Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary information for

Fluorine-driven amorphous solid-state polycondensation: Phosgene-free synthesis of high-molecular weight polycarbonate from fluorinated carbonate

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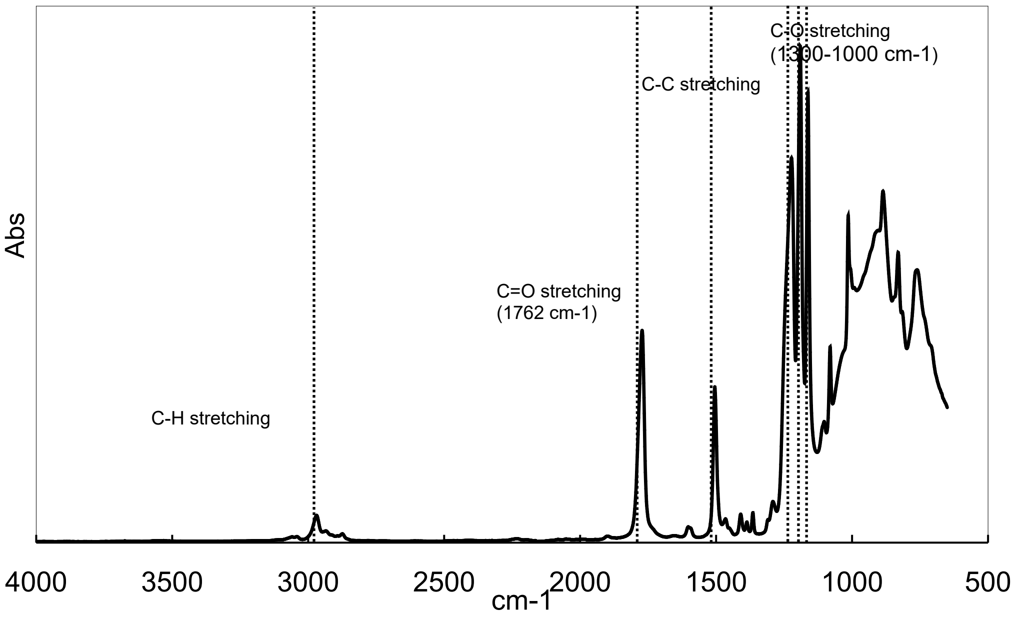

Figure S1. FT-IR spectrum of the polymer (entry 2, SSP5)

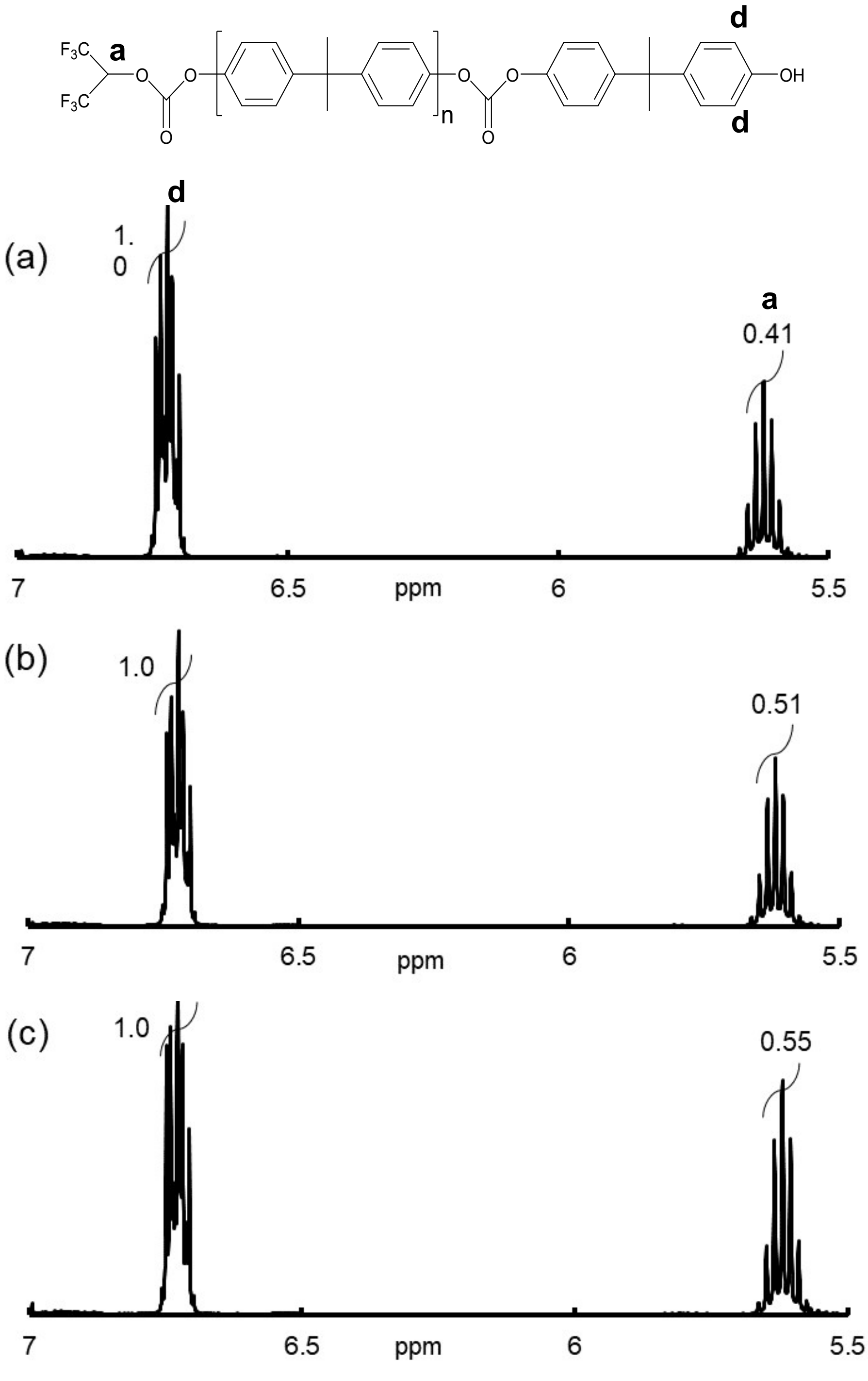
F3C
a
F3C
O
O
O
n
O
O
O
d
OH
d
(a)
d
1.
0
a
0.41
7
6.5
ppm
6
5.5
(b)
1.0
0.51
7
6.5
ppm
6
5.5
(c)
1.0
0.55
7
6.5
ppm
6
5.5

Figure S2. Expanded ^{1}H NMR spectra (5.5–7.0 ppm) of the reaction mixture of the prepolymer syntheses with the different feed molar ratios of BHFC and BPA: (a) 1.00:1.00 (entry 1); (b) 1.05:1.00 (entry 2); and (c) 1.07:1.00 (entry 3)

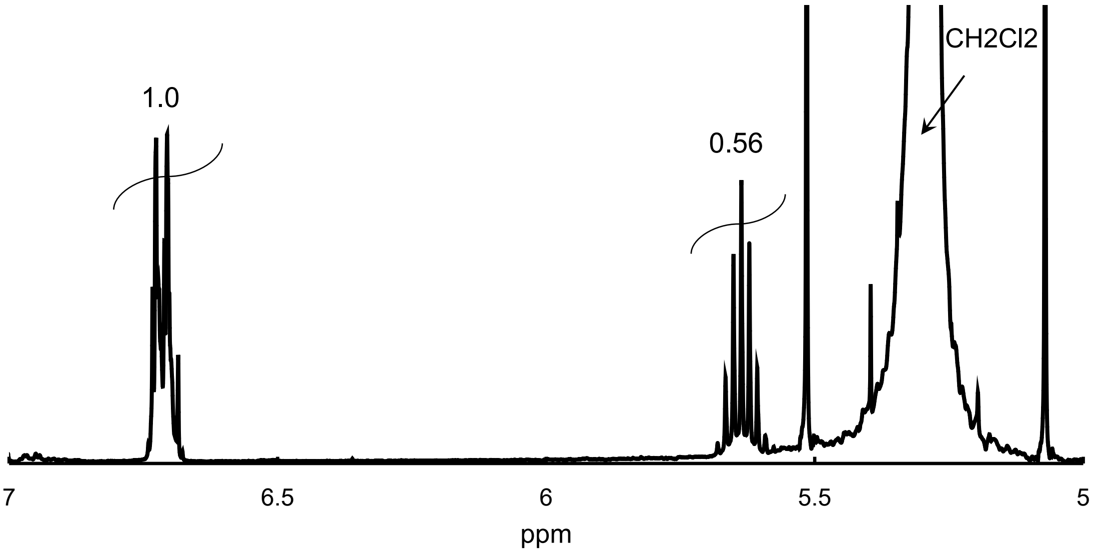

Figure S3. ^{1}H NMR spectrum of the reaction mixtures of the prepolymer synthesis (entry 2) before vacuum drying

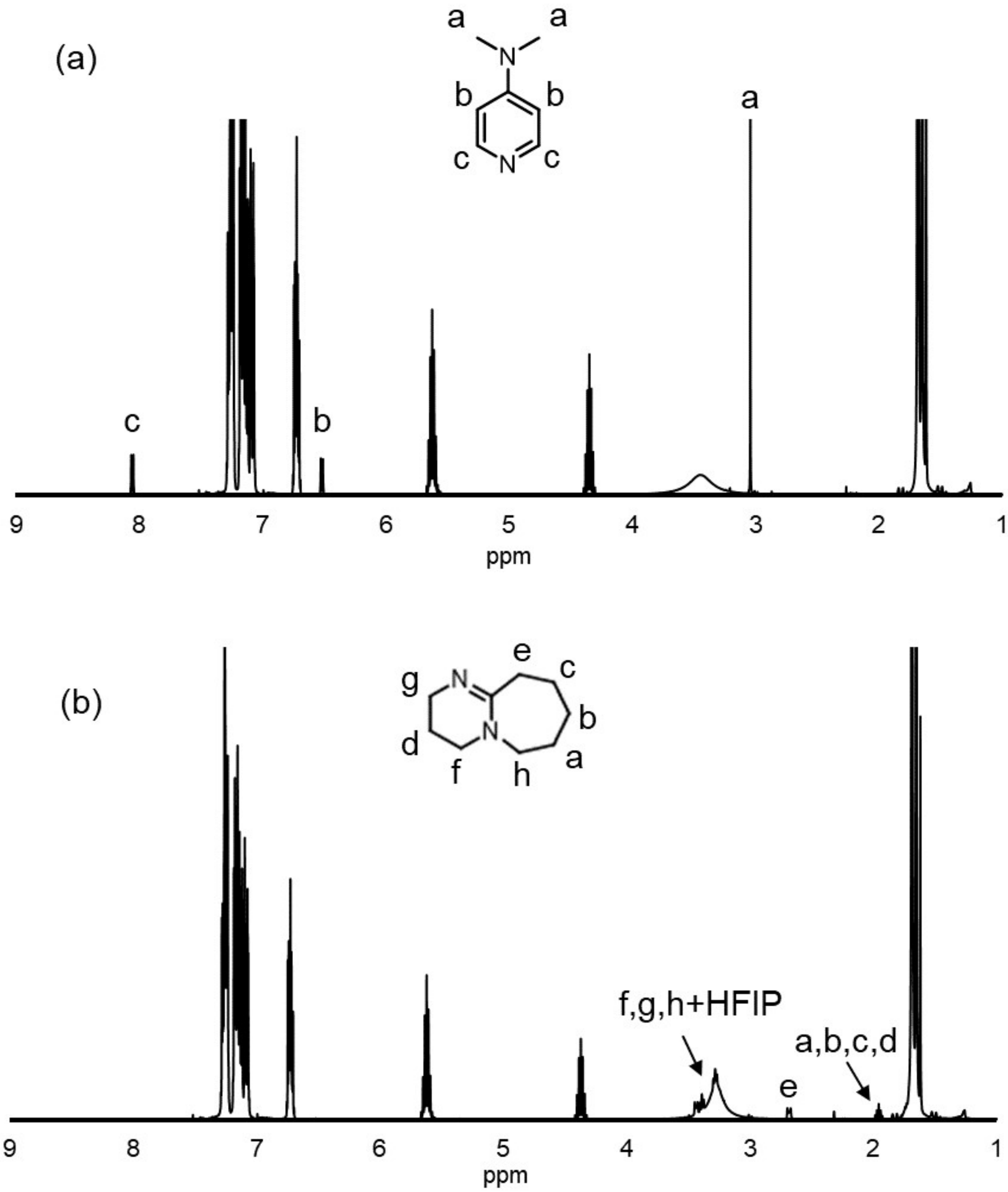

Figure S4. ^{1}H NMR spectra of the reaction mixtures of the prepolymer synthesis (entries 6 and 7)) after vacuum drying

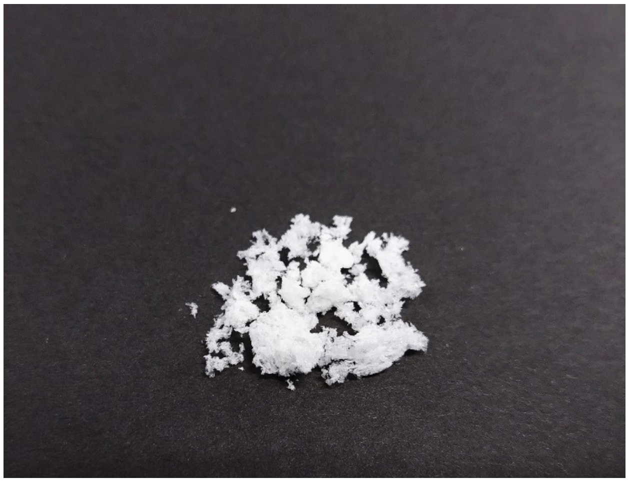

Figure S5. A picture of the polymer (entry 2, SSP5)

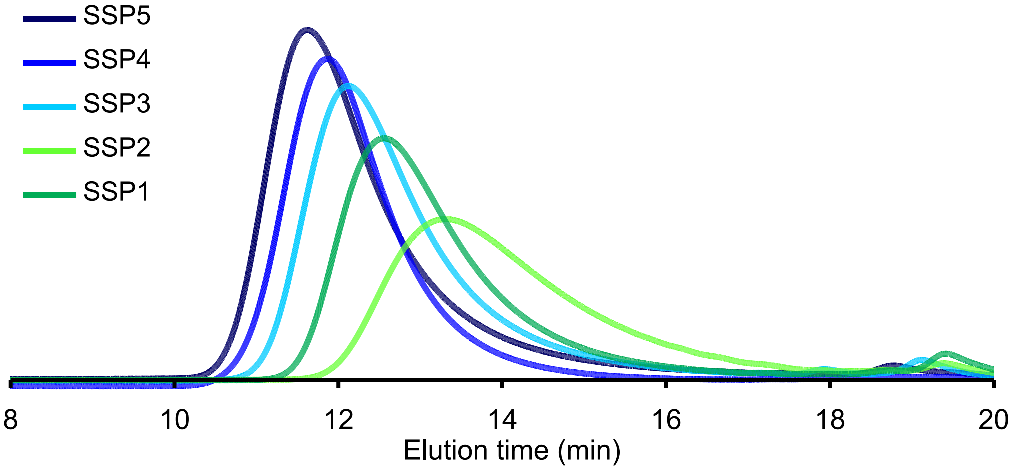

Figure S6. GPC profiles of the polymers (entry 2) from SSP1 to SSP5

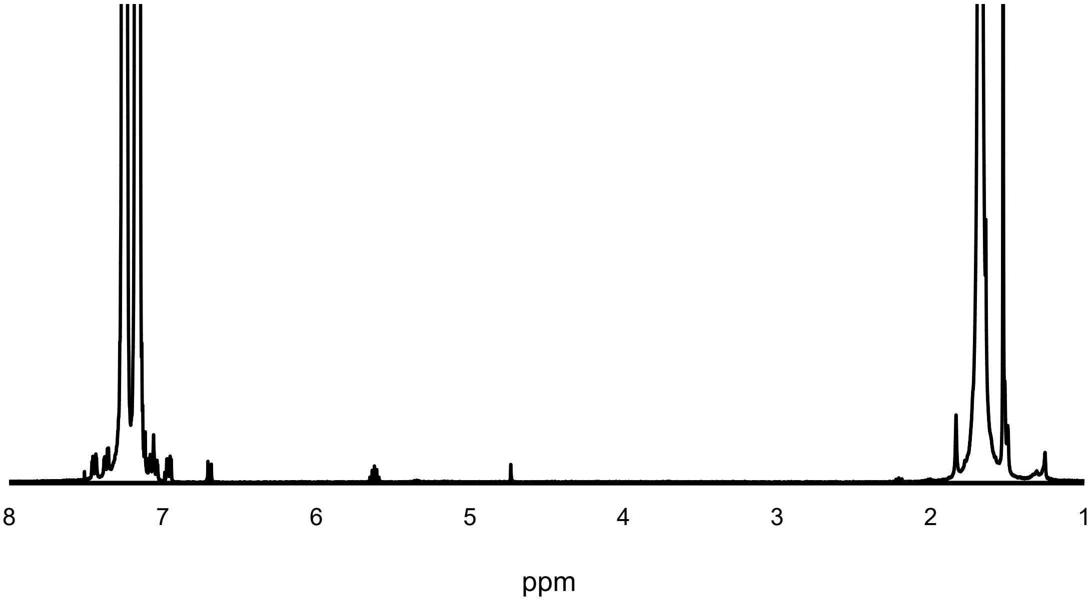

Figure S7. ^{1}H NMR spectrum of the reaction mixture after the SSP5 (entry 2)

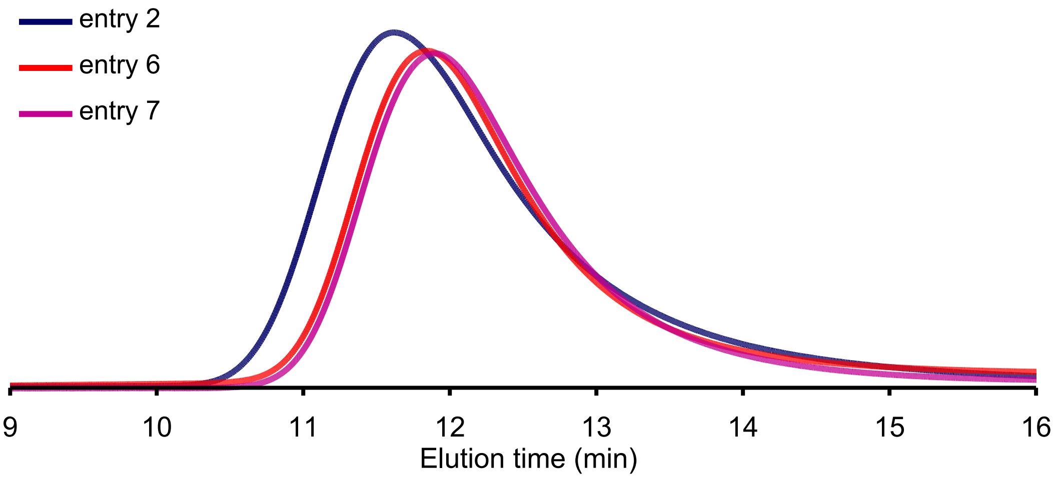

Figure S8. GPC profiles of the polymers (entries 2, 6, and 7) after SSP5

Table S1. M_n and M_w values and residual catalyst contents at entries 2, 6, and 7 (Figure 3))

Cat.	TBA			DMAP			DBU		
	M_n	M_w	Residual cat. (mol %)	M_n	M_w	Residual cat. (mol%)	M_n	M_w	Residual cat. (mol%)
SSP 1	4500	11,000	3.9	3800	9000	1.1	3600	8900	3.9
SSP 2	13,000	24,000	3.0	9000	23,000	0.08	9000	24,000	3.9
SSP 3	19,000	40,000	0.7	14,000	32,000	0	15,000	38,000	2.1
SSP 4	27,000	67,000	0.05	20,000	49,000	0	24,000	65,000	1.2
SSP 5	38,000[a]	83,000	0	25,000	61,000	0	21,000	58,000	1.0

[a] M_n 35,000 calculated from the ^{1}H NMR spectrum

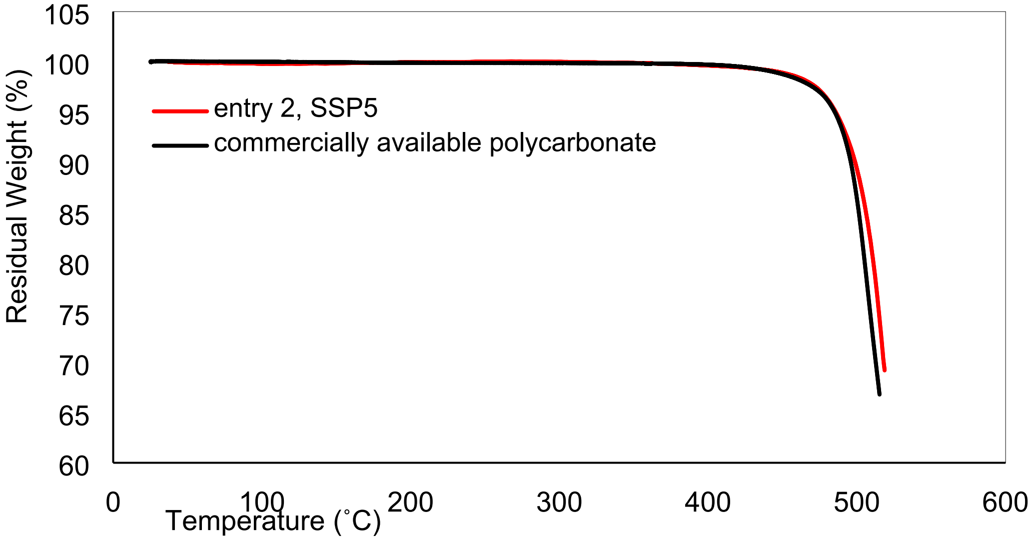

Figure S9. TGA curve of the polymers (red line: entry 2, SSP5; black line: commercially available polycarbonate)

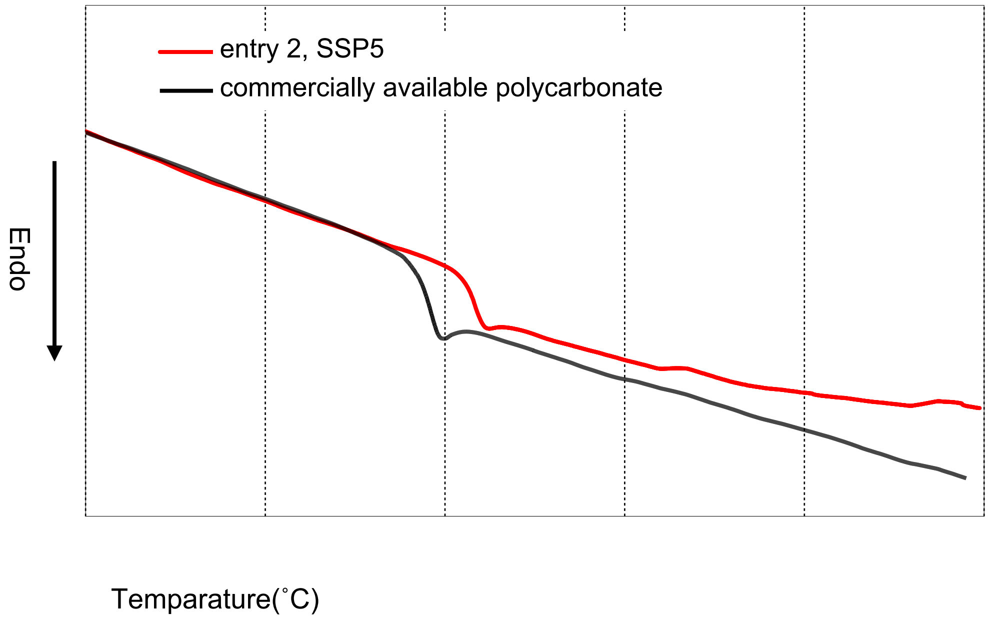

Figure S10. DSC profiles of the polymer (red line: entry 2, SSP5; black line: commercially available polycarbonate)

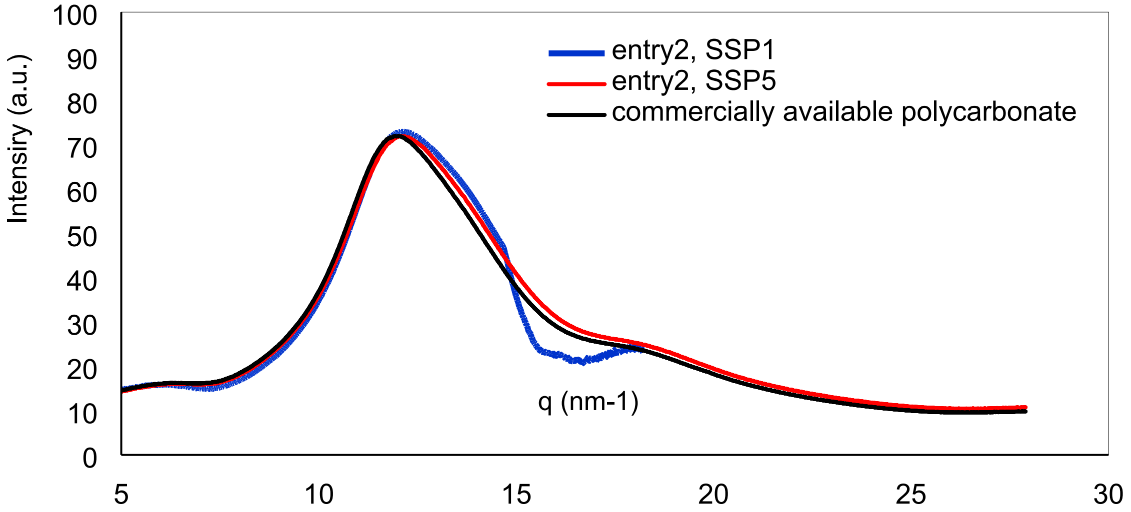

Figure S11. WAXD chart of the polymer (entry 2) after SSP1 and SSP5 and of commercially available polycarbonate.

Figure S12. Images of the water droplets on the polymer films (entry 2) obtained by SSP2, 3, 4, and 5

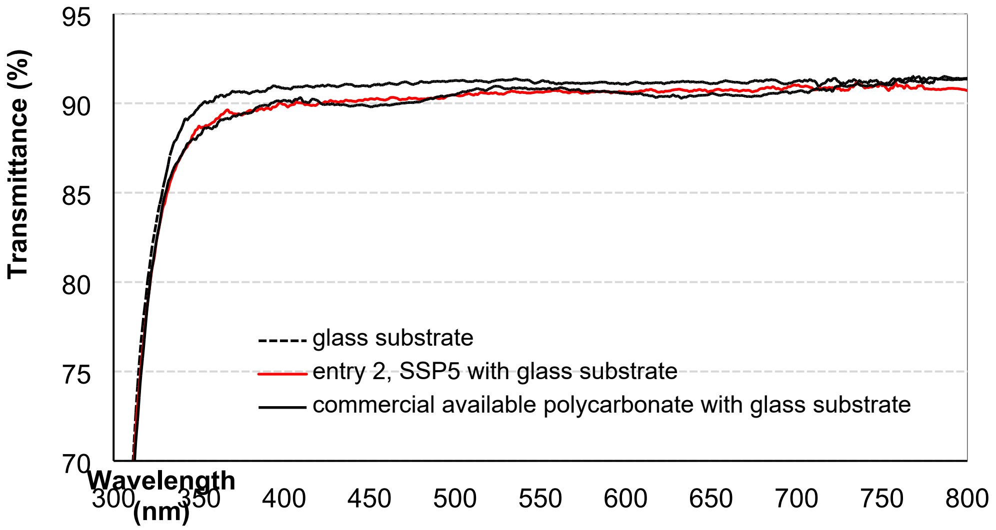

Figure S13. Transmittance of the polymer films (entry2, SSP5)

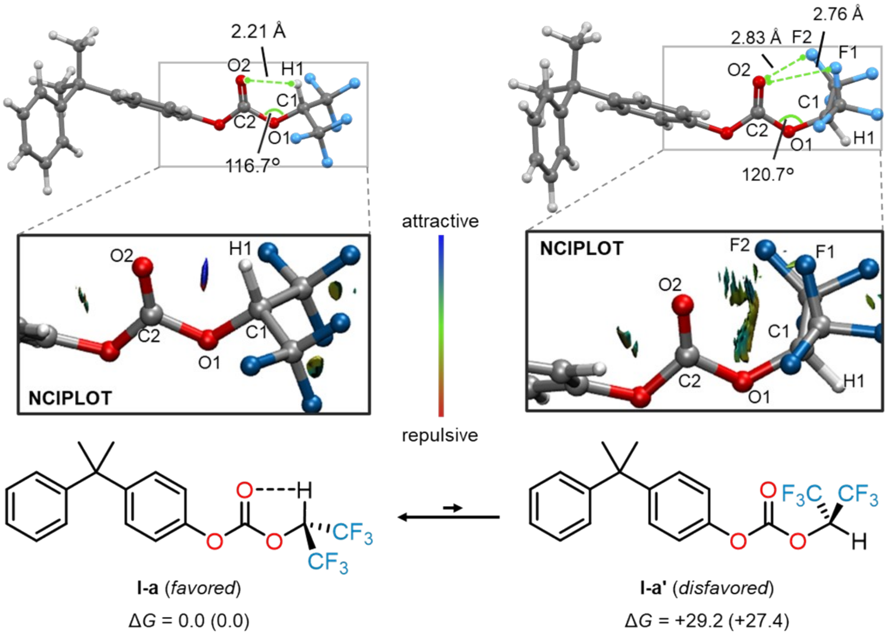

Figure S14. Conformation analysis of the mono HFIP-carbonate

The DFT calculation of the two representative conformations I-a and I-a′ of the model HFIP-terminated carbonate was performed to investigate the origin of the unique reactivity of the HFIP-terminated carbonate. The calculation results indicated that conformation I-a was highly stable compared to I-a′ (Δ*G* = +29.2 kcal/mol). This energy difference was caused by the intramolecular hydrogen bond between the carbonyl oxygen (O_2) and the hydrogen of the HFIP moiety (H1) in I-a (H1-O_2: 2.21 Å). The highly electron-deficient proton atom H1 by the trifluoromethyl groups is a good hydrogen bond acceptor. This attractive interaction reflects the bond angle of C1–O1–C2. The I-a angle is smaller than that of I-a′ (I-a: 116.7°, I-a′: 120.7°). Another conformation I-a′, in which the hydrogen atom H1 is distal from the carbonyl oxygen atom O_2, is disfavored because of the electronic repulsion between the fluorine atoms (F1 and F2) and oxygen O_2.

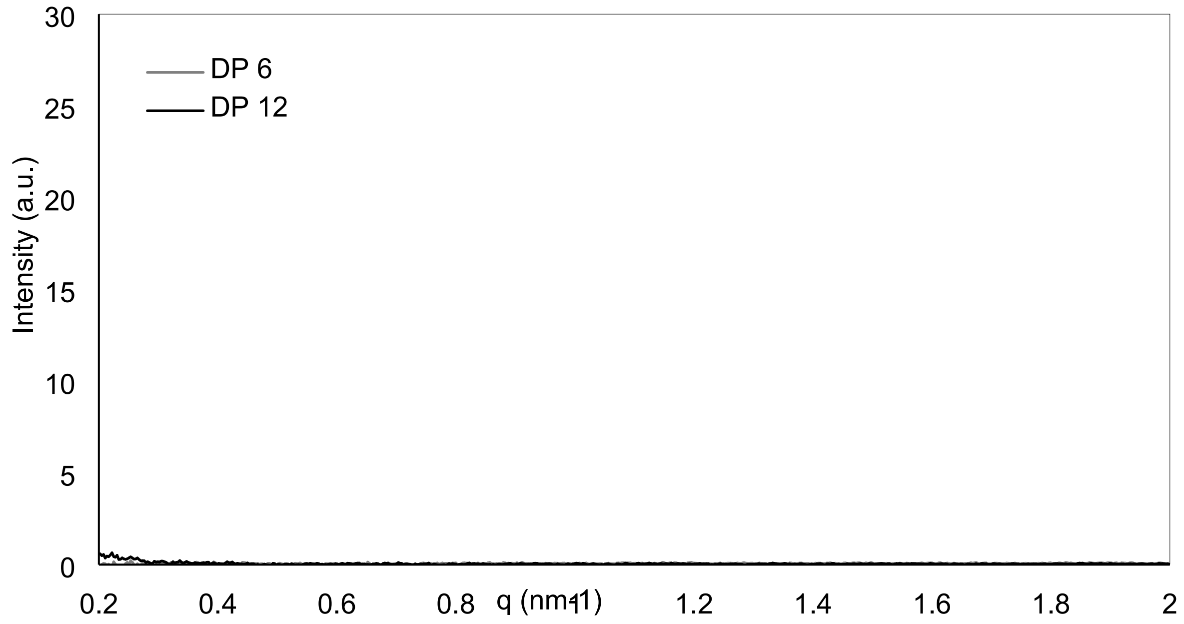

Figure S15. SAXS chart of the polymers of DP6 and 12 (entry 2)