Emulsion Copolymerization of vinylidene fluoride (VDF) with perfluoromethyl vinylether (PMVE)

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Supplementary RMN spectra

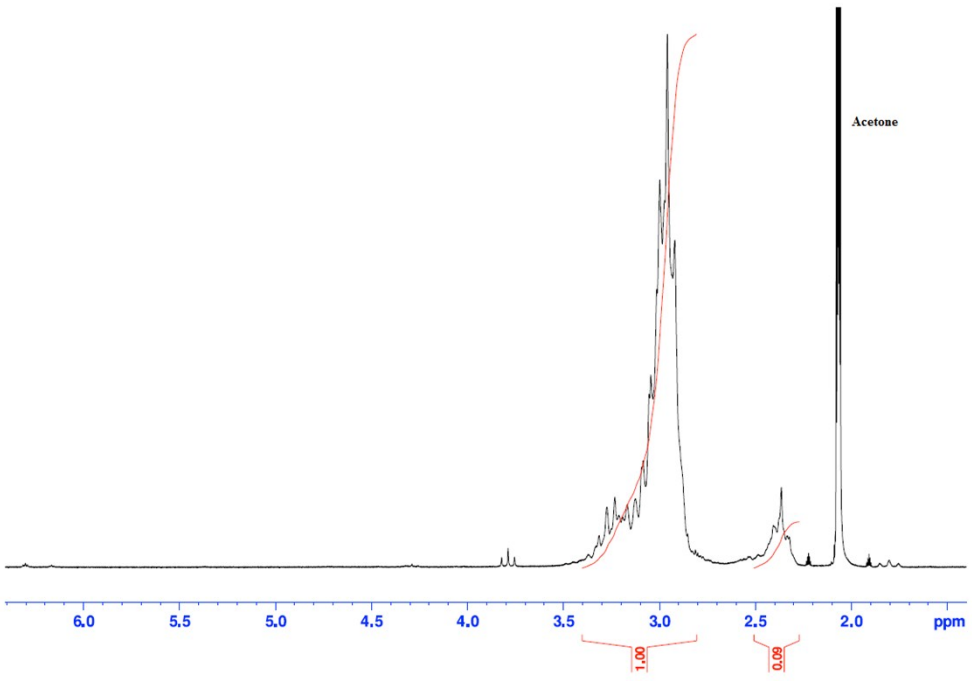

Fig. S1: ^{1}H NMR spectrum of poly(VDF-*co*-PMVE) copolymer (Entry 2, Table 1).

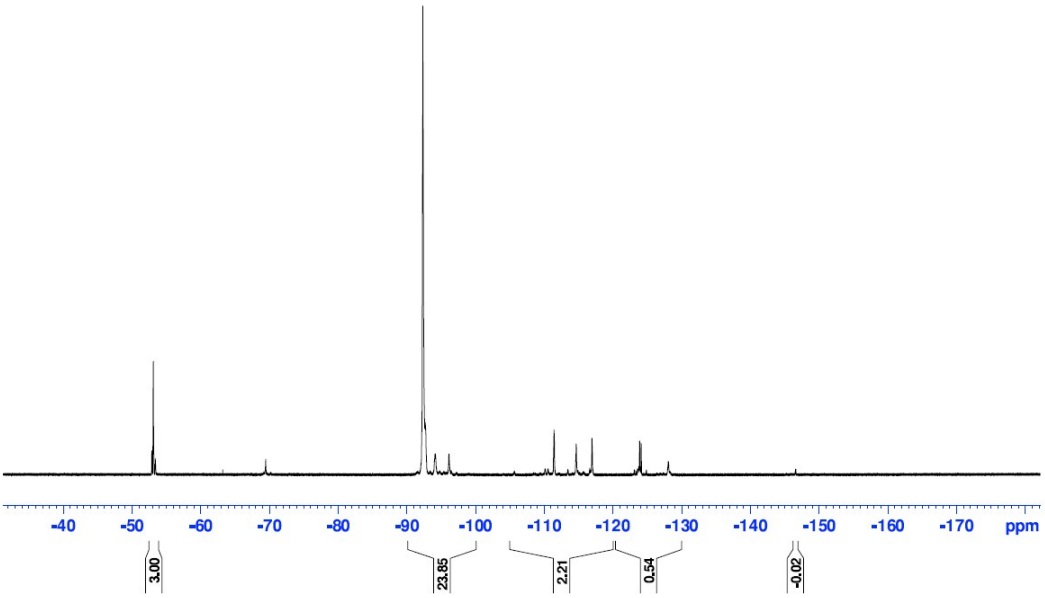

Fig. S2: ^{19}F NMR spectrum of poly(VDF-*co*-PMVE) copolymer (Entry 2, Table 1)

Supplementary chromatogram

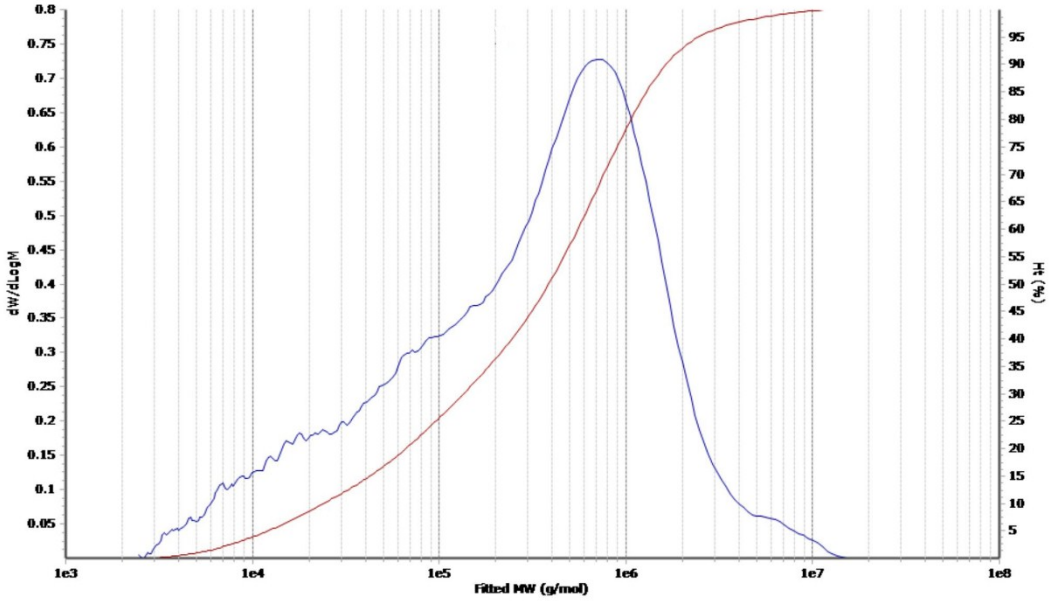

Fig. S3: Typical mass distribution curve by GPC (Entry 7, Table 1).

Supplementary TGA curves

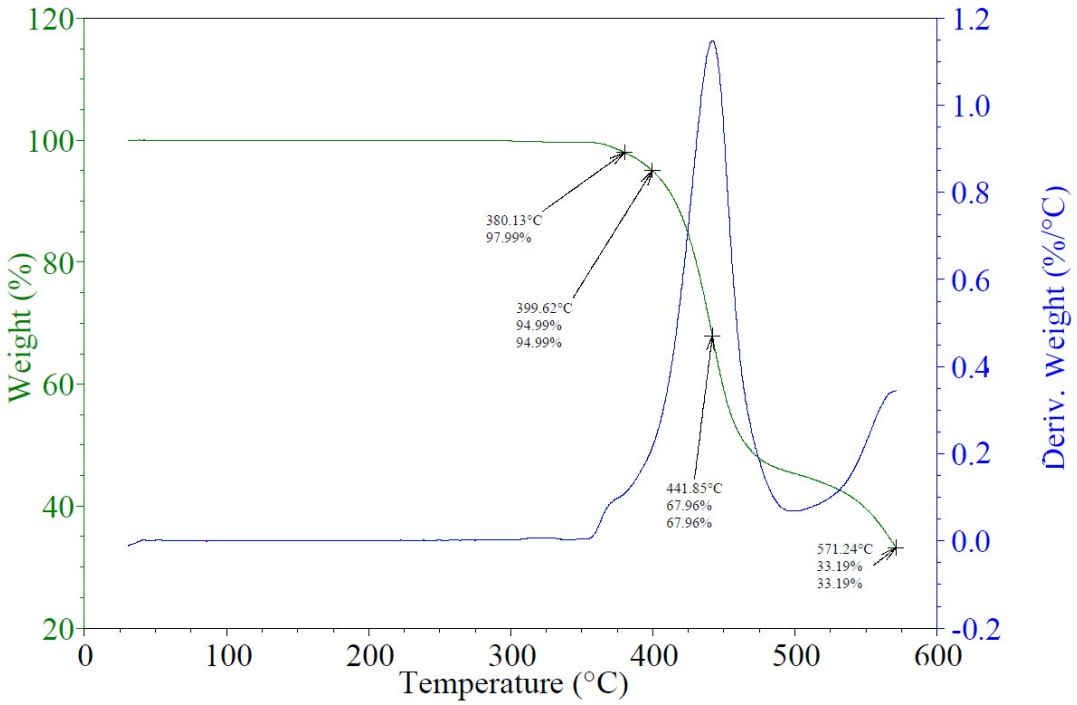

Fig. S4: Thermogravimetric analysis under air and heating at 10 °C/min for Entry 10, Table 1.

Supplementary DSC Thermograms

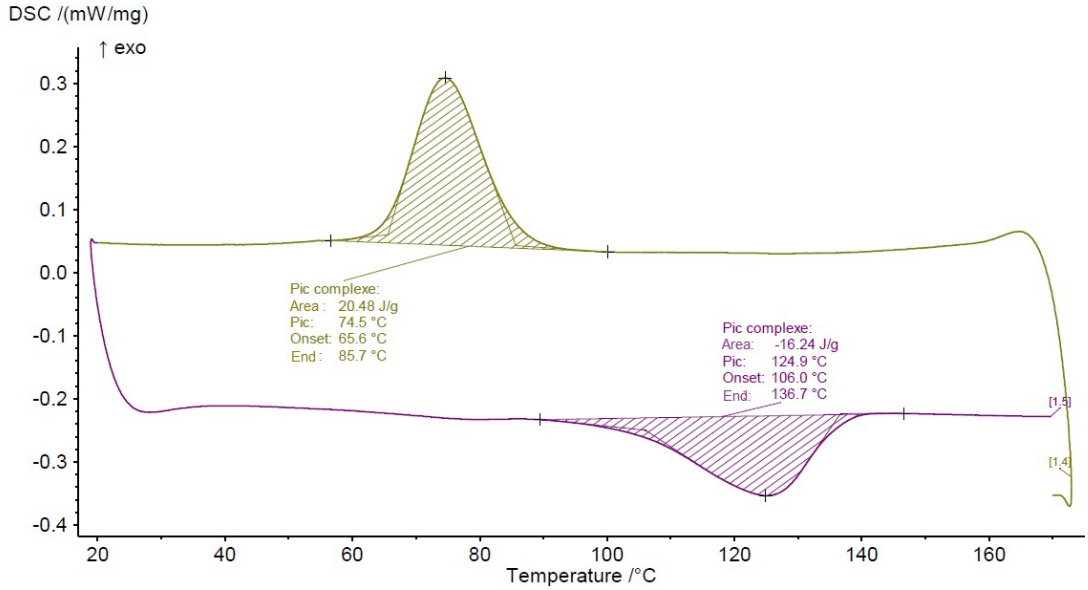

Fig S.5: Differential Scanning Calorimetry thermogram for Entry 2, Table 1. First cooling and second heating program.

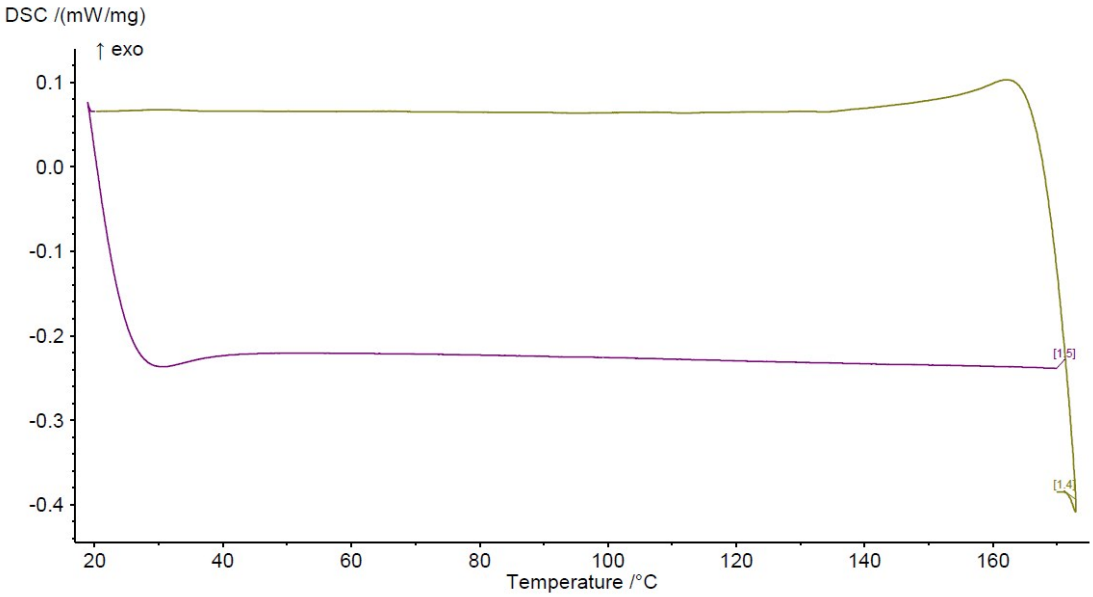

Fig S.6: Differential Scanning Calorimetry thermogram for Entry 5, Table 1. First cooling and second heating program.

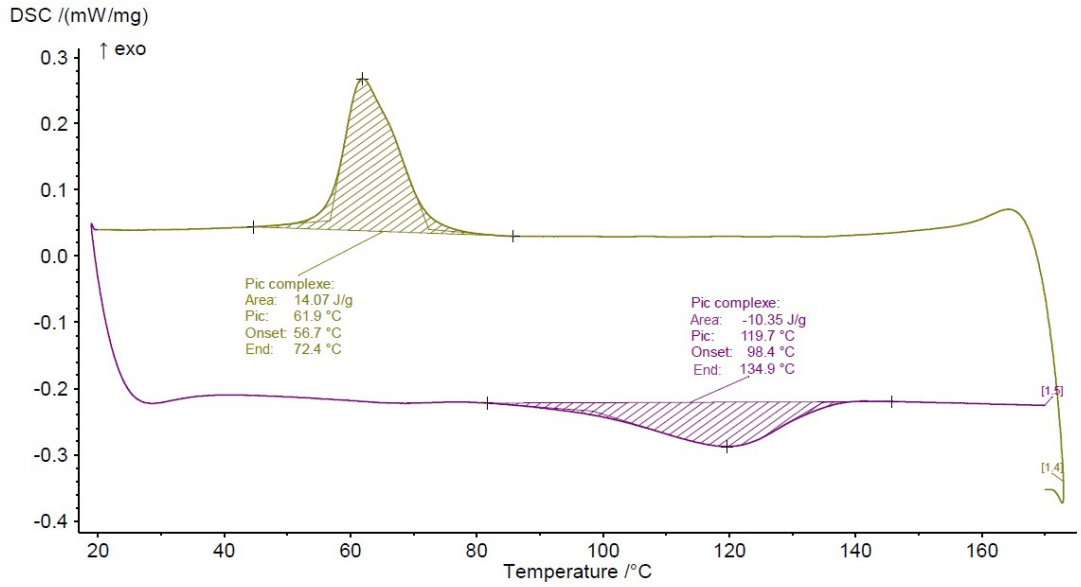

Fig S.7: Differential Scanning Calorimetry curve for Entry 9, Table 1. First cooling and second heating program for T_m and T_c and ΔH_m and ΔH_c determination.

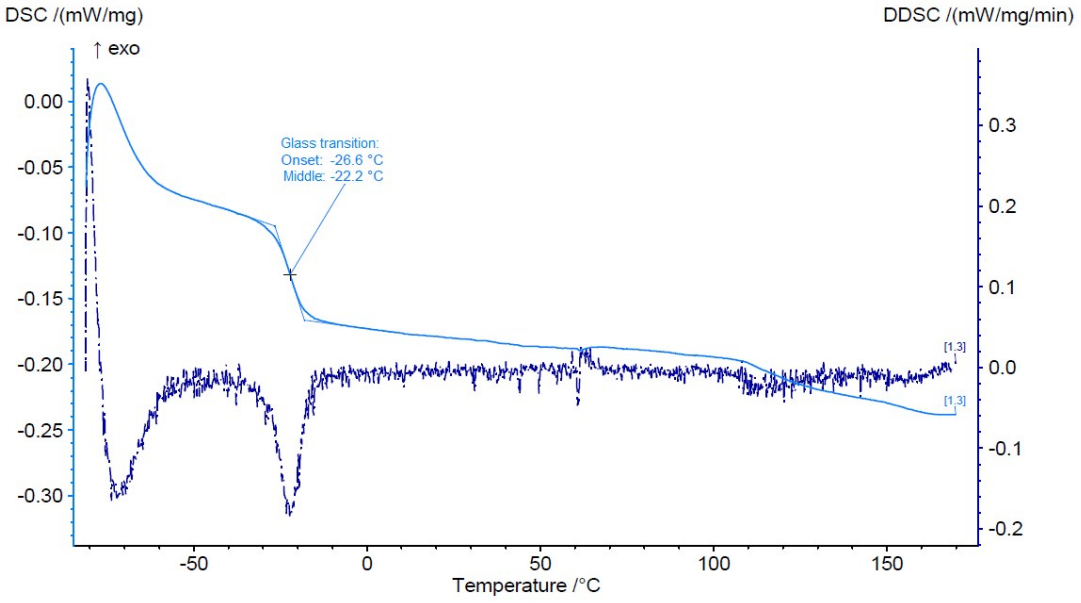

Fig. S8: Differential Scanning Calorimetry thermogram for Entry 6. First cooling and second heating program for T_g determination.

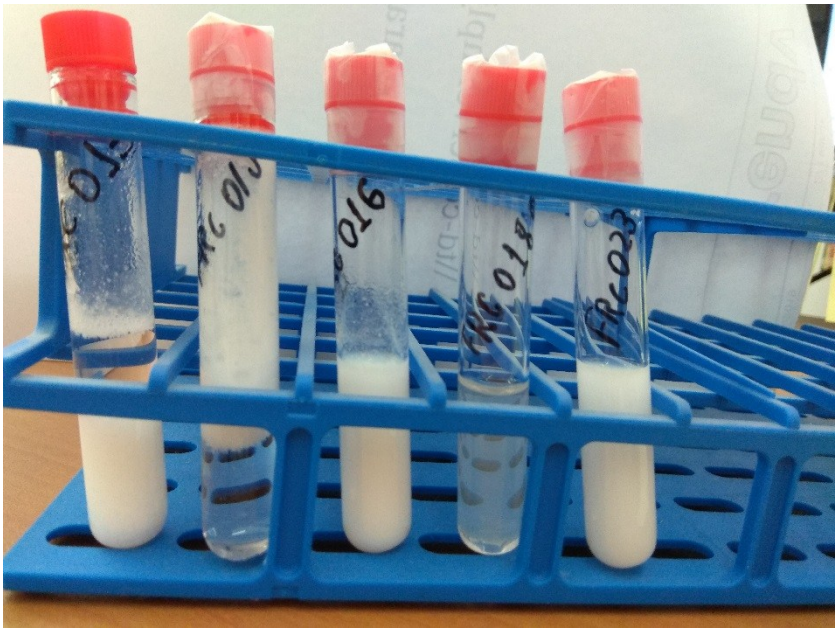

Fig. S9: pictures of samples after copolymerization. Samples 8, 7, 6, 1, and 11 Table 1, from left to right

Supplementary Tables

Table S1: ANOVA for copolymerization yield.

Source of variation	Sum of squares	Degree of freedom	Squared mean	F_0	*P-value*	$F_{critical}$
VDF	155.76125	1	155.76125	2.52900227	0.252737	0.005013
MAF-OH	1423.11125	1	1423.11125	23.1062064	0.040657	
mol	427.78125	1	427.78125	6.94562835	0.118849	
VDFxMAF-OH	296.46125	1	296.46125	4.81346404	0.159486	
VDFxmol	120.90125	1	120.90125	1.9630013	0.296202	
MAF-Ohxmol	1428.45125	1	1428.45125	23.1929088	0.040514	
Pure quadratic	1047.6167	1	1047.6167	17.009526	0.054067	
Error	123.18	2	61.59	-	-	
Total	5023.2642	9	558.1405	-	-	

Table S2: ANOVA for the incorporated VDF assessed from ^{19}F NMR spectroscopy.

Source of variation	Sum of squares	Degree of freedom	Squared mean	F_0	*P-value*	$F_{critical}$
VDF	1277.65125	1	1277.651	110.875145	0.008899	0.005013
MAF-OH	0.45125	1	0.45125	0.03915968	0.861422	
mol	140.28125	1	140.2813	12.1736694	0.073235	
VDFxMAF-OH	0.03125	1	0.03125	0.00271189	0.963202	
VDFxmol	89.11125	1	89.11125	7.73311397	0.108644	
MAF-Ohxmol	0.36125	1	0.36125	0.03134944	0.875771	
Pure quadratic	70.1636742	1	70.16367	6.08883491	0.132391	
Error	23.0466667	2	11.52	-	-	
Total	1601.09784	9	177.8998	-	-	

Table S3: ANOVA for the glass transition temperature.

Source of variation	Sum of squares	Degree of freedom	Squared mean	F_0	*P-value*	$F_{critical}$
VDF	68.445	1	68.445	50.9516129	0.019067	0.005013
MAF-OH	0.98	1	0.98	0.72952854	0.483016	
mol	1.28	1	1.28	0.9528536	0.431943	
VDFxMAF-OH	0.845	1	0.845	0.62903226	0.510854	
VDFxmol	3.125	1	3.125	2.32630273	0.266712	
MAF-Ohxmol	5.12	1	5.12	3.81141439	0.190155	
Pure quadratic	5.82061	1	5.82	4.33295737	0.172841	
Error	2.68666667	2	1.34	-	-	
Total	88.3022727	9	9.8114	-	-	

Table S4: ANOVA for the 5% mass loss in thermal degradation

Source of variation	Sum of squares	Degree of freedom	Squared mean	F_0	*P-value*	$F_{critical}$
VDF	16.18805	1	16.18805	0.02956947	0.879297	0.005013
MAF-OH	330.50205	1	330.5021	0.60370269	0.518478	
mol	467.87405	1	467.874	0.85462957	0.45284	
VDFxMAF-OH	403.8482	1	403.8482	0.73767847	0.48091	
VDFxmol	997.2578	1	997.2578	1.82161418	0.309594	
MAF-Ohxmol	195.2288	1	195.2288	0.35660944	0.610997	
Pure quadratic	13.365	1	13.365	0.02441282	0.890186	
Error	1094.9166	2	547.46	-	-	
Total	3519.18055	9	391.0201	-	-	

Table S5: ANOVA for melting enthalpy

Source of variation	Sum of squares	Degree of freedom	Squared mean	F_0	*P-value*	$F_{critical}$
VDF	351.522613	1	351.522613	31.5606546	0.030254	0.005013
MAF-OH	9.3096125	1	9.3096125	0.83584229	0.457098	
mol	3.2640125	1	3.2640125	0.2930519	0.642509	
VDFxMAF-OH	9.3096125	1	9.3096125	0.83584229	0.457098	
VDFxmol	3.2640125	1	3.2640125	0.2930519	0.642509	
MAF-Ohxmol	0.4095125	1	0.4095125	0.03676714	0.865643	
Pure quadratic	3.73517274	1	3.73517274	0.33535395	0.621056	
Error	22.2760027	2	11.14	-	-	
Total	403.09055	9	44.7878	-	-	

Table S6: ANOVA for crystallization enthalpy

Source of variation	Sum of squares	Degree of freedom	Squared mean	F_0	*P-value*	$F_{critical}$
VDF	631.368113	1	631.368113	15.2424237	0.059784	0.005013
MAF-OH	4.5753125	1	4.5753125	0.11045672	0.771225	
mol	7.9800125	1	7.9800125	0.19265264	0.703583	
VDFxMAF-OH	4.5753125	1	4.5753125	0.11045672	0.771225	
VDFxmol	7.9800125	1	7.9800125	0.19265264	0.703583	
MAF-Ohxmol	1.2720125	1	1.2720125	0.03070879	0.877028	
Pure quadratic	1.53004	1	1.53004	0.03693798	0.865337	
Error	82.8435327	2	41.42	-	-	
Total	742.124344	9	82.4583	-	-	

Table S7: ANOVA for crystallinity rate

Source of variation	Sum of squares	Degree of freedom	Squared mean	F_0	*P-value*	$F_{critical}$
VDF	322.58	1	322.58	22.0793977	0.042429	0.005013
MAF-OH	8.405	1	8.405	0.5752909	0.52736	
mol	2.88	1	2.88	0.19712526	0.700468	
VDFxMAF-OH	8.405	1	8.405	0.5752909	0.52736	
VDFxmol	2.88	1	2.88	0.19712526	0.700468	
MAF-Ohxmol	0.405	1	0.405	0.02772074	0.883077	
Pure quadratic	1.6	1	1.6	0.10789621	0.773755	
Error	29.22	2	14.61	-		
Total	376.35	9	41.817	-	-	

Table S8: ANOVA for VDF-VDF% dyads

Source of variation	Sum of squares	Degree of freedom	Squared mean	F_0	*P-value*	$F_{critical}$
VDF	6418.445	1	6418.45	439.318617	0.002269	0.005013
MAF-OH	6.845	1	6.845	0.46851472	0.564344	
mol	72	1	72	4.92813142	0.156601	
VDFxMAF-OH	3.38	1	3.38	0.23134839	0.678005	
VDFxmol	0.125	1	0.125	0.00855578	0.934734	
MAF-Ohxmol	13.005	1	13.005	0.89014374	0.445029	
Pure quadratic	319.4	1	319.44	21.8644764	0.04282	
Error	27.44	2	13.72	-		
Total	6860.68	9	762.298		-	

Table S9: ANOVA for Tail-to-Tail inversions

Source of variation	Sum of squares	Degree of freedom	Squared mean	F_0	*P-value*	$F_{critical}$
VDF	11.3404551	1	11.34046	159.5705	0.006209	0.005013
MAF-OH	0.25169609	1	0.251696	3.54159	0.200567	
mol	0.31923268	1	0.319233	4.49189	0.168181	
VDFxMAF-OH	0.20458576	1	0.204586	2.87871	0.231849	
VDFxmol	0.0134422	1	0.013442	0.18914	0.70606	
MAF-OHxmol	0.06218238	1	0.062182	0.87496	0.448331	
Pure quadrtic	1.90974057	1	1.909741	26.8718	0.035257	
Error	0.14213727	2	0.071069	-	-	
Total	14.2434721	9	82.4583	-	-	

Table S10: ANOVA for number molar mass (M_n)

Source of variation	Sum of squares	Degree of freedom	Squared mean	F_0	*P-value*	$F_{critical}$
VDF	98.70125	1	98.70125	0.93455293	0.435673	0.005013
MAF-OH	2383.95125	1	2383.951	22.5724459	0.04156	
mol	2370.16125	1	2370.161	22.4418752	0.041786	
VDFxMAF-OH	44.65125	1	44.65125	0.42278043	0.582265	
VDFxmol	635.46125	1	635.4613	6.01686577	0.133671	
MAF-Ohxmol	686.35125	1	686.3513	6.49871781	0.125546	
Pure quadratic	448.0	1	447.9819	4.24171685	0.175636	
Error	211.226667	2	105.6133	-	-	
Total	6878.48602	9	764.2762	-	-	

Table S11: ANOVA for the weight molar mass (M_w)

Source of variation	Sum of squares	Degree of freedom	Squared mean	F_0	P-value	$F_{critical}$
VDF	59.95125	1	59.95125	0.00774462	0.937892	0.005013
MAF-OH	16,4996.401	1	164996.4	21.3145464	0.043853	
mol	23,0215.051	1	230215.1	29.7396147	0.032019	
VDFxMAF-OH	8,109.01125	1	8109.011	1.04753737	0.413713	
VDFxmol	859.05125	1	859.0513	0.11097386	0.770719	
MAF-Ohxmol	124.725.151	1	124725.2	16.1122304	0.056826	
Pure quadratic	38229.9	1	38229.9	4.93861062	0.156343	
Error	15.482.0467	2	7741.02	-	-	
Total	582.676.564	9	64741.84	-	-	

Table S12: ANOVA for dispersity

Source of variation	Sum of squares	Degree of freedom	Squared mean	F_0	P-value	$F_{critical}$
VDF	6.51605	1	6.51605	11.3652035	0.077852	0.005013
MAF-OH	0.49005	1	0.49005	0.85473837	0.452816	
mol	5.81405	1	5.81405	10.1407849	0.086071	
VDFxMAF-OH	13.05605	1	13.05605	22.7721802	0.041217	
VDFxmol	4.23405	1	4.23405	7.38497093	0.11293	
MAF-Ohxmol	7.56605	1	7.56605	13.1965988	0.068125	
Pure quadratic	1.7	1	1.744438	3.04262421	0.223224	
Erreur	1.14666667	2	0.57	-	-	
Total	40.5674	9	4.5075	-	-	

Table S13: ANOVA for H % transfer

Source of variation	Sum of squares	Degree of freedom	Squared mean	F_0	P-value	$F_{critical}$
VDF	0.04714	1	0.04714	6.69035	0.1226	0.005013
MAF-OH	0.00988	1	0.00988	1.40182	0.3581	
mol	0.02212	1	0.02212	3.13990	0.2184	
VDFxMAF-OH	0.00730	1	0.00730	1.03639	0.4158	
VDFxmol	0.00590	1	0.00590	0.83770	0.4567	
MAF-Ohxmol	1.5312×10^{-6}	1	1.5312×10^{-6}	0.00021	0.9896	
Pure quadratic	0.03770	1	0.03770	5.35024	0.1468	
Erreur	0.01409	2	0.00705	-	-	
Total	0.144136	9	0.01602	-	-	