Electronic Supplementary Material (ESI) for Polymer Chemistry.

Hydrogen bonding in radical solution copolymerization kinetics of acrylates and methacrylates: A comparison of hydroxy- and methoxy- functionality

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Supporting information

NMR Analysis of MEA containing samples

Copolymers containing MEA were analyzed via ^{1}H NMR by taking the ratio of the signals arising from the distinct monomer ester side chains. Fig. S1 shows the spectrum of polyMEA, and a copolymer of BA and MEA (poly(BA-co-MEA)). The CH_2 group adjacent to the ester group creates a signal at 4.20 ppm in polyMEA, whereas the same group in polyBA produces a peak at 4.05 ppm. The deshielding effect introduced by the methoxy group in MEA creates a resonance of the adjacent CH_2 and CH_3 groups at 3.57 ppm and 3.36 ppm, respectively. In contrast, the butyl chain in polyBA produces multiplets at lower chemical shifts, notably the triplet at 0.95 ppm arising from the terminal CH_3 group. Integrating these resolved peaks allows for calculation of relative monomer composition following equation 1:

$$F_{MEA} = \frac{\int CH_2(3.57\ ppm)}{\int CH_2(4.20\ ppm) + \int CH_2(4.05\ ppm)} \quad \text{(eq. 1)}$$

The results were verified with the triplet at 0.95 ppm to determine the BA (or BMA) content using equation 2:

$$F_{BA/BMA} = \frac{\frac{2}{3}\int CH_3(0.95\ ppm)}{\int CH_2(4.20\ ppm) + \int CH_2(4.05\ ppm)} \quad \text{(eq. 2)}$$

The calculations were in good agreement, and the reported composition is the average of the two values.

The sharp peak at 3.94 ppm stems from monomethyl ether hydroquinone inhibitor, while the peak at 3.23 ppm is attributed to DMPA photoinitiator residue. The region spanning form 1.4-2.5 ppm contains the resonance from protons in the polymer backbone. Monomers configured with *meso* tacticity give rise to the peaks centred at 1.95 ppm and 1.52 ppm, whereas those in a *racemo* arrangement produce the peak at 1.69 ppm.[1] Note that no residual monomer peaks are found after isolation.

[1] J. F. J. Coelho, J. Gois, A. C. Fonseca, R. A. Carvalho, A. V. Popov, V. Percec, M. H. Gil, *J. Polym. Sci. Part A-Polym. Chem.,* 2009, *47,* 4454-4463.

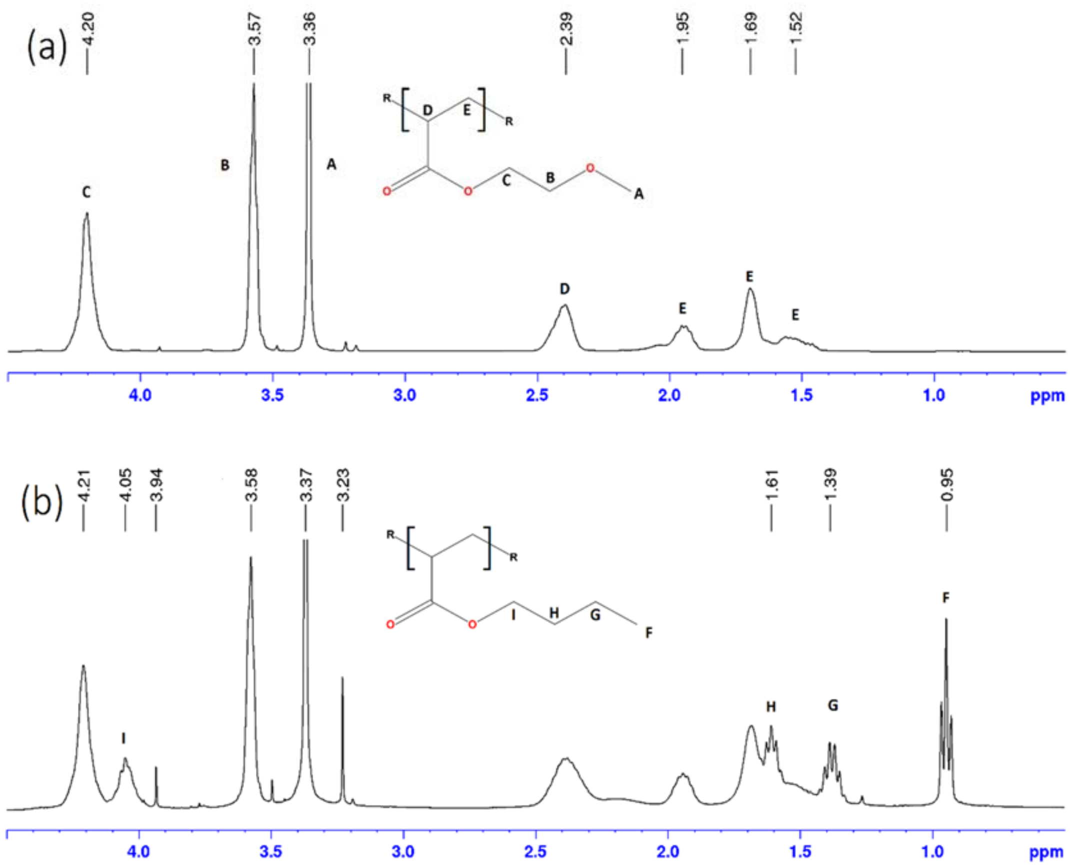


Fig. S1. ^{1}H NMR peaks assigned to protons (a) of polyMEA in $CDCl_3$ and (b) poly(BA-co-MEA) in $CDCl_3$. Low-conversion polymers produced at 50 ^{o}C from bulk MEA for (a) and a mixture of 30 vol% BA (balance MEA) for (b).

Tabulated NMR data for copolymer composition analysis

All polymer samples for NMR were synthesized at 50 °C, as previous studies demonstrated a negligible effect of temperature on relative monomer reactivity (within experimental error).

Table S1: Copolymer composition for BA/HEA samples produced by PLP in bulk, xylenes, MIBK, BuOH and DMF

Bulk		Xylenes		MIBK		BuOH		DMF	
f_{HEA}	F_{HEA}	f_{HEA}	F_{HEA}	f_{HEA}	F_{HEA}	f_{HEA}	F_{HEA}	f_{HEA}	F_{HEA}
0.13	0.27	0.13	0.16	0.13	0.17	0.13	0.14	0.13	0.11
0.25	0.44	0.25	0.34	0.25	0.281	-	-	0.25	0.22
0.36	0.52	0.36	0.50	0.36	0.484	0.36	0.40	0.36	0.35
0.47	0.65	-	-	-	-	-	-	0.47	0.47
0.57	0.69	0.57	0.75	0.57	0.681	0.57	0.62	0.57	0.58
0.66	0.82	0.66	0.82	0.66	0.77	-	-	0.66	0.65
-	-	0.75	0.86	-	-	0.75	0.79	0.75	0.73
0.84	0.91	-	-	0.84	0.883	-	-	-	
0.92	0.96	0.92	0.95	0.92	0.9517	0.92	0.95	-	

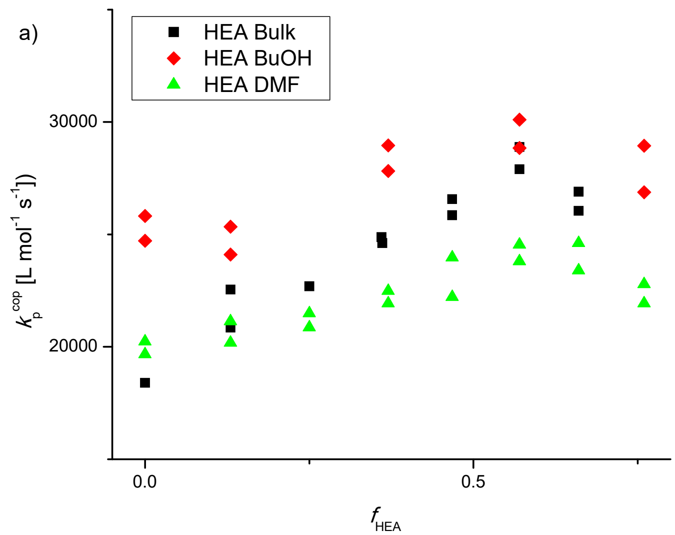
Table S2: Copolymer composition for BA/MEA samples produced by PLP in bulk, BuOH and DMF

Bulk		BuOH		DMF	
f_{MEA}	F_{MEA}	f_{MEA}	F_{MEA}	f_{MEA}	F_{MEA}
0.11	0.09	0.11	0.10	0.11	0.11
0.32	0.31	0.32	0.32	0.32	0.30
0.52	0.53	0.52	0.53	0.52	0.51
0.72	0.74	0.72	0.73	0.72	0.70
0.91	0.91	0.91	0.92	0.91	0.92

Table S3: Copolymer composition for BMA/MEA samples produced by PLP in bulk, xylenes, MIBK, BuOH and DMF

Bulk		BuOH		**DMF**	
f_{MEA}	F_{MEA}	f_{MEA}	F_{MEA}	f_{MEA}	F_{MEA}
0.12	0.09	0.12	0.06	0.12	0.05
0.35	0.21	0.35	0.19	0.35	0.18
0.55	0.35	0.55	0.35	0.55	0.33
0.74	0.55	0.74	0.53	0.74	0.52
0.92	0.81	0.92	0.82	0.92	0.79

Tabulated PLP data for k_p^{cop} and supplementary graphs



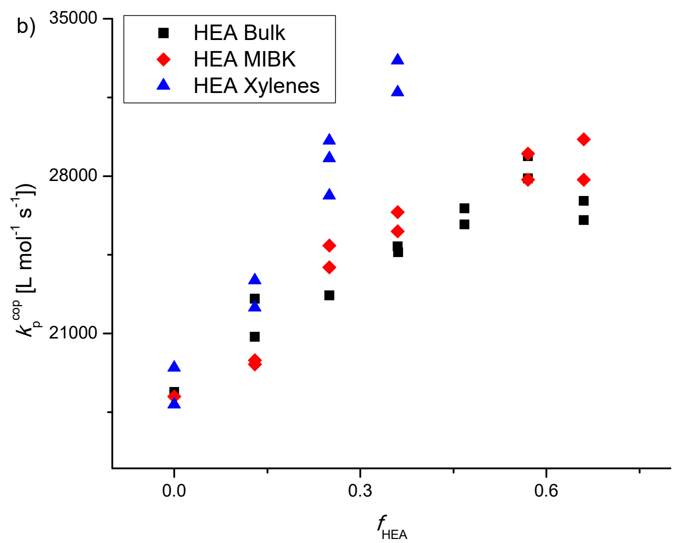
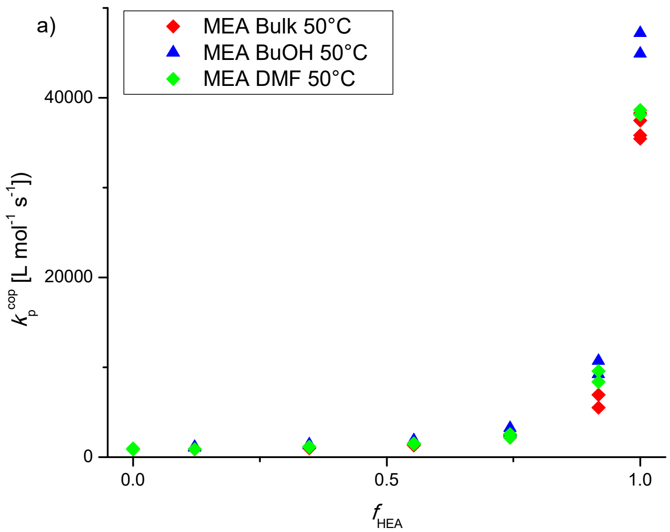


Fig. S2: a) Evolution of k_p^{cop} for BA/HEA as a function of HEA monomer mole fraction at 30 °C in (a) bulk (black), BuOH (red) and DMF (green), and (b) in bulk (black), MIBK (red) and xylenes (blue).



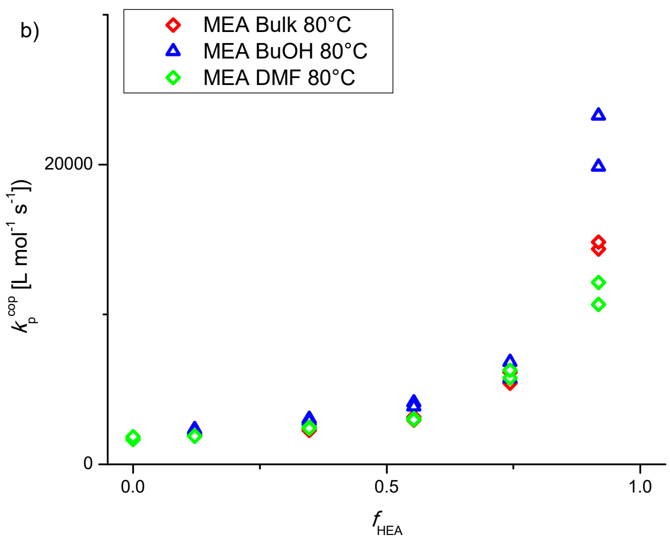


Fig. S3: a) Evolution of k_p^{cop} for BMA/MEA as a function of MEA monomer mole fraction at 50 °C in (a) bulk (red), BuOH (blue) and DMF (green), and (b) at 80 °C in the respective solvents.

Table S4: k_p^{cop} values for BA/HEA PLP copolymerizations in bulk

f_{HEA}	$\boldsymbol{\upsilon}$ (Hz)	T (°C)	k_p^{DRI} (L·mol^{-1}·s^{-1})	L1/L2	k_p^{LS} (L·mol^{-1}·s^{-1})
0	400	30	18400	0.514	19005
0.13	400	30	20847	0.571	21417
0.13	500	30	22549	0.524	25063
0.25	500	30	22694	0.529	22240
0.36	400	30	24871	0.495	26767
0.36	500	30	24617	0.567	27110
0.47	400	30	25854	0.555	26237
0.47	500	30	26568	0.492	28219
0.57	400	30	27895	0.559	27789
0.57	500	30	28884	0.527	28910
0.66	400	30	26050	0.503	29501
0.66	500	30	26903	0.559	27374
0	450	50	26246	0.522	25666
0	500	50	27620	0.553	28304
0.13	450	50	30836	0.515	32934
0.13	500	50	31943	0.497	34510
0.25	450	50	34699	0.511	36775
0.25	500	50	34215	0.512	35183
0.36	400	50	38229	0.544	41540
0.36	500	50	40221	0.517	40854
0.47	450	50	41346	0.495	41278
0.47	500	50	42446	0.550	46380
0.60	450	50	41971	0.530	44917
0.60	500	50	44090	0.499	43223

Table S5: k_p^{cop} values for BA/HEA PLP copolymerizations in 50 v% BuOH

f_{HEA}	$\boldsymbol{\upsilon}$ (Hz)	T (°C)	k_p^{DRI} (L·mol^{-1}·s^{-1})	L1/L2	k_p^{LS} (L·mol^{-1}·s^{-1})
0	300	30	25813	0.501	25715
0	400	30	24717	0.513	24189
0.13	300	30	24106	0.515	25521
0.13	400	30	25338	0.499	26179
0.36	300	30	27820	0.533	29698
0.36	400	30	28956	0.537	30515
0.57	300	30	28845	0.558	28388
0.57	400	30	30104	0.541	32744
0.76	300	30	26873	0.510	27268
0.76	400	30	28938	0.544	29821
0	420	50	33142	0.515	35506
0	500	50	35714	0.548	34909
0.13	420	50	33379	0.554	32868
0.13	500	50	36004	0.516	37282
0.37	420	50	37912	0.507	40157
0.37	500	50	40407	0.561	40180
0.58	420	50	41416	0.506	41954
0.58	500	50	44410	0.571	47102

Table S6: k_p^{cop} values for BA/HEA PLP copolymerizations in 50 v% DMF

f_{HEA}	υ (Hz)	T (°C)	k_p^{DRI} (L·mol^{-1}·s^{-1})	L1/L2	k_p^{LS} (L·mol^{-1}·s^{-1})
0	300	30	19672	0.567	19171
0	400	30	20241	0.535	21773
0.13	300	30	20179	0.554	20054
0.13	400	30	21139	0.528	22855
0.25	300	30	20860	0.518	22638
0.25	400	30	21484	0.501	22277
0.36	300	30	21926	0.559	23094
0.36	400	30	22484	0.575	23282
0.47	380	30	22217	0.521	22957
0.47	480	30	23977	0.564	24319
0.57	380	30	23812	0.545	24060
0.57	480	30	24549	0.570	23832
0.66	380	30	23395	0.551	25197
0.66	480	30	24617	0.570	24506
0.76	380	30	21933	0.509	23112
0.76	480	30	22782	0.500	22725
0	380	50	29221	0.503	30620
0	500	50	31204	0.530	31870
0.13	380	50	29797	0.499	29407
0.13	500	50	32439	0.530	33298
0.25	380	50	31794	0.532	33780
0.25	500	50	34244	0.564	37196
0.36	380	50	32751	0.514	32664
0.36	500	50	36234	0.553	37301
0.47	400	50	35246	0.518	36118
0.47	500	50	35349	0.530	37921
0.57	400	50	34916	0.494	36012
0.57	500	50	36593	0.538	35854
0.66	400	50	35453	0.550	37388
0.66	500	50	36248	0.498	39318
0.76	400	50	31621	0.556	32015
0.76	500	50	33180	0.540	35093

Table S7: k_p^{cop} values for BA/HEA PLP copolymerizations in 50 v% MIBK

f_{HEA}	$\boldsymbol{\upsilon}$ (Hz)	T (°C)	k_p^{DRI} (L·mol^{-1}·s^{-1})	L1/L2	k_p^{LS} (L·mol^{-1}·s^{-1})
0	420	30	18195	0.542	18805
0.13	320	30	19623	0.528	19194
0.13	420	30	19802	0.522	20327
0.25	320	30	24913	0.509	26128
0.25	420	30	23947	0.545	24157
0.36	320	30	25547	0.554	26283
0.36	420	30	26398	0.551	26184
0.57	320	30	27844	0.523	29850
0.57	420	30	29005	0.527	28826
0.66	320	30	27845	0.499	27577
0.66	420	30	29637	0.540	31513
0	400	50	29833	0.561	29989
0	500	50	30493	0.537	32525
0.13	400	50	28589	0.564	31097
0.13	500	50	29292	0.564	30149
0.25	400	50	30123	0.520	30799
0.25	500	50	32476	0.573	34135
0.36	400	50	37757	0.526	38059
0.36	500	50	38554	0.498	41707
0.57	400	50	37816	0.557	39040
0.57	500	50	41593	0.573	45252

Table S8: k_p^{cop} values for BA/HEA PLP copolymerizations in 50 v% Xylenes

f_{HEA}	$\boldsymbol{\upsilon}$ (Hz)	T (°C)	k_p^{DRI} (L·mol^{-1}·s^{-1})	L1/L2	k_p^{LS} (L·mol^{-1}·s^{-1})
0	320	30	17841	0.515	18414
0	420	30	19477	0.499	20528
0.13	330	30	22156	0.569	23248
0.13	430	30	23361	0.499	22748
0.25	400	30	28800	0.504	29051
0.25	500	30	27139	0.547	28571
0.25	500	30	29580	0.523	28966
0.36	340	30	31729	0.536	31667
0.36	440	30	33148	0.503	35816
0	400	50	28732	0.511	27986
0	500	50	30514	0.571	29643
0.13	400	50	33647	0.529	35846
0.13	500	50	35788	0.506	37776
0.25	400	50	41421	0.523	43241
0.25	500	50	42045	0.569	45606
0.37	400	50	46098	0.500	48455
0.37	500	50	49919	0.571	53319

Table S9: k_p^{cop} values for BA/MEA PLP copolymerizations in bulk; [a] samples polymerized with 7 mM/L photoinitiator

f_{MEA}	υ (Hz)	T (°C)	k_p^{DRI} (L·mol^{-1}·s^{-1})	L1/L2	k_p^{LS} (L·mol^{-1}·s^{-1})
0	400	30	18400	0.514	19005
0.11	380	30	18165	0.535	19439
0.11	480	30	18900	0.534	19379
0.32	380	30	19212	0.564	20235
0.32	480	30	20137	0.562	20992
0.53	380	30	20228	0.503	20107
0.53	480	30	20902	0.497	21286
0.72	380	30	21251	0.495	21519
0.72	480	30	22784	0.560	22558
0.91	380	30	23095	0.536	24876
0.91	480	30	24362	0.534	24145
1	380	30	22819	0.563	22171
1	480	30	24459	0.516	26472
1	380 [a]	30	23525	0.502	22885
1	480 [a]	30	24459	0.570	23732
0	450	50	26246	0.522	27438
0.11	400	50	23927	0.549	24263
0.11	500	50	26391	0.567	28842
0.32	400	50	25903	0.562	26720
0.32	500	50	27681	0.567	28404
0.53	400	50	29765	0.518	32460
0.53	500	50	30273	0.568	31474
0.72	400	50	32807	0.567	33693
0.72	500	50	32532	0.502	32697
0.91	400	50	35147	0.512	37468
0.91	500	50	35384	0.527	36642
1	400	50	38285	0.548	40858
1	500	50	37479	0.509	39395
1	400 [a]	50	35822	0.491	35285
1	500 [a]	50	35468	0.555	36308

Table S10: k_p^{cop} values for BA/MEA PLP copolymerizations in 50 v% BuOH

f_{MEA}	υ (Hz)	T (°C)	k_p^{DRI} (L·mol^{-1}·s^{-1})	L1/L2	k_p^{LS} (L·mol^{-1}·s^{-1})
0	300	30	22396	0.526	22841
0	400	30	22867	0.544	23047
0.11	380	30	22938	0.522	22791
0.11	480	30	24072	0.560	25114
0.32	380	30	25022	0.504	25697
0.32	480	30	26261	0.566	27683
0.53	380	30	27302	0.523	27451
0.53	480	30	28453	0.494	30445
0.72	380	30	29310	0.496	31342
0.72	480	30	30963	0.512	30795
0.91	380	30	31184	0.560	33705
0.91	480	30	32726	0.543	31896
1	380	30	31921	0.573	33846
1	480	30	33284	0.557	36195
0	420	50	33295	0.542	36306
0	500	50	35689	0.516	34943
0.11	450	50	34580	0.519	34811
0.11	500	50	35007	0.515	34325
0.32	450	50	36120	0.556	36128
0.32	500	50	37639	0.493	37914
0.53	450	50	39417	0.523	42446
0.53	500	50	39919	0.530	40779
0.72	450	50	41703	0.521	43222
0.72	500	50	44391	0.507	46893
0.91	450	50	44673	0.555	47634
0.91	500	50	45890	0.520	48339
1	450	50	44907	0.544	46390
1	500	50	47226	0.512	48872

Table S11: k_p^{cop} values for BMA/MEA PLP copolymerizations in bulk

f_{MEA}	υ (Hz)	T (°C)	k_p^{DRI} (L·mol^{-1}·s^{-1})	L1/L2	k_p^{LS} (L·mol^{-1}·s^{-1})
0.12	20	50	803	0.539	833
0.12	40	50	886	0.548	875
0.35	23	50	993	0.525	1029
0.35	43	50	1107	0.543	1172
0.55	26	50	1313	0.492	1395
0.55	46	50	1449	0.480	1470
0.74	75	50	2196	0.507	2306
0.74	120	50	2481	0.540	2505
0.92	150	50	5521	0.546	5983
0.92	300	50	6932	0.537	7404
0.12	50	80	1734	0.515	1776
0.12	100	80	1927	0.535	2095
0.35	55	80	2264	0.492	2402
0.35	105	80	2392	0.549	2595
0.55	60	80	2946	0.501	3184
0.55	110	80	3161	0.498	3235
0.74	300	80	6156	0.527	6265
0.74	400	80	5419	0.539	5851
0.92	400	80	14366	0.520	15595
0.92	500	80	14833	0.538	16019

Table S12: k_p^{cop} values for BMA/MEA PLP copolymerizations in 50 v% BuOH

f_{MEA}	υ (Hz)	T (°C)	k_p^{DRI} ($L \cdot mol^{-1} \cdot s^{-1}$)	L1/L2	k_p^{LS} ($L \cdot mol^{-1} \cdot s^{-1}$)
0.12	20	50	1048	0.540	1032
0.12	40	50	1139	0.536	1111
0.35	40	50	1434	0.517	1501
0.35	60	50	1338	0.505	1426
0.55	60	50	1859	0.550	1970
0.55	80	50	1865	0.550	1864
0.74	100	50	2721	0.507	2860
0.74	150	50	3243	0.495	3341
0.92	380	50	9227	0.531	9619
0.92	480	50	10702	0.492	11091
0.12	50	80	2332	0.493	2372
0.12	100	80	2249	0.512	2255
0.35	70	80	3016	0.527	3082
0.35	120	80	2872	0.503	3000
0.55	90	80	4118	0.510	4254
0.55	140	80	3847	0.533	3864
0.74	200	80	5727	0.532	5697
0.74	300	80	6823	0.501	6838
0.92	400	80	19850	0.490	20626
0.92	500	80	23262	0.512	23688

Table S13: k_p^{cop} values for BMA/MEA PLP copolymerizations in 50 v% DMF

f_{MEA}	υ (Hz)	T (°C)	k_p^{DRI} (L·mol^{-1}·s^{-1})	L1/L2	k_p^{LS} (L·mol^{-1}·s^{-1})
0.12	20	50	869	0.510	880
0.12	40	50	891	0.513	891
0.35	40	50	1159	0.547	1131
0.35	60	50	1120	0.509	1170
0.55	60	50	1440	0.501	1458
0.55	80	50	1523	0.506	1497
0.74	150	50	2188	0.521	2384
0.74	200	50	2556	0.496	2727
0.92	400	50	8380.	0.518	8886
0.92	500	50	9562	0.548	10245
1	450	50	38638	0.554	38632
1	500	50	38133	0.538	38831
0.12	50	80	1899	0.506	1873
0.12	100	80	1879	0.496	2000
0.35	70	80	2464	0.534	2408
0.35	120	80	2404	0.540	2479
0.55	90	80	3051	0.507	3052
0.55	140	80	2985	0.515	3106
0.74	150	80	5764	0.546	5746
0.74	200	80	6277	0.507	6214
0.92	450	80	11664	0.492	12209
0.92	500	80	12143	0.554	12219