

Supporting Information

Photocrosslinked PVDF-based star polymer coatings:

An all-in-one alternative to PVDF/PMMA blends for outdoor applications

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Experimental Section. *Materials:* Vinylidene fluoride (VDF) and Solef[®] (PVDF) were kindly supplied by Arkema and Solvay, respectively. Amyl peroxy-2-ethylhexanoate (Trigonox[®] 121) was purchased from AkzoNobel. ReagentPlus grade dimethyl carbonate (DMC), 2-butanone (MEK), dimethylformamide (DMF), 3-(acryloyloxy)-2-hydroxypropyl methacrylate (AHPMA), butyl acrylate, triethylamine (Et₃N), Darocur[®] 1173, poly(methyl methacrylate) $M_n = 120,000 \text{ g mol}^{-1}$, and hexylamine were purchased from Sigma Aldrich. The solvents used for NMR spectroscopy were purchased from Euroiso-top. Fluorolink[®] E10H $M_n = 1800 \text{ g mol}^{-1}$ (precursor of PFPE-DMA) was purchased from ACOTA. *Characterizations:* ¹H and ¹⁹F NMR spectra were recorded on a Bruker AC 400 spectrometer. Number-average molar masses and dispersities were assessed with triple-detection SEC from Agilent Technologies using DMF (containing 0.1 wt.% of LiCl) as the eluent at a flow rate of 0.8 mL min⁻¹ at 35 °C (PMMA narrow standards were used for the universal calibration). The PVDF functionality was assessed using the Agilent branching module with a PVDF₅₁ as the linear reference,¹ the Intrinsic Viscosity (IV) as the source data, and a star-branching regular model (structure parameter = 0.5 and repeating units = 103).² The thermogravimetric analyses (under air) were performed using a TA Instruments TGA

51 apparatus and the samples were heated in aluminum pans from room temperature to 580 °C with a heating rate of 10 °C min⁻¹. DSC analyses were carried out under nitrogen using a Netzsch DSC 200 F3 instrument. Two scans were recorded at a heating/cooling rate of 10 °C min⁻¹ from -150 °C to 250 °C under inert atmosphere (N₂) using aluminum standard crucibles with aluminum piercing lids. Water contact angle measurements were carried out at ambient temperature on Contact Angle System OCA-Data Physics using the water sessile drop method. Adhesion property was characterized using the D3359 ASTM standard test method (tape test). The film thickness and the surface roughness were determined using a smarWLI-basic profilometer from Schaefer. The formulation of the coating was achieved as follows: 4-arm star PVDF (20 mg), PFPE-DMA (optional), Darocur[®] 1173 (2 wt.%), and MEK (100 mg) were heated at 50 °C until complete dissolution, the solution was cast (glass or steel plate), and allowed to dry at room temperature (*ca.* 20 °C). The coating was UV-cured for 5 min using a Fusion UV system equipped with a F300/HP6 lamp ($\lambda = 200\text{-}400$ nm, 300 W/inch). The PVDF/PMMA 70/30 wt.% coating was prepared as follows: Solef[®] (100 mg), PMMA (30 mg), and DMF (200 mg) were heated until complete dissolution, the solution was cast onto a steel plate and allowed to dry at room temperature (*ca.* 20 °C). *Syntheses:* The R-core tetrafunctional CTA was synthesized according to a previously reported two-step procedure.³ The experimental procedure for the synthesis of the 4-arm star PVDF is similar to that reported for its linear counterpart.¹ The 4-arm star PVDF methacrylate and butyl ester were also prepared according to method reported previously.⁴

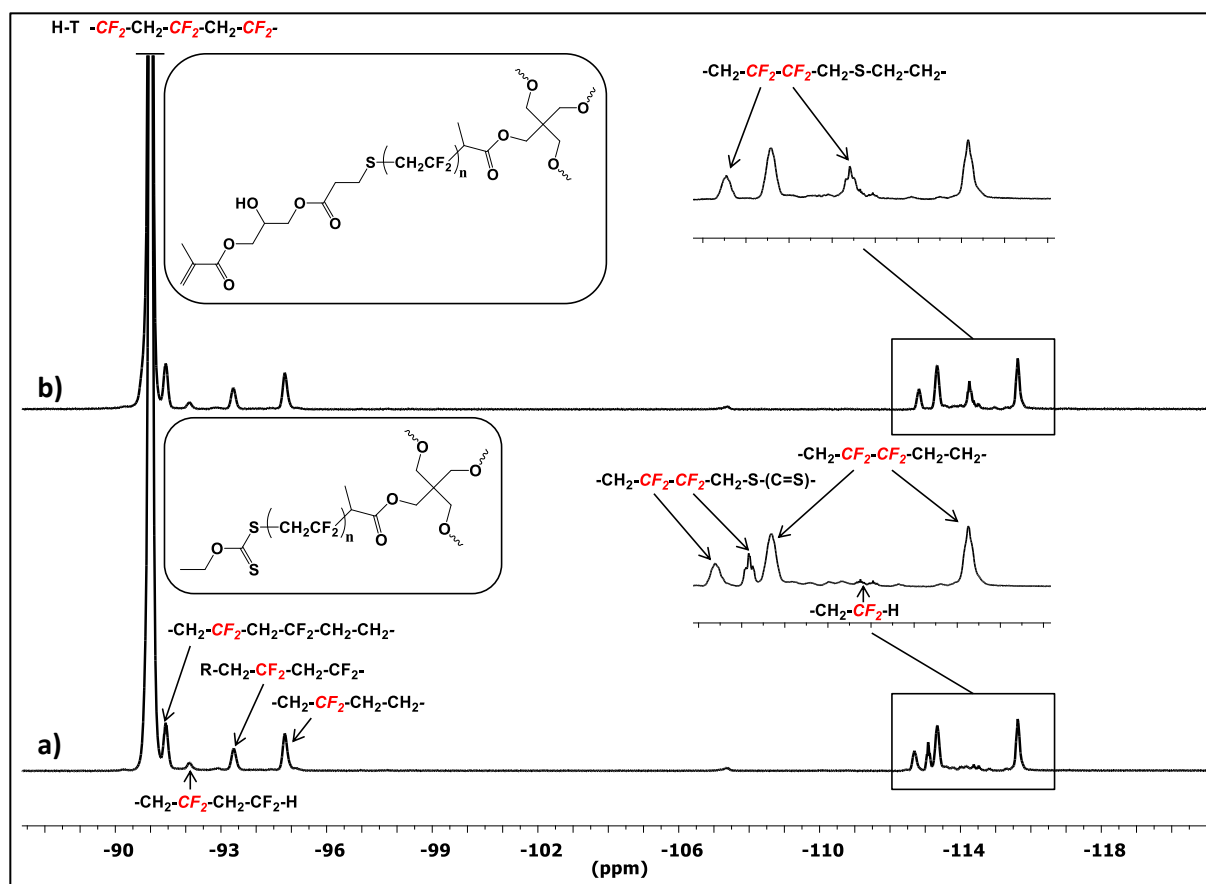


Figure S1. ^{19}F NMR spectra recorded in $(\text{CD}_3)_2\text{CO}$ for a) 4-arm star PVDF made by RAFT, and b) 4-arm star PVDF methacrylate prepared *via* one-pot aminolysis and thia-Michael addition.

Calculation of DP and M_n by ^1H NMR

$$(S1) \quad DP_{total} = \frac{\int_{2.70}^{3.19} \text{CH}_2 (\text{HT}) + \int_{2.28}^{2.43} \text{CH}_2 (\text{TT}) + \int_{4.37}^{4.52} \text{CH}_2 (\text{End - group})}{1/6 \times \int_{1.19}^{1.24} \text{CH}_3 (\text{R - CTA})}$$

$$(S2) \quad DP_{arm} = \frac{DP_{total}}{3.2}$$

$$(S3) \quad M_{nNMR} = M_{nCTA} + DP_{total} \times M_{nVDF}$$

with $M_{nVDF} = 64.04 \text{ g mol}^{-1}$ and $M_{nCTA} = 841.14 \text{ g mol}^{-1}$

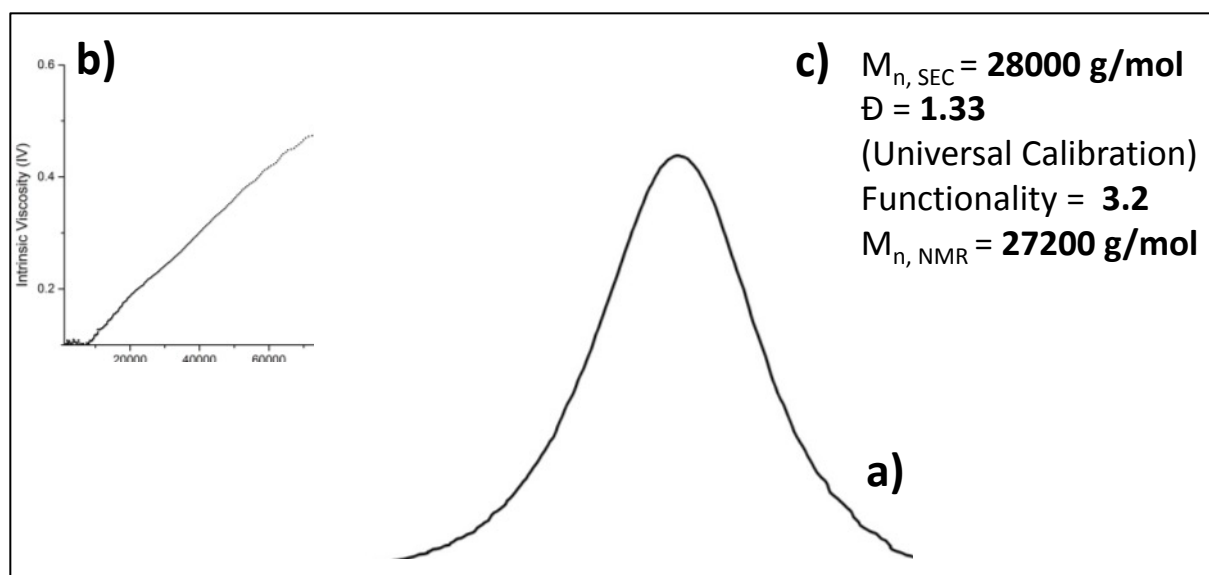


Figure S2. a) SEC trace for the 4-arm star PVDF methacrylate, b) evolution of the intrinsic viscosity, c) $M_{n, SEC}$, $M_{n, NMR}$ and PDI for the 4-arm star PVDF methacrylate.

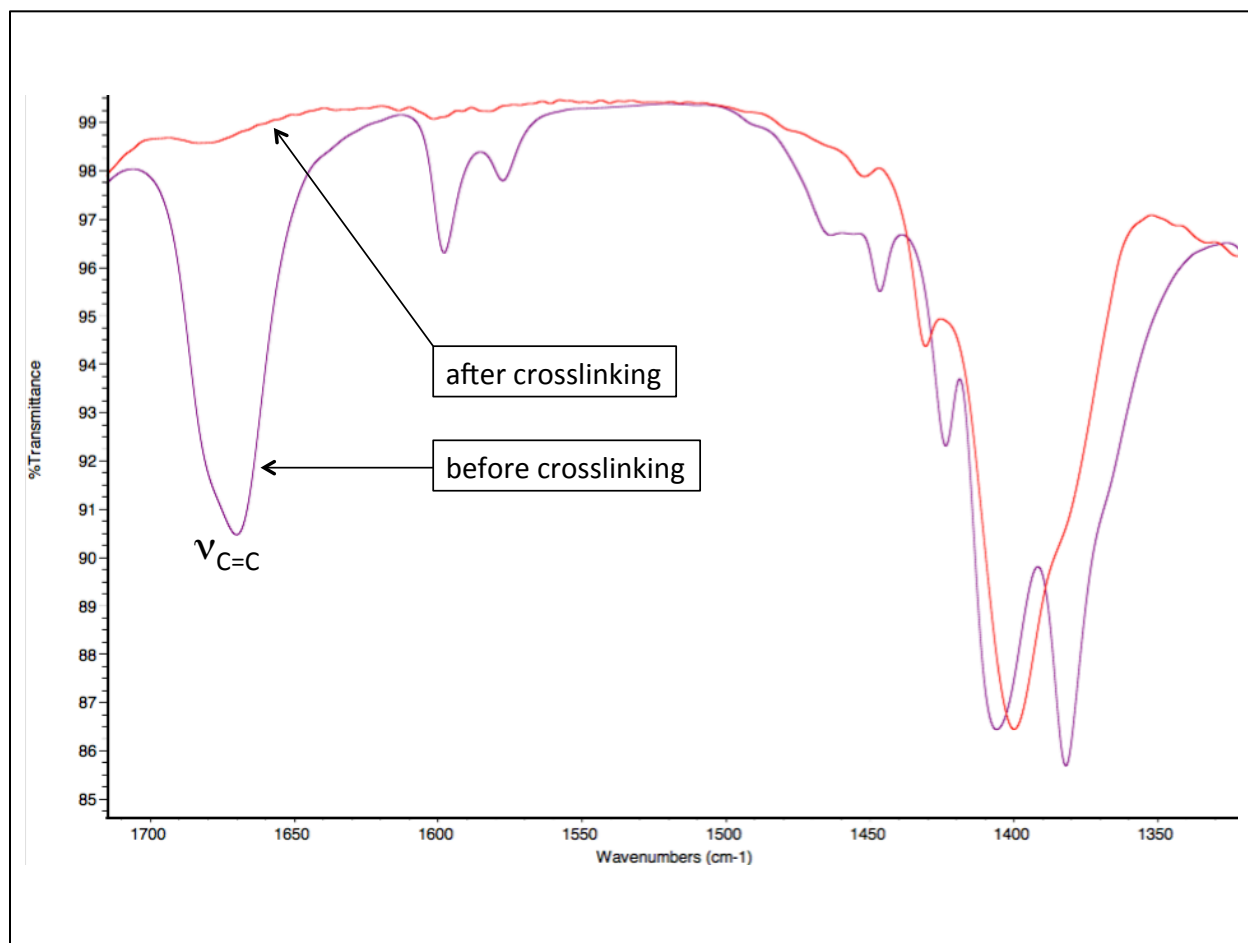


Figure S3. FTIR spectra of 4-arm star PVDF methacrylate-based coatings before and after photocrosslinking.

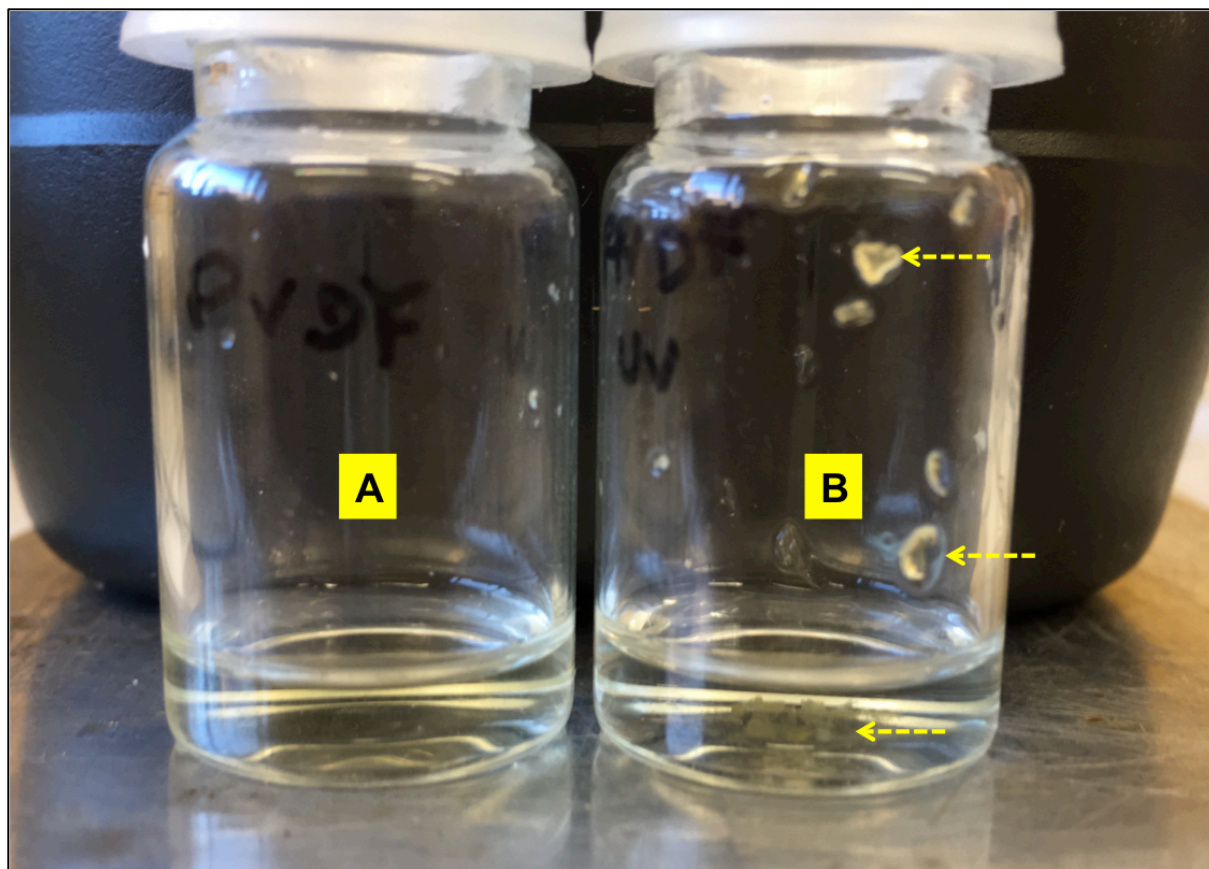
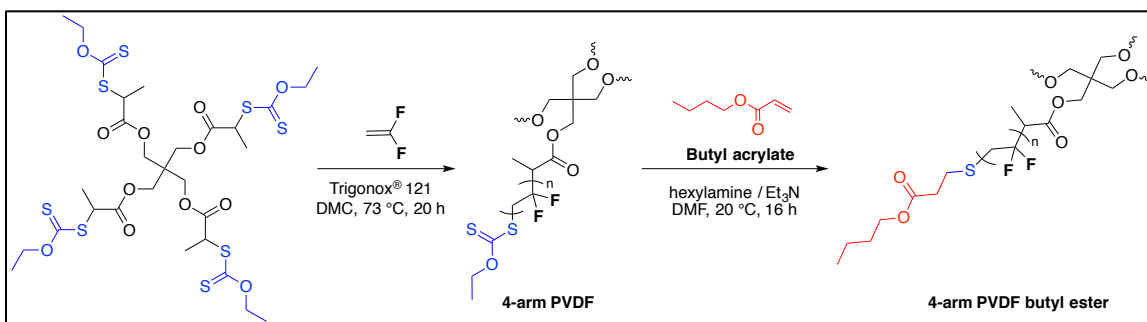


Figure S4. Pictures of a 4-arm star PVDF methacrylate coating immersed in MEK (**A**) before UV treatment, and (**B**) after UV-treatment. Yellow arrows shows the crosslinked polymer.



Scheme S1. Synthesis of butyl ester-functionalized 4-arm star PVDF

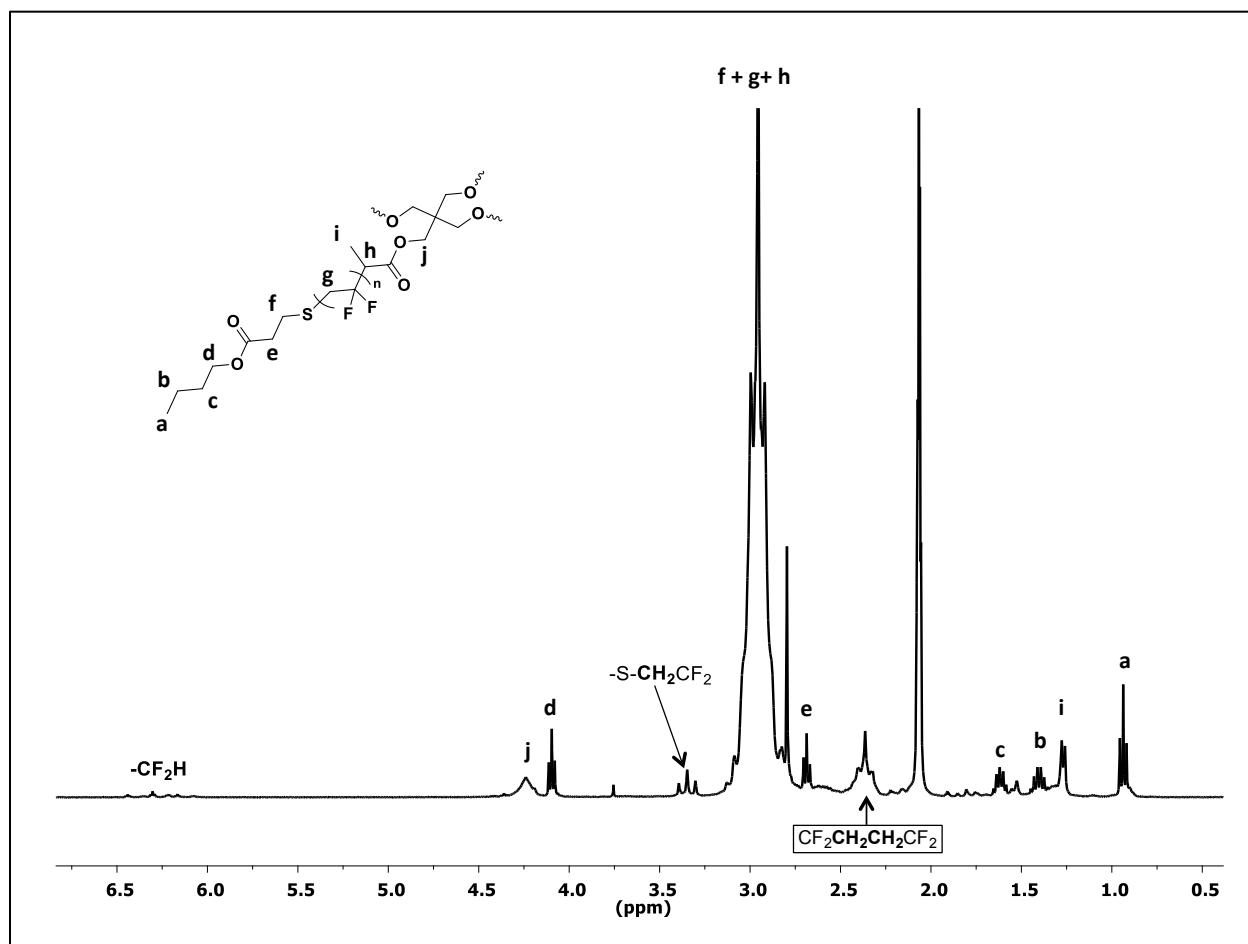


Figure S5. ¹H NMR spectra recorded in (CD₃)₂CO for the 4-arm star PVDF butyl ester.

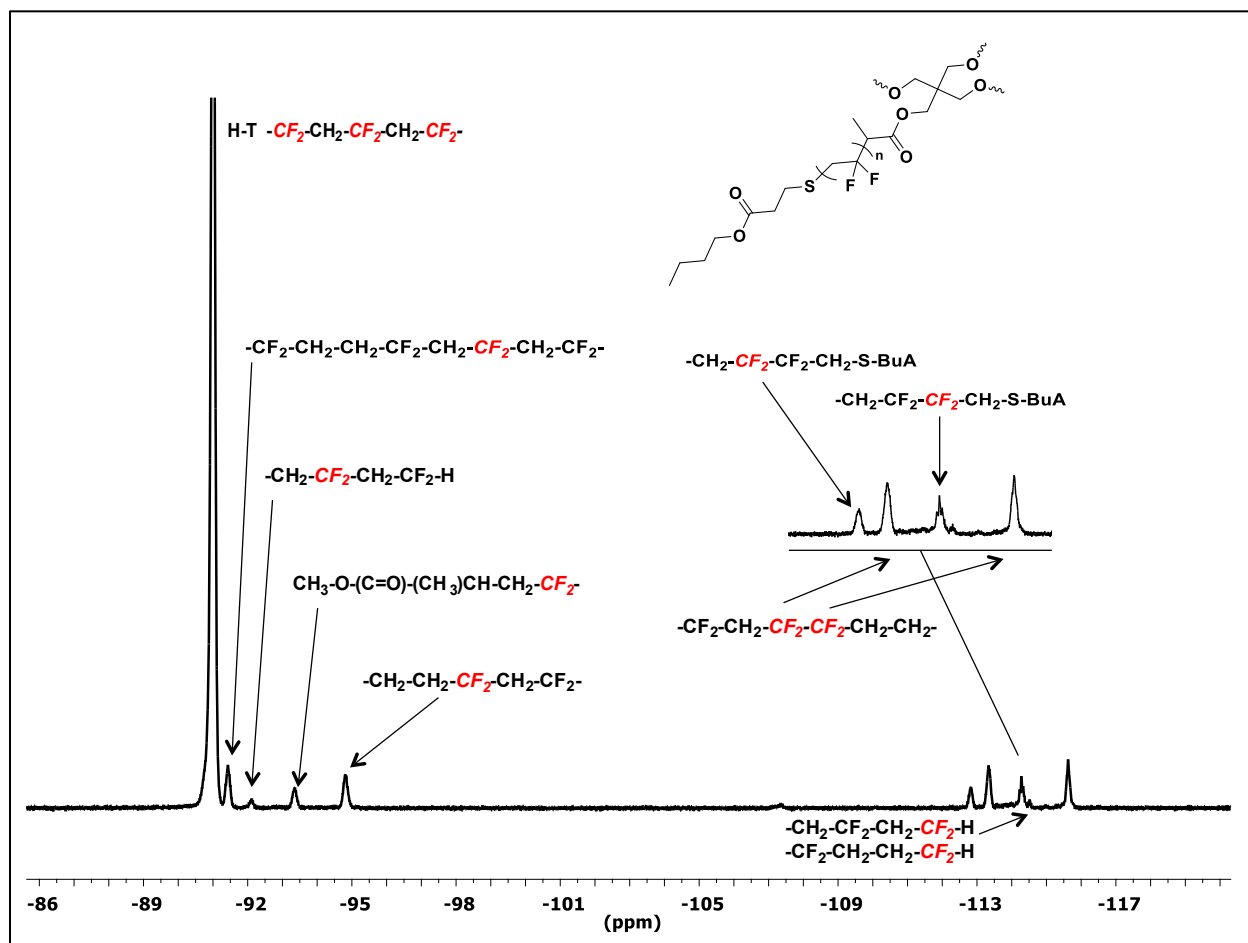


Figure S6. ^{19}F NMR spectra recorded in $(\text{CD}_3)_2\text{CO}$ for the 4-arm star PVDF butyl ester.

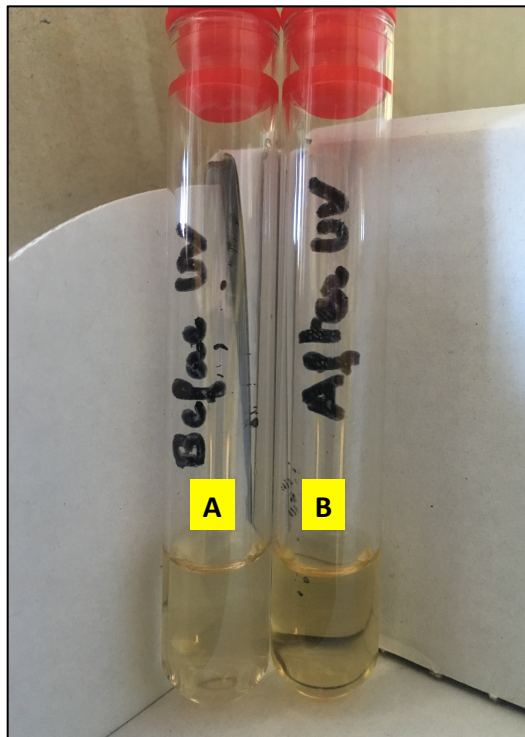


Figure S7. Pictures of a 4-arm star PVDF butyl ester coating immersed in MEK **(A)** before UV treatment, and **(B)** after UV-treatment.

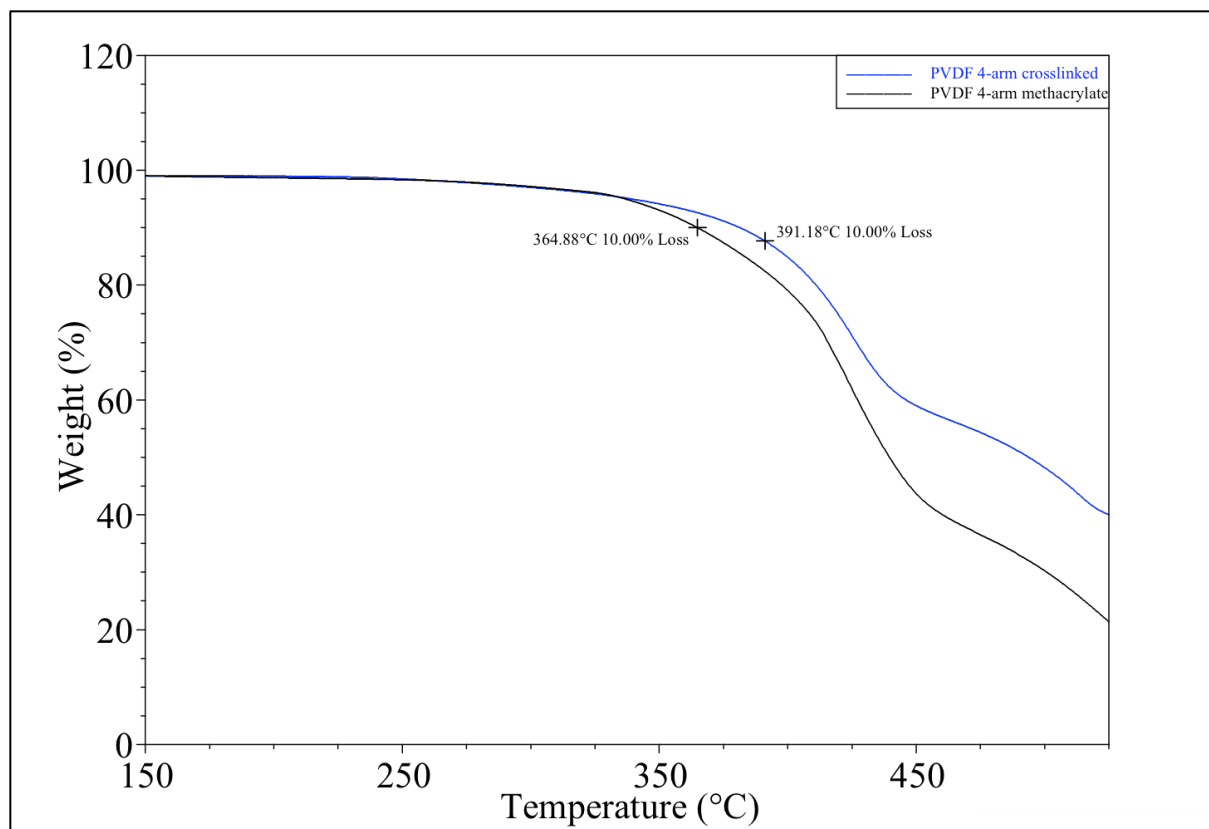


Figure S8. TGA thermograms under air for 4-arm star PVDF methacrylate before (black curve) and after (blue curve) crosslinking.

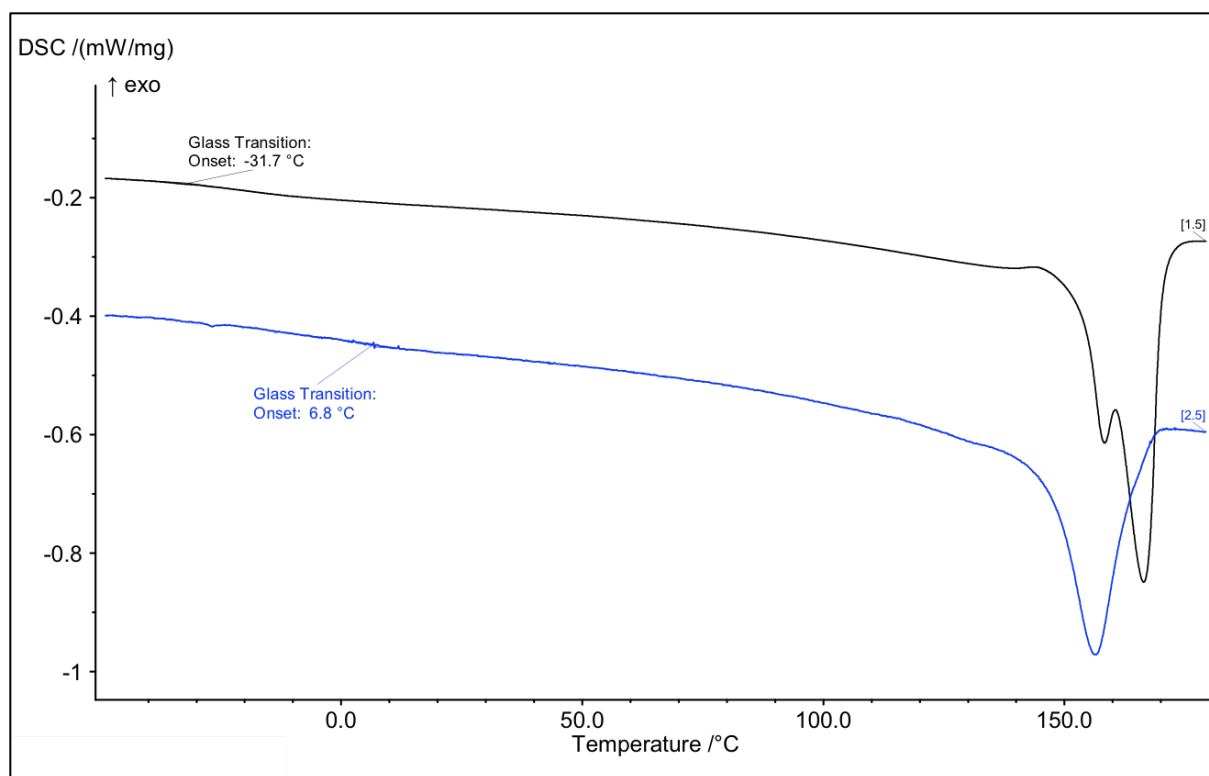


Figure S9. DSC thermograms for the 4-arm star PVDF methacrylate before (black curve) and after (blue curve) crosslinking.

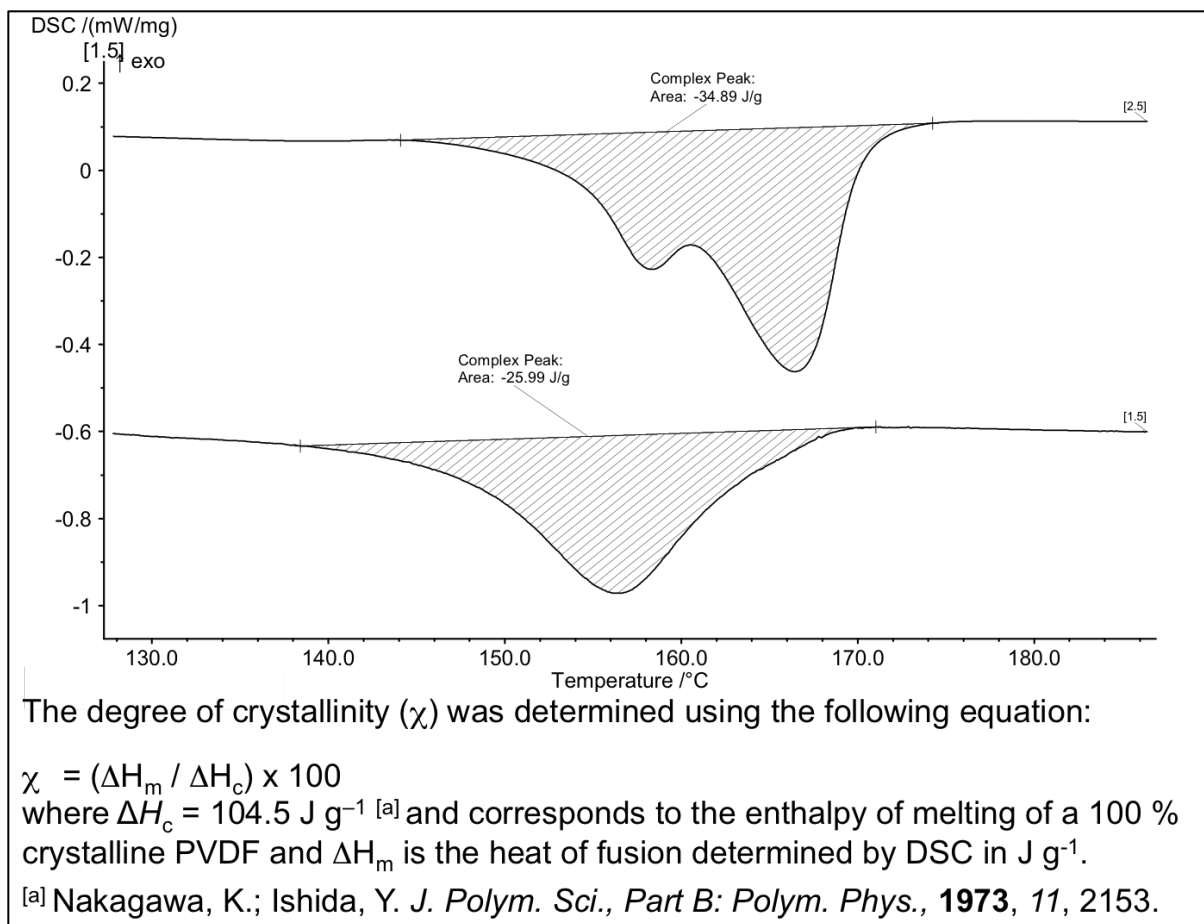


Figure S10. DSC thermograms for the 4-arm star PVDF methacrylate before (top) and after (bottom) crosslinking and equation for the determination of the degree of crystallinity.

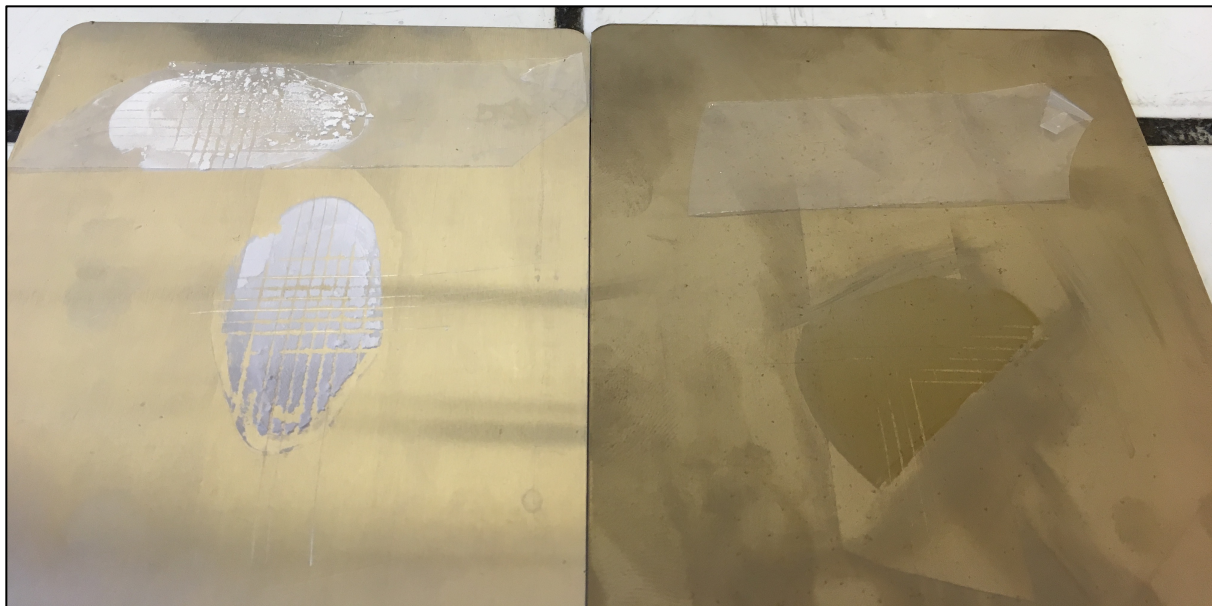


Figure S11. Adhesion properties characterized using the D3359 ASTM standard test method for (a) Solef[®] PVDF coating (left), and (b) photocrosslinked 4-arm star PVDF methacrylate coating (right).

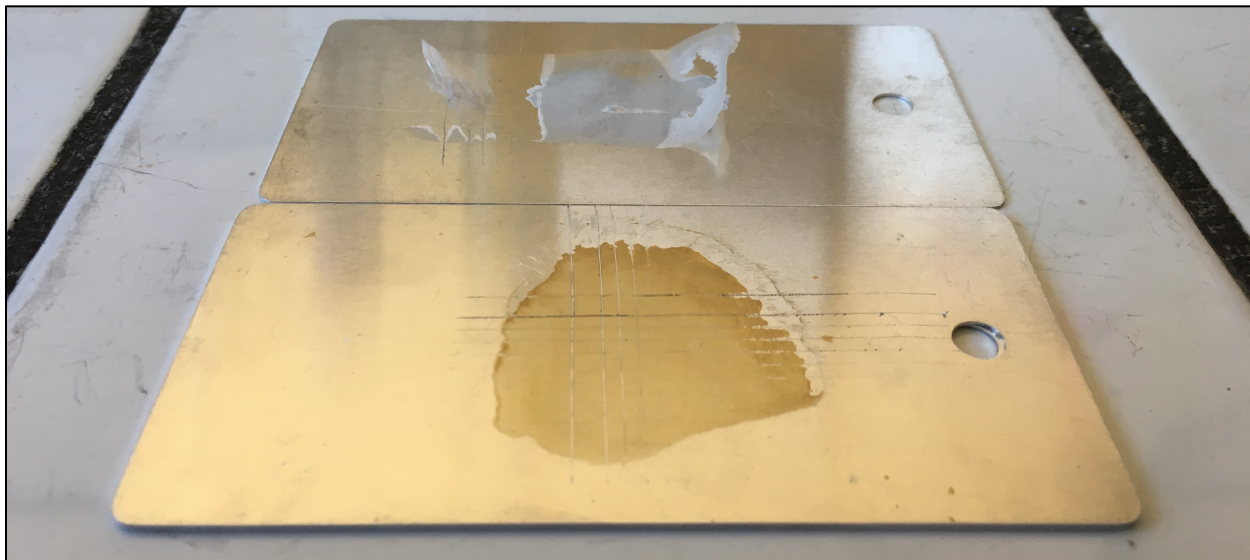


Figure S12. Adhesion properties characterized using the D3359 ASTM standard test method for (a) PVDF/PMMA 70/30 wt.% blend (up), and (b) photocrosslinked 4-arm star PVDF methacrylate coating (down).

References

- (1) Guerre, M. *et al. Macromolecules* **2015**, *48*, 7810–7822.
- (2) <http://www.agilent.com/cs/library/primers/public/5990-7196EN.pdf>, accessed: 02, 2017.
- (3) Bernard, J. *et al. Macromolecules*, **2005**, *38*, 5475–5484.
- (4) Guerre, M. *et al. Polym. Chem.*, **2016**, *7*, 441–450.