Support information

Investigation of the Effect of Grafting Density on Surface Properties for Sequence-Determined Fluoropolymer Films

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Synthesis of sequence-determined polymers

Three base polymers (BP1, BP5 and BP7) with different sequence intervals were synthesized in different feed ratios of St/Ugi-DPE. After hydrolysis of above polymers, the amine groups were introduced in polymer chains of sequence-determined amine functionalized polymers (SD1, SD5 and SD7). The characteristics of BP and SD were listed in Table S1. The ^{1}H NMR and SEC curves are shown in Figure S1. The peak at δ 0.1- 0.3 ppm in ^{1}H NMR spectra of BP disappeared completely, while the peak of amines appeared at δ 3.2-3.7 ppm simultaneously in ^{1}H NMR spectra of SD. It meant that the hydrolysis of BP was highly efficient. All the SEC curves remained narrow and unimodal, which proved that no side reaction happened in the LAP.

Table S1. Structural characteristics of sequence-determined functionalized polymers

Run	M_n[a] (kg/mol)	$Đ$[a]	N_S/N_D[b]	N_D[b]
BP1	5.1	1.14	1.4	10.4
SD1	4.2	1.12		
BP5	6.3	1.14	4.6	8.2
SD5	5.5	1.14		
BP7	7.0	1.15	6.7	7.1
SD7	6.3	1.14		

[a] The molecular weights and dispersions were determined by SEC. [b] The ratios of St/DPE units in the chain (N_S/N_D) and the average number of DPE units (N_D) were calculated by ^{1}H NMR.

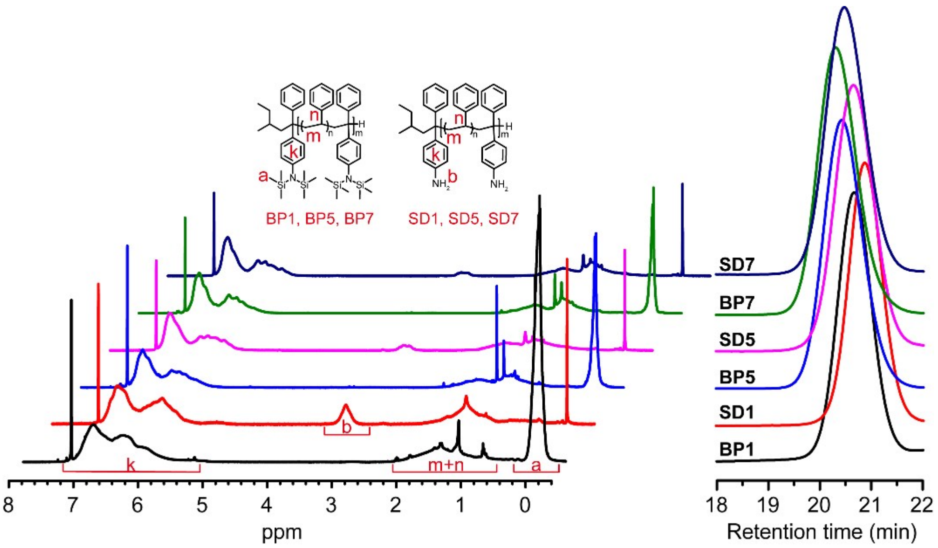

Figure S1. ^{1}H-NMR spectra and SEC curves of base polymers (BP) and sequence-determined amine functionalized polymers (SD)

Post-modification of SD via epoxy-amine reaction

The epoxy-amine reaction was chosen to modify the SD with fluorine functionalized epoxides. Two fluorine functionalized epoxides bearing different numbers of fluorine atoms reacted with the amines in three SD respectively to synthesize six SD-F. The fluorinated groups followed different grafting densities along the chains and varied the lengths of pendant groups. Without catalyst, the post-modification of SD possessed for 5 days to obtain high conversions of fluorination. Although the reaction time was long, it was guaranteed that nearly all amines were converted to fluorinated groups. The FT-IR spectra (Figure S2) showed that the fluorinated groups were grafted on the polymer chains successfully.

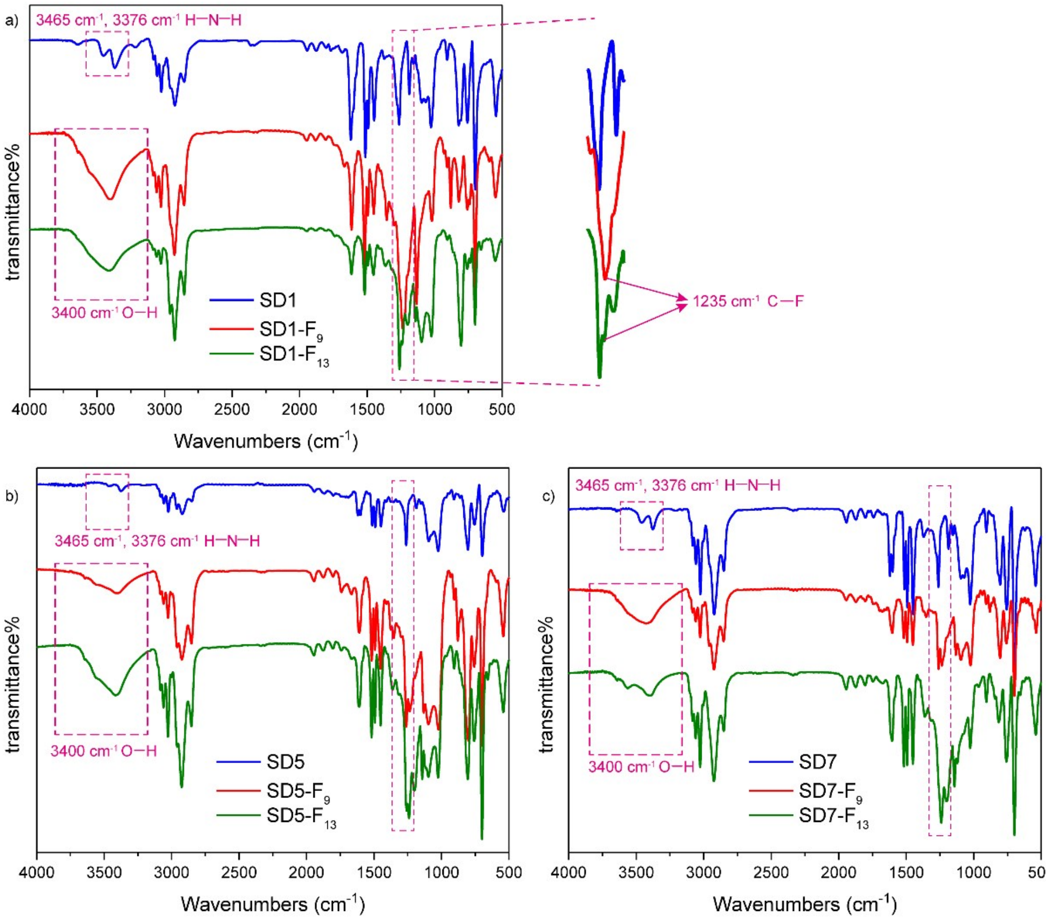

Figure S2. FT-IR spectra of SD and SD-F

The conversions of the epoxy-amine reaction could be calculated using ^{1}H-NMR spectra. The ^{1}H-NMR spectra of SD-F were shown in Figure S3. However, the peaks in ^{1}H-NMR spectra were hardly analyzed, because as shown in Scheme 1(b), the amines might attack either of the two carbon atoms on the epoxides, which were called α- and β-addition respectively. Hence, the peaks must be distinguished by the HSQC of SD1-F_9 in Figure S4, firstly. The independent peak at δ 4.1-4.4 ppm in ^{1}H-NMR spectra of SD-F was belong to the proton (c in Figure S3) on the tertiary carbon (2 in Figure S4) beside the hydroxyl of β-addition. The peaks at δ 2.1-2.5 ppm were belong to the protons (h, i in Figure S3) on the secondary carbon (3, 6 in Figure S4). If only β-addition had happened, the integral ratio of peak (h+i) and peak (c) would have been 2. However, in all ^{1}H-NMR spectra of SD1-F, the integral ratios are larger than 2 (2.30 in SD1-F_9 and 2.48 in SD1-F_{13}) so that both of the α- and β-additions happened simultaneously. The ratio of α-addition and β-addition can also be calculated by the ^{1}H-NMR spectra. As the peaks overlapped at the area of δ 2.1-2.5 ppm in the ^{1}H-NMR spectra of SD5-F and SD7-F, a necessary assumption was put forward that the ratio of β-addition to total addition was constant for the same epoxide derivatives, i.e. the values calculated in SD1-F could be taken as standard. Meanwhile, because the number of protons on phenyl did not change after modification, the total conversions of epoxy-amine reaction (C_{total}) could be calculated by ^{1}H-NMR spectra, as following:

$$\frac{Area(\delta\ 5.0-7.2\ ppm)_{in\ SD}}{Area(\delta\ 5.0-7.2\ ppm)_{in\ SD-F}}=\frac{C_{\beta-addition}\times Area(\delta\ 3.2-3.7\ ppm)_{in\ SD}}{2\times Area(\delta\ 4.1-4.4\ ppm)_{in\ SD-F}}$$

$$C_{total} = \frac{C_{\beta-addition} \times Area(\delta\ 2.1-2.5\ ppm)_{in\ SD-F}}{Area(\delta\ 4.1-4.4\ ppm)_{in\ SD-F}}$$

As listed in Table 1, the C_{total} values were larger than 95%, in which the percentages of β-addition were 87% for EO-F_9 and 80% for EO-F_{13}. The C_{total} values of SD1-F_9, SD5-F_9 and SD5-F_{13} were slightly above 100%. It should be acceptable according the ^{1}H NMR error and potential double-addition reaction[1].

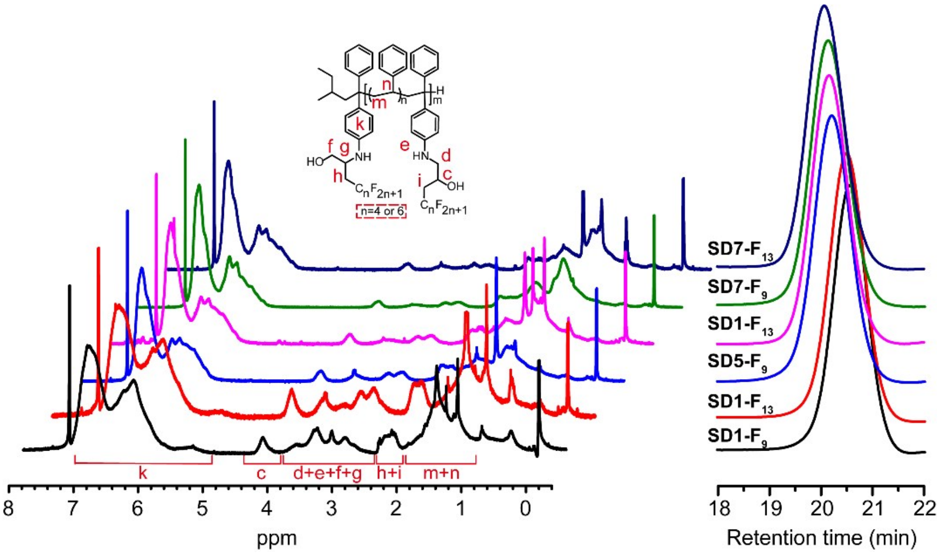

Figure S3. ^{1}H-NMR spectra and SEC curves of SD-F

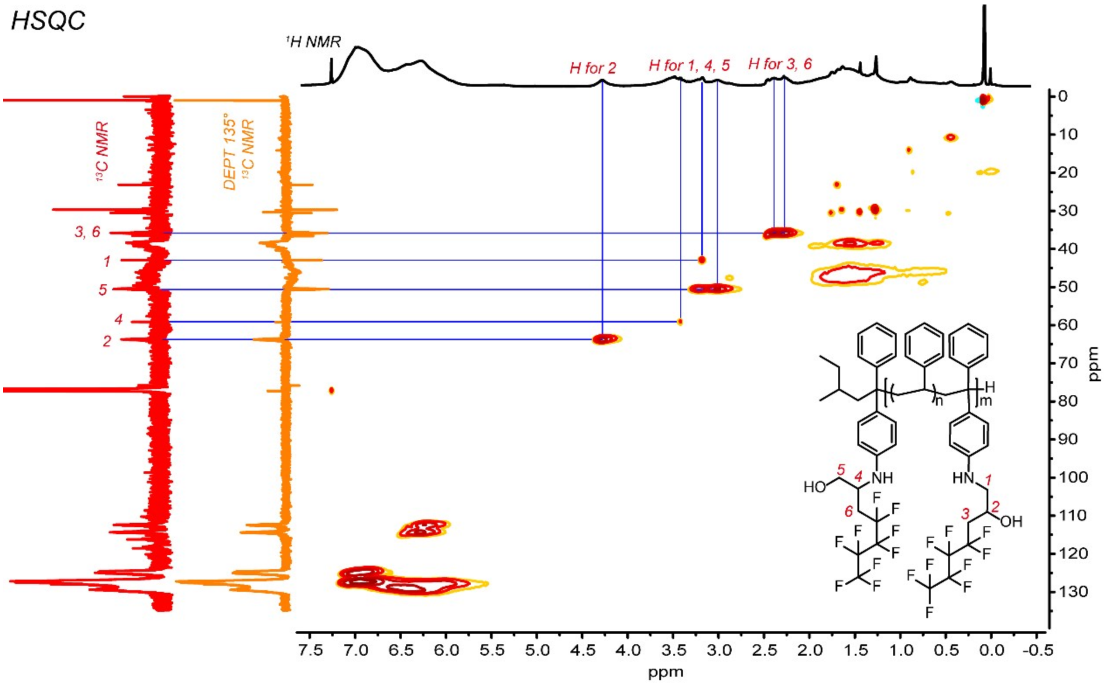

Figure S4. ^{1}H NMR, ^{13}C NMR, DEPT 135° ^{13}C NMR and HSQC spectra of SD1-F_9

1 Zhou C, Truong V X, Qu Y, Lithgow T, Fu G D, Forsythe J S. J Polym Sci Pol Chem, 2016, 54(5): 656-667