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Self-wrinkling induced by the photopolymerization and self-assembly of fluorinated polymer at air/liquid interface

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1. Experimental section

1.1 Materials.

Trimethylolpropane triacrylate (TMPTA), 2,2'-(4,4'-(propane-2,2-diyl)bis (4,1-phenylene))bis(oxy)bis(ethane-2,1-diyl) diacrylate (A-BPE-10) and poly(propylene oxide) diacrylate (PPGDA) were provided by Shin-Nakamura Chemical; 2-(perfluorooctyl) Ethyl Acrylate (CFA_8) were obtained from ALDRICH chemical; Photoinitiator I-907 was obtained from Tronly (Changzhou, China); Other chemicals were obtained from China National Pharmaceutical Group (Shanghai, China). All reagents were used as received except as noted.

1.2 Synthesis and characterization of PMMA-F. As shown in Figure S1, a solution of MMA (0.08 mol, 8g), CFA8 (0.0038 mol, 2g) and 0.1 g AIBN were added in 20 mL of dioxane, the mixed solution were stirring and reacted at 70 °C for 6 h, and then 200 mL methanol was added, the white precipitate were separated and wash by methanol for 6 times and then dried in the vacuum condition at 70 °C for 24 h.

Figure S2 presents the ^1H NMR spectrum of the obtained PMMA-F, and the characteristic signals and their corresponding groups were marked in the spectrum and the inserted structural formula. The molecular weight of The PMMA-F was also determined by GPC. As shown in Figure S3 and Table S1, the Mn and the PDI of the PMMA-F are about 2.46×10^4 and 1.67, respectively.

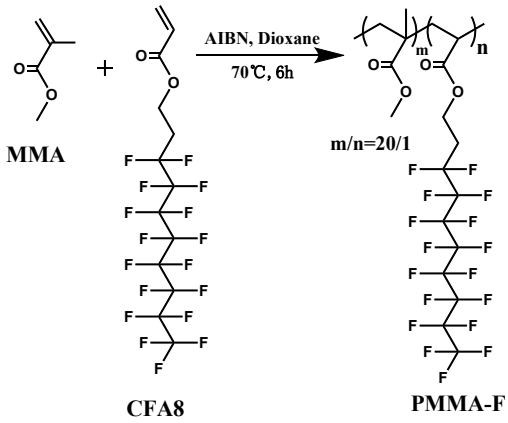

Figure S1. The schematic process for synthesis of PMMA-F.

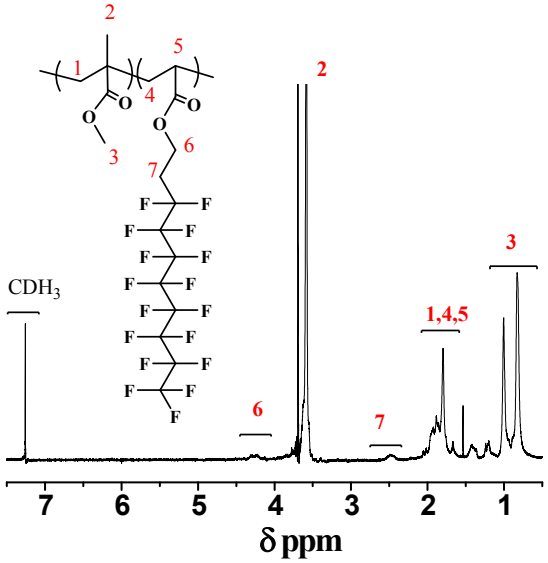

Figure S2. The ^{1}H NMR spectrum of the PMMA-F in $CDCl_3$

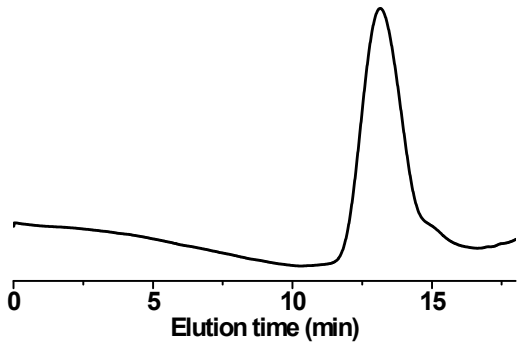

Figure S3 The GPC curve of PMMA-F, THF as eluent.

1.3 Synthesis of PnBA-F.

PnBA-F was synthesized according to Figure S4. A solution of nBA (0.08 mol, 10.24g), CFA8 (0.0038 mol, 2g) and 0.12 g AIBN were added in 30 mL of dioxane, the mixed solution were stirring and reacted at 70 °C for 6 h, and then 200 mL methanol/water (4/1) was added, the ropy precipitate were separated and wash by methanol/water for many times and then dried in the vacuum condition at 70 °C for 24 h.

Figure S5 shows the ^{1}H NMR spectrum of the prepared PnBA-F, and the characteristic signals and their corresponding groups were marked in the spectrum and the inserted structural formula. As shown in Figure S6 and Table S1, the Mn and the PDI of the PMMA-F are about 3.0×10^{4} and 2.18, respectively.

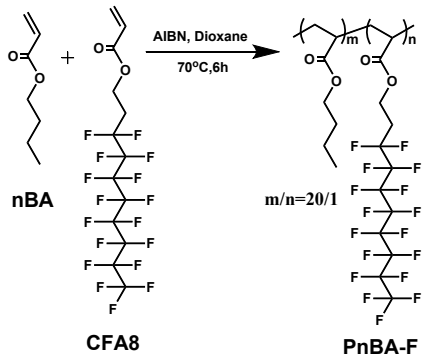

Figure S4. The schematic process for synthesis of PnBA-F.

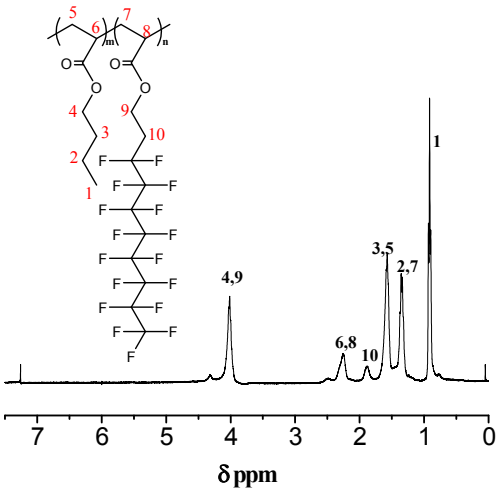

Figure S5. The ^{1}H NMR spectrum of the PnBA-F in $CDCl_3$.

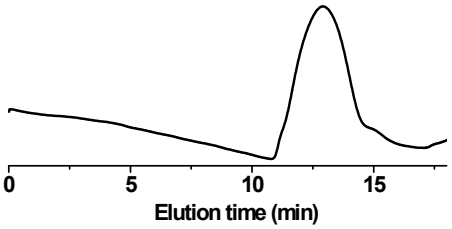

Figure S6. The GPC curve of PnBA-F, THF as eluent.

Table S1 The molecule weight and PDI of fluorinated polymer (PMMA-F and PnBA-F)

Sample	$M_n/10^4$	$M_w/10^4$	M_w/M_n
PMMA-F	2.46	4.13	1.67
PnBA-F	3.04	6.62	2.18

1.4 Synthesis of reactive fluorinated polymer (MAA-PMA-F)

As shown in Figure S7, a solution of MMA (0.08 mol, 8g), CFA8 (0.0072 mol, 4g) HEMA (0.04 mol, 5.92g) and 0.1 g AIBN were added in 20 mL of dioxane, the mixed solution were stirring and reacted at 70 °C for 6 h, and then 200 mL methanol was added, the white precipitate were separated and wash by methanol for 6 times and then dried in the vacuum condition at 70 °C for 24 h. Then the 3g of the dried precipitated and 1.5 mL dried triethylamine were dissolved in 50 mL CH_2Cl_2 solution and added into 10 mL methacryloyl chloride solution in 1 hour with stirring at 0 °C, the mixed solution were stirring for 24 h and filtered to remove the precipitates. The collected CH_2Cl_2 solution was added into cold diethyl ether solution to obtain the white precipitates, the precipitates were dissolved in CH_2Cl_2 solution and added in the fresh cold diethyl ether solution again, and the same operation was repeated for 3 times to remove the excess methacryloyl chloride and triethylamine. The obtained white precipitates were dissolved in 40 mL CH_2Cl_2 solution and washed by 20 mL deionized water with stirring for 5 times to remove the residual triethylamine hydrochloride, and the CH_2Cl_2 phase was collected and dried by anhydrous magnesium sulfate. At last, the objective product of MMA-PMMA-F was obtained by removing the CH_2Cl_2 solution using reduced pressure distillation at room temperature.

Figure S8 shows the ^1H NMR spectrum of the prepared MMA-PMMA-F, and the characteristic signals and their corresponding groups were marked in the spectrum

and the inserted structural formula.

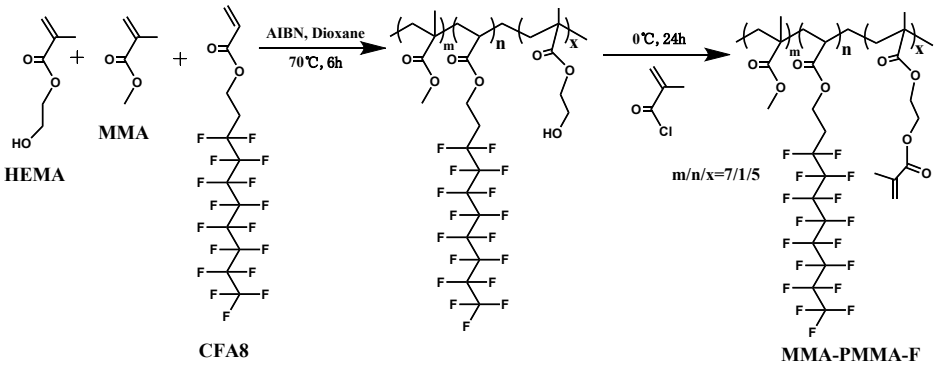

Figure S7. The schematic process for synthesis of MMA-PMMA-F.

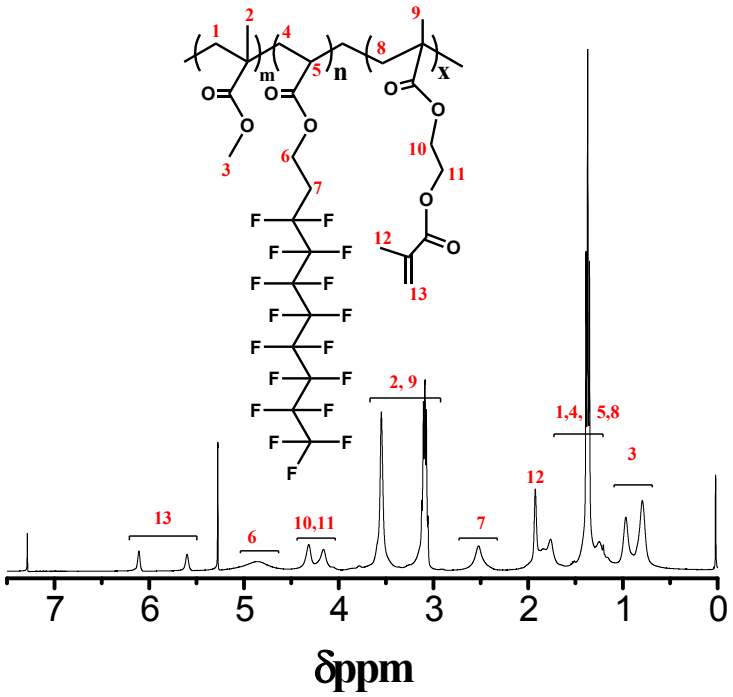

Figure S8. The ^{1}H NMR spectrum of the MMA-PMMA-F in $CDCl_3$.

2. Results

2.1 AFM analysis of cured TMPTA resins with 12wt% PMMA

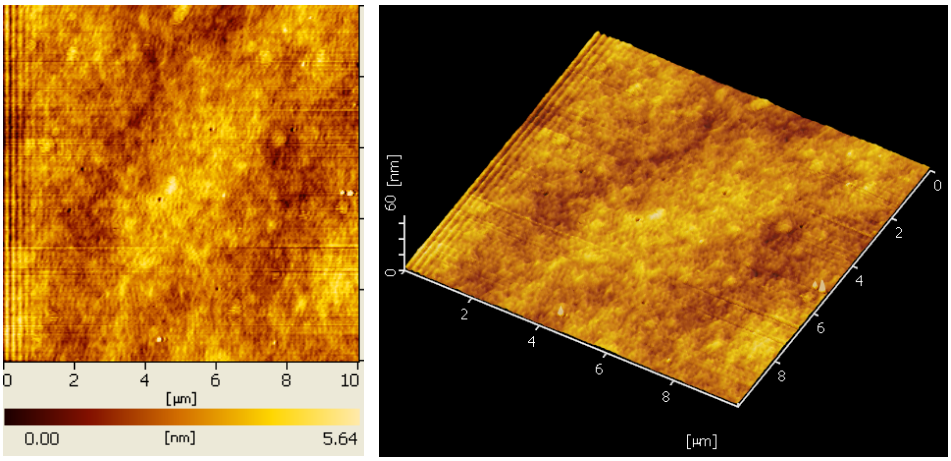

Figure S9. AFM images of the cured TMPTA resin with 12wt% pure PMMA.

2.2 AFM analysis of cured blank cured TMPTA resins

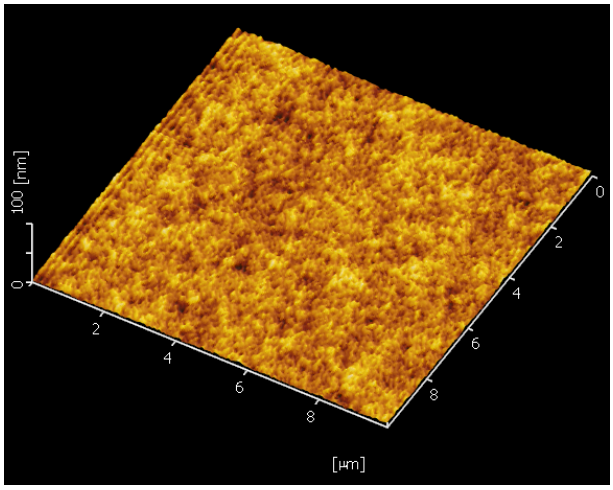

Figure S10. 3D AFM image of the blank cured TMPTA resins without additives of polymer.

2.3 Measuring the modulus of the UV-curing films by AFM system

The modulus of the cured films were calculated using the AFM force curves based on the Hertz model according to reported literatures. [1-4] The Hertz model gives the relationship of the loading force (F), the indentation (δ) and elastic modulus (E) of the film as the follows: [1]

$$F = (2/\pi)[E/(1-\nu^2)]\ \delta^2 \tan(\alpha) \qquad (1)$$

Where, ν is the Poisson ratio of the film, α is the half opening angle of the indenting cone.

The δ can be given by equation 2 according to the Hooke's law: [1]

$$F = kd = k\,(z-\delta) \qquad (2)$$

Here, k is the force constant of the cantilever, d is the deflection of the cantilever. To an infinitely stiff sample, the deflection d of the cantilever is identical to the movement of the piezo in z direction: d = z.

To combine eq 1 and 2 yields:

$$\Delta F = (2/\pi)E/(1-\nu^2)\delta^2 \tan(\alpha) = (2/\pi)E/(1-\nu^2)[\Delta z - (\Delta F/k)]^2 \tan(\alpha) \qquad (3)$$

Here the ΔF and Δz can be determined independently by taking two different deflection values and their corresponding F and z values from a force curve, as shown in Figure S9.

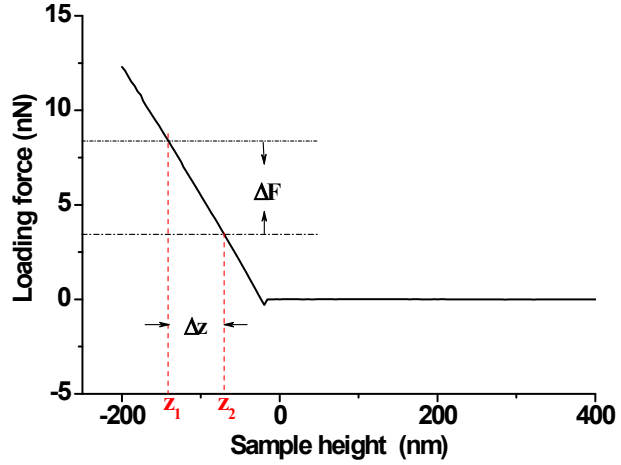

Figure S11. Force curve on the curing TMPTA film.

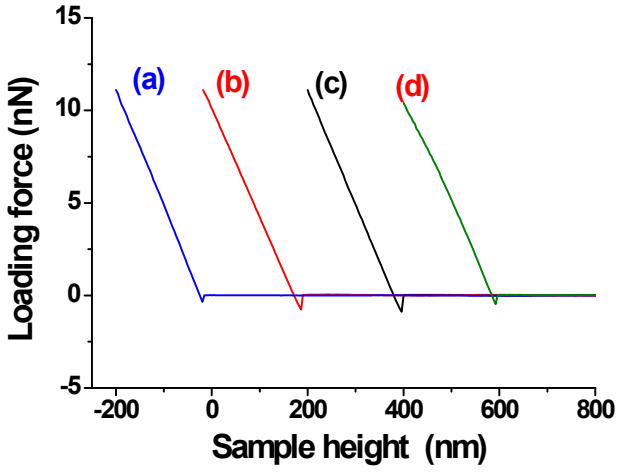

Figure S12. Force curve on the curing TMPTA film with (a) 2% PMMA-F; (b) 6% PMMA-F; (c) 12% PMMA-F and (d) 12% PnBA-F, respectively.

2.4 AFM analysis of TMPT resins with 4wt% PMMA-F under UV for 5s

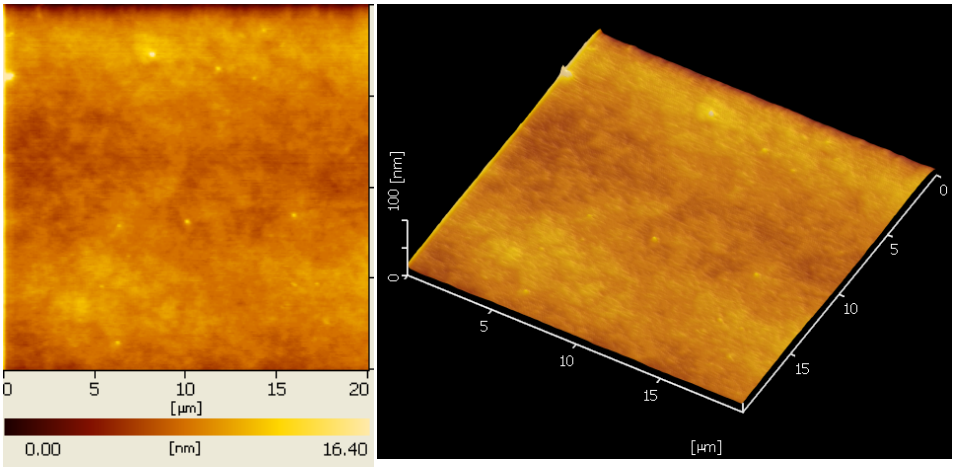

Figure S13. AFM images of the TMPT resins with 4wt% PMMA-F under UV for 5s.

3.2 AFM analysis of cured TMPT resins with 6wt% and 12wt% MMA-PMMA-F, respectively.

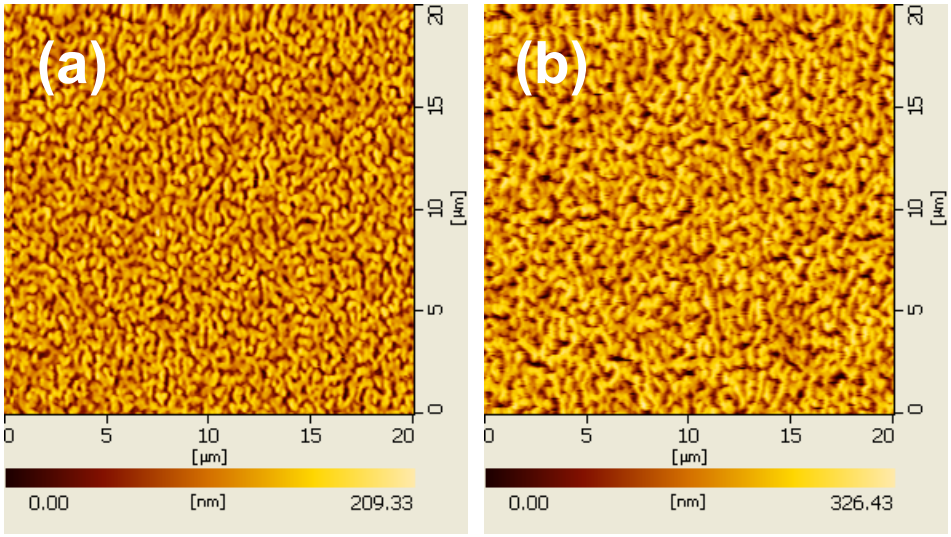

Figure S14. AFM images of the cured TMPTA resin with (a) 6wt% MMA-PMMA-F and (b) 12wt% MMA-PMMA-F.

Table S1 The modulus and volume shrinkage of cured TMPTA and A-BPE-10 mixed resins.

Curing Samples	Young modulus (Gpa)[a]	Volume shrinkage (%)[b]
TMPTA/A-BPE-10 (4/1)	2.3±0.1	14.6
TMPTA/A-BPE-10 (3/2)	1.7±0.2	11.3
TMPTA/A-BPE-10 (2/3)	1.1±0.15	8.2
A-BPE-10	0.04±0.013	6.5

[a] The Young modulus is calculated by AFM force curves.

[b] The volumetric shrinkage was calculated using the formula: $\Delta V\% = (1 - \frac{\rho_{uncured}}{\rho_{cured}}) \times 100\%$.

References

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[2] P. J. Nowatzki, C. Franck, S. A. Maskarinec, G. Ravichandran, D. A. Tirrell, *Macromolecules* **2008**, 41, 1839.

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[4] H. Liu, N. Chen, S. Fujinami, D. Louzguine-Luzgin, K. Nakajima, T. Nishi, *Macromolecules* **2012**, 45, 8770.