Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPORTING INFORMATION

Laccase-catalyzed Controlled Radical Polymerization of *N*-Vinylimidazole

Csaba Fodor,[a,b†] Bernadetta Gajewska,[a] Omar Rifaie-Graham,[a] Edward A. Apebende,[a] Jonas Pollard[a] and Nico Bruns[a]*

[a]Adolphe Merkle Institute, University of Fribourg
Chemin des Verdiers 4, 1700 Fribourg, Switzerland

[b]Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences
H-1117 Budapest, Magyar tudósok krt. 2, Hungary

[†]Present address: Department of Polymer Chemistry, Zernike Institute for Advanced Materials, University of Groningen
Nijenborgh 4, 9747 AG Groningen, The Netherlands

*Correspondence to: nico.bruns@unifr.ch

Supporting Tables and Figures

Table S1. Synthetic parameters and polymerization data of biocatalytic NVIm polymerizations under ATRP conditions in aqueous media.

Entry	I/M/RA/Cat[a]	Catalyst	pH	T (°C)	t (h)	conv. (%)	$M_{n,th}$	$M_{n,NMR}$	$M_{n,GPC}$	$M_{w,GPC}$	$Đ$
1	1/50/1/0.002	HRP	6	RT	24	2.9	140	390	-	-	-
2	1/50/1/0.002	HRP	6	RT	68	7.4	350	390	-	-	-
3	1/50/1/0.002	Hb	7	RT	24	2.1	99	270	-	-	-
4	1/50/0.2/0.005	LacTv	4	RT	1	4.8	220	1140	-	-	-
5	1/50/0.2/0.005	LacTv	4	RT	3	8.7	410	1140	1660	2110	1.27
6	1/50/0.2/0.005	LacTv	4	RT	5	29.3	1380	2380	2710	3890	1.43
7	1/50/0.2/0.005	LacTv	4	RT	6	31.3	1470	2510	3480	5140	1.48
8	1/50/0.2/0.005	LacTv	4	RT	7	36.3	1710	3350	3550	5030	1.41
9	1/50/0.2/0.005	LacTv	4	RT	8	42.7	2010	3850	4080	6200	1.52
10	1/50/0.2/0.005	LacTv	4	RT	24	70.0	3290	4270	5070	8090	1.56
11	1/100/0.2/0.005	LacTv	4	RT	1	6.5	620	1430	-	-	-
12	1/100/0.2/0.005	LacTv	4	RT	3.5	20.9	1970	2450	2930	4010	1.37
13	1/100/0.2/0.005	LacTv	4	RT	5	26.5	2490	3280	3100	4090	1.32
14	1/100/0.2/0.005	LacTv	4	RT	6	39.4	3710	3890	3210	4360	1.36
15	1/100/0.2/0.005	LacTv	4	RT	7	39.9	3760	3900	3090	4160	1.35
16	1/100/0.2/0.005	LacTv	4	RT	8	43.7	4110	5400	3680	5060	1.38
17	1/100/0.2/0.005	LacTv	4	RT	24	41.3	3890	6140	5540	8630	1.56
18	1/100/0.2/0.010	LacTv	4	RT	1	48.6	4570	4390	4020	5934	1.48
19	1/100/0.2/0.010	LacTv	4	RT	3	64.7	6090	6940	6040	10390	1.72
20	1/100/0.2/0.010	LacTv	4	RT	5	81.2	7640	8460	6760	13380	1.98
21	1/100/0.2/0.010	LacTv	4	RT	7	80.4	7570	9980	5890	11640	1.98
22	1/100/0.2/0.010	LacTv	4	RT	8	80.5	7570	9540	5770	10730	1.86
23	1/100/0.2/0.010	LacTv	4	RT	24	86.3	8120	12140	5780	11670	2.09
24	1/50/0.2/0.005	LacTv	4	40	1	9.1	428	592	2500	5890	2.36
25	1/50/0.2/0.005	LacTv	4	40	2	13.4	632	863	4850	11200	2.31
26	1/50/0.2/0.005	LacTv	4	40	3	31.5	1483	2360	5920	16290	2.81
27	1/50/0.2/0.005	LacTv	4	40	5	52.8	2486	4014	8790	40720	4.61
28	1/50/0.2/0.005	LacTv	4	40	6	63.2	2976	4503	8900	45760	5.14
29	1/50/0.2/0.005	LacTv	4	40	7	65.9	3103	4551	8870	45440	5.12
30	1/50/0.2/0.005	LacTv	4	40	8	64.4	3031	5999	8850	45330	5.12
31	1/50/0.2/0.005	LacTv	3	RT	24	79	3719	5373	8910	13880	1.56
32	1/50/0.2/0.005	LacTv	4	RT	24	91	4303	5415	8930	14110	1.58
33	1/50/0.2/0.005	LacTv	5	RT	24	84	3931	6595	9970	15430	1.55
34	1/50/0.2/0.005	LacTv	6	RT	24	86	4060	7759	9100	14680	1.61

[a)] I/M/RA/Cat = molar ratio of HEBIB:NVIm:NaAsc:enzyme in the reaction mixture at the beginning of the reaction.

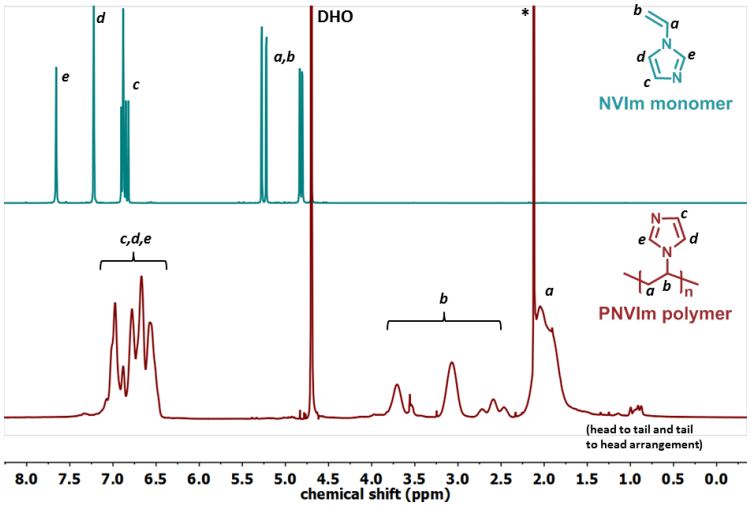

Figure S1. Phase and baseline-corrected ^{1}H NMR spectra of the monomer NVIm and PNVIm synthetized under conditions of ATRP. (ratio of HEBIB:NVIm:NaAsc:LacTv 1:50:0.2:0.005 at pH 4.0, polymerization time: 24 h, purified from the polymerization mixture as described in the materials and methods section) (solvent: D_2O, number of transients (nt): 256, relaxation time (d1): 1 for NVIm and 10 for PNVIm and RT).

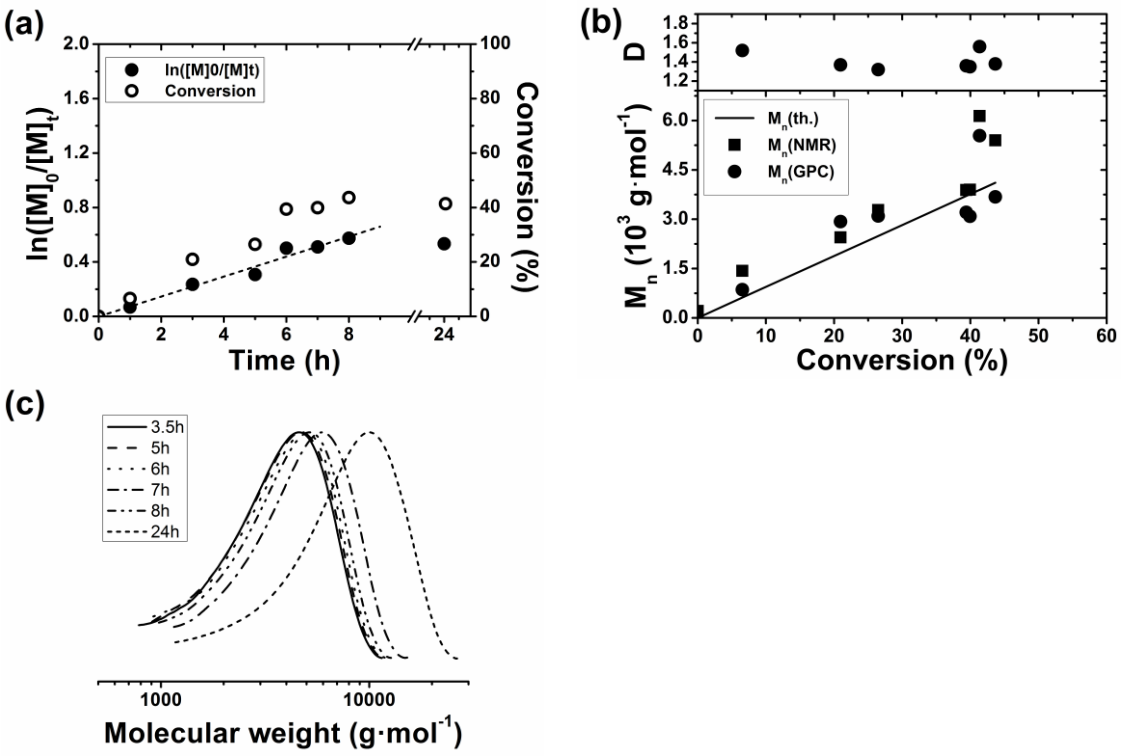

Figure S2. Kinetic investigations of polymerizations catalyzed by LacTv under conditions of ATRP. (a) First order kinetic plot of $\ln([M]_0/[M]$ as a function of reaction time, (b) evolution of molecular weights and dispersity with monomer conversion and (c) GPC traces (experimental conditions of the polymerization: ratio of HEBIB:NVIm:NaAsc:LacTv 1:100:0.2:0.005 at pH 4.0, RT).

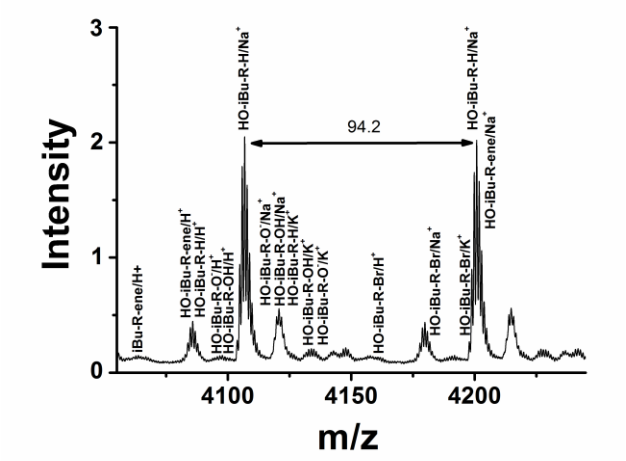

Figure S3. Magnification of a set of peaks of the MALDI-ToF MS spectrum of PNVIm, with repeating set of peaks starting with HO-iBu-R-ene/H^+, where R = $(NVIm)_n$.

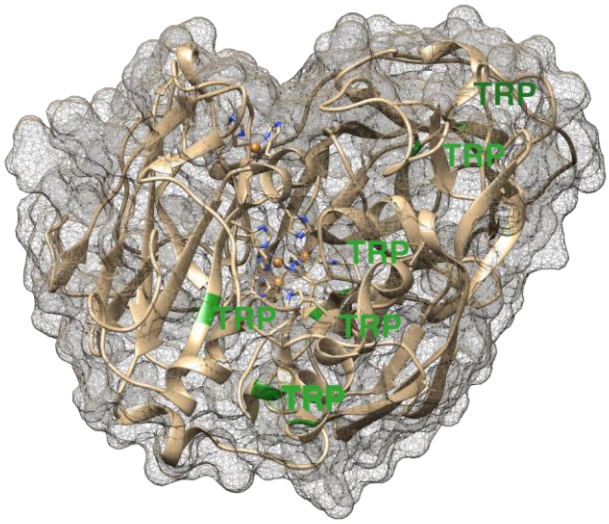

Figure S4. Three-dimensional structure of LacTv, showing its tryptophan residues in green (Protein Data Bank; ID: 1GYC[1]).

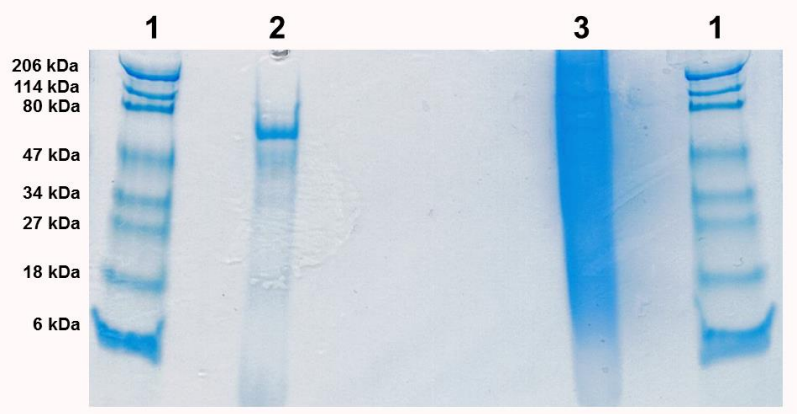

Figure S5. SDS-PAGE gel of pure LacTv and of LacTv recovered after a polymerization of NVIm (lane 1: prestained SDS PAGE standards, lane 2: LACTV, lane 3: purified, recovered LacTv).

The sample from the polymerization (lane 3 in Figure S5) resulted in a strong smear which is caused by the polycationic polymer. This shows that the polymer cannot be removed completely from the enzyme, most likely because electrostatic complexes between the enzyme and the polycationic polymer formed. Please note that, while it was not possible to obtain purified LacTv after the polymerization, the complete removal of the enzyme (and any polymer that complexed it) from the polymer was possible, because the majority of polymer chains did not bind to the enzyme (see ICP-OES and UV-*vis* data in the manuscript).

Notes and references

1. K. Piontek, M. Antorini and T. Choinowski, *J. Biol. Chem.*, 2002, **277**, 37663-37669.