Electronic Supporting Information (ESI)

Controlled Copolymerization of *n*-Butyl Acrylate with Semifluorinated Acrylates by RAFT Polymerization

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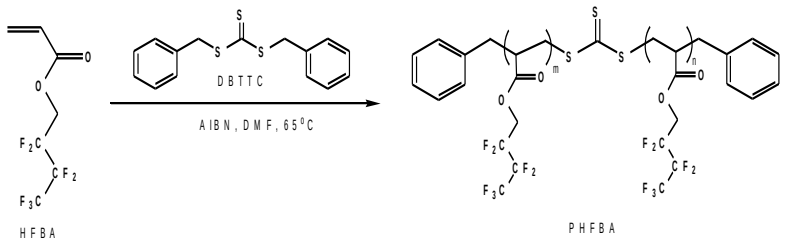

Scheme S1: Synthetic route to semifluorinated homopolymer PHFBA mediated by DBTTC in DMF at 65 °C.

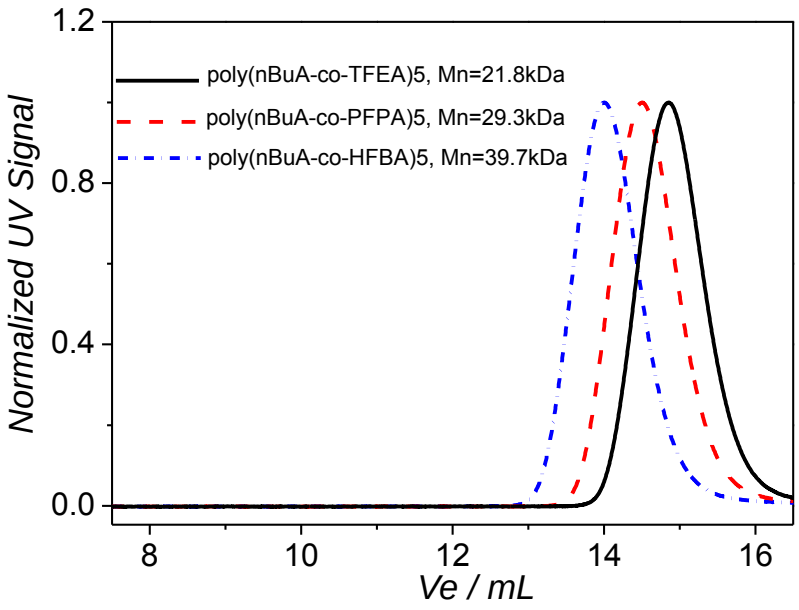

Figure S1: SEC traces of normalized UV signals for the obtained semifluorinated copolymers.

Table S1: ESI-TOF MS results of poly(*n*BuA-*co*-HFBA).

Series	Species	m/z $_{measured}$ $g \cdot mol^{-1}$	m/z $_{simulated}$ $g \cdot mol^{-1}$
①	$[(C_7H_7)_2(C_7H_{12}O_2)_5(C_7H_5F_7O_2)_2CS_3 + H + Br + Cl]^-$	1552.3892	1552.3666
②	$[(C_7H_7)_2(C_7H_{12}O_2)_5(C_7H_5F_7O_2)_2CS_3 - H_2 + Na_2 + Br]^-$	1561.3804	1561.3618
③	$[(C_7H_7)_2(C_7H_{12}O_2)_5(C_7H_5F_7O_2)_2CS_3 - H_2 + Na + K + Br]^-$	1577.3592	1577.3356
④	$[(C_7H_7)_2(C_7H_{12}O_2)_5(C_7H_5F_7O_2)_2CS_3 + H + Br_2]^-$	1597.3545	1597.3239
⑤	$[(C_7H_7)_2(C_7H_{12}O_2)_7(C_7H_5F_7O_2)_1CS_3 - H_4 + Na_3 + K + Br]^-$	1623.4610	1623.4475
⑥	$[(C_7H_7)_2(C_7H_{12}O_2)_5(C_7H_5F_7O_2)_2CS_3 - H_4 + Na_2 + K_2 + Br]^-$	1637.3995	1637.3717
⑦	$[(C_7H_7)_2(C_7H_{12}O_2)_4(C_7H_5F_7O_2)_3CS_3 + H + Br + Cl]^-$	1681.4319	1681.4186
⑧	$[(C_7H_7)_2(C_7H_{12}O_2)_4(C_7H_5F_7O_2)_3CS_3 - H_2 + Na_2 + Br]^-$	1687.3098	1687.2941
⑨	$[(C_7H_7)_2(C_7H_{12}O_2)_4(C_7H_5F_7O_2)_3CS_3 - H_2 + Na + K + Br]^-$	1703.2867	1703.2696
⑩	$[(C_7H_7)_2(C_7H_{12}O_2)_4(C_7H_5F_7O_2)_3CS_3 + H + Br_2]^-$	1723.2751	1723.2579
⑪	$[(C_7H_7)_2(C_7H_{12}O_2)_6(C_7H_5F_7O_2)_2CS_3 + (CH_3OH)_3 + Br]^-$	1741.5866	1741.5601
⑫	$[(C_7H_7)_2(C_7H_{12}O_2)_6(C_7H_5F_7O_2)_2CS_3 - H_4 + Na_3 + K + Br]^-$	1749.4014	1749.3831
⑬	$[(C_7H_7)_2(C_7H_{12}O_2)_4(C_7H_5F_7O_2)_3CS_3 - H_4 + Na_2 + K_2 + Br]^-$	1763.2259	1763.2075
⑭	$[(C_7H_7)_2(C_7H_{12}O_2)_3(C_7H_5F_7O_2)_4CS_3 + H + Br + Cl]^-$	1805.2581	1805.2347
⑮	$[(C_7H_7)_2(C_7H_{12}O_2)_5(C_7H_5F_7O_2)_3CS_3 - H_2 + Na_2 + Br]^-$	1815.3991	1815.3794
⑯	$[(C_7H_7)_2(C_7H_{12}O_2)_5(C_7H_5F_7O_2)_3CS_3 + H + Br_2]^-$	1851.3675	1851.3407
⑰	$[(C_7H_7)_2(C_7H_{12}O_2)_5(C_7H_5F_7O_2)_3CS_3 - H_4 + Na_3 + K + Br]^-$	1875.3327	1875.3156
⑱	$[(C_7H_7)_2(C_7H_{12}O_2)_5(C_7H_5F_7O_2)_3CS_3 - H_4 + Na_2 + K_2 + Br]^-$	1891.3068	1891.2895
⑲	$[(C_7H_7)_2(C_7H_{12}O_2)_4(C_7H_5F_7O_2)_4CS_3 + H + Br + Cl]^-$	1933.3457	1933.3263
⑳	$[(C_7H_7)_2(C_7H_{12}O_2)_6(C_7H_5F_7O_2)_3CS_3 - H_2 + Na_2 + Br]^-$	1943.4685	1943.4416

Table S2: ESI-TOF MS results of poly(*n*BuA-*co*-PFPA).

Series	Species	m/z $_{measured}$ $g \cdot mol^{-1}$	m/z $_{simulated}$ $g \cdot mol^{-1}$
①	$[(C_7H_7)_2(C_7H_{12}O_2)_6(C_6H_5F_5O_2)_3CS_3 + Na]^+$	1693.5582	1693.5803
②	$[(C_7H_7)_2(C_7H_{12}O_2)_6(C_6H_5F_5O_2)_3CS_3 - H + Li + Na]^+$	1699.5649	1699.5886
③	$[(C_7H_7)_2(C_7H_{12}O_2)_6(C_6H_5F_5O_2)_3CS_3 + K]^+$	1709.5253	1709.5542
④	$[(C_7H_7)_2(C_7H_{12}O_2)_3(C_6H_5F_5O_2)_5CS_3 + Na]^+$	1717.3495	1717.3710
⑤	$[(C_7H_7)_2(C_7H_{12}O_2)_3(C_6H_5F_5O_2)_5CS_3 - H + Li + Na]^+$	1723.3501	1723.3793
⑥	$[(C_7H_7)_2(C_7H_{12}O_2)_3(C_6H_5F_5O_2)_5CS_3 + K]^+$	1733.3223	1733.3450
⑦	$[(C_7H_7)_2(C_7H_{12}O_2)_8(C_6H_5F_5O_2)_2CS_3 + Na]^+$	1745.7029	1745.7268
⑧	$[(C_7H_7)_2(C_7H_{12}O_2)_8(C_6H_5F_5O_2)_2CS_3 - H + Li + Na]^+$	1751.7201	1751.7349
⑨	$[(C_7H_7)_2(C_7H_{12}O_2)_8(C_6H_5F_5O_2)_2CS_3 + K]^+$	1761.6842	1761.7007
⑩	$[(C_7H_7)_2(C_7H_{12}O_2)_5(C_6H_5F_5O_2)_4CS_3 + Na]^+$	1769.4965	1769.5157
⑪	$[(C_7H_7)_2(C_7H_{12}O_2)_5(C_6H_5F_5O_2)_4CS_3 - H + Li + Na]^+$	1775.5013	1775.5257
⑫	$[(C_7H_7)_2(C_7H_{12}O_2)_5(C_6H_5F_5O_2)_4CS_3 + K]^+$	1785.4697	1785.4915
⑬	$[(C_7H_7)_2(C_7H_{12}O_2)_5(C_6H_5F_5O_2)_4CS_3 - H + Li + K]^+$	1791.4763	1791.4996
⑭	$[(C_7H_7)_2(C_7H_{12}O_2)_7(C_6H_5F_5O_2)_3CS_3 + Na]^+$	1821.6307	1821.6640
⑮	$[(C_7H_7)_2(C_7H_{12}O_2)_7(C_6H_5F_5O_2)_3CS_3 + K]^+$	1837.6175	1837.6349
⑯	$[(C_7H_7)_2(C_7H_{12}O_2)_4(C_6H_5F_5O_2)_5CS_3 + Na]^+$	1745.4299	1745.4548
⑰	$[(C_7H_7)_2(C_7H_{12}O_2)_4(C_6H_5F_5O_2)_5CS_3 - H + Li + Na]^+$	1752.4486	1752.4709
⑱	$[(C_7H_7)_2(C_7H_{12}O_2)_4(C_6H_5F_5O_2)_5CS_3 + K]^+$	1861.3943	1861.4287
⑲	$[(C_7H_7)_2(C_7H_{12}O_2)_6(C_6H_5F_5O_2)_4CS_3 - H_2 + Li + Na + K]^+$	1889.4017	1889.4266
⑳	$[(C_7H_7)_2(C_7H_{12}O_2)_6(C_6H_5F_5O_2)_4CS_3 + Na]^+$	1897.5739	1897.6012

Table S3: ESI-TOF MS results of poly(*n*BuA-*co*-TFEA).

Series	Species	m/z $_{measured}$ $g \cdot mol^{-1}$	m/z $_{simulated}$ $g \cdot mol^{-1}$
①	$[(C_7H_7)_2(C_7H_{12}O_2)_{15}(C_5H_5F_3O_2)_7CS_3 + 2Na]^{2+}$	1667.6951	1667.7146
②	$[(C_7H_7)_2(C_7H_{12}O_2)_7(C_5H_5F_3O_2)_3CS_3 + Na]^{+}$	1671.6514	1671.6736
③	$[(C_7H_7)_2(C_7H_{12}O_2)_7(C_5H_5F_3O_2)_3CS_3 - H + Na + Li]^{+}$	1677.6661	1677.6817
	& $[(C_7H_7)_2(C_7H_{12}O_2)_{14}(C_5H_5F_3O_2)_8CS_3 + 2Na]^{2+}$	1680.6719	1680.6849
④	$[(C_7H_7)_2(C_7H_{12}O_2)_{13}(C_5H_5F_3O_2)_9CS_3 + 2Na]^{2+}$	1693.6275	1693.6550
⑤	$[(C_7H_7)_2(C_7H_{12}O_2)_6(C_5H_5F_3O_2)_4CS_3 + Na]^{+}$	1697.5921	1697.6140
⑥	$[(C_7H_7)_2(C_7H_{12}O_2)_6(C_5H_5F_3O_2)_4CS_3 - H + Na + Li]^{+}$	1703.6045	1703.6224
	& $[(C_7H_7)_2(C_7H_{12}O_2)_{12}(C_5H_5F_3O_2)_{10}CS_3 + 2Na]^{2+}$	1706.6067	1706.6253
⑦	$[(C_7H_7)_2(C_7H_{12}O_2)_{11}(C_5H_5F_3O_2)_{11}CS_3 + 2Na]^{2+}$	1719.5716	1719.5955
⑧	$[(C_7H_7)_2(C_7H_{12}O_2)_5(C_5H_5F_3O_2)_5CS_3 + Na]^{+}$	1723.5319	1723.5545
⑨	$[(C_7H_7)_2(C_7H_{12}O_2)_5(C_5H_5F_3O_2)_5CS_3 - H + Na + Li]^{+}$	1729.5465	1729.5626
	& $[(C_7H_7)_2(C_7H_{12}O_2)_{10}(C_5H_5F_3O_2)_{12}CS_3 + 2Na]^{2+}$	1732.5428	1732.5657
⑩	$[(C_7H_7)_2(C_7H_{12}O_2)_9(C_5H_5F_3O_2)_{13}CS_3 + 2Na]^{2+}$	1745.5154	1745.5360
⑪	$[(C_7H_7)_2(C_7H_{12}O_2)_4(C_5H_5F_3O_2)_6CS_3 + Na]^{+}$	1749.4648	1749.4949
⑫	$[(C_7H_7)_2(C_7H_{12}O_2)_4(C_5H_5F_3O_2)_6CS_3 - H + Na + Li]^{+}$	1755.4862	1755.5030
	&$[(C_7H_7)_2(C_7H_{12}O_2)_8(C_5H_5F_3O_2)_{14}CS_3 + 2Na]^{2+}$	1751.4848	1758.5061
⑬	$[(C_7H_7)_2(C_7H_{12}O_2)_7(C_5H_5F_3O_2)_{15}CS_3 + 2Na]^{2+}$	1771.4593	1771.4764
⑭	$[(C_7H_7)_2(C_7H_{12}O_2)_9(C_5H_5F_3O_2)_2CS_3 + Na]^{+}$	1773.7945	1773.8169
⑮	$[(C_7H_7)_2(C_7H_{12}O_2)_9(C_5H_5F_3O_2)_2CS_3 - H + Na + Li]^{+}$	1799.8067	1799.8250
	& $[(C_7H_7)_2(C_7H_{12}O_2)_6(C_5H_5F_3O_2)_{16}CS_3 + 2Na]^{2+}$	1784.4248	1784.4466
⑯	$[(C_7H_7)_2(C_7H_{12}O_2)_5(C_5H_5F_3O_2)_{17}CS_3 + 2Na]^{2+}$	1797.3981	1797.4168
⑰	$[(C_7H_7)_2(C_7H_{12}O_2)_8(C_5H_5F_3O_2)_3CS_3 + Na]^{+}$	1799.7386	1799.7573
⑱	$[(C_7H_7)_2(C_7H_{12}O_2)_8(C_5H_5F_3O_2)_3CS_3 - H + Na + Li]^{+}$	1805.7438	1805.7675
	& $[(C_7H_7)_2(C_7H_{12}O_2)_4(C_5H_5F_3O_2)_{18}CS_3 + 2Na]^{2+}$	1810.3674	1810.3870
⑲	$[(C_7H_7)_2(C_7H_{12}O_2)_3(C_5H_5F_3O_2)_{19}CS_3 + 2Na]^{2+}$	1823.3361	1823.3573
⑳	$[(C_7H_7)_2(C_7H_{12}O_2)_7(C_5H_5F_3O_2)_4CS_3 + Na]^{+}$	1825.6685	1825.6978

Table S4: Fineman-Ross and Kelen-Tüdos parameters for the RAFT copolymerization of *n*BuA with HFBA at 65 °C.

[*n*BuA + HFBA]/[DBTTC] = 50, [DBTTC/AIBN] = 10, V_{DMF} = 0.7 mL.

f_{nBuA}	f_{HFBA}	x (f_{nBuA}/f_{HFBA})	F_{nBuA}	F_{HFBA}	X (F_{nBuA}/F_{HFBA})	G x(X-1)/X	H x^2/X	η* G/(H+α)	ζ H/(H+α)
0.21	0.79	0.265822785	0.204	0.796	0.256281407	-0.771407	0.2757194	-0.621241	0.2220465
0.44	0.56	0.785714286	0.431	0.569	0.757469244	-0.251574	0.8150125	-0.141254	0.4576119
0.52	0.48	1.083333333	0.541	0.459	1.178649237	0.164202	0.995726	0.083703	0.507576
0.62	0.38	1.631578947	0.639	0.361	1.770083102	0.7098262	1.5039124	0.2873892	0.608893
0.79	0.21	3.761904762	0.807	0.193	4.18134715	2.8622175	3.3845378	0.6578997	0.7779585

* $\alpha = (H_{min} \times H_{max})^{1/2}$

In the Fineman-Ross laws, the following equation was used:

$$G = r_{nBuA}H - r_{HFBA}$$

Where, G = x(X-1)/X.

$H = x^2/X$.

$x = f_{nBuA}/f_{HFBA}$ (f_{nBuA} and f_{HFBA} are the molar fractions of *n*BuA and HFBA in the feed).

$X = F_{nBuA}/F_{HFBA}$ (F_{nBuA} and F_{HFBA} are the molar fractions of *n*BuA and HFBA in the final obtained copolymer).

In the Kelen-Tüdos laws, the following equation was used:

$$\eta = (r_{nBuA}+r_{HFBA}/\alpha)\zeta - r_{HFBA}/\alpha$$

Where, $\eta = G/(\alpha + H)$

$\zeta = H/(\alpha + H)$

$\alpha = (H_{min} \times H_{max})^{1/2}$

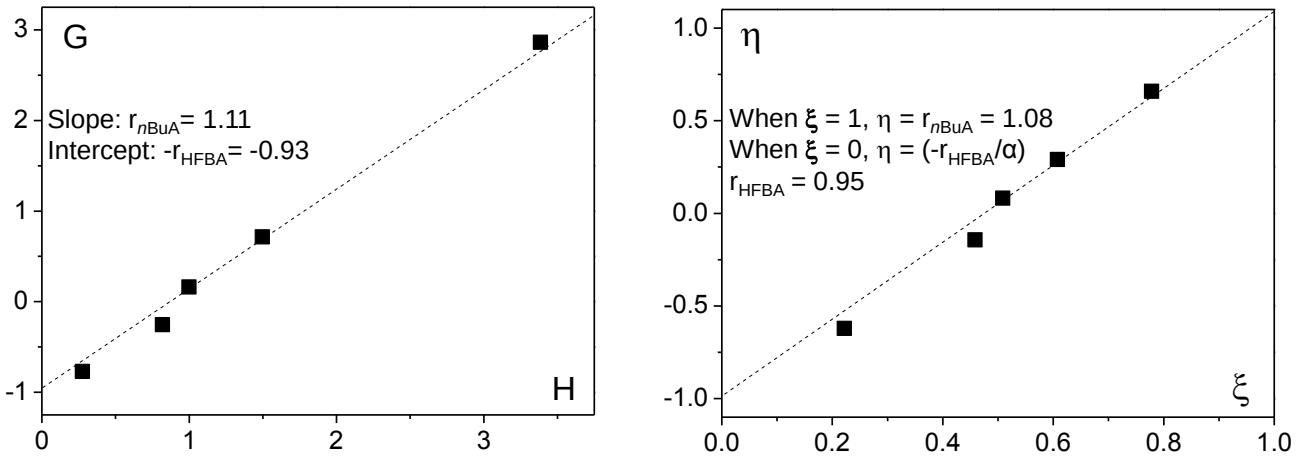

Figure S2: **Fineman-Ross graphic method [G = f(H)] (left), and Kelen-Tüdos graphic method [η = f(ξ)] (right) for the determination of *n*BuA with HFBA reactivity ratios at 65 °C.**

Table S5: Fineman-Ross and Kelen-Tüdos parameters for the RAFT copolymerization of *n*BuA with PFPA at 65 °C.

[*n*BuA + HFPA]/[DBTTC] = 50, [DBTTC/AIBN] = 10, V_{DMF} = 0.7 mL.

f_{nBuA}	f_{PFPA}	x (f_{nBuA}/f_{PFPA})	F_{nBuA}	F_{PFPA}	X (F_{nBuA}/F_{PFPA})	G x(X-1)/X	H x^2/X	η* G/(H+α)	ζ H/(H+α)
0.21	0.79	0.265822785	0.202	0.798	0.253132832	-0.784309	0.2791489	-0.568066	0.2021842
0.36	0.64	0.56250000	0.332	0.668	0.497005988	-0.569277	0.6366246	-0.327521	0.3662674
0.51	0.49	1.040816327	0.473	0.527	0.897533207	-0.11882	1.206973	-0.05147	0.522841
0.68	0.32	2.12500000	0.689	0.311	2.225806452	1.1702899	2.0287591	0.3738615	0.6481086
0.81	0.19	4.263157895	0.807	0.193	4.18134715	3.2435923	4.3465693	0.5953636	0.7978158

* $\alpha = (H_{min} \times H_{max})^{1/2}$

In the Fineman-Ross laws, the following equation was used:

$$G = r_{nBuA}H - r_{PFPA}$$

Where, G = x(X-1)/X.

H = x^2/X.

x = f_{nBuA}/f_{PFPA} (f_{nBuA} and f_{PFPA} are the molar fractions of *n*BuA and PFPA in the feed).

X = F_{nBuA}/F_{PFPA} (F_{nBuA} and F_{PFPA} are the molar fractions of *n*BuA and PFPA in the final obtained copolymer).

In the Kelen-Tüdos laws, the following equation was used:

$$\eta = (r_{nBuA}+r_{PFPA}/\alpha)\zeta - r_{PFPA}/\alpha$$

Where, $\eta = G/(\alpha + H)$

$\zeta = H/(\alpha + H)$

$\alpha = (H_{min} \times H_{max})^{1/2}$

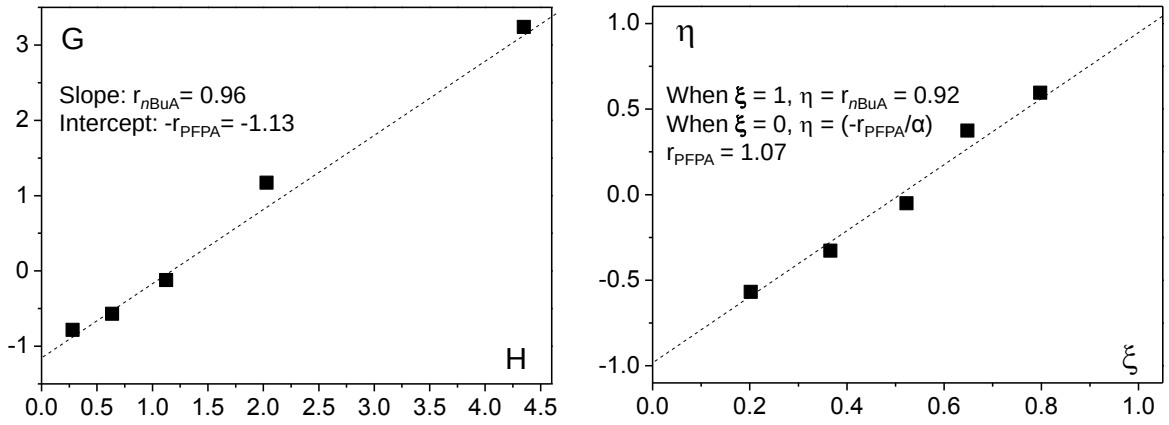

Figure S3: **Fineman-Ross graphic method [G = f(H)] (left), and Kelen-Tüdos graphic method [η = f(ξ)] (right) for the determination of *n*BuA and PFPA reactivity ratios at 65 °C.**

Table S6: Fineman-Ross and Kelen-Tüdos parameters for the RAFT copolymerization of *n*BuA with TFEA at 65 °C.

[*n*BuA + TFEA]/[DBTTC] = 50, [DBTTC/AIBN] = 10, V_{DMF} = 0.7 mL.

f_{nBuA}	f_{TFEA}	x (f_{nBuA}/f_{TFEA})	F_{nBuA}	F_{TFEA}	X (F_{nBuA}/F_{TFEA})	G x(X-1)/X	H x^2/X	η* G/(H+α)	ζ H/(H+α)
0.23	0.77	0.298701299	0.171	0.829	0.206272618	-1.149389	0.4325463	-0.618666	0.2328211
0.36	0.64	0.562501552	0.306	0.694	0.44092219	-0.713241	0.7176012	-0.332842	0.3348735
0.49	0.51	0.960784314	0.429	0.571	0.751313485	-0.318022	1.2286569	-0.119829	0.4629524
0.62	0.38	1.631578947	0.639	0.361	1.770083102	0.7098262	1.5039124	0.2873892	0.6088934
0.78	0.22	3.545454545	0.728	0.272	2.676470588	2.2207792	4.6965762	0.3627611	0.7671789

* $\alpha = (H_{min} \times H_{max})^{1/2}$

In the Fineman-Ross laws, the following equation was used:

$$G = r_{nBuA}H - r_{TFEA}$$

Where, G = x(X-1)/X.

$H=x^2/X$.

$x = f_{nBuA}/f_{TFEA}$ (f_{nBuA} and f_{TFEA} are the molar fractions of *n*BuA and TFEA in the feed).

$X = F_{nBuA}/F_{TFEA}$ (F_{nBuA} and F_{TFEA} are the molar fractions of *n*BuA and TFEA in the final obtained copolymer).

In the Kelen-Tüdos laws, the following equation was used:

$$\eta = (r_{nBuA}+r_{TFEA}/\alpha)\zeta - r_{TFEA}/\alpha$$

Where, $\eta = G/(\alpha + H)$

$\zeta = H/(\alpha + H)$

$\alpha = (H_{min} \times H_{max})^{1/2}$

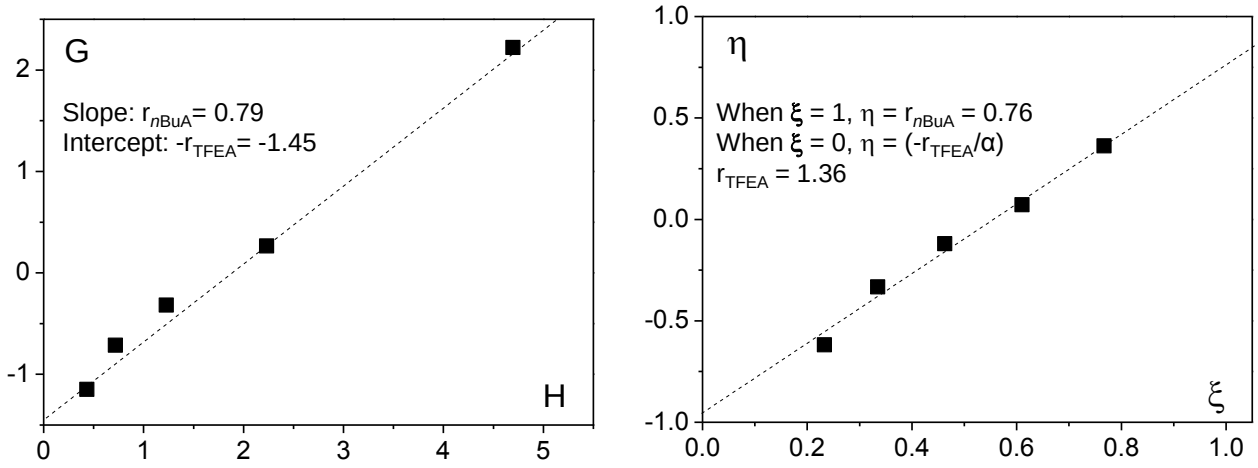

Figure S4: Fineman-Ross graphic method [G = f(H)] (left), and Kelen-Tüdos graphic method [η = f(ξ)] (right) for the determination of *n*BuA and TFEA reactivity ratios at 65 °C.