Methods to prepare Quaternary Ammonium Groups-Containing Alternating Poly(chlorotrifluoroethylene-*alt*-vinyl ether) Copolymers

Guillaume Couture, Vincent Ladmiral, Bruno Améduri*

Institut Charles Gerhardt Montpellier, UMR 5253 CNRS-UM2-ENSCM-UM1 Ingénierie et Architectures Macromoléculaires (IAM) 8, rue de l'école normale, Montpellier , 34296 cedex 5, France.

Corresponding author: Tel. +33 (0)4 67 14 43 68; fax: +33 (0)4 67 14 72 20

Supplementary information



Figure S1. ¹H NMR spectrum of vinyloxy-3-dimethylamino-2,2-dimethylpropane recorded in acetone d6. Red arrows indicate traces of alcohol precursor. The crossed-out signal is assigned to acetone



Figure S2. DEPT-135 ¹³C NMR spectrum of vinyloxy-3-dimethylamino-2,2-dimethylpropane recorded in acetone d6. The crossed-out signals are assigned to acetone.



Figure S3. FTIR transmittance spectrum of poly(CTFE-*alt*-2MeNEV) copolymer.

Structure and compositions of copolymers.

Elemental composition for each product was first calculated using the following equation (1):

$$\%_m X = \frac{\left(N_{X, CTFE} + N_{X, EV}\right) \times M_X}{M_{CTFE} + M_{EV}} \tag{1}$$

Where $\%_m X$, $N_{X,CTFE}$, $N_{X,EV}$, M_X , M_{CTFE} and M_{EV} represent the mass percentage of element X in the product, the number of atoms of element X in CTFE, the number of atoms of element X in the vinyl ether, the molar mass of element X, the molar mass of CTFE and the molar mass of the vinyl ether, respectively. This calculation provides an accurate value for copolymer with relatively high molar molecular weight, as it does not take into account the chain end-groups. These theoretical values were then compared with the results obtained from elemental analysis (C, F and heteroatoms present in the vinyl ethers). The results are presented in Table S1 and allow calculating the amount of each monomer in the copolymer thanks to equations (2) and (3):

$$\frac{\%_m F}{\%_m C} = \frac{M_F}{M_C 2 \times \%_n CTFE} + N_{C,EV} \times \%_n EV$$
(2)
$$\%_n CTFE + \%_n EV = 1$$
(3)

Where $%_n Y$ (Y = CTFE, EV) stands for the molar percentage of monomer Y in the copolymer. The equations can also be written as follows:

$$\frac{\%_m FM_C}{\%_m CM_F} = B \Rightarrow (2B - 3)\%_n CTFE + B \times N_{C,EV} \times \%_n EV = 0$$
⁽⁴⁾

$$\%_n CTFE + \%_n EV = 1 \tag{5}$$

EV	% _m C		% _m N		% _m F		% _m Cl	
	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.
CEVE	32.3	32.8	/	/	25.6	24.6	31.8	30.7
2MeNEV	48.2	42.5	5.1	3.8	20.8	26.3	13.0	16.3
	48.2	44.8	5.1	4.1	20.8	25.0	13.0	15.3
GcEV	38.9	37.1	/	/	26.3	26.3	16.4	17.2
CCEV	32.2	31.9	/	/	21.9	28.0	13.6	18.7

Table S1. Elemental analysis results for poly(CTFE-alt-VE) copolymers.

Nucleophilic substitution on benzyl chloride :

Tert-butoxide (1.96 g, 17.40 mmol) was introduced into a round bottom flask along with 20 mL of THF. 3-(Dimethylamino)-2,2-dimethylpropan-1-ol (2.18 g, 16.60 mmol) was then added dropwise to the solution over the course of 2 hr. The mixture was then added dropwise to a THF solution of benzyl chloride (2.00 g, 15.80 mmol,) at 0 °C. The reaction mixture was stirred at 0 °C for 12 hr. The solvent was removed under reduced pressure and the resulting residue was characterized by ¹H NMR.



Figure S4. Functionalisation of benzyl chloride by nucleophiplic substitution using potassium 3-(dimethylamino)-2,2-dimethylpropan-1-olate.



Figure S5. ¹H NMR spectra in acetone d6 of 3-dimethylamino-2,2-dimethylpropan-1-ol (bottom), of benzyl chloride (middle), and of the nucleophilic substitution product (top). The crossed-out signals are assigned to acetone

$$\% Conversion = \frac{\int_{4,5}^{0} (-CH_2O - 1)}{\int_{4,5}^{0} (-CH_2O - 1) + \int_{4,7}^{0} (-CH_2Cl)}$$

Equation used for the calculation of the conversion of the nucleophilic substitution of benzyl chloride.



Figure S6. 2D (COSY ¹H-¹H) NMR spectrum of poly(CTFE-*alt*-CkEVE) copolymer in acetone d6.

% Conversion =
$$\frac{2 * \int_{7,4}^{7,9} CH_{triazole}}{\int_{3,9}^{4,4} OCH_2}$$



Equations used to calculate the conversion of the thermal Huisgen cycloaddition and the proportion of isomers obtained.



Figure S7. ¹H NMR spectrum of poly(CTFE-*alt*-CkN⁺EVE) copolymer (recorded in D₂O). The crossed-out signal is assigned to D₂O.