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Solid polymer electrolytes from a fluorinated copolymer bearing cyclic carbonate pendant groups

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NMR characterization of MAF-cyCB

The purified MAF-cyCB was characterized by ^{1}H and ^{19}F NMR spectroscopies. ^{1}H NMR spectrum (Fig. S1) of MAF-cyCB exhibits characteristic signals centred at 3.74, 4.54, 4.29, 4.96, 6.47, and 6.72 ppm assigned to $-O-CH_2-CH(O)-C\underline{H}_2-O-$, $-O-C\underline{H}_2-CH(O)-CH_2-O-$, $-O-CH_2-C\underline{H}(O)-CH_2-O-$ and $\underline{H}_2C=C(CF_3)(CO_2CH_2-$, respectively. The ^{19}F NMR spectrum (Figure S1) shows a singlet at -65.8 ppm, attributed to $-C\underline{F}_3$ group in MAF.

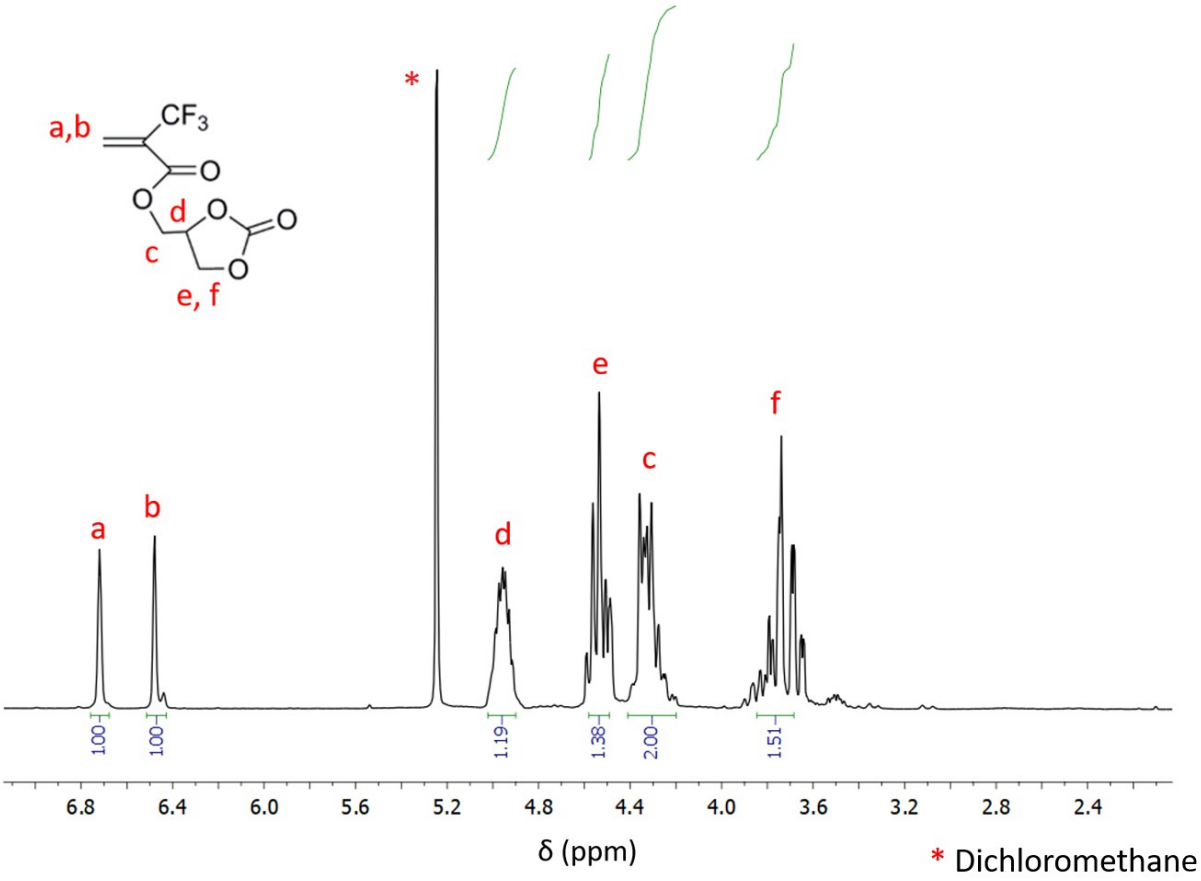

Fig. S1. ^{1}H NMR spectrum of MAF-cyCB recorded in $CDCl_3$ at 20 °C.

NMR characterization of poly(VDF-*co*-MAF-cyCB)

The ^{1}H NMR spectrum of the poly(VDF-*co*-MAF-cyCB) copolymer (Fig. S2) exhibits seven characteristic signals: (i) in 2.15-2.40 ppm range attributed to the reverse (tail-to-tail, T-T) addition of VDF repeat units (−$CF_2\underline{CH_2}$−$\underline{CH_2}CF_2$−), (ii) a small signal at 2.62 ppm assigned to the [−CH_2CF_2−$\underline{CH_2}C(CF_3)${$CO_2CH_2CH(O)CH_2O$}−]; (iii) a broad one ranging between 2.70 and 3.20 ppm corresponding to normal (head-to-tail, H-T) addition of VDF (−$C\underline{H_2}CF_2$−$C\underline{H_2}CF_2$−), (iv) at 3.73 ppm attributed to one of the two protons in −$CO_2CH_2CH(O)C\underline{H_2}O$ in the cyclic carbonate function, and (v) between 4.2 and 4.55 ppm characteristic of the −$CO_2C\underline{H_2}CH(O)CH_2O$; (vi) at around 4.6 ppm attributed to the second protons of −$CO_2CH_2CH(O)C\underline{H_2}O$ and (vii) at 5.07 ppm assigned to −$CO_2CH_2C\underline{H}(O)CH_2O$ in the cyclic carbonate function. A tiny triplet of triplets, centered at 6.3 ppm, corresponding to -CH_2CF_2-$\underline{H}$ end-group, suggested negligible back-biting or transfer to monomer, solvent, or to copolymer.

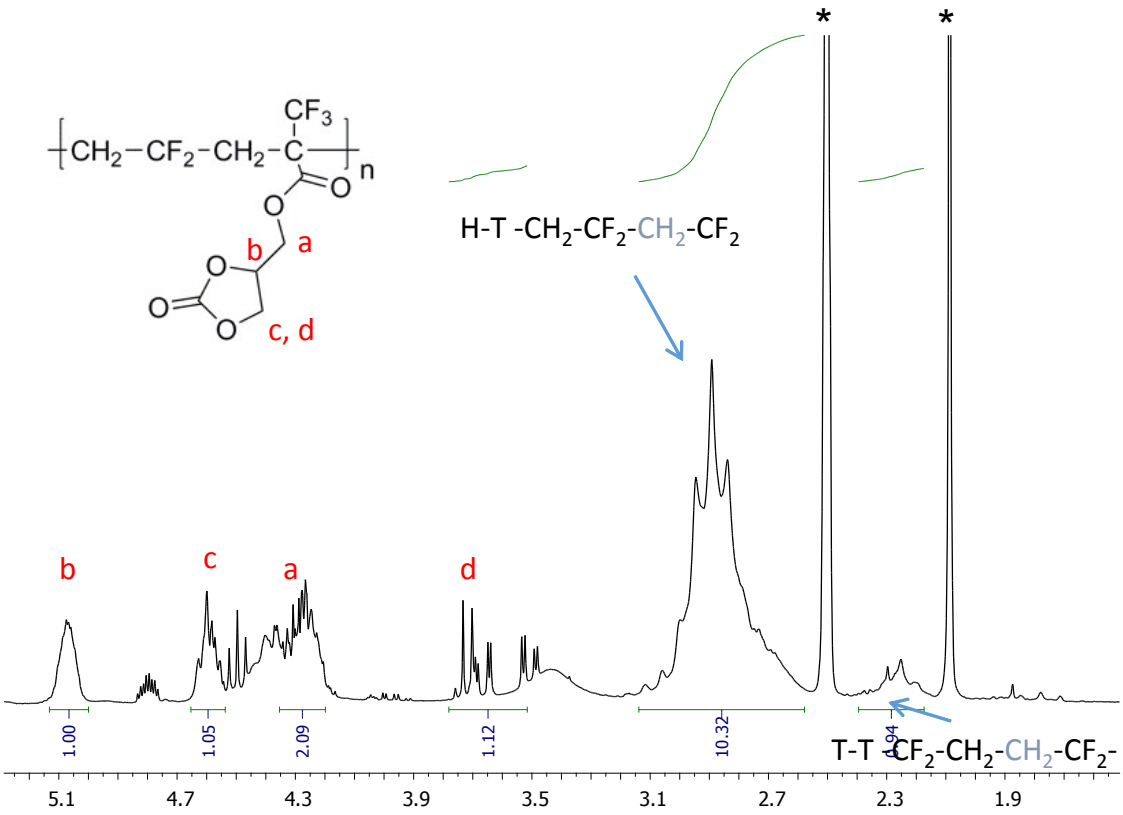

Fig. S2. ^{1}H NMR spectrum of poly(VDF-*co*-MAF-cyCB) copolymer prepared by free radical copolymerization of VDF and MAF-cyCB initiated by TAPE in DMC at 74 °C, recorded in DMSO-d_6 at 20 °C. (*) Solvent (DMSO) signals.

The ^{19}F NMR spectrum of the poly(VDF-*co*-MAF-cyCB) copolymer (Fig. S3) mainly exhibits the following characteristic signals: (i) a broad signal centered at −66 ppm assigned to $-CF_3$ in MAF-cyCB units in the copolymer; (ii) at −91.5 ppm attributed to the normal or Head-to-Tail (H-T) VDF-VDF dyads ($-CH_2\underline{CF_2}-CH_2\underline{CF_2}-$) of the PVDF chains; (iii) at −95 ppm corresponding to the fluorine atoms of the $-CF_2$ groups of VDF in VDF-MAF-cyCB alternating dyads, (iv) at −113.2 and −116.5 ppm assigned to the reverse or H-H VDF-VDF dyads ($-CH_2\underline{CF_2}-\underline{CF_2}CH_2-$), and (v) a doublet ($^2J_{FH}$ = 55 Hz) of triplets ($^3J_{FH}$ = 16 Hz) of triplets ($^4J_{FF}$ = 6 Hz) centered at -114.8 ppm as fingerprint of the $-CH_2\underline{CF_2}$-H chain-ends. The molar fractions of VDF base units in the copolymer were determined from equation (1).

$$mol\%\ VDF\ in\ copolymers = \frac{(\int_{-91}^{-96} CF_2 + \int_{-113}^{-118} CF_2)/2}{(\int_{-91}^{-96} CF_2 + \int_{-113}^{-118} CF_2)/2 + \int_{-66}^{-71} CF_3/3} \times 100 \quad (1)$$

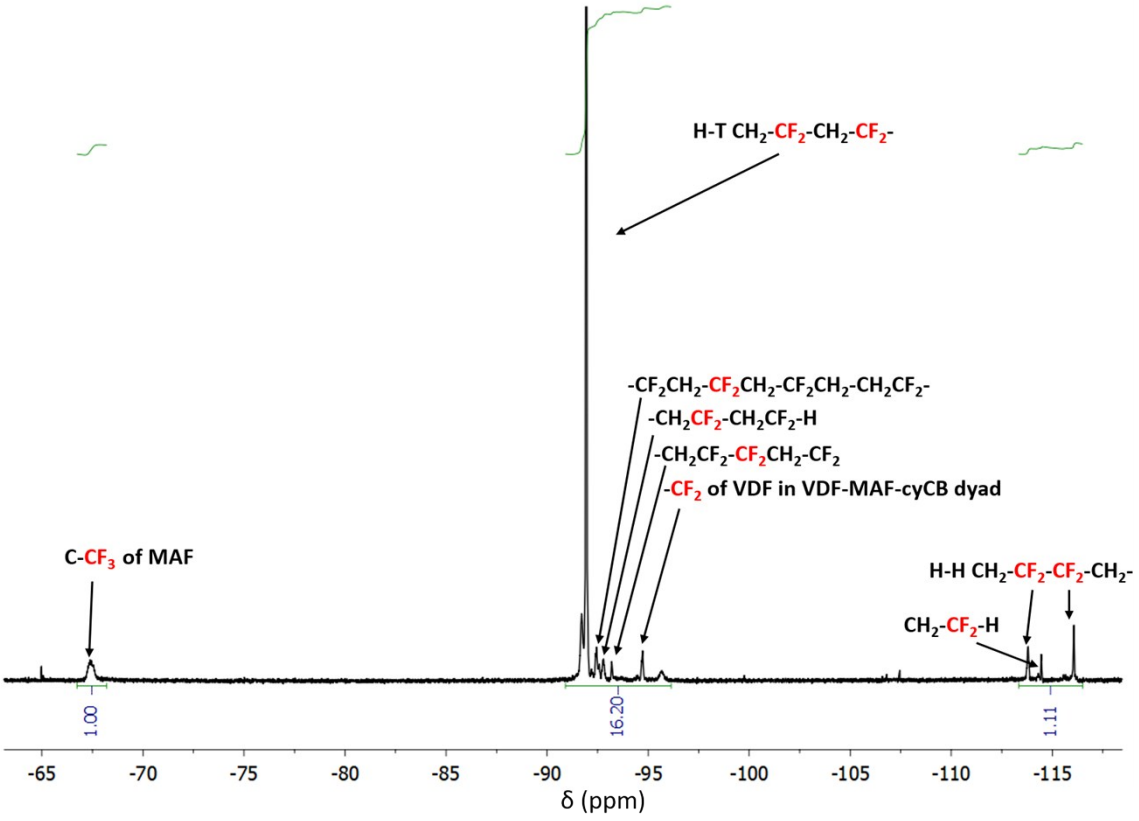

Fig. S3. ^{19}F NMR spectrum of poly(VDF-*co*-MAF-cyCB) copolymer prepared by free radical copolymerization of VDF and MAF-cyCB initiated by TAPE in dimethylcarbonate at 74 °C, recorded in DMSO-d_6 at 20 °C.

Differential Scanning Calorimetry measurements.

The degrees of crystallinity of the pure copolymer and of the SPEs were determined using equation 2:

$$Degree\ of\ crystallinity\ (\chi) = \frac{\Delta H_m}{\Delta H_c} \times 100 \qquad (2)$$

Where ΔH_c (104.6 J g^{-1}) corresponds to the melting enthalpy of 100% crystalline PVDF.[1,2]

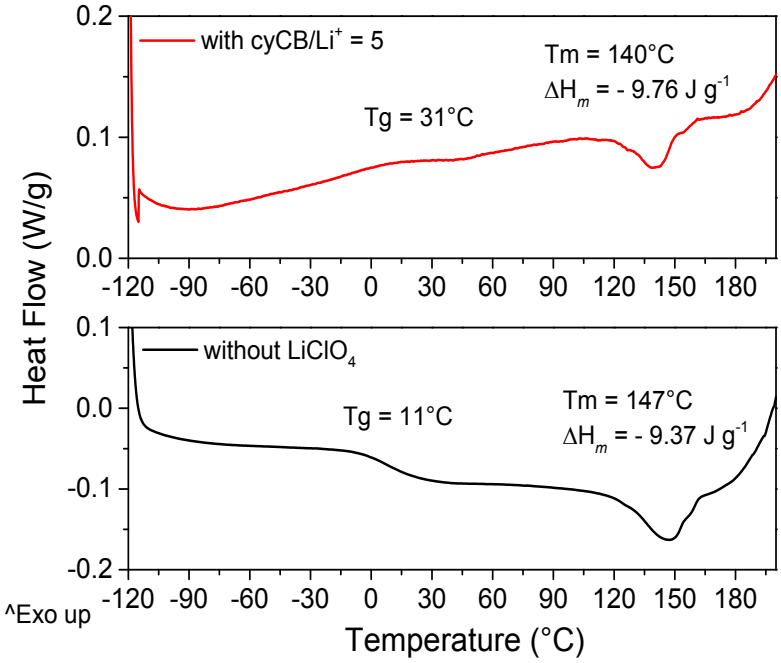

Fig. S4. DSC thermograms of poly(VDF-*co*-MAF-cyCB) with and without salt in the second heating cycle.

Morphology characterization.

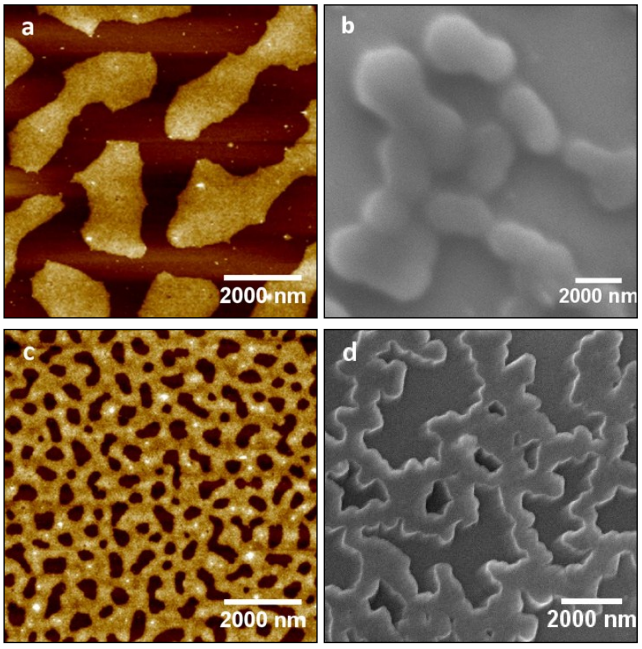

Fig. S5. AFM (height contrast) and SEM images of poly(VDF-*co*-MAF-cyCB) copolymer **(a-b)** without $LiClO_4$ and **(c-d)** with added $LiClO_4$ (cyCB/Li^+ = 5).

Oscillatory rheology measurements.

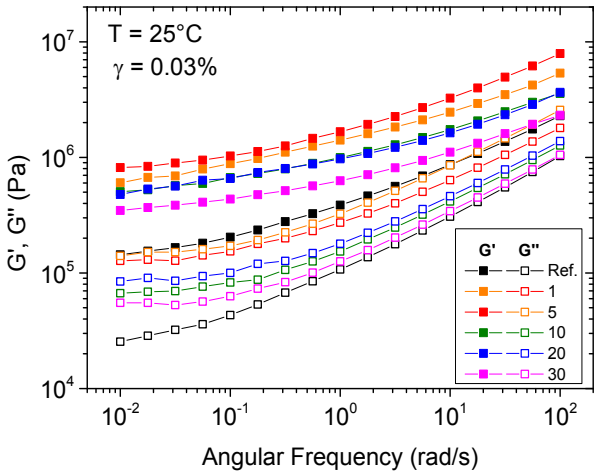

Fig. S6. Frequency sweeps displaying the influence of the salt concentration on the SPEs at T = 25 °C. The storage modulus G′ is represented by filled symbols and the loss modulus G″ by unfilled symbols. The reference black curves represent the poly(VDF-co-MAF-cyCB) copolymer without any $LiClO_4$ and the colored curves represent the polymer mixed with different salt amounts. The numbers indicated in the insert correspond to the cyCB/Li^+ ratio.

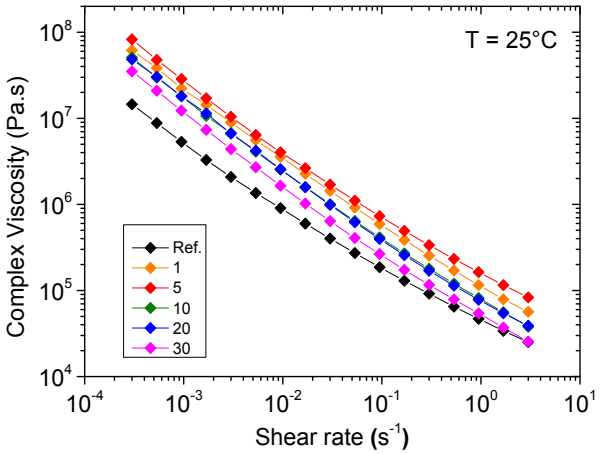

Fig. S7. Complex viscosity vs shear rate showing the influence of the added salt at T = 25 °C. The reference black curve represents the poly(VDF-*co*-MAF-cyCB) copolymer without any added salt and the colored curves represent this polymer mixed with different salt amounts. The numbers indicated in the insert correspond to the cyCB/Li^+ ratio.

Galvanostatic cycling test.

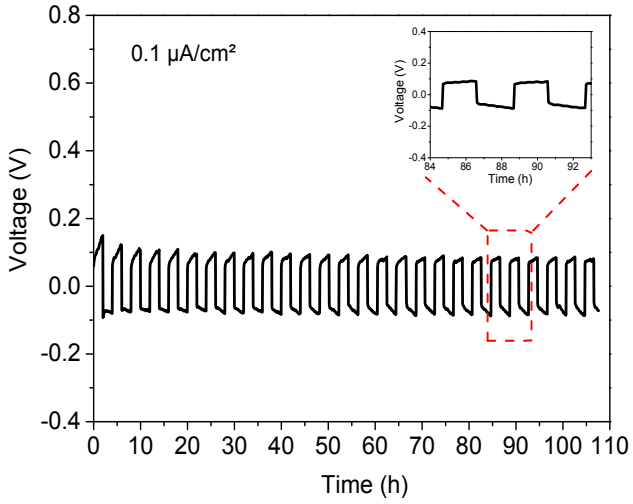

Fig. S8. Galvanostatic cycling curve of Li/SPE/Li symmetrical cell at 40°C and at current density of 0.1µA/cm² with charge/discharge cycle time of 4 hours. The inset shows 2 cycles of charge/discharge between 84 and 93 hours.

References

1. K. Nakagawa, Y. Ishida, *J. Polym. Sci.* 1973, **11**, 2153.
2. P. Maccone, G. Brinati, V. Arcella, *Polym. Eng. Sci.* 2000, **40**, 761.