

Supplementary Material (ESI) for Polymer Chemistry
This journal is (c) The Royal Society of Chemistry 2010

Metalloenzymatic Radical Polymerization Using Alkyl Halides as Initiators

Yeap-Hung Ng, Fabio di Lena* and Christina L. L. Chai

*Institute of Chemical and Engineering Sciences, Agency of Science, Technology and Research, 1
Pesek Road, Jurong Island, 627833 Singapore*

Table S1. Free radical polymerization of PEGMA in the presence of LTV for different cysteine/EBiB molar ratios at 40°C

<u>Entry 1- [PEGMA]/[EBiB]/[VitC]/[Cysteine]=50/1/8/1</u>			
Time (hour)	Conversion (%)	M_n	M_w/M_n
1.5	21.9	307909	2.87
3	37.8	348487	4.08
5	51.0	341473	5.18
8	61.1	256026	7.72
22	Gel		
<u>Entry 2- [PEGMA]/[EBiB]/[VitC]/[Cysteine]=50/1/8/2</u>			
Time (hour)	Conversion (%)	M_n	M_w/M_n
4	43.8	212015	3.41
8	59.6	202205	5.51
22	76.3	194016	15.4
<u>Entry 3- [PEGMA]/[EBiB]/[VitC]/[Cysteine]=50/1/8/5</u>			
Time (hour)	Conversion (%)	M_n	M_w/M_n
1.5	18.6	107488	1.88
3	29.0	111728	1.79
5	39.2	108766	1.81
8	49.0	101299	2.07
22	67.9	96756	2.49
<u>Entry 4- [PEGMA]/[EBiB]/[VitC]/[Cysteine]=50/1/8/10</u>			
Time (hour)	Conversion (%)	M_n	M_w/M_n
4	32.3	60809	1.70
8	40.5	60713	1.71
22	51.8	60195	1.83
PEGMA=0.5mL, Water=2mL, EBiB=5μL, Laccase=10mg, VitC=50mg, Temperature=40°C			

Table S2. Effect of the amount of cysteine on the molecular weight in the free radical polymerization of PEGMA in the presence of LTV

Entry	Conv. (%)	[Cysteine]/ [EBiB]	[Cysteine]/ [OEGMA]	M_n	M_w/M_n	DP_n	$10^5/DP_n$
1	51.0 (5Hr)	1	0.0195	341473	5.18	1138	87
2	43.8 (4Hr)	2	0.0389	212015	3.41	707	141
3	49.0 (8Hr)	5	0.0973	101299	2.07	338	296
4	40.5 (8Hr)	10	0.1947	60713	1.71	202	494

Table S3. Free radical polymerization of PEGMA in the presence of LTV for two different temperatures and CPDB/2BPN molar ratios

<u>Entry 5- [PEGMA]/[2PBN]/[VitC]/[CPDB]=50/1/8/1 (40°C)</u>			
Time (hour)	Conversion (%)	M_n	M_w/M_n
1	2.1	2709	1.24
3	8.8	3462	1.27
5	23.9	4946	1.23
8	43.3	5897	1.23
22	52.5	6547	1.33
<u>Entry 6- [PEGMA]/[2PBN]/[VitC]/[CPDB]=50/1/8/0.25 (40°C)</u>			
Time (hour)	Conversion (%)	M_n	M_w/M_n
1	9.1	7060	1.38
3	34.0	15058	1.35
5	47.3	20366	1.37
8	61.1	24801	1.38
22	82.1	28746	1.66
<u>Entry 7- [PEGMA]/[2PBN]/[VitC]/[CPDB]=50/1/8/0.25 (50°C)</u>			
Time (hour)	Conversion (%)	M_n	M_w/M_n
1	21.8	11807	1.37
3	52.8	23069	1.38
5	66.9	28546	1.43
8	77.4	31507	1.59
22	87.0	36232	1.75
PEGMA=0.5mL, Water=2mL, 2BPN=2.9μL, Laccase=10mg, VitC=50mg			