Supplemental Information

Controlled Hydrogenation of P(VDF-*co*-CTFE) to Prepare

P(VDF-*co*-TrFE-*co*-CTFE) in the Presence of CuX(X=Cl, Br) Complexes

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Experimental section

Materials and synthesis procedure

P(VDF-co-CTFE) (31508) with 9 mol% CTFE (containing 2.6 mmol Cl atom) was purchased from Solvay Solexis. CuCl (99.99% from Sigma-Aldrich) and CuBr (99.999% from Sigma-Aldrich) were stored in N_2 atmosphere and used as received. All the other chemicals were commercial available and used as received.

Into a N_2 purged 250 mL three-necked glass bottle, 2 g P(VDF-co-CTFE), 60 mL N-methyl pyrrolidone (NMP), 2.6 mmol CuCl or CuBr, and 5.2 mmol 2,20-bipyridine (BPy) are introduced and heated at 120 ^{o}C for 12 h in an N_2 atmosphere. The reaction solution is precipitated in H_2O–CH_3OH (1 : 1 in volume) mixture with about 5 vol% concentrated hydrochloric acid to remove Cu species as $CuCl_2$. The resultant copolymer in light yellow is obtained via dissolving in acetone and precipitating in methanol for 3 times.

Characterization

^{1}H NMR (400 MHz) spectra were obtained using a Bruker (Advance II) 400M Hz spectrometer with tetramethylsilane as an internal standard. GPC analysis was

conducted with a Waters GPC 2410 in tetrahydrofuran (THF) using a calibration curve of polystyrene standards. The limiting viscosity of the copolymer was measured in DMAc at 25°C.

Results and discussion

When BPy is served as ligand, no obvious molecular weight improvement is observed in the resultant copolymer prepared at 110°C for 4h as shown in Figure S1, where the molecular weight of P(VDF-*co*-CTFE) and the resultant P(VDF-*co*-TrFE-*co*-CTFE) measured with GPC are compared. However, the molecular weight of the hydrogenated copolymer obtained at 120°C for 4h is slightly enhanced. Meanwhile, the limiting viscosity measured in DMAc of the resultant polymer hydrogenated at 120°C increases slowly against reaction time as shown in Figure S2. When the reaction temperature is improved to 140°C (Run 2 in Table 1), the crosslinked polymer gel with much lower TrFE content than expected is obtained although CTFE units have disappeared in the final product. All the experimental evidence strongly suggests the coupling reaction of macromolecular free radicals at high temperature.
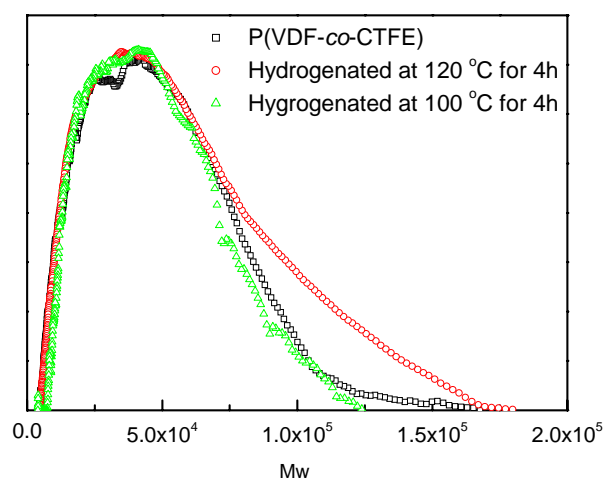

Figure S1. Molecular weight and distribution of P(VDF-co-CTFE) and P(VDF-co-TrFE-co-CTFE) prepared at 100°C and 120°C.
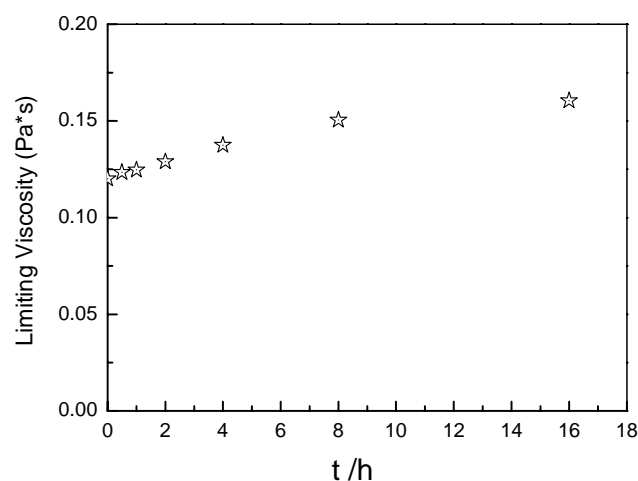
Figure S2. The limiting viscosity of P(VDF-co-TrFE-co-CTFE) prepared at 120°C as a function of reaction time.

It has been well known that the amine is originally utilized as the crosslinking agent of VDF containing fluoropolymer, where elimination reaction of F-H in fluoropolymer is catalyzed by amine followed by the addiction reaction of C=C formed[1]. In this case, PMEDTA, as a tertiary amine, may also catalyze the elimination reaction of Cl-H or F-H and leads to the crosslinking of the final product at high temperature. As a result, some of Cl atoms on polymer chain are eliminated instead of substituted by H as designed, which results in much lower TrFE content in the final product. The elimination reaction of Cl-H or F-H could be confirmed by the structure of -CF=CH- generated, which exhibits a multiple peak at 6.5ppm on ^{1}H NMR spectra as shown in Figure S3. Meanwhile, the poor solubility of the hydrogenated polymer with CuCl/PMEDTA indicates the molecular weight improvement of final product, which may also confirm the elimination and crosslinking reaction mechanism. However, no obvious elimination and crosslinking reactions are observed in the polymer hydrogenated with CuX/BPy complex. Therefore, the aromatic N containing ligands with less alkalinity are more desirable for the hydrogenation of Cl containing PVDF based fluoropolymer via ATRCT process in view of the elimination of Cl-H or F-H.
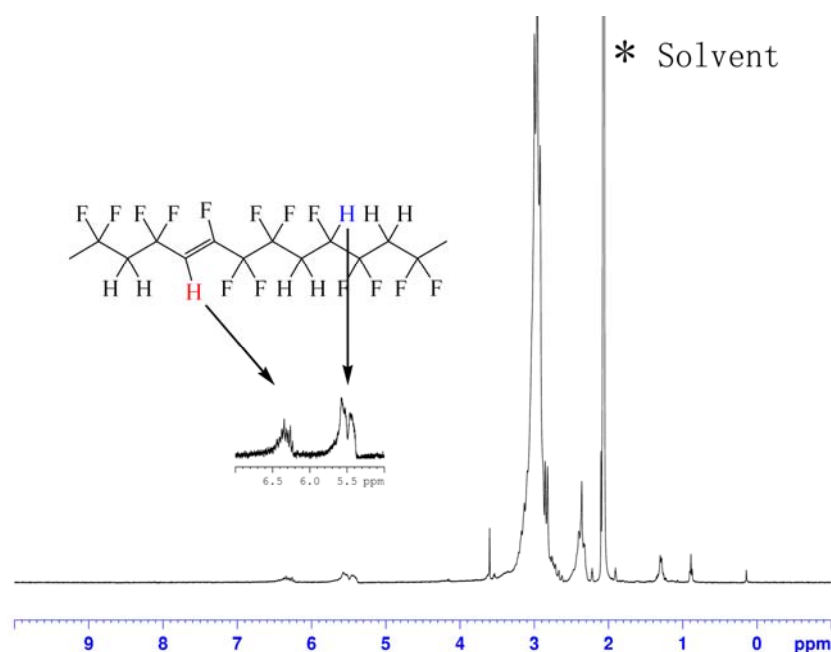
Figure S3. ^{1}H NMR spectra of P(VDF-*co*-TrFE-*co*-CTFE) prepared at 100°C with CuCl/PMEDTA complex. Reaction conditions: 2g polymer, 60mL NMP as solvent, CuCl/PMEDTA=2.6:5.2 mmol.

The structure of the solvents is rather close as shown in Scheme S1. C-H bond on –CHO group of DMF, C-H bond on -CO-CH$_3$ of DMAc and C-H bond on -N-CO-CH$_2$- of NMP are expected to be broken and donate H atom during the chain transfer reaction for their lower bond energy than the other C-H bonds. As a result, *C(O)-N(CH$_3$)$_2$, *CH$_2$-C(O)-N(CH$_3$)$_2$ and -N-CO-CH*- free radicals would be generated, respectively. According to the references, the bond energy of C-H on -C(O)-H of DMF and C-H on -CO-CH$_3$ of DMAc is about 350 kJ/mol and 380kJ/mol. The bond energy of C-H on -N-CO-CH$_2$- of NMP should be higher than that on DMAc (380kJ/mol) for the electron donating effect of -CH$_2$- group adjacent. Therefore, the broken priority of C-H bond in these solvents should be in the order of DMF>DMAc>NMP, and the chain transfer reaction priority of macromolecular radicals to these solvents should be in the same trend.

However, the free radicals generated from the solvent (S*) are still very active comparing to the Cu-Cl bond on CuCl$_2$/Lignads formed. Therefore, the chain transfer

reaction of S* to Cl of CuCl$_2$/Lignads may happen and S-Cl may be formed as shown in Scheme S1. According to the references[2], bond energy of Cl-C on Cl-C(O)- and Cl-CH$_2$-C(O)- is about 310kJ/mol and 302kJ/mol respectively, which is lower than that of Cl-C (about 330kJ/mol) on P(VDF-*co*-CTFE). Therefore, S-Cl formed may also involve the reduction reaction of CuCl/Ligands and establish a compete equilibrium (k_{act2}/k_{deact2}) as shown in Scheme S1. Meanwhile, the reaction activity between CuCl/Ligands and S-Cl is even higher than that between CuCl/Ligands and P(VDF-*co*-CTFE) for the lower bond energy of S-Cl. As a result, P(VDF-*co*-CTFE) could hardly be further hydrogenated even at rather low CTFE conversion. Meanwhile, the slightly higher CTFE conversion in DMF than that in DMAc may be attributed to the lower bond energy of Cl-CH$_2$-C(O)- formed in DMAc than that of Cl-C(O)- formed in DMF.
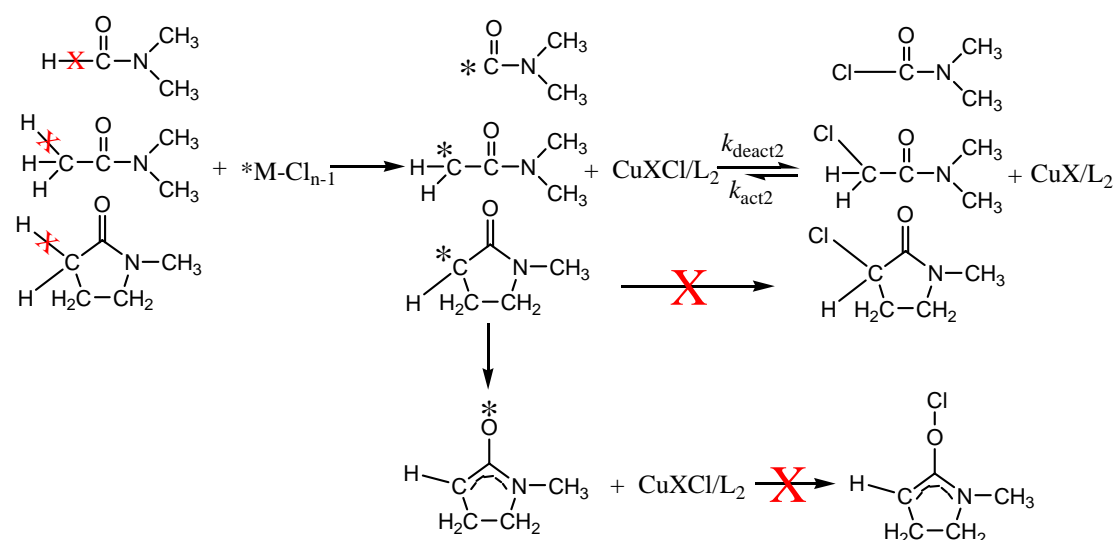
Scheme S1. Reaction route of S* with CuX/L$_2$.

In the case of NMP, two reasons may reduce the competition oxidation reaction of CuCl/Ligands with solvent-Cl and P(VDF-*co*-CTFE). Firstly, the free radicals generated in NMP are in a 5-membered ring which may stabilize the free radicals by structure rearrangement and reduce its reaction activity with CuCl$_2$/Ligands as shown in Scheme S1. As a result, NMP* stable radicals instead of NMP-Cl compounds would be preferred in the reaction system. Therefore, the competition reaction between S-Cl and P(VDF-*co*-CTFE) with CuCl/Ligands in NMP is less desirable than

that in DMF or DMAc. The other reason may be that the bond energy of NMP-Cl formed is higher than that of Cl-C on P(VDF-*co*-CTFE), which allows the reduction of CTFE units in P(VDF-*co*-CTFE) to be continued. However, the experimental evidence that the molar ratio of TrFE obtained to CuCl input is always lower than 1:1 strongly suggests that the oxidized Cu species (CuCl$_2$/Ligands) could not be regenerated via the reaction between CuCl$_2$/Ligands and NMP*. Therefore, stable NMP* free radicals mechanism is preferred to address the much higher CTFE conversion in NMP than that in DMF and DMAc.

References

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(2) Yuran Luo. Comprehensive Handbook of Chemical Bond Energies. Science press in China. Beijing, **2005**.