Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information for

Going beyond the barriers of Aza-Michael reaction: controlling the selectivity of acrylates towards primary amino-PDMS

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Table S1: Influence of the Michael acceptor on the aza-Michael addition with α,ω-amino-PDMS (NH40D). Room temperature, bulk, $r \sim 0.5$

Michael donor	Michael acceptor[a]	r	time (h)	Conv. (%)	Composition (mol-%)		
					MA[b]	*DA*[c]	*R-NH*$_2$[d]
NH40D	BA	0.53	25	80	73	3.5	23.5
			1080	100	87	7.0	6.0
	AN	0.50	1	6	6	0	94
			4	20	20	0	80
			8	34	34	0	66
	MeA	0.50	1	15	15	0	85
			4	39	38	1	61
			7	52	50	2	48
	tBA	0.5	1	9	9	0	91
			264	91	87	4	9

(a) BA: butyl acrylate; AN: acrylonitrile; MeA: methyl acrylate; tBA: t-butyl acrylate, (b) Mono-adduct , (c) Di-adduct, (d) Primary amine groups

Table S2: Influence of the IPOH content on the kinetics and amine composition, with NH40D and BA as reactants (T = 25°C).

Entry	*r*	Solvent (mol%)	Time (h)	Conv. (%)	Composition (mol-%)		
					MA[a]	*DA*[b]	*R-NH*$_2$[c]
S1	0.51	14	1	31	31	0	69
			4	61	59	2	39
			8	77	71	3	26
S2	0.53	36	5	87	82	2.5	16
S3	0.50	40	1	57	55	1	44
			4	83	79	2	19
			8	91	85	3	12
S4	0.51	57	1	70	68	1	30
			4	89	85	2	13
			8	94	90	2	8
S5	0.51	77	1	74	72	1	27
			4	91	89	1	9
			8	94	92	1	6
S6	0.51	85	2	85.5	84	1	15
			48	99.5	96	1.5	2
S7	0.51	93	1	69	69	0	31
			4	90	88	1	11
			8	94	92	1	6
S8	0.53	98	7	85.5	88	0	11.5
			28	95	97	0	2.5
			48	96.5	97	1	2

(a) Mono-adduct, (b) Di-adduct, (c) Primary amine groups

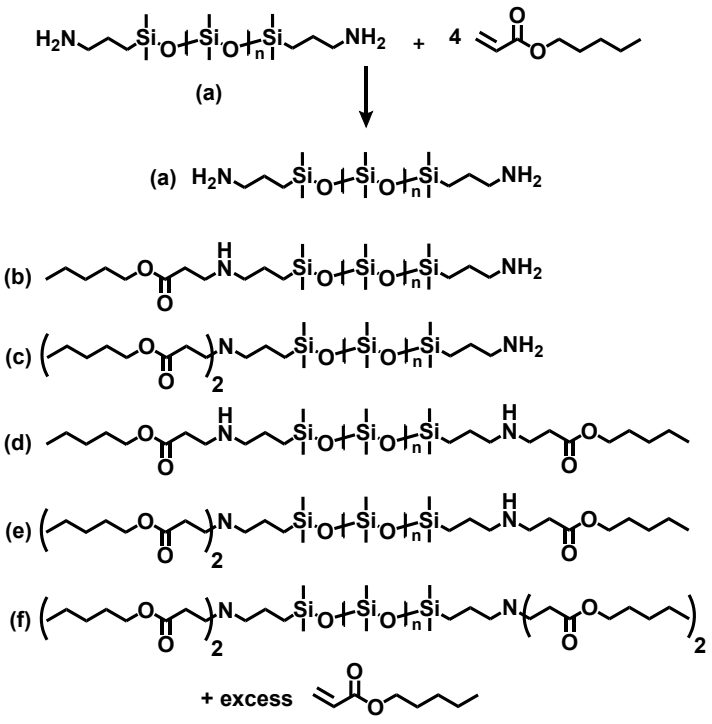

Figure S1: Possible structures obtained in the aza-Michael reaction of a bis(aminopropyl)-terminated PDMS with butyl acrylate.

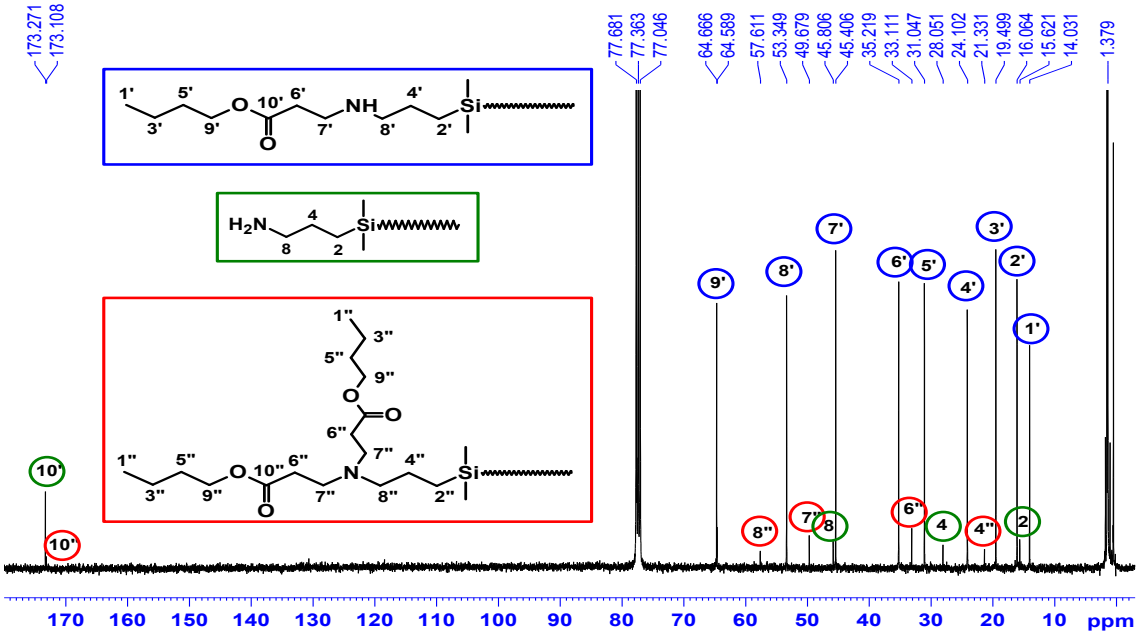

Figure S2: ^{13}C NMR analysis of the mixture of amines after removal of residual butyl acrylate (entry s1, Table s1 (t = 25h)).

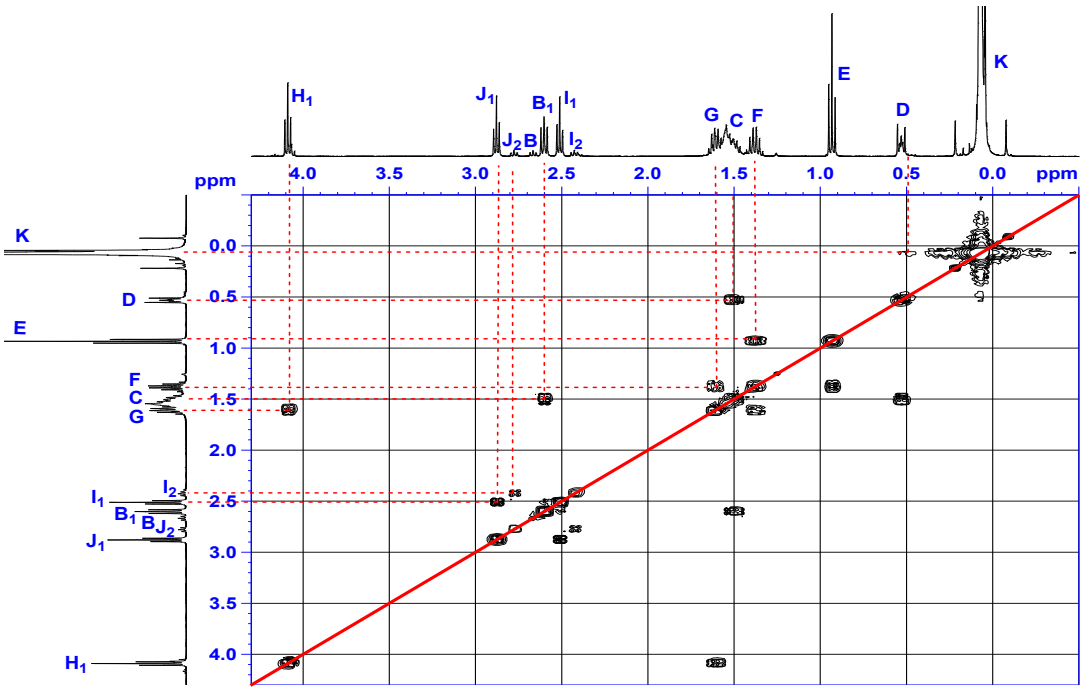

Figure S3 : COSY analysis (J_{HH}) of the mixture of amines after removal of residual butyl acrylate (entry s1, Table s1 (t = 25h))

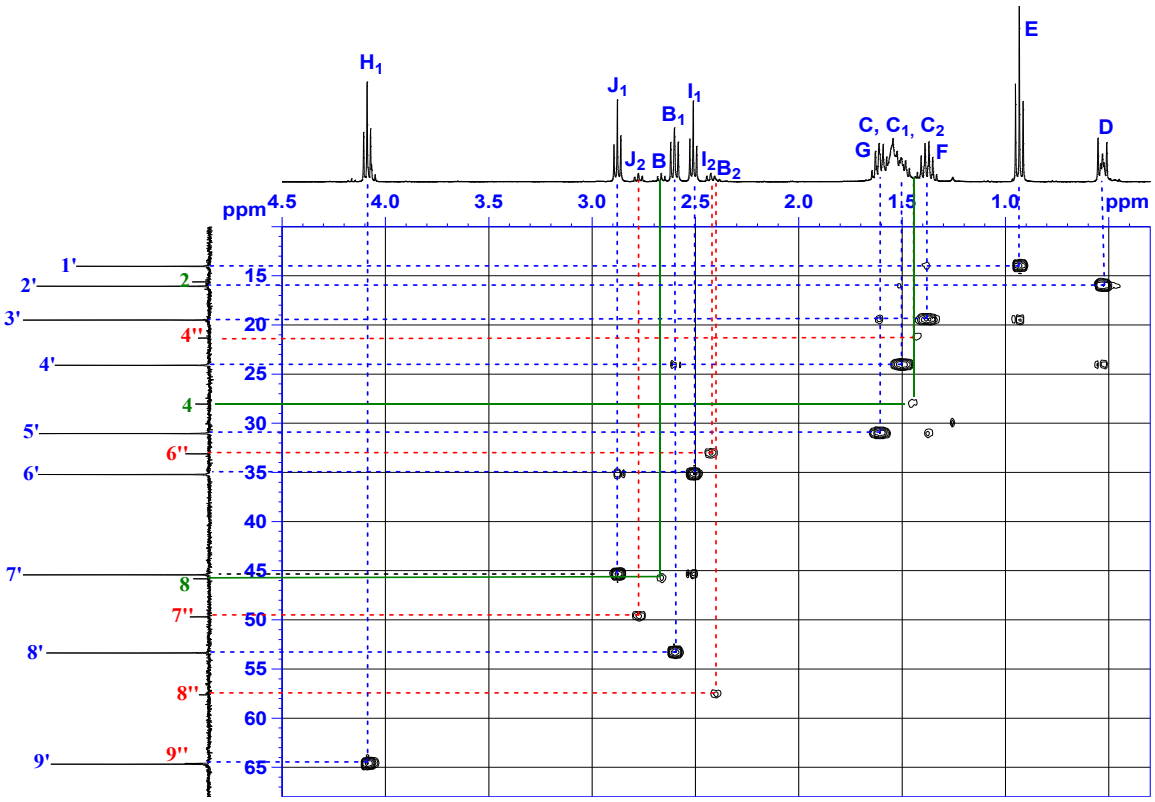

Figure S4: HSQC analysis ($^1J_{CH}$) of the mixture of amines after removal of residual butyl acrylate (entry s1, Table s1 (t = 25h))

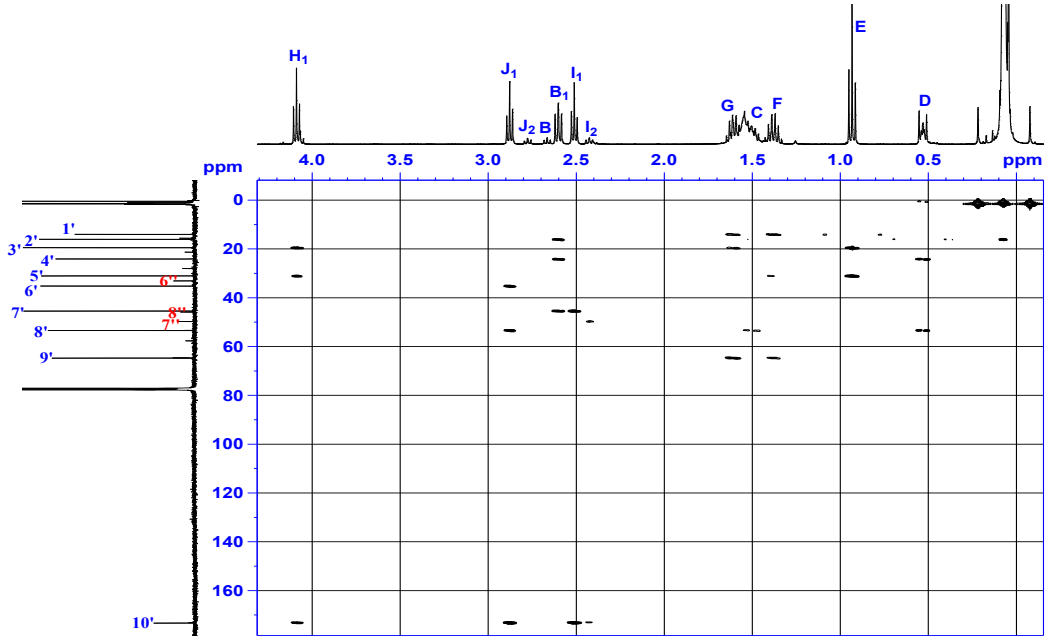

Figure S5: HMBC analysis ($^2J_{CH}$, $^3J_{CH}$) of the mixture of amines after removal of residual butyl acrylate (entry s1, Table s1 (t = 25h)).

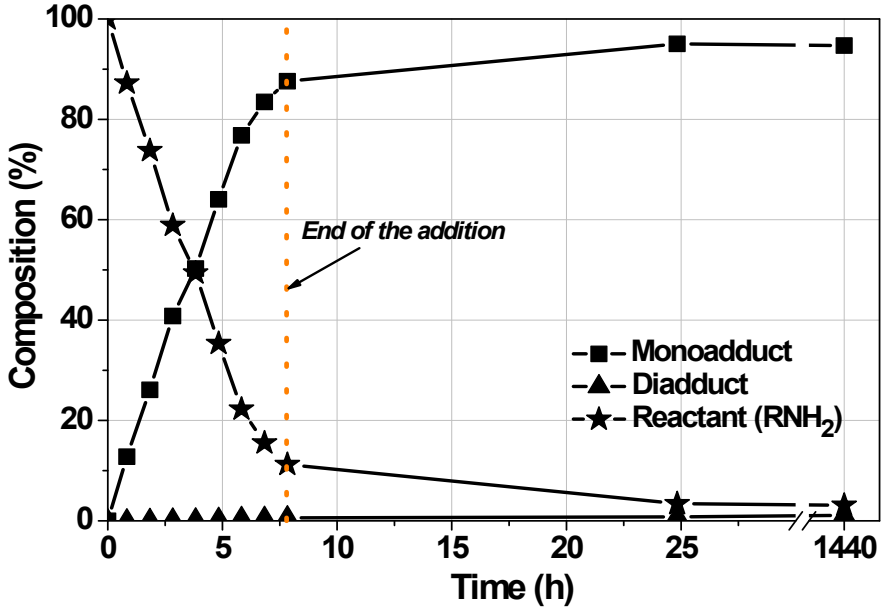

Figure S6: Composition change in amine for a starve-fed addition of a butylacrylate/isopropanol solution to an aminopropyl-terminated PDMS (r=0.5, 25°C). Final content in IPA: 85mol%