Solvent Effects on Radical Copolymerization Kinetics of 2-Hydroxyethyl Methacrylate and Butyl Methacrylate

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Supporting Information

Table S1: Molar fraction of HEMA (F_{HEMA}) in BMA/HEMA copolymers produced of low conversion by PLP in bulk and in *n*-butanol (BUOH) and dimethyl formamide (DMF) (vol% monomer) as a function of HEMA molar fraction (f_{HEMA}) in the monomer mixture.

	F_{HEMA}	F_{HEMA}	F_{HEMA}	F_{HEMA}	F_{HEMA}	F_{HEMA}	F_{HEMA}
f_{HEMA}	BULK	50% mon in BUOH	20% mon in BUOH	10% mon in BUOH	50% mon in DMF	20% mon in DMF	10% mon in DMF
0.13	0.22	0.14	-	0.17	-	0.12	0.13
0.25	0.35	0.32	0.30	0.31	0.29	0.26	0.25
0.36	0.50	0.45	0.44	0.45	0.46	0.37	0.38
0.47	0.63	0.59	0.55	0.59	0.53	0.43	0.45
0.57	0.72	0.74	0.67	0.66	0.64	0.59	0.56
0.66	0.81	-	0.75	0.75	0.81	0.68	0.66
0.75	0.88	-	0.87	0.80	0.85	0.77	0.75
0.84	-	-	-	0.86	0.95	0.86	0.85
0.92	-	-	-	0.94	-	0.96	0.95

Table S2: Molar fraction of HEMA (F_{HEMA}) in BMA/HEMA copolymers produced at low conversion by PLP in xylene (XYL) as a function of HEMA molar fraction (f_{HEMA}) in the monomer mixture.

	F_{HEMA}	F_{HEMA}	F_{HEMA}
f_{HEMA}	50% mon in XYL	20% mon in XYL	10% mon in XYL
0.13	0.21	0.27	0.32
0.25	0.43	0.42	0.69
0.36	0.63	0.85	0.75
0.47	0.81	0.88	0.89
0.57	0.91	-	-
0.66	0.97	-	-
0.75	-	-	-

Table S3: k_p^{cop} values obtained from PLP-SEC experiments of BMA/HEMA in bulk with 5 mmol/L DMPA photoinitiator as a function of mol fraction HEMA in the monomer mixture (f_{HEMA}), temperature and laser pulse repetition rate (ν). L_1/L_2 is the ratio of the first two inflection points on the PLP-produced MMD.

f_{HEMA}	T (°C)	ν (Hz)	k_p (L/mol s)	L_1/L_2	f_{HEMA}	T (°C)	ν (Hz)	k_p (L/mol s)	L_1/L_2
0	50	20	764	0.51	**0**	80	35	1626	0.51
0.13	50	20	863	0.49	**0.13**	80	35	1793	0.50
0.25	50	20	1043	0.50	**0.25**	80	35	2069	0.50
0.36	50	20	1150	0.49	**0.36**	80	35	2333	0.49
0.47	50	20	1267	0.49	**0.47**	80	35	2511	0.49
0	50	40	840	0.52	**0.57**	80	35	2702	0.48
0.13	50	40	927	0.52	**0**	80	70	1668	0.52
0.25	50	40	1070	0.52	**0.13**	80	70	1970	0.52
0.36	50	40	1264	0.52	**0.25**	80	70	2274	0.52
0.47	50	40	1393	0.51	**0.36**	80	70	2564	0.52
0.57	50	40	1432	0.51	**0.47**	80	70	2635	0.51
0	50	80	842	0.49	**0.57**	80	70	2836	0.52
0.13	50	80	929	0.49	**0.66**	80	70	2913	0.51
0.25	50	80	1123	0.51	**0**	80	100	1726	0.52
0.36	50	80	1327	0.54	**0.13**	80	100	2039	0.54
0.47	50	80	1429	0.52	**0.25**	80	100	2300	0.52
0.57	50	80	1574	0.52	**0.36**	80	100	2476	0.52
0.66	50	80	1655	0.54	**0.47**	80	100	2791	0.52
					0.57	80	100	2935	0.51
					0.66	80	100	3085	0.52

Table S4: k_p^{cop} values obtained from PLP-SEC experiments of BMA/HEMA in *n*-butanol with 5 mmol/L DMPA photoinitiator as a function of mol fraction HEMA in the monomer mixture (f_{HEMA}), temperature and laser pulse repetition rate (ν). L_1/L_2 is the ratio of the first two inflection points on the PLP-produced MMD.

		50 vol% Monomer in BUOH			20 vol% Monomer in BUOH			10 vol% Monomer in BUOH		
f_{HEMA}	T (°C)	ν (Hz)	k_p (L/mol s)	L_1/L_2	ν (Hz)	k_p (L/mol s)	L_1/L_2	ν (Hz)	k_p (L/mol s)	L_1/L_2
0	50	20	968	0.52	4	1037	0.50	8	1198	0.51
0.13	50	20	1068	0.54	4	1093	0.49	8	1292	0.51
0.25	50	20	1075	0.52	4	1152	0.49	8	1300	0.52
0.36	50	20	1213	0.52	4	1241	0.48	8	1278	0.52
0.47	50	20	1306	0.52	4	1337	0.48	8	1285	0.50
0.57	50	20	1313	0.51	4	1408	0.47	8	1552	0.52
0	50	40	971	0.50	8	1114	0.52	12	1187	0.48
0.13	50	40	1047	0.50	8	1174	0.52	12	1251	0.48
0.25	50	40	1154	0.51	8	1237	0.51	12	1259	0.47
0.36	50	40	1273	0.51	8	1333	0.52	12	1326	0.47
0.47	50	40	1436	0.54	8	1404	0.51	12	1462	0.47
0.57	50	40	1443	0.52	8	1444	0.51	12	1503	0.48
0	80	35	1891	0.54	7	1942	0.49	10	2213	0.52
0.13	80	35	1992	0.52	7	2094	0.49	10	2387	0.51
0.25	80	35	2050	0.52	7	2107	0.49	10	2294	0.52
0.36	80	35	2260	0.51	7	2271	0.49	10	2307	0.52
0.47	80	35	2434	0.52	7	2561	0.48	10	2726	0.52
0.57	80	35	2502	0.51	7	2634	0.48	10	2740	0.51
0	80	70	1895	0.50	14	2086	0.52	15	2144	0.49
0.13	80	70	1907	0.48	14	2198	0.52	15	2477	0.51
0.25	80	70	2202	0.51	14	2263	0.51	15	2221	0.49
0.36	80	70	2484	0.52	14	2439	0.52	15	2286	0.50
0.47	80	70	2675	0.54	14	2627	0.50	15	2764	0.51
0.57	80	70	2750	0.54	14	2765	0.51	15	2977	0.51

Table S5: k_p^{cop} values obtained from PLP-SEC experiments of BMA/HEMA in dimethylformamide with 5 mmol/L DMPA photoinitiator as a function of mol fraction HEMA in the monomer mixture (f_{HEMA}), temperature and laser pulse repetition rate (ν). L_1/L_2 is the ratio of the first two inflection points on the PLP-produced MMD.

		50 vol% Monomer in DMF			20 vol% Monomer in DMF			10 vol% Monomer in DMF		
f_{HEMA}	T (°C)	ν (Hz)	k_p (L/mol s)	L_1/L_2	ν (Hz)	k_p (L/mol s)	L_1/L_2	ν (Hz)	k_p (L/mol s)	L_1/L_2
0	50	40	712	0.49	4	734	0.50	4	749	0.50
0.13	50	40	768	0.49	4	738	0.49	4	789	0.50
0.25	50	40	828	0.49	4	760	0.49	4	812	0.50
0.36	50	40	892	0.49	4	782	0.49	4	855	0.50
0.47	50	40	983	0.50	4	823	0.49	4	880	0.48
0.57	50	40	1034	0.50	4	866	0.48	4	864	0.49
0.66	50	40	1088	0.51	4	831	0.48	4	868	0.49
0.75	50	40	1117	0.51	4	797	0.50	4	795	0.47
0	50	80	820	0.54	8	825	0.52	8	786	0.49
0.13	50	80	884	0.52	8	812	0.49	8	828	0.49
0.25	50	80	931	0.52	8	835	0.50	8	833	0.49
0.36	50	80	980	0.51	8	821	0.50	8	877	0.49
0.47	50	80	1031	0.51	8	844	0.50	8	882	0.49
0.57	50	80	1085	0.50	8	868	0.50	8	846	0.47
0.66	50	80	1141	0.49	8	893	0.50	8	831	0.48
0.75	50	80	1173	0.49	8	856	0.50	8	797	0.47

Table S5 continued on following page

Table S5 (continued from previous page)

		50 vol% Monomer in DMF			20 vol% Monomer in DMF			10 vol% Monomer in DMF		
f_{HEMA}	**T (°C)**	**ν (Hz)**	**k_p (L/mol s)**	**L_1/L_2**	**ν (Hz)**	**k_p (L/mol s)**	**L_1/L_2**	**ν (Hz)**	**k_p (L/mol s)**	**L_1/L_2**
0	80	70	1376	0.49	7	1447	0.49	10	1424	0.50
0.13	80	70	1553	0.50	7	1490	0.49	10	1501	0.51
0.25	80	70	1636	0.50	7	1464	0.49	10	1509	0.51
0.36	80	70	1762	0.50	7	1577	0.49	10	1553	0.51
0.47	80	70	1897	0.51	7	1586	0.50	10	1561	0.51
0.57	80	70	2042	0.51	7	1593	0.49	10	1569	0.51
0.66	80	70	2098	0.51	7	1600	0.49	10	1576	0.50
0.75	80	70	2205	0.52	7	1607	0.49	10	1511	0.50
0	80	100	1458	0.49	14	1450	0.50	15	1411	0.49
0.13	80	100	1608	0.49	14	1493	0.50	15	1453	0.47
0.25	80	100	1654	0.49	14	1502	0.50	15	1462	0.47
0.36	80	100	1782	0.49	14	1618	0.50	15	1504	0.49
0.47	80	100	1875	0.48	14	1589	0.50	15	1478	0.48
0.57	80	100	1927	0.48	14	1672	0.50	15	1485	0.48
0.66	80	100	2026	0.49	14	1680	0.50	15	1526	0.48
0.75	80	100	2081	0.49	14	1610	0.50	15	1498	0.48

Table S6: k_p^{cop} values obtained from PLP-SEC experiments of BMA/HEMA in xylene with 5 mmol/L DMPA photoinitiator as a function of mol fraction HEMA in the monomer mixture (f_{HEMA}), temperature, laser pulse repetition rate (ν) and vol % monomer. L_1/L_2 is the ratio of the first two inflection points on the PLP-produced MMD.

f_{HEMA}	T (°C)	ν (Hz)	Vol% Mon	k_p (L/mol s)	L_1/L_2	f_{HEMA}	T (°C)	ν (Hz)	Vol% Mon	k_p (L/mol s)	L_1/L_2
0.00	50	20	50	822	0.52	**0.00**	80	35	50	809	0.52
0.13	50	20	50	1115	0.51	**0.13**	80	35	50	1156	0.50
0.25	50	20	50	1513	0.49	**0.25**	80	35	50	1533	0.51
0.36	50	20	50	1960	0.55	**0.36**	80	35	50	1940	0.66
0.47	50	20	50	2369	0.48	**0.47**	80	35	50	2457	0.46
0.57	50	20	50	3287	0.47	**0.57**	80	35	50	3368	0.44
0.66	50	20	50	4664	0.44	**0.00**	80	70	50	1875	0.50
0.00	50	40	50	796	0.49	**0.13**	80	70	50	2588	0.51
0.13	50	40	50	1198	0.51	**0.25**	80	70	50	3297	0.51
0.25	50	40	50	1552	0.54	**0.36**	80	70	50	4078	0.48
0.36	50	40	50	1920	0.50	**0.47**	80	70	50	5403	0.48
0.47	50	40	50	2545	0.49	**0.57**	80	70	50	7156	0.48
0.57	50	40	50	3450	0.49	**0.00**	80	7	20	1725	0.52
0.66	50	40	50	4675	0.46	**0.13**	80	7	20	1948	0.50
0.00	50	4	20	801	0.52	**0.25**	80	7	20	2356	0.49
0.13	50	4	20	1039	0.52	**0.00**	80	14	20	1811	0.55
0.00	50	8	20	881	0.55	**0.13**	80	14	20	2092	0.52
0.13	50	8	20	1090	0.51	**0.25**	80	14	20	2531	0.54
0.00	50	8	10	805	0.50	**0.00**	80	10	10	1468	0.50
0.13	50	8	10	1255	0.51	**0.13**	80	10	10	2236	0.54
0.00	50	12	10	855	0.52	**0.00**	80	15	10	1559	0.51
0.13	50	12	10	1215	0.47	**0.13**	80	15	10	2152	0.49