2D-NMR Characterization of Sequence Distributions in the Backbone of Poly(vinylidene fluoride-*co*-tetrafluoroethylene)

Supporting Material

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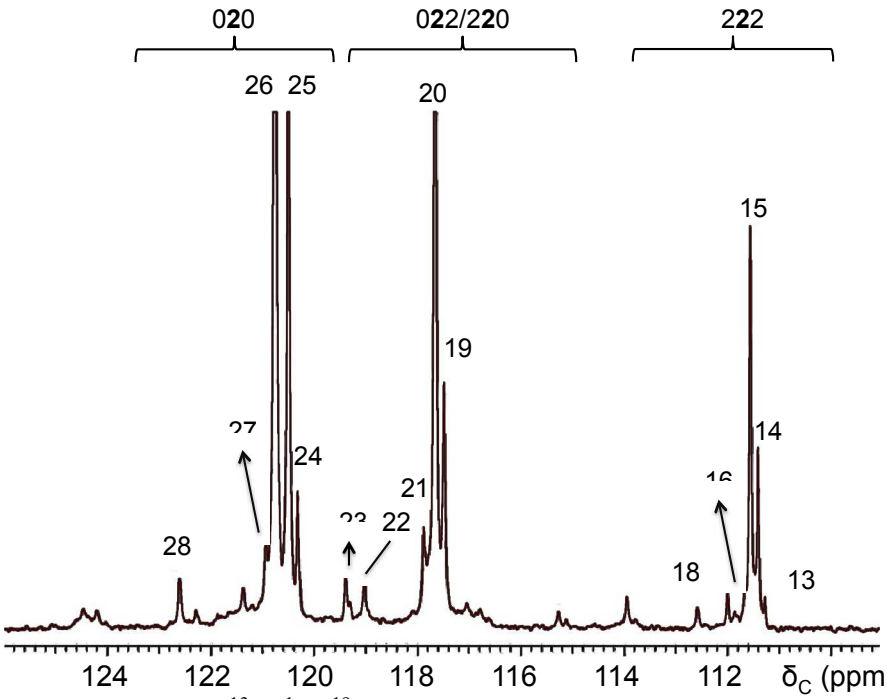
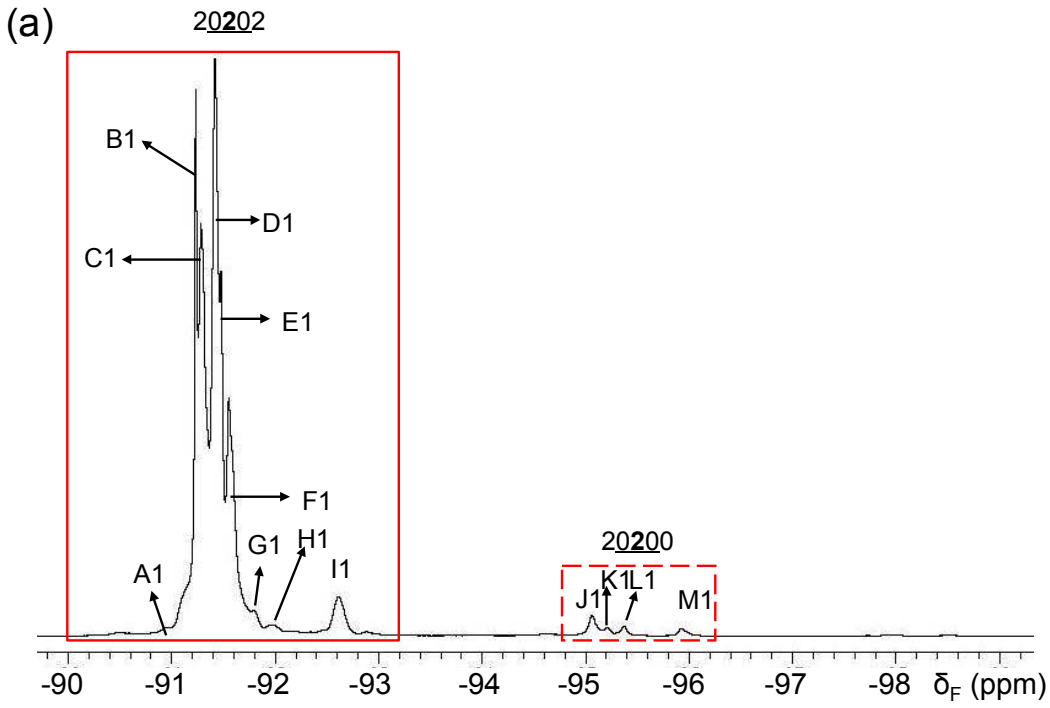
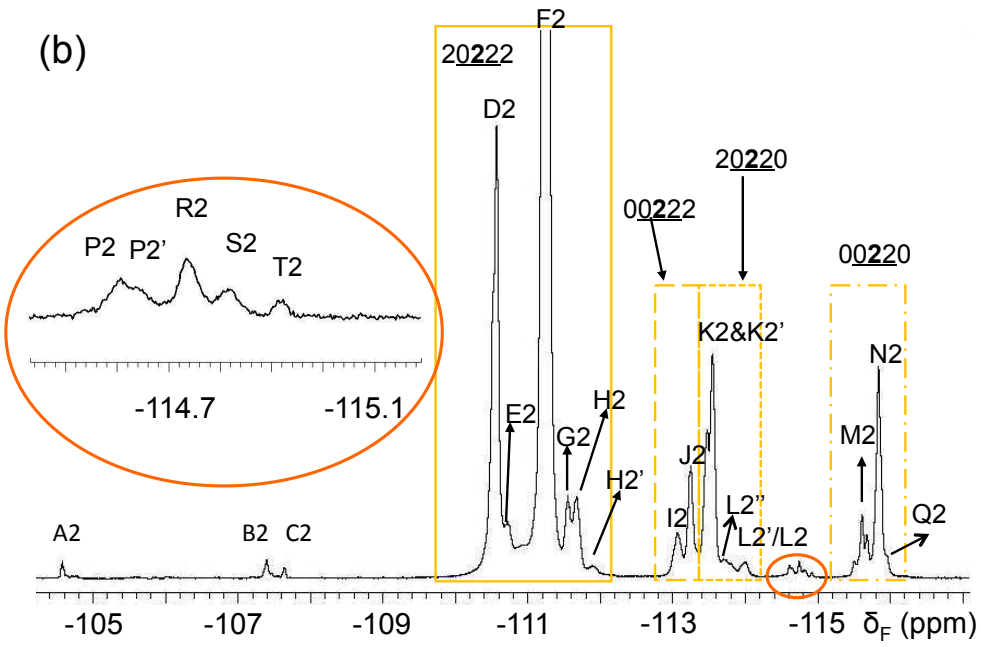


Figure S1. 125 MHz $^{13}C\{^{1}H, ^{19}F\}$ NMR spectrum of poly(VDF-*co*-TFE) (84:16 mole%).


(a)
20202
B1
D1
C1
E1
F1
G1
H1
I1
A1
20200
K1
L1
J1
M1
-90
-91
-92
-93
-94
-95
-96
-97
-98
δF (ppm)


(b)
F2
20222
D2
20220
00222
00220
R2
P2
P2'
S2
T2
-114.7
-115.1
K2&K2'
N2
E2
G2
H2
J2'
M2
H2'
I2
L2"
L2'/L2
Q2
A2
B2
C2
-105
-107
-109
-111
-113
-115
δF (ppm)

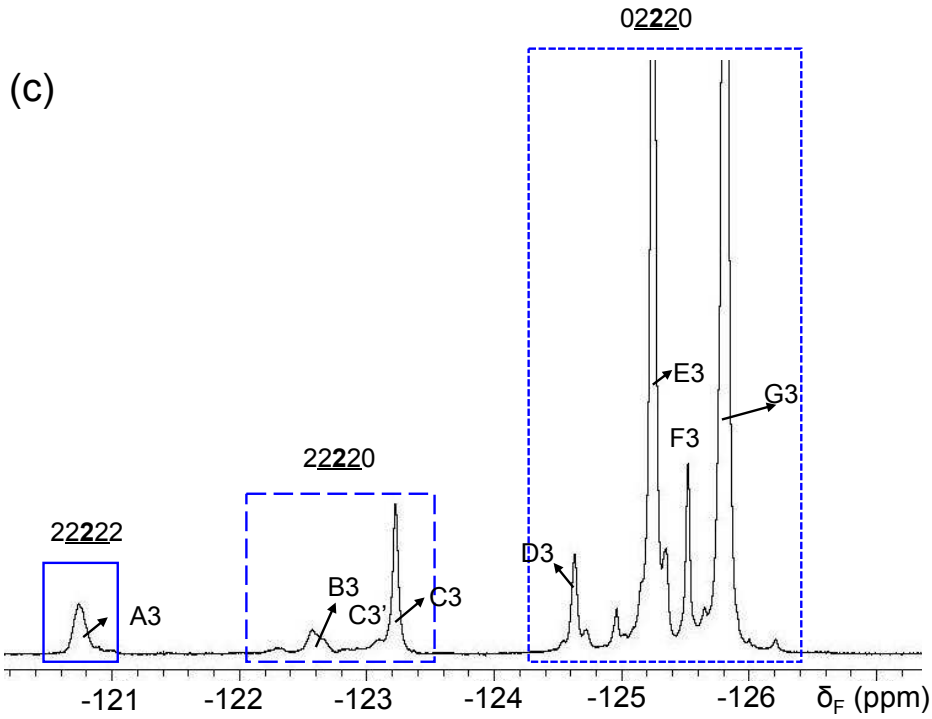


Figure S2. Expansions from 470 MHz $^{19}F\{^{1}H\}$ NMR spectra of poly(VDF-*co*-TFE) (84:16 mole%). (a) region 1 from 0**2**0 sequences, (b) region 2 from 0**2**2/2**2**0 sequences and (c) region 3 from 2**2**2 sequences.

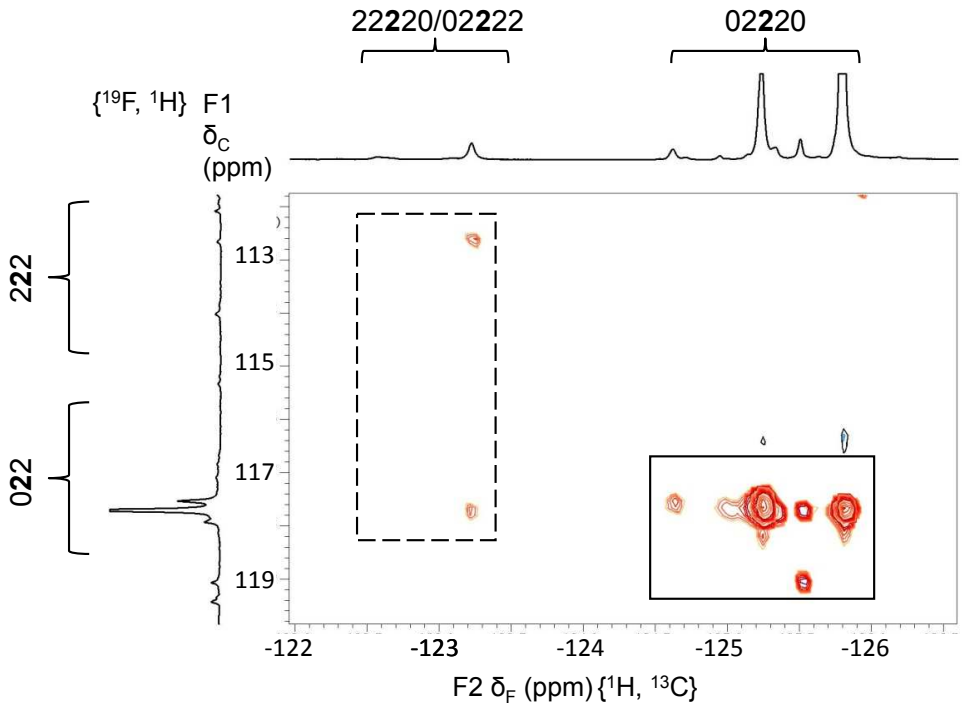


Figure S3. Selected region of two bond ^{19}F-^{13}C gHSQC NMR spectrum of poly(VDF-*co*-TFE) (84:16 mole%).

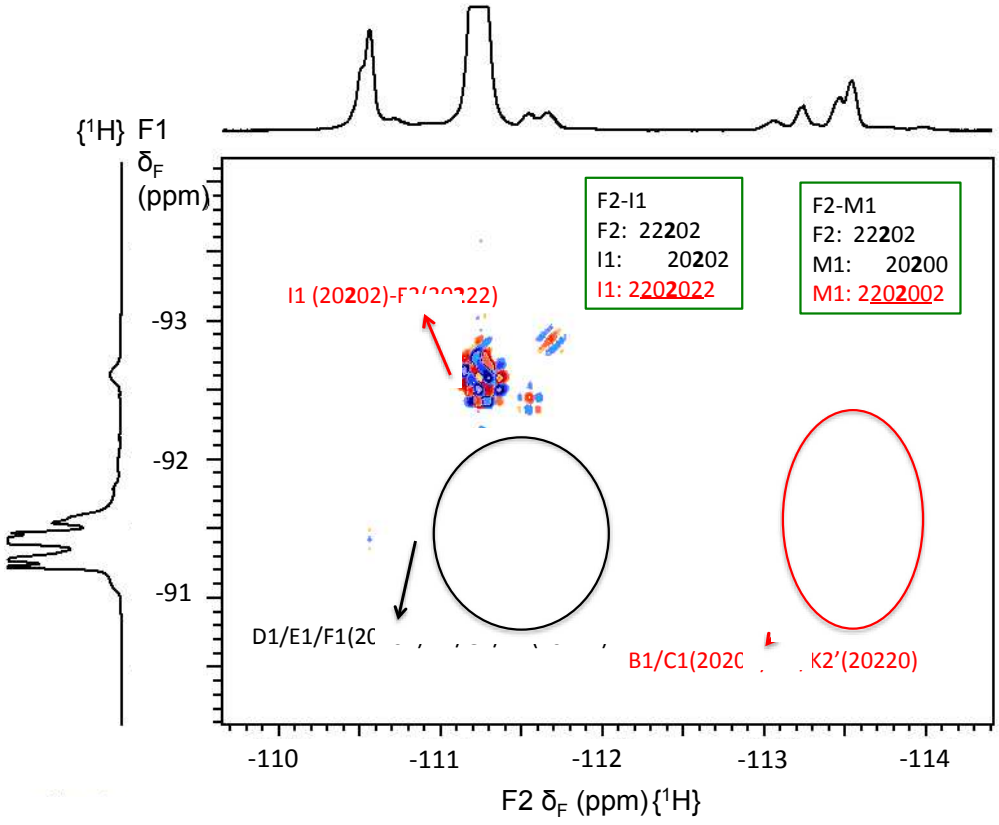


Figure S4: Selected region of ^{19}F-^{19}F gdqCOSY spectrum of poly(VDF-*co*-TFE) (84:16 mole%).

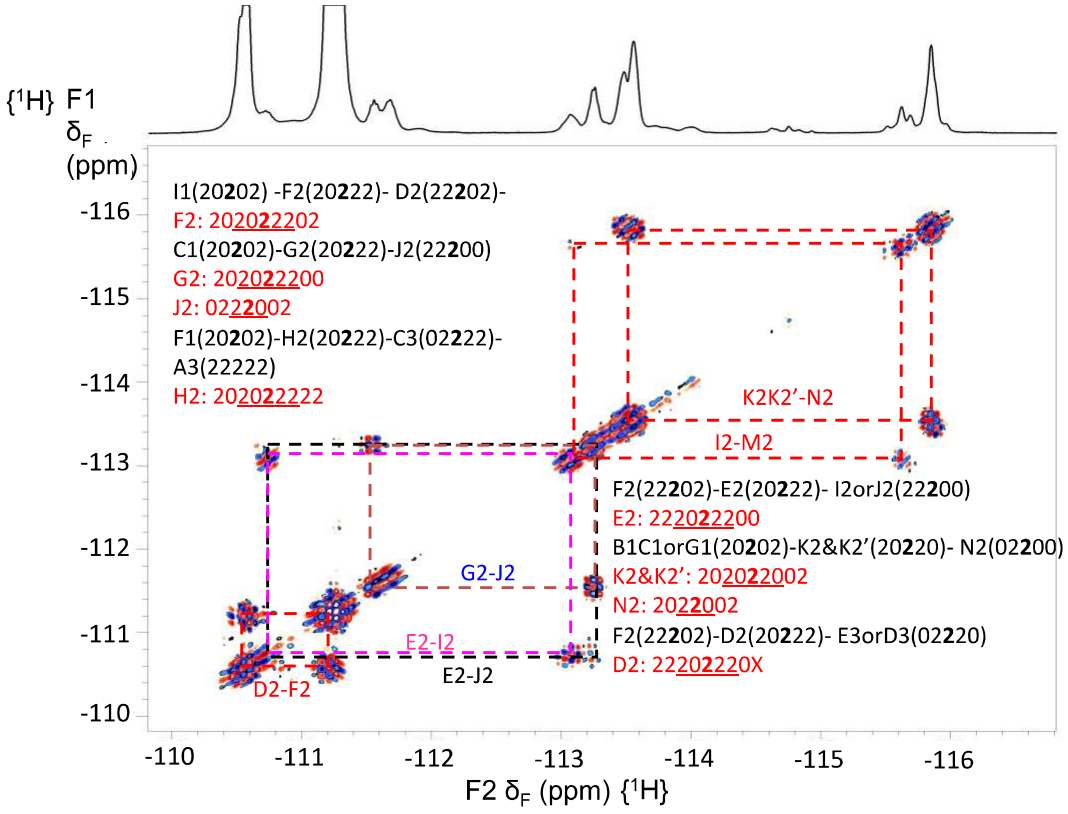


Figure S5. Selected region of ^{19}F-^{19}F gdqCOSY spectrum of poly(VDF-*co*-TFE) (84:16 mole%).

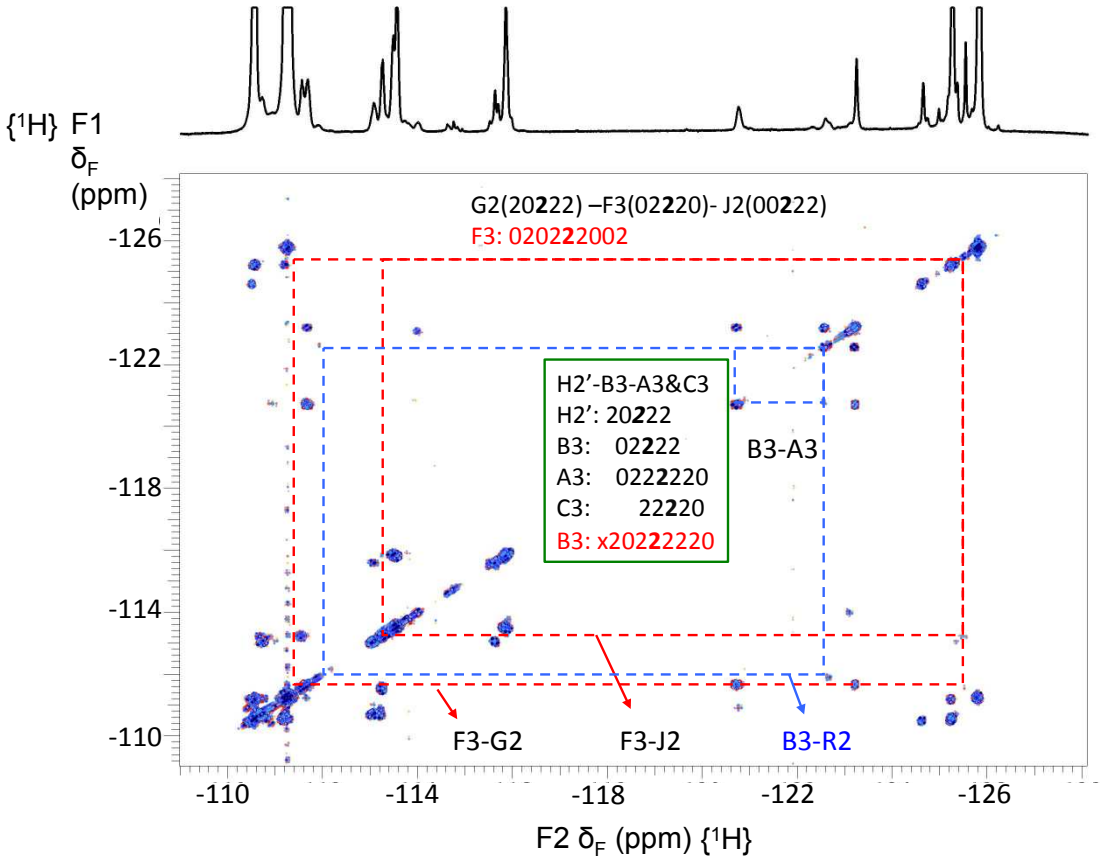


Figure S6. Selected region of ^{19}F-^{19}F gdqCOSY spectrum of poly(VDF-*co*-TFE) (84:16 mole%).

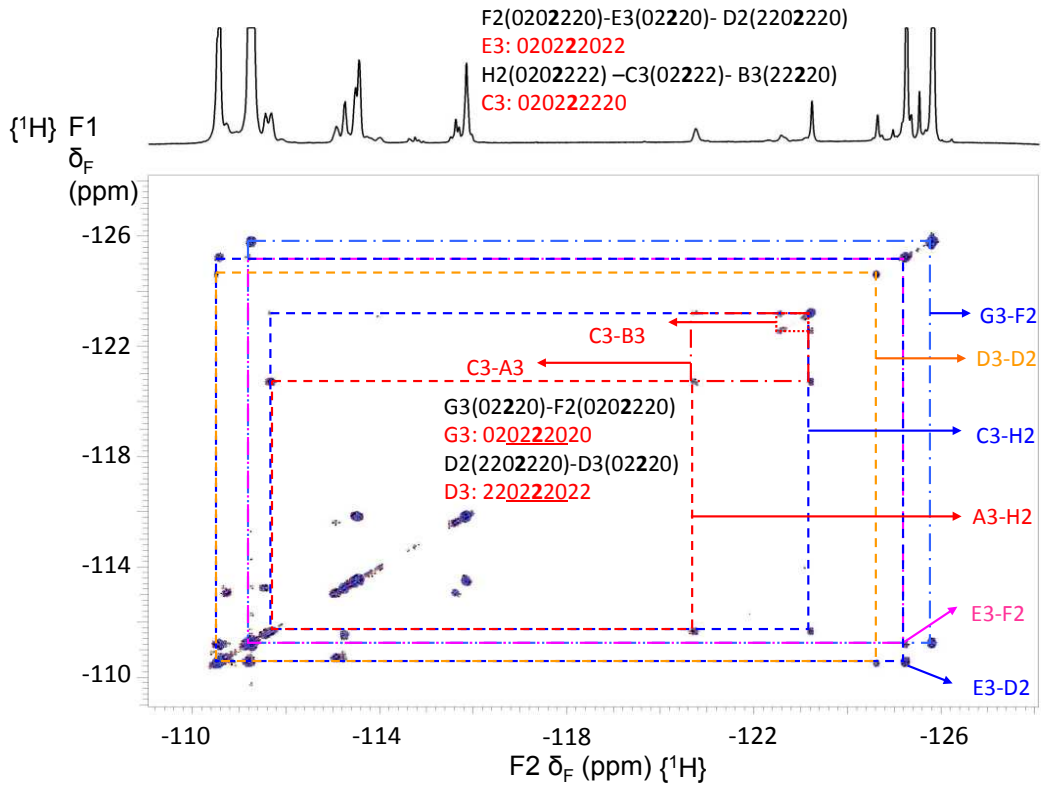


Figure S7. Selected region of ^{19}F-^{19}F gdqCOSY spectrum of poly(VDF-*co*-TFE) (84:16 mole%).

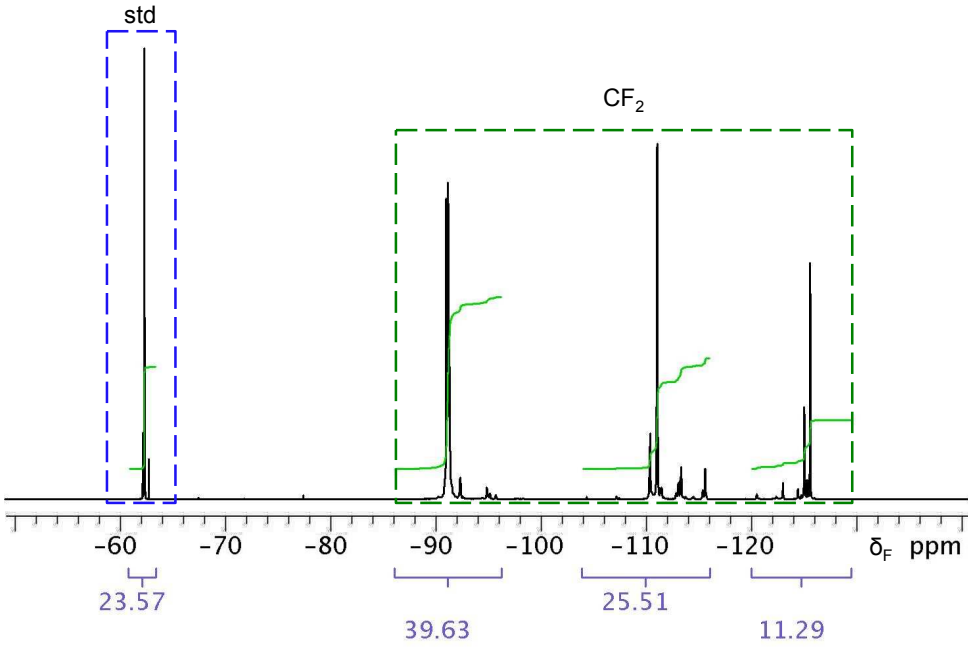


Figure S8. Quantitative 470 MHz $^{19}F\{^{1}H\}$ NMR spectrum of poly(VDF-*co*-TFE) (84:16 mole%).

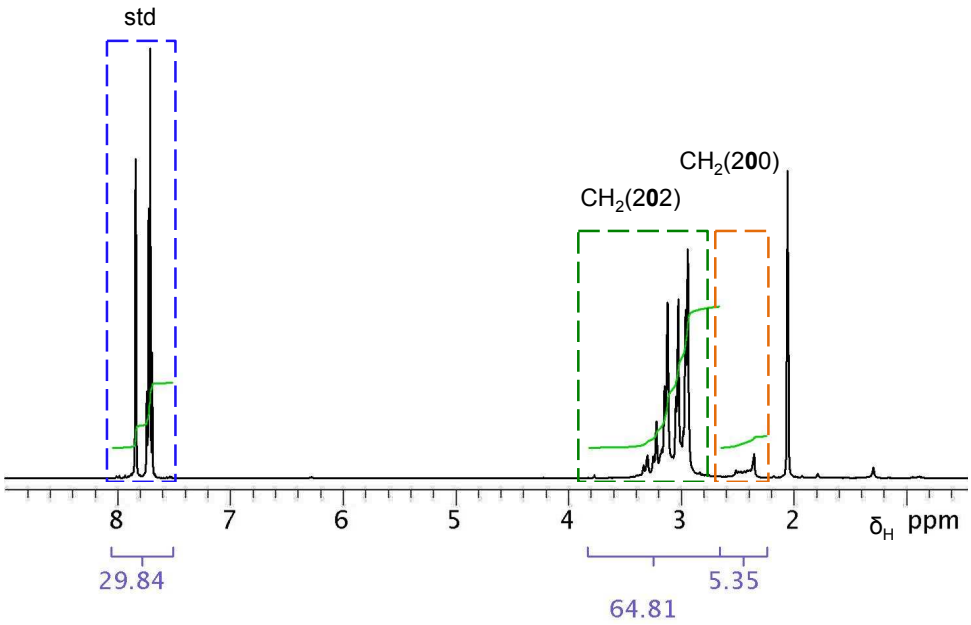


Figure S9. Quantitative 500MHz $^{1}H\{^{19}F\}$ NMR spectrum of poly(VDF-*co*-TFE) (84:16 mole %).

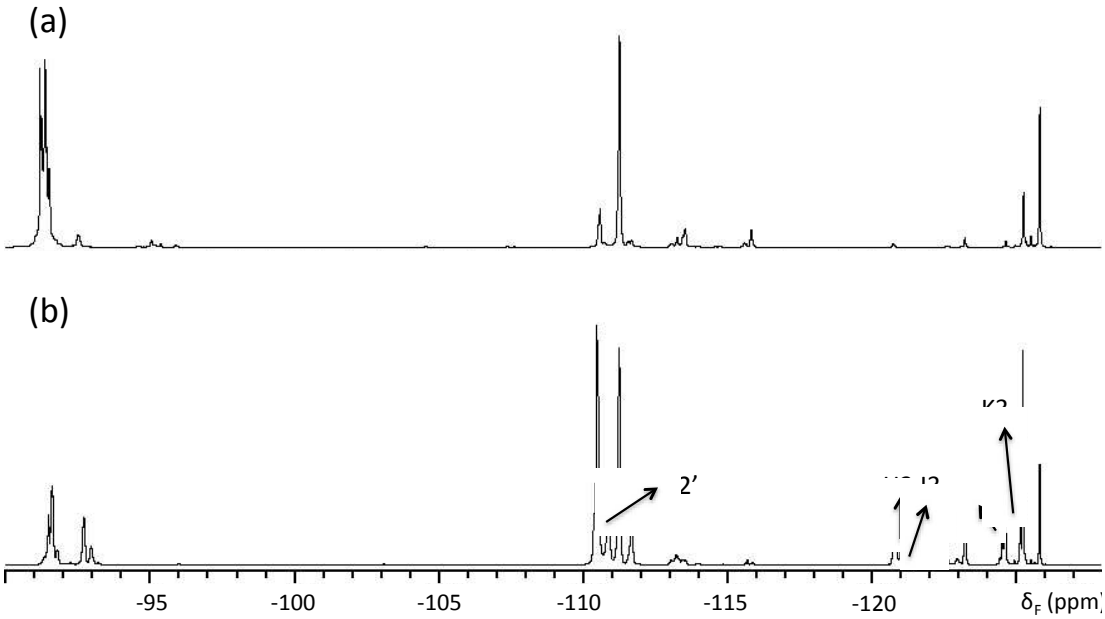


Figure S10. 470 MHz $^{19}F\{^{1}H\}$ NMR spectra of (a) poly(VDF-*co*-TFE) (84:16 mol%) and (b) poly(VDF-*co*-TFE) (56:44 mole %).

Table S1. Assignments of extra peaks shown in the ^{19}F 1D-NMR spectrum of poly(VDF-*co*-TFE) (56:44 mole %)

Peak	^{19}F Chemical shift (ppm)	Assignment
E2'	-110.89	220**2**222
H3	-121.01	022**2**222
I3	-121.42	222**2**222
J3	-124.51	2202**2**2022
K3	-125.14	2202**2**2020

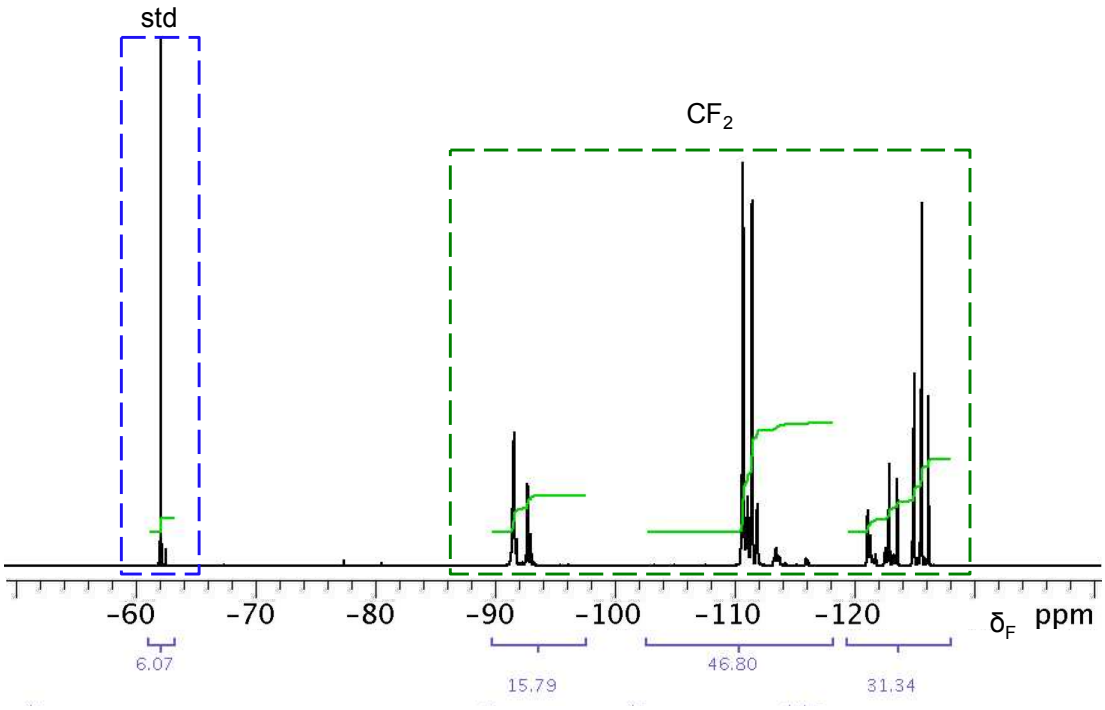


Figure S11. Quantitative 470 MHz $^{19}F\{^{1}H\}$ NMR spectrum of poly(VDF-*co*-TFE) (56:44 mole %).

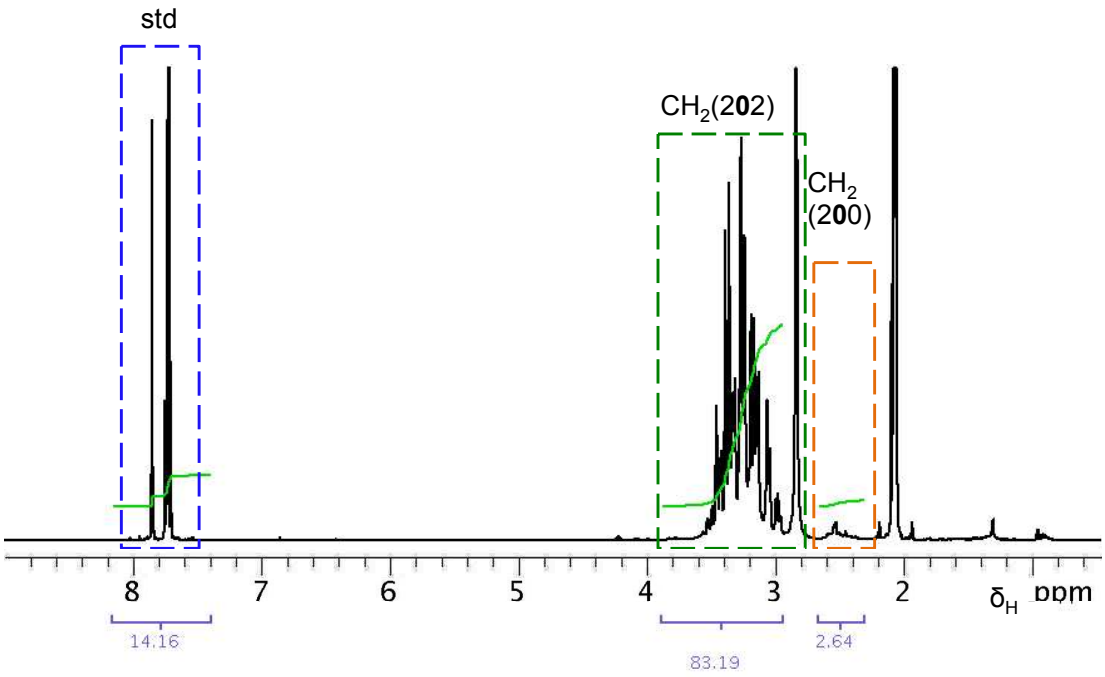


Figure S12. Quantitative 500MHz $^{1}H\{^{19}F\}$ NMR spectrum of poly(VDF-*co*-TFE) (56:44 mole %).

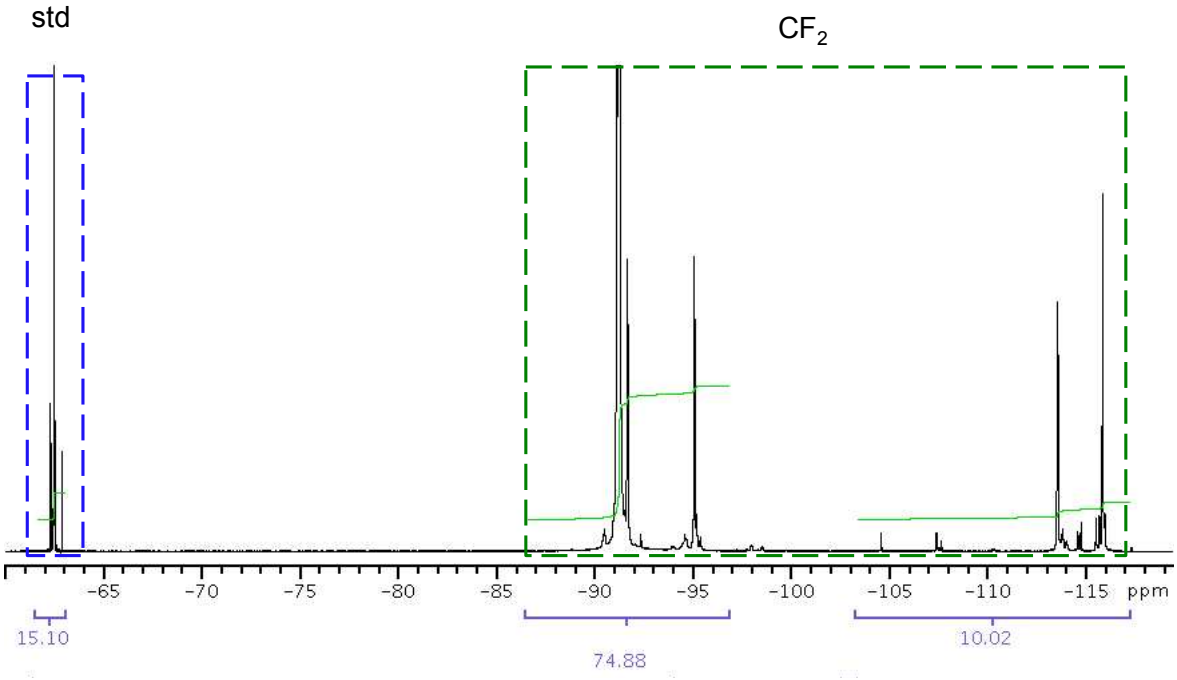


Figure S13. Quantitative 470 MHz $^{19}F\{^{1}H\}$ NMR spectrum of PVDF.

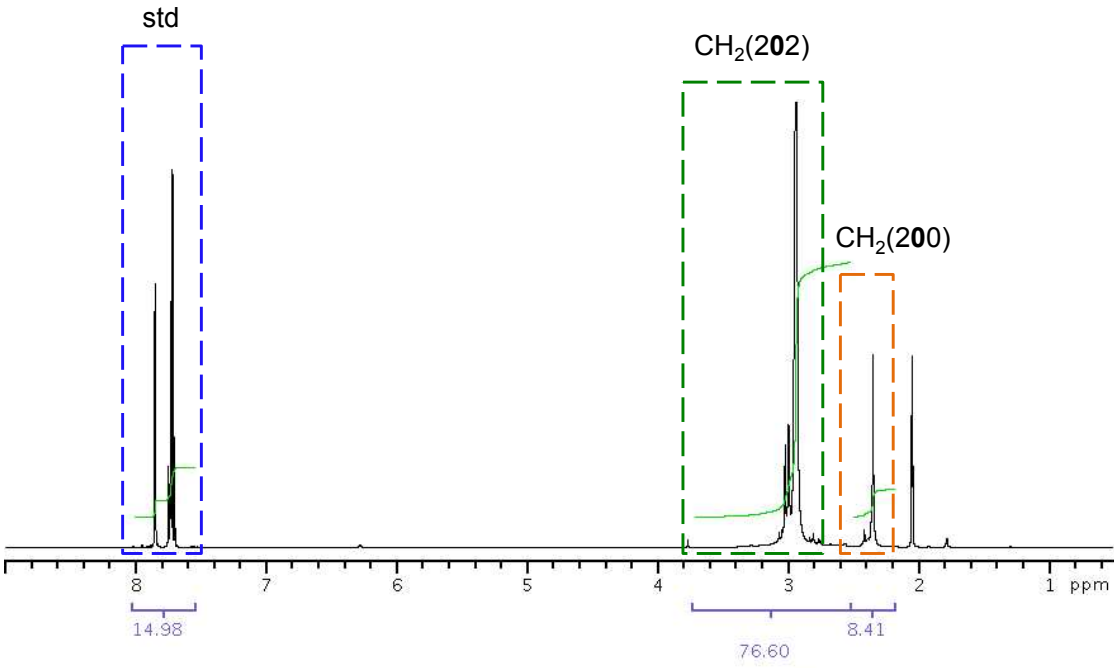


Figure S14. Quantitative 500MHz $^{1}H\{^{19}F\}$ NMR spectrum of PVDF.

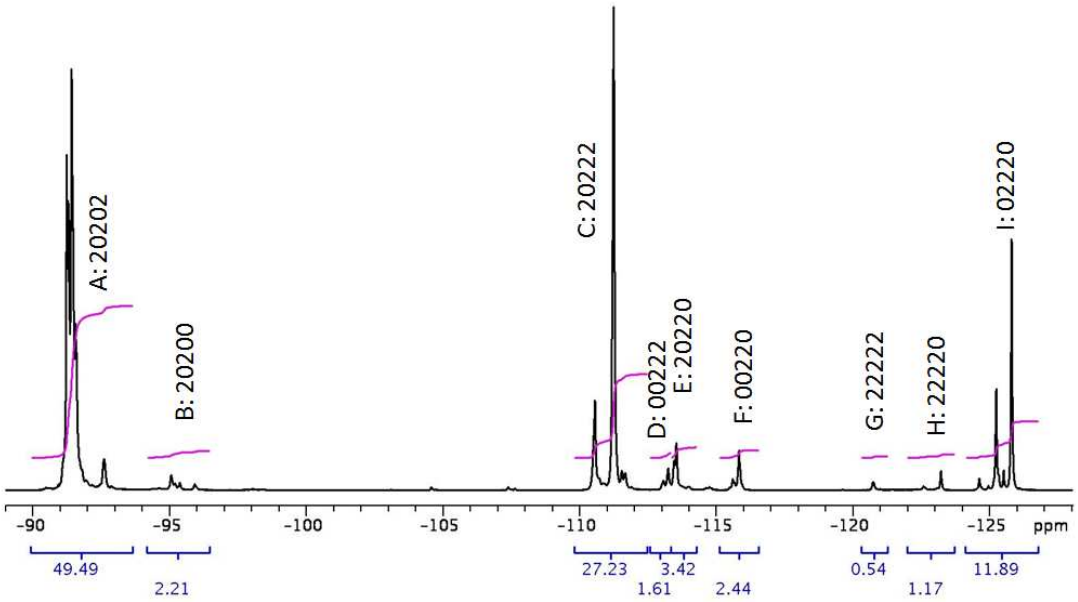


Figure S15. Quantitative 470 MHz $^{19}F\{^{1}H\}$ NMR spectrum of poly(VDF-*co*-TFE) (84:16 mole %).

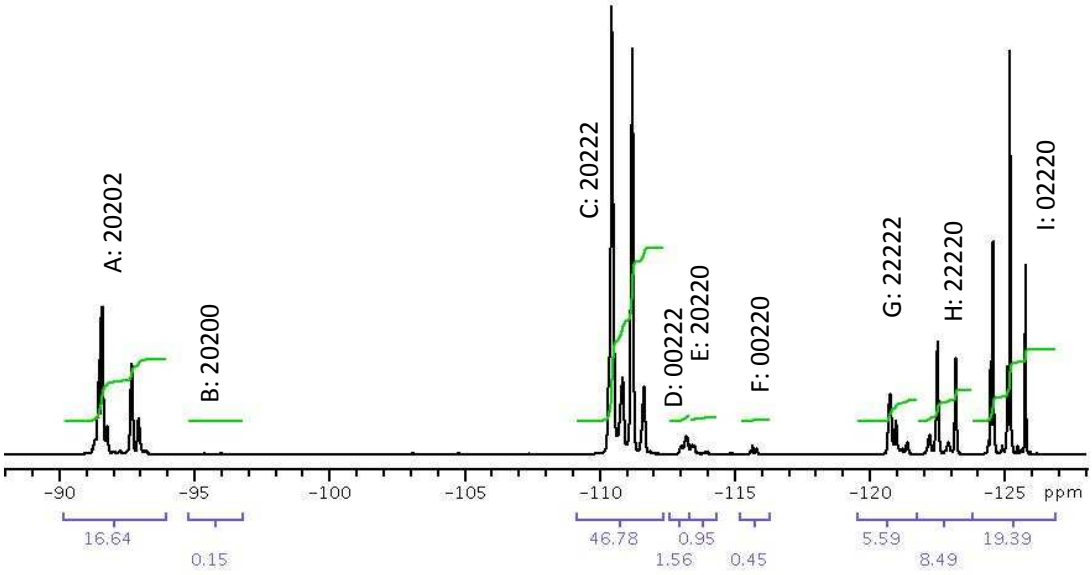


Figure S16. Quantitative 470 MHz $^{19}F\{^{1}H\}$ NMR spectrum of poly(VDF-*co*-TFE) (56:44 mole %).

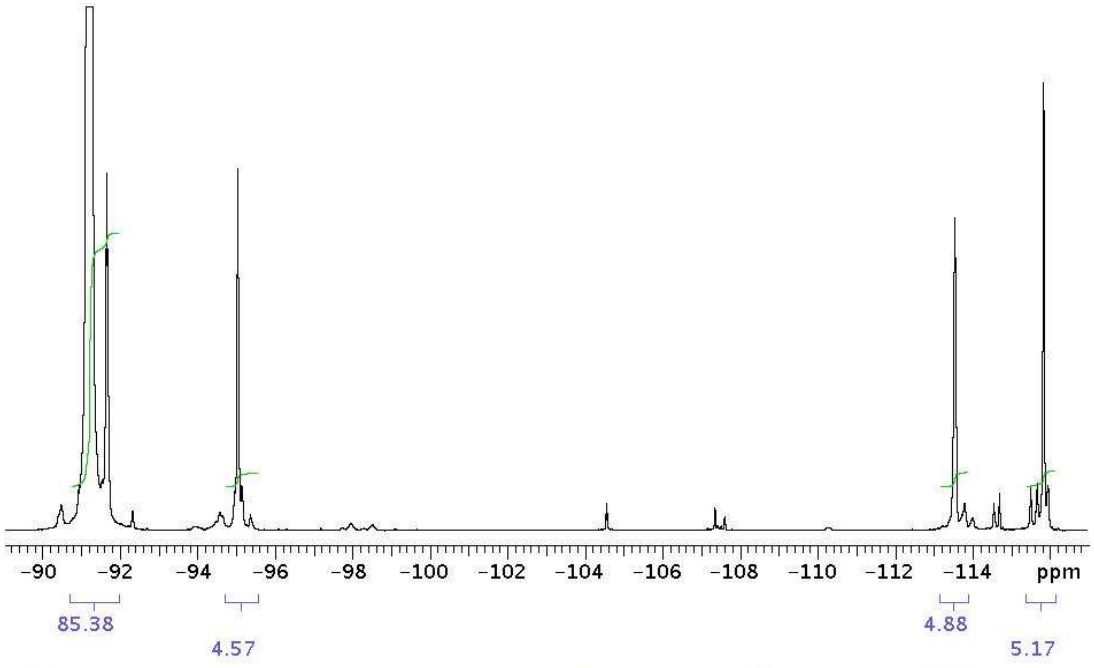


Figure S17. Quantitative 470 MHz $^{19}F\{^{1}H\}$ NMR spectrum of PVDF.

Table S2. Quantitative results of VDF-containing polymers obtained by internal standard method.

	PVDF	P(VDF-TFE) (84:16 mole %)	P(VDF-TFE) (56:44 mole %)
N_{CF2}/N^{F}_{std}	5.62	4.86	23.21
N_{CH2}/N^{H}_{std}	5.67	3.53	9.09

Table S3. Probabilities of triad sequences in VDF-containing polymers.

Triad\Region	PVDF	poly(VDF-*co*-TFE) (ca. 84:16 mole %)	poly(VDF-*co*-TFE) (ca. 56:44 mole %)
VVV (02**020**2)	0.85315	0.46270	0.08875
VVB (02**02**20)	0.04655	0.02636	0.00389
BVV (200202)	0.04746	0.02003	0.00320
BVB (200220)	0.00259	0.00114	0.00014
TVV (220202)		0.11245	0.14341
VVT (020222)		0.12276	0.12930
TVT (220222)		0.02983	0.20895
TVB (220220)		0.00641	0.00628
BVT (200222)		0.00531	0.00466
BBB (202020)	0.00003	0.00090	0.00000
VBB (022020)	0.00110	0.00584	0.00000
BBV (202002)	0.00112	0.00444	0.00000
VBV (022002)	0.04799	0.02885	0.00972
TBB (222020)		0.00097	0.00000
BBT (202022)		0.00003	0.00000
TBT (222022)		0.00003	0.00000
TBV (222002)		0.00481	0.01146
VBT (022022)		0.00016	0.00000
TTT (222222)		0.00013	0.01024
VTT (022222)		0.00460	0.04950
TTV (222202)		0.00421	0.05491
VTV (022202)		0.15179	0.26537
BTT (202222)		0.00000	0.00000
TTB (222220)		0.00016	0.00175
BTB (202220)		0.00001	0.00000
VTB (022220)		0.00593	0.00848
BTV (202202)		0.00014	0.00000

Table S4. Percent relative errors between calculated and measured integrals for 5-carbon sequences in VDF-containing polymers.

Sample	Model	A (20202)	B (20200)	C (20222)	D (00222)	E (20220)	F (00220)	G (22222)	H (22220)	I (02220)
PVDF	Bernoullian	0%	-6%	NA	NA	1%	6%	NA	NA	NA
	First order Markovian	0%	-6%	NA	NA	2%	2%	NA	NA	NA
poly(VDF-*co*-TFE) (84:16 mole%)	Bernoullian	-2%	24%	8%	51%	5%	31%	-608%	-406%	16%
	First order Markovian	0%	5%	2%	46%	2%	-6%	20%	-53%	-10%
poly(VDF-*co*-TFE) (56:44 mole%)	Bernoullian	-59%	184%	26%	111%	148%	128%	-182%	-58%	46%
	First order Markovian	0%	-52%	0%	26%	24%	-56%	8%	-3%	2%

Spreadsheet A. Statistical simulation for PVDF with the Bernoullian model.

1	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
2															
3		fV=	**0.949**												
4		fB=	**0.051**												
5															
6															
7															
8	Triad probablility	Triad\Region	A (20202)	B (20200)	E (20220)	F (00220)									
9	0.85413	VVV (02**020**2)	0.4271												
10	0.04609	VVB (02**02**20)			0.0230										
11	0.04609	BVV (200202)		0.0230											
12	0.00249	BVB (200220)				0.0012									
13	0.00013	BBB (202020)	0.0001												
14	0.00249	VBB (022020)			0.0012										
15	0.00249	BBV (202002)		0.0012											
16	0.04609	VBV (022002)				0.0230									
17	1.00000	Calculated Integral	0.4271	0.0243	0.0243	0.0243	0.5000								
18		Measured Integral	0.4272	0.0229	0.0244	0.0259	0.5004								
19		Difference	0.0001	-0.0014	0.0001	0.0016									
20		Difference Squared	9.40E-09	2.02E-06	1.70E-08	2.50E-06	**2.13E-03**								
21		Relative Error %	0%	-6%	1%	6%									
22															
23	**DOCUMENTATION**														
24	**Entered Data**														
25	Cells C18 to F18 are measured integrated areas after normalization.														
26	Normalization: measured integral=A(XX2XX)/A_{total}, where A_{total} is the total intensities of all 3-carbon sequences and obtained by equation A_{total}=2a+3*b/2+c+(d+e+f)/2=199.85.														
27	In this equation, a=A(020) b=A(220/022) c=A(222) d=A(20200) e=A(00222) f=A(00220)) (Ref: Polymer 1992 V33 P4920)														
28															
29	**Results**														
30	Cell C3 is the independent variable: the fractions of normal VDF (fV).														
31															
32	Cell C4 is the fraction of reverse VDF (fB), and is obtained by the equation C4=1-C3, assuming that the sum of the components fV + fB = 1														
33															
34	**Parameters Varied by Solver**														
35	Cells C3 is the independent variable that is varied by Solver to minimize the cell L39.														
36															

37	**Calculated Fields**
38	A9 to A16 are the probabilities of triads, obtained by Bernoullian model. e.g.: A10(VVB)=C3*C3*C4 (i.e. fV * fV * fB)
39	
40	A17 is a sum of the probabilities of all triads, which should be 1. A17=Sum(A9:A16)
41	
42	The Matrix containing cells C9 through F16 (i.e. cells C-F/9-16) contains columns C through F representing the integral regions of 5-carbon sequences from the 19F NMR spectrum, and rows corresponding to the different triads.
43	
44	If the center monomer in a triad contributes to the resonances of a 5-carbon sequence region, its contribution (based on its statistical probability and number of atoms contributing to the resonance) is entered at the intersection of the corresponding row and column.
45	
46	Cells C17 to F17 are the calculated integrated areas of 5-carbon sequences, which are obtained by adding the probabilities of triads contributing the integrated area of each 5-carbon sequence. e.g.: Cell C17 =Sum(C9:C16) ….
47	
48	Cells C19 to F19 are the differences between the calculated integral areas and the measured integral areas of the 5-carbon sequences e.g.: Cell C19 =C18-C17
49	
50	Cells C20 to F20 are the difference squared so that the sign of the difference can be removed. e.g.: C20=POWER(C19,2)
51	
52	Cells C21 to F21 are the percent relative errors between calculated and measured integral areas of each 5-carbon sequence. e.g.: C21=C19/C18
53	
54	Cell G17 is the total of calculated integral areas for 5-carbon sequences, G17=Sum(C17:F17)
55	
56	Cell G18 is the total of measured integral areas for 5-carbon sequences after normalization, G18=Sum(C18:F18)
57	
58	Cell G20 is the square root of the total of differences squared, G20=SQRT(Sum(C20:F20)).
59	G20 is minimized by Solver to obtain the best values of the independent variables (fV, and indirectly fB, in cells C3, and C4).

Spreadsheet B. Statistical simulation for poly(VDF-*co*-TFE) (ca. 84:16 mole %) with the Bernoullian model.

1	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
2																				
3		fV=	**0.777**																	
4		fB=	**0.031**																	
5		fT=	**0.192**																	
6			1																	
7																				
8	Triad probablility	Triad\Region	A (20202)	B (20200)	C (20222)	D (00222)	E (20220)	F (00220)	G (22222)	H (22220)	I (02220)									
9	0.46927	VVV (02**020**2)	0.2346																	
10	0.01871	VVB (02**02**20)					0.0094													
11	0.01871	BVV (200202)		0.0094																
12	0.00075	BVB (200220)						0.0004												
13	0.11589	TVV (220202)	0.0579																	
14	0.11589	VVT (020222)			0.0579															
15	0.02862	TVT (220222)			0.0143															
16	0.00462	TVB (220220)					0.0023													
17	0.00462	BVT (200222)				0.0023														
18	0.00003	BBB (202020)	0.0000																	
19	0.00075	VBB (022020)					0.0004													
20	0.00075	BBV (202002)		0.0004																
21	0.01871	VBV (022002)						0.0094												
22	0.00018	TBB (222020)			0.0001															
23	0.00018	BBT (202022)	0.0001																	
24	0.00114	TBT (222022)			0.0006															
25	0.00462	TBV (222002)				0.0023														
26	0.00462	VBT (022022)					0.0023													
27	0.00707	TTT (222222)							0.0071											
28	0.02862	VTT (022222)							0.0143	0.0143										
29	0.02862	TTV (222202)			0.0143					0.0143										
30	0.11589	VTV (022202)			0.0579						0.0579									
31	0.00114	BTT (202222)			0.0006					0.0006										
32	0.00114	TTB (222220)							0.0006	0.0006										
33	0.00018	BTB (202220)			0.0001						0.0001									
34	0.00462	VTB (022220)								0.0046										
35	0.00462	BTV (202202)					0.0046													
36	1	Calculated Integral	0.2927	0.0097	0.1458	0.0046	0.0190	0.0097	0.0219	0.0344	0.0580	0.5960								
37		Measured Integral	0.2874	0.0128	0.1581	0.0094	0.0199	0.0142	0.0031	0.0068	0.0691	0.5808								

38		Difference	-0.0053	0.0031	0.0123	0.0048	0.0009	0.0045	-0.0188	-0.0276	0.0111	-0.0152								
39		Difference Squared	2.80E-05	9.43E-06	1.50E-04	2.28E-05	8.60E-07	2.00E-05	3.55E-04	7.61E-04	1.22E-04	**3.83E-02**								
40		Relative Error %	-2%	24%	8%	51%	5%	31%	-608%	-406%	16%									
41																				
42																				
43	**DOCUMENTATION**																			
44	**Entered Data**																			
45	Cells C37 to K37 are measured integrated areas after normalization.																			
46	Normalization: measured integral=A(XX2XX)/A_{total}, where A_{total} is the total intensities of all 3-carbon sequences and obtained by equation A_{total}=2a+3*b/2+c+(d+e+f)/2=172.18.																			
47	In this equation, a=A(020) b=A(220/022) c=A(222) d=A(20200) e=A(00222) f=A(00220)) (Ref: Polymer 1992 V33 P4920)																			
48																				
49	**Results**																			
50	Cells C3 and C4 are the independent variables: the fractions of normal VDF (fV) and reverse VDF (fB).																			
51																				
52	Cell C5 is the fraction of T (fT), and is obtained by the equation C5=1-C3-C4, assuming that the sum of the components fV + fB + fT = 1																			
53																				
54	**Parameters Varied by Solver**																			
55	Cells C3 and C4 are the independent variables that are varied by Solver to minimize the cell L39.																			
56																				
57	**Calculated Fields**																			
58	A9 to A35 are the probabilities of triads, obtained by Bernoullian model. e.g.: A14(VVT)=C3*C3*C4 (i.e. fV * fB * fT)																			
59																				
60	A36 is a sum of the probabilities of all triads, which should be 1. A36=Sum(A9:A35)																			
61																				
62	The Matrix containing cells C9 through K35 (i.e. cells C-K/9-35) contains columns C through K representing the integral regions of 5-carbon sequences from the 19F NMR spectrum, and rows corresponding to the different triads.																			
63	If the center monomer in a triad contributes to the resonances of a 5-carbon sequence region, its contribution (based on its statistical probability and number of atoms contributing to the resonance) is entered at the intersection																			
64	of the corresponding row and column.																			
65																				
66	Cells C36 to K36 are the calculated integrated areas of 5-carbon sequences, which are obtained by adding the probabilities of triads contributing the integrated area of each 5-carbon sequence. e.g.: Cell C36 =Sum(C9:C35) ….																			
67																				
68	Cells C38 to K38 are the differences between the calculated integral areas and the measured integral areas of the 5-carbon sequences e.g.: Cell C38 =C37-C36																			
69																				
70	Cells C39 to K39 are the difference squared so that the sign of the difference can be removed. e.g.: C39=POWER(C38,2)																			
71																				
72	Cells C40 to K40 are the percent relative errors between calculated and measured integral areas of each 5-carbon sequence. e.g.: C40=C38/C37																			
73																				

74	Cell L36 is the total of calculated integral areas for 5-carbon sequences, L36=Sum(C36:K36)
75	
76	Cell L37 is the total of measured integral areas for 5-carbon sequences after normalization, L37=Sum(C37:K37)
77	
78	Cell L39 is the square root of the total of differences squared, L39=SQRT(Sum(C39:K39)).
79	L39 is minimized by Solver to obtain the best values of the independent variables (fV and fB, and indirectly fΓ, in cells C3, C4 and C5).

Spreadsheet C. Statistical simulation for poly(VDF-*co*-TFE) (56:44 mole %) with the Bernoullian model.

1	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
2																				
3		fV=	**0.607**																	
4		fB=	**-0.005**																	
5		fT=	**0.397**																	
6			1																	
7																				
8	Triad probablility	Triad\Region	A (20202)	B (20200)	C (20222)	D (00222)	E (20220)	F (00220)	G (22222)	H (22220)	I (02220)									
9	0.22406	VVV (02**020**2)	0.1120																	
10	-0.00177	VVB (02**02**20)					-0.0009													
11	-0.00177	BVV (200202)		-0.0009																
12	0.00001	BVB (200220)						0.0000												
13	0.14661	TVV (220202)	0.0733																	
14	0.14661	VVT (020222)			0.0733															
15	0.09594	TVT (220222)			0.0480															
16	-0.00116	TVB (220220)					-0.0006													
17	-0.00116	BVT (200222)				-0.0006														
18	0.00000	BBB (202020)	0.0000																	
19	0.00001	VBB (022020)					0.0000													
20	0.00001	BBV (202002)		0.0000																
21	-0.00177	VBV (022002)						-0.0009												
22	0.00001	TBB (222020)			0.0000															
23	0.00001	BBT (202022)	0.0000																	
24	-0.00076	TBT (222022)			-0.0004															
25	-0.00116	TBV (222002)				-0.0006														
26	-0.00116	VBT (022022)					-0.0006													
27	0.06278	TTT (222222)							0.0628											
28	0.09594	VTT (022222)							0.0480	0.0480										
29	0.09594	TTV (222202)			0.0480					0.0480										
30	0.14661	VTV (022202)			0.0733						0.0733									
31	-0.00076	BTT (202222)			-0.0004					-0.0004										
32	-0.00076	TTB (222220)							-0.0004	-0.0004										
33	0.00001	BTB (202220)			0.0000						0.0000									
34	-0.00116	VTB (022220)								-0.0012										
35	-0.00116	BTV (202202)					-0.0012													
36	1.00000	Calculated Integral	0.1853	-0.0009	0.2418	-0.0012	-0.0032	-0.0009	0.1104	0.0940	0.0733	0.6987								

37		Measured Integral	0.1166	0.0011	0.3277	0.0109	0.0067	0.0032	0.0392	0.0595	0.1358	0.7006								
38		Difference	-0.0688	0.0019	0.0859	0.0121	0.0099	0.0040	-0.0712	-0.0345	0.0625	0.0019								
39		Difference Squared	4.73E-03	3.72E-06	7.38E-03	1.46E-04	9.71E-05	1.63E-05	5.07E-03	1.19E-03	3.91E-03	**1.50E-01**								
40		Relative Error %	-59%	184%	26%	111%	148%	128%	-182%	-58%	46%									
41																				
42																				
43	**DOCUMENTATION**																			
44	**Entered Data**																			
45	Cells C37 to K37 are measured integrated areas after normalization.																			
46	Normalization: measured integral=A(XX2XX)/A_{total}, where A_{total} is the total intensities of all 3-carbon sequences and obtained by equation A_{total}=2a+3*b/2+c+(d+e+f)/2=142.74.																			
47	In this equation, a=A(020) b=A(220/022) c=A(222) d=A(20200) e=A(00222) f=A(00220)) (Ref: Polymer 1992 V33 P4920)																			
48																				
49	**Results**																			
50	Cells C3 and C4 are the independent variables: the fractions of normal VDF (fV) and reverse VDF (fB).																			
51																				
52	Cell C5 is the fraction of T, and is obtained by the equation C5=1-C3-C4, assuming that the sum of the components V + B + T = 1																			
53																				
54	**Parameters Varied by Solver**																			
55	Cells C3 and C4 are the independent variables that are varied by Solver to minimize the cell L39.																			
56																				
57	**Calculated Fields**																			
58	A9 to A35 are the probabilities of triads, obtained by Bernoullian model. e.g.: A14(VVT)=C3*C3*C4 (i.e. fV * fB * fT)																			
59																				
60	A36 is a sum of the probabilities of all triads, which should be 1. A36=Sum(A9:A35)																			
61																				
62	The Matrix containing cells C9 through K35 (i.e. cells C-K/9-35) contains columns C through K representing the integral regions of 5-carbon sequences from the 19F NMR spectrum, and rows corresponding to the different triads.																			
63	If the center monomer in a triad contributes to the resonances of a 5-carbon sequence region, its contribution (based on its statistical probability and number of atoms contributing to the																			
64	resonance) is entered at the intersection of the corresponding row and column.																			
65																				
66	Cells C36 to K36 are the calculated integrated areas of 5-carbon sequences, which are obtained by adding the probabilities of triads contributing the integrated area of each 5-carbon sequence. e.g.: Cell C36 =Sum(C9:C35) ….																			
67																				
68	Cells C38 to K38 are the differences between the calculated integral areas and the measured integral areas of the 5-carbon sequences e.g.: Cell C38 =C37-C36																			
69																				
70	Cells C39 to K39 are the difference squared so that the sign of the difference can be removed. e.g.: C39=POWER(C38,2)																			
71																				
72	Cells C40 to K40 are the percent relative errors between calculated and measured integral areas of each 5-carbon sequence. e.g.: C40=C38/C37																			

73	
74	Cell L36 is the total of calculated integral areas for 5-carbon sequences, L36=Sum(C36:K36)
75	
76	Cell L37 is the total of measured integral areas for 5-carbon sequences after normalization, L37=Sum(C37:K37)
77	
78	Cell L39 is the square root of the total of differences squared, L39=SQRT(Sum(C39:K39)).
79	L39 is minimized by Solver to obtain the best values of the independent variables (fV and fB, and indirectly fT, in cells C3, C4 and C5).

Spreadsheet D. Statistical simulation for PVDF with the first order Markov model.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y
1							P(V/V)=	**0.9483**	P(B/V)=	0.9775															
2							P(V/B)=	**0.0517**	P(B/B)=	0.0225															
3		fV=	**0.949**																						
4		fB=	**0.051**				P(VV)=	0.8997	P(BV)=	0.0500															
5							P(VB)=	0.0491	P(BB)=	0.0012															
6																									
7																									
8	Triad probablility	Triad\Region	A (20202)	B (20200/00202)	E (20220/02202)	F (00220/02200)																			
9	0.8532	VVV (02**020**2)	0.4266																						
10	0.0466	VVB (02**02**20)			0.0233																				
11	0.0475	BVV (200202)		0.0237																					
12	0.0026	BVB (200220)				0.0013																			
13	0.0000	BBB (202020)	0.0000																						
14	0.0011	VBB (022020)			0.0006																				
15	0.0011	BBV (202002)		0.0006																					
16	0.0480	VBV (022002)				0.0240																			
17	1.0000	Calculated Integral	0.4266	0.0243	0.0238	0.0253	0.5000																		
18		Measured Integral	0.4272	0.0229	0.0244	0.0259	0.5004																		
19		Difference	0.0006	-0.0014	0.0006	0.0006	0.0004																		
20		Difference Squared	4.11E-07	2.03E-06	3.49E-07	3.36E-07	**1.77E-03**																		
21		Relative Error %	0%	-6%	2%	2%																			
22																									
23																									
24	**DOCUMENTATION**																								
25	**Entered Data**																								
26	Cells C18 to F18 are measured integrated areas after normalization.																								
27	Normalization: measured integral=A(XX2XX)/A_{total}, where A_{total} is the total intensities of all 3-carbon sequences and obtained by equation A_{total}=2a+3*b/2+c+(d+e+f)/2=199.85.																								
28	In this equation, a=A(020) b=A(220/022) c=A(222) d=A(20200) e=A(00222) f=A(00220)) (Ref: Polymer 1992 V33 P4920)																								
29																									
30	**Results**																								
31	The cells H1-H2 and J1-J2 are the conditional probabilities of monomer addition.																								
32	Among them, cells H1 and J1 are the independent variables, corresponding to P(V/V) and P(B/V), respectively.																								

33	Cells H2 and J2 can be obtained by equations H2=1-H1 and J2-1-J1, assuming the P(V/V)+P(V/B)=1 and P(B/V)+P(B/B)=1.
34	
35	Cells H4-H5 and J4-J5 are the probabilities of dyads calculated based on fractions of monomers and the conditional probabilities of monomer addition.
36	
37	**Parameters Varied by Solver**
38	Cells H1 and J1 are the independent variables that are varied by Solver to minimize the cell G20.
39	
40	**Calculated Fields**
41	A9 to A16 are the probabilities of triads, obtained by 1st order Markovian model. e.g.: A10(VVB)=C3*H1*H2 (i.e. fV * P(V/V) * P(V/B))
42	
43	A17 is a sum of the probabilities of all triads, which should be 1. A17=Sum(A9:A16)
44	
45	The Matrix containing cells C9 through F16 (i.e. cells C-F/9-16) contains columns C through F representing the integral regions of 5-carbon sequences from the 19F NMR spectrum, and rows corresponding to the different triads.
46	If the center monomer in a triad contributes to the resonances of a 5-carbon sequence region, its contribution (based on its statistical probability and number of atoms contributing to the resonance) is entered at the intersection of the corresponding row and column.
47	
48	Cells C17 to F17 are the calculated integrated areas of 5-carbon sequences, which are obtained by adding the probabilities of triads contributing the integrated area of each 5-carbon sequence. e.g.: Cell C17 =Sum(C9:C16) ….
49	
50	Cells C19 to F19 are the differences between the calculated integral areas and the measured integral areas of the 5-carbon sequences e.g.: Cell C19 =C18-C17
51	
52	Cells C20 to F20 are the difference squared so that the sign of the difference can be removed. e.g.: C20=POWER(C19,2)
53	
54	Cells C21 to F21 are the percent relative errors between calculated and measured integral areas of each 5-carbon sequence. e.g.: C21=C19/C18
55	
56	Cell G17 is the total of calculated integral areas for 5-carbon sequences, G17=Sum(C17:F17)
57	
58	Cell G18 is the total of measured integral areas for 5-carbon sequences after normalization, G18=Sum(C18:F18)
59	
60	Cell G20 is the square root of the total of differences squared, G20=SQRT(Sum(C20:F20)).
61	G20 is minimized by Solver to obtain the best values of the independent variables (P(V/V), and indirectly P(V/B), in cells H1, and H2, P(B/V), and indirectly P(B/B), in cells J1, and J2.)

Spreadsheet E. Statistical simulation for poly(VDF-*co*-TFE) (84:16 mole %) with the first order Markov model.

1	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
2																		
3		fV=	**0.809**				P(V/V)=	**0.7563**	P(B/V)=	**0.8278**	P(T/V)=	**0.9351**						
4		fB=	**0.032**				P(V/B)=	**0.0431**	P(B/B)=	**0.1675**	P(T/B)=	**0.0365**						
5		fT=	**0.159**				P(V/T)=	**0.2006**	P(B/T)=	**0.0047**	P(T/T)=	**0.0283**						
6			1					1.0000		1.0000		1.0000						
7							PVV=	0.6118	PBV=	0.0265	PTV=	0.1487						
8							PVB=	0.0349	PBB=	0.0054	PTB=	0.0058						
9							PVT=	0.1623	PBT=	0.0002	PTT=	0.0045						
10																		
11	Triad probablility	Triad\Region	A (20202)	B (20200/00202)	C (20222/22202)	D (00222/22200)	E (20220/02202)	F (00220/02200)	G (22222)	H (22220/02222)	I (02220)							
12	0.46270	VVV (02**020**2)	0.2313															
13	0.02636	VVB (02**02**20)					0.0132											
14	0.02003	BVV (200202)		0.0100														
15	0.00114	BVB (200220)						0.0006										
16	0.11245	TVV (220202)	0.0562															
17	0.12276	VVT (020222)			0.0614													
18	0.02983	TVT (220222)			0.0149													
19	0.00641	TVB (220220)					0.0032											
20	0.00531	BVT (200222)				0.0027												
21	0.00090	BBB (202020)	0.0004															
22	0.00584	VBB (022020)					0.0029											
23	0.00444	BBV (202002)		0.0022														
24	0.02885	VBV (022002)						0.0144										
25	0.00097	TBB (222020)			0.0005													
26	0.00003	BBT (202022)	0.0000															
27	0.00003	TBT (222022)			0.0000													
28	0.00481	TBV (222002)				0.0024												
29	0.00016	VBT (022022)					0.0001											
30	0.00013	TTT (222222)							0.0001									
31	0.00460	VTT (022222)							0.0023	0.0023								
32	0.00421	TTV (222202)			0.0021					0.0021								
33	0.15179	VTV (022202)			0.0759						0.0759							
34	0.00000	BTT (202222)			0.0000					0.0000								
35	0.00016	TTB (222220)							0.0001	0.0001								
36	0.00001	BTB (202220)			0.0000						0.0000							

37	0.00593	VTB (022220)								0.0059								
38	0.00014	BTV (202202)					0.0001											
39	1.00000	Calculated Integral	0.2880	0.0122	0.1548	0.0051	0.0195	0.0150	0.0025	0.0104	0.0759	0.5835						
40		Measured Integral	0.2874	0.0128	0.1581	0.0094	0.0199	0.0142	0.0031	0.0068	0.0691	0.5808						
41		Difference	-0.0006	0.0006	0.0033	0.0043	0.0003	-0.0008	0.0006	-0.0036	-0.0068							
42		Difference Squared	3.78E-07	3.60E-07	1.12E-05	1.84E-05	1.12E-07	6.84E-07	3.93E-07	1.31E-05	4.68E-05	**9.56E-03**						
43		Relative Error %	0%	5%	2%	46%	2%	-6%	20%	-53%	-10%							
44																		
45																		
46	**DOCUMENTATION**																	
47	**Entered Data**																	
48	Cells C40 to K40 are measured integrated areas after normalization.																	
49	Normalization: measured integral=A(XX2XX)/A_{total}, where A_{total} is the total intensities of all 3-carbon sequences and obtained by equation A_{total}=2a+3*b/2+c+(d+e+f)/2=172.18.																	
50	In this equation, a=A(020) b=A(220/022) c=A(222) d=A(20200) e=A(00222) f=A(00220)) (Ref: Polymer 1992 V33 P4920)																	
51																		
52	C3 and C4 are the fractions of normal VDF and reverse VDF, which are obtained by internal standard method. C5 is the fraction of TFE and obtained by equation C5=1-C3-C4																	
53																		
54	**Results**																	
55	The cells H3-H5, J3-J5 and L3-L5 are the conditional probabilities of monomer addition.																	
56	Among them, cells H3 and H4, J3 and J4, and L3 and L4 are the independent variables, corresponding to P(V/V), P(V/B), P(B/V), P(B/B), P(T/V) and P(T/B), respectively.																	
57	Cells H5, J5 and L5 can be obtained by equations H5=1-H3-H4, J5-1-J3-J4, and L5=1-L3-L4, assuming the P(V/V)+P(V/B)+P(V/T)=1, P(B/V)+P(B/B)+P(B/T)=1 and P(T/V) +P(T/B)+P(T/T)=1.																	
58																		
59	Cells H7-H9, J7-J9 and L7-L9 are the probabilities of dyads calculated based on fractions of monomers and the conditional probabilities of monomer addition.																	
60																		
61	**Parameters Varied by Solver**																	
62	Cells H3 and H4, J3 and J4, and L3 and L4 are the independent variables that are varied by Solver to minimize the cell L42.																	
63																		
64	**Calculated Fields**																	
65	A12 to A38 are the probabilities of triads, obtained by first order Markovian model. e.g.: A17(VVT)=C3*H3*H5 (i.e. fV*P(V/V)*P(V/T))																	
66																		
67	A39 is a sum of the probabilities of all triads, which should be 1. A39=Sum(A12:A38)																	
68																		
69	The Matrix containing cells C12 through K38 (i.e. cells C-K/12-38) contains columns C through K representing the integral regions of 5-carbon sequences from the 19F NMR spectrum, and rows corresponding to the different triads.																	
70	If the center monomer in a triad contributes to the resonances of a 5-carbon sequence region, its contribution (based on its statistical probability and number of atoms contributing to the resonance) is																	
71	entered at the intersection of the corresponding row and column.																	
72																		

73	Cells C39 to K39 are the calculated integrated areas of 5-carbon sequences, which are obtained by adding the probabilities of triads contributing the integral areas of each 5-carbon sequence. e.g.: Cell C39 =Sum(C12:C38).
74	
75	Cells C41 to K41 are the differences between the calculated integrated areas and the measured integral areas of the 5-carbon sequences e.g.: Cell C41 =C40-C39
76	
77	Cells C42 to K42 are the difference squared so that the sign of the difference can be removed. e.g.: C42=POWER(C41,2)
78	
79	Cells C43 to K43 are the percent relative error between calculated and measured integral areas of each 5-carbon sequence. e.g.: C43=C41/C40
80	
81	Cell L39 is the total of calculated integral areas for 5-carbon sequences, L39=Sum(C39:K39)
82	
83	Cell L40 is the total of measured integral areas for 5-carbon sequences after normalization, L40=Sum(C40:K40)
84	
85	Cell L42 is the square root of the total of difference squared, L42=SQRT(Sum(C42:K42)).
86	L42 is minimized by Solver to obtain the values of independent variables. (P(V/V) and P(V/B), and indirectly P(V/T) in cells H3, H4 and H5.
87	P(B/V) and P(B/B), and indirectly P(B/T) in cells J3, J4 and J5. P(T/V) and P(T/B), and indirectly P(T/T) in cell L3, L4 and L5.)

Spreadsheet F. Statistical simulation for poly(VDF-*co*-TFE) (56:44 mole %) with the first order Markov model.

1	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
2																		
3		V=	**0.555**				P(V/V)=	**0.3999**	P(B/V)=	**1.0000**	P(T/V)=	**0.8207**						
4		B=	**0.008**				P(V/B)=	**0.0175**	P(B/B)=	**0.0000**	P(T/B)=	**0.0262**						
5		T=	**0.437**				P(V/T)=	**0.5826**	P(B/T)=	**0.0000**	P(T/T)=	**0.1531**						
6			1					1.0000		1.0000		1.0000						
7							PVV=	0.2219	PBV=	0.0080	PTV=	0.3586						
8							PVB=	0.0097	PBB=	0.0000	PTB=	0.0115						
9							PVT=	0.3234	PBT=	0.0000	PTT=	0.0669						
10																		
11	Triad probablility	Triad\Region	A (20202)	B (20200/00202)	C (20222/22202)	D (00222/22200)	E (20220/02202)	F (00220/02200)	G (22222)	H (22220/02222)	I (02220)							
12	0.08875	VVV (02**020**2)	0.0444															
13	0.00389	VVB (02**02**20)					0.0019											
14	0.00320	BVV (200202)		0.0016														
15	0.00014	BVB (200220)						0.0001										
16	0.14341	TVV (220202)	0.0717															
17	0.12930	VVT (020222)			0.0647													
18	0.20895	TVT (220222)			0.1045													
19	0.00628	TVB (220220)					0.0031											
20	0.00466	BVT (200222)				0.0023												
21	0.00000	BBB (202020)	0.0000															
22	0.00000	VBB (022020)					0.0000											
23	0.00000	BBV (202002)		0.0000														
24	0.00972	VBV (022002)						0.0049										
25	0.00000	TBB (222020)			0.0000													
26	0.00000	BBT (202022)	0.0000															
27	0.00000	TBT (222022)			0.0000													
28	0.01146	TBV (222002)				0.0057												
29	0.00000	VBT (022022)					0.0000											
30	0.01024	TTT (222222)							0.0102									
31	0.04950	VTT (022222)							0.0248	0.0248								
32	0.05491	TTV (222202)			0.0275					0.0275								
33	0.26537	VTV (022202)			0.1327						0.1327							
34	0.00000	BTT (202222)			0.0000					0.0000								
35	0.00175	TTB (222220)							0.0009	0.0009								
36	0.00000	BTB (202220)			0.0000						0.0000							

37	0.00848	VTB (022220)								0.0085								
38	0.00000	BTV (202202)					0.0000											
39	1.00000	Calculated Integral	0.1161	0.0016	0.3293	0.0081	0.0051	0.0049	0.0359	0.0616	0.1327	0.6951						
40		Measured Integral	0.1166	0.0011	0.3277	0.0109	0.0067	0.0032	0.0392	0.0595	0.1358	0.7006						
41		Difference	0.0005	-0.0005	-0.0015	0.0029	0.0016	-0.0018	0.0033	-0.0021	0.0032							
42		Difference Squared	2.47E-07	3.01E-07	2.35E-06	8.24E-06	2.47E-06	3.15E-06	1.08E-05	4.32E-06	9.96E-06	**6.47E-03**						
43		Relative Error %	0%	-52%	0%	26%	24%	-56%	8%	-3%	2%							
44																		
45																		
46	**DOCUMENTATION**																	
47	**Entered Data**																	
48	Cells C40 to K40 are measured integrated areas after normalization.																	
49	Normalization: measured integral=A(XX2XX)/A_{total}, where A_{total} is the total intensities of all 3-carbon sequences and obtained by equation A_{total}=2a+3*b/2+c+(d+e+f)/2=142.74.																	
50	In this equation, a=A(020) b=A(220/022) c=A(222) d=A(20200) e=A(00222) f=A(00220)) (Ref: Polymer 1992 V33 P4920)																	
51																		
52	C3 and C4 are the fractions of normal VDF and reverse VDF, which are obtained by internal standard method. C5 is the fraction of TFE and obtained by equation C5=1-C3-C4																	
53																		
54	**Results**																	
55	The cells H3-H5, J3-J5 and L3-L5 are the conditional probabilities of monomer addition.																	
56	Among them, cells H3 and H4, J3 and J4, and L3 and L4 are the independent variables, corresponding to P(V/V), P(V/B), P(B/V), P(B/B), P(T/V) and P(T/B), respectively.																	
57	Cells H5, J5 and L5 can be obtained by equations H5=1-H3-H4, J5-1-J3-J4, and L5=1-L3-L4, assuming the P(V/V)+P(V/B)+P(V/T)=1, P(B/V)+P(B/B)+P(B/T)=1 and P(T/V) +P(T/B)+P(T/T)=1.																	
58																		
59	Cells H7-H9, J7-J9 and L7-L9 are the probabilities of dyads calculated based on fractions of monomers and the conditional probabilities of monomer addition.																	
60																		
61	**Parameters Varied by Solver**																	
62	Cells H3 and H4, J3 and J4, and L3 and L4 are the independent variables that are varied by Solver to minimize the cell L42.																	
63																		
64	**Calculated Fields**																	
65	A12 to A38 are the probabilities of triads, obtained by first order Markovian model. e.g.: A17(VVT)=C3*H3*H5 (i.e. fV*P(V/V)*P(V/T))																	
66																		
67	A39 is a sum of the probabilities of all triads, which should be 1. A39=Sum(A12:A38)																	
68																		
69	The Matrix containing cells C12 through K38 (i.e. cells C-K/12-38) contains columns C through K representing the integral regions of 5-carbon sequences from the 19F NMR spectrum, and rows corresponding to the different triads.																	
70	If the center monomer in a triad contributes to the resonances of a 5-carbon sequence region, its contribution (based on its statistical probability and number of atoms contributing to the resonance) is entered at the intersection of the corresponding row and column.																	

71	
72	Cells C39 to K39 are the calculated integrated areas of 5-carbon sequences, which are obtained by adding the probabilities of triads contributing the integral areas of each 5-carbon sequence. e.g.: Cell C39 =Sum(C12:C38).
73	
74	Cells C41 to K41 are the differences between the calculated integrated areas and the measured integral areas of the 5-carbon sequences e.g.: Cell C41 =C40-C39
75	
76	Cells C42 to K42 are the difference squared so that the sign of the difference can be removed. e.g.: C42=POWER(C41,2)
77	
78	Cells C43 to K43 are the percent relative error between calculated and measured integral areas of each 5-carbon sequence. e.g.: C43=C41/C40
79	
80	Cell L39 is the total of calculated integral areas for 5-carbon sequences, L39=Sum(C39:K39)
81	
82	Cell L40 is the total of measured integral areas for 5-carbon sequences after normalization, L40=Sum(C40:K40)
83	
84	Cell L42 is the square root of the total of difference squared, L42=SQRT(Sum(C42:K42)).
85	L42 is minimized by Solver to obtain the values of independent variables. (P(V/V) and P(V/B), and indirectly P(V/T) in cells H3, H4 and H5.
86	P(B/V) and P(B/B), and indirectly P(B/T) in cells J3, J4 and J5. P(T/V) and P(T/B), and indirectly P(T/T) in cell L3, L4 and L5.)