Electronic Supplementary Material (ESI) for Faraday Discussions.

Supplementary Information for:

Mechanochemical Solid-State Vinyl Polymerization with Anionic Initiator

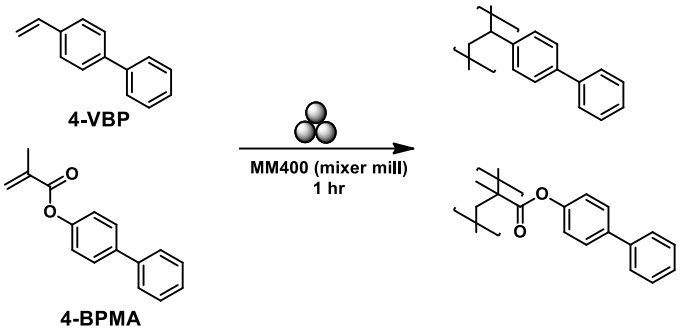
Kwangho Yoo[a,b,†], Gue Seon Lee[a,†], Hyo Won Lee[a,†], Byeong-Su Kim[b], and Jeung Gon Kim*[,a]

[a] Department of Chemistry and Research Institute of Physics and Chemistry, Jeonbuk National University, Jeonju 54896, Republic of Korea.

[b] Department of Chemistry, Yonsei University, Seoul 03722, Republic of Korea.

[†] These authors are contributed equally.

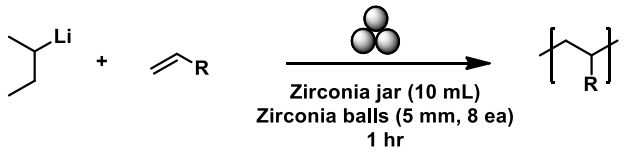
Table S1. Mechanochemical radical polymerization of 4-VBP and 4-BPMA without an external initiator (Raw Data of Table 1)



Entry	Container	Balls	Hz	Conv. (%)[a]	
				4-VBP	4-BPMA
1-1	Zirconia (10 mL)	Zirconia 8 mm, 2 ea	30	99	97
1-2				99	93
2-1	Zirconia (10 mL)	Zirconia 8 mm, 2 ea	20	37	< 1
2-2				17	< 1
3-1	Zirconia (10 mL)	Zirconia 10 mm, 1 ea	20	75	< 1
3-2				66	< 1
4-1	Zirconia (10 mL)	Zirconia 5 mm, 8 ea	20	< 1	< 1
4-2				< 1	< 1
5-1	Zirconia (10 mL)	Zirconia 5 mm, 8 ea	25	< 1	< 1
5-2				< 1	< 1
6-1	Zirconia (10 mL)	Zirconia 5 mm, 8 ea	30	< 1	< 1
6-2				< 1	< 1

[a] Determined by ^{1}H NMR spectroscopy with CH_2Br_2 as an internal standard.

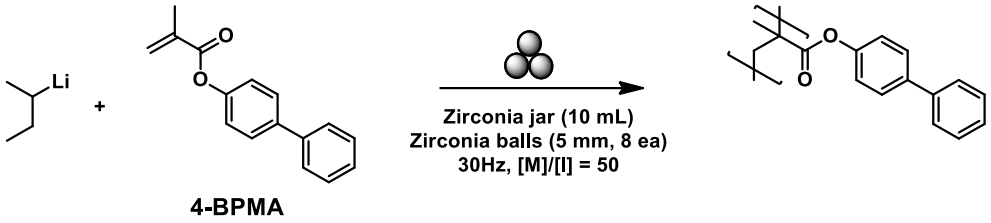
Table S2. Polymerization of 4-vinyl biphenyl with *s*-BuLi initiator.[a] (Raw Data of Table 2)



Entry	Monomer	Hz	[M]/[I]	Conv.(%)[b]	DP_{exp}[c]	M_n[d] (kg/mol)	M_w[d] (kg/mol)	$Đ$[d]
[M]/[I] variation set								
1-1	4-VBP	30	25	99	25	12.6	23.5	1.87
1-2				99	25	12.6	24.7	1.96
2-1	4-VBP	30	50	88	44	36.8	83.4	2.27
2-2				78	39	44.5	116	2.60
3-1	4-VBP	30	100	53	53	110	282	2.57
3-2				55	55	99.9	254	2.54
4-1	4-BPMA	30	25	69	17	35.7	62.0	1.74
4-2				76	19	35.5	62.4	1.76
5-1	4-BPMA	30	50	54	27	42.8	76.9	1.80
5-2				45	23	41.6	75.7	1.82
6-1	4-BPMA	30	100	42	42	44.6	84.7	1.90
6-2				45	45	45.9	85.5	1.86
Vibration energy variation set								
1-1	4-VBP	30	50	88	44	36.8	83.4	2.27
1-2				78	39	44.5	116	2.60
2-1	4-VBP	25	50	51	26	48.7	133	2.73
2-2				56	28	41.1	101	2.46
3-1	4-VBP	20	50	17	9	47.0	210	4.46
3-2				19	10	135	309	2.29
4-1	4-BPMA	30	50	54	27	42.8	76.9	1.80
4-2				45	23	41.6	75.7	1.82
5-1	4-BPMA	25	50	< 1	-	-	-	-
5-2				6	-	-	-	-
6-1	4-BPMA	20	50	< 1	-	-	-	-
6-2				< 1	-	-	-	-

[a] *s*-BuLi solution (1.4 M in cyclohexane) was used. [b] Determined by ^{1}H NMR spectroscopy with CH_2Br_2 as an internal standard.
[c] DP_{exp}=[M]/[I] X conversion. [d] Determined by SEC calibrated with polystyrene standards in THF at 40℃.

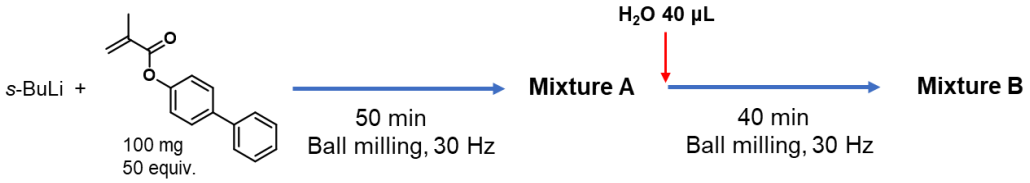
Table S3. A raw data of the polymerization time vs. conversion (Raw data of Figure 3)[a]



Entry	Time	Conv.(%)	DP_{exp}[c]	M_n[d] (kg/mol)	M_w[d] (kg/mol)	$Đ$[d]
1-1	10	< 1	-	-	-	-
1-2		< 1	-	-	-	-
2-1	20	< 1	-	-	-	-
2-2		2	-	-	-	-
3-1	30	6	3	59.6	89.6	1.50
3-2		8	4	62.9	94.4	1.50
4-1	40	8	4	56.0	70.1	1.25
4-2		13	7	55.2	75.1	1.36
5-1	50	33	17	45.6	78.0	1.71
5-2		33	17	45.4	77.6	1.71
6-1	60	47	24	42.7	76.0	1.78
6-2		56	28	45.8	84.0	1.83
7-1	90	93	47	24.6	59.8	2.43
7-2		93	47	24.8	62.9	2.53
8-1	120	97	49	20.4	47.3	2.32
8-2		97	49	20.4	46.1	2.26

[a] *s*-BuLi solution (1.4 M in cyclohexane) was used. [b] Determined by ^{1}H NMR spectroscopy with CH_2Br_2 as an internal standard.
[c] DP_{exp}=[M]/[I] X conversion. [d] Determined by SEC calibrated with polystyrene standards in THF at 40℃.

Table S4. Anion quenching experiments (Raw data of Figure 4.)[a]



Entry	Time	Conv.(%)	DP_{exp}[b]	M_n[c] (kg/mol)	M_w[c] (kg/mol)	$Đ$
1-1	50	43[d]	22	47.3	89.6	1.89
1-2		38[d]	19	47.1	83.0	1.76
2-1	50 + 40	99[e]	50	12.6	25.0	1.99
2-2		99[e]	50	12.7	25.3	1.99

[a] s-BuLi solution (1.4 M in cyclohexane) was used. [b] DP_{exp}=[M]/[I] X conversion. [c] Determined by SEC calibrated with polystyrene standards in THF at 40℃. [d] Determined by ^{1}H NMR spectroscopy using conv. (%) = 1 – [(unreacted 4-BPMA)/(total products)] [e] Determined by ^{1}H NMR spectroscopy with CH_2Br_2 as an internal standard.