

Supporting information

Pd(II)-catalyzed ethylene/methyl acrylate copolymerization: toward catalyst recovery and recycle.

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Ethylene/methyl acrylate copolymerization experiments

Table S1 Ethylene/methyl acrylate copolymerization: effect of solvent composition.^[a]

Precatalyst: [Pd(1)(Me)(MeCN)][PF₆] **Pd1b**.

entry	$\chi_{\text{TFE}}^{[b]}$	yield [g]	kg CP/mol Pd ^[c]	mol % MA ^[d]	M(MA):T(MA) ^[e]	$M_n^{[f]}$ [kDa] (M_w/M_n)	Bd ^[g]
1 ^[h]	0.00	1.04	49.4	4.8	12:88	5.0 (2.00)	93
2	0.09	2.42	114.9	3.0	14:85	16.6 (1.69)	99
3	0.17	2.97	141.8	2.4	15:85	18.2 (1.72)	101
3BIS		2.92	139.0	2.2	15:85		103
4	0.26	2.67	126.9	2.8	13:87	18.2 (1.70)	102
5	0.35	1.89	89.7	4.1	10:90	18.8 (1.53)	99
5BIS		1.92	91.2	3.6	11:89		100
6	0.47	2.86	136.1	2.3	18:82	18.5 (1.54)	104
7	0.59	2.41	115.1	2.4	21:79	19.3 (1.60)	103
8	0.79	1.94	92.3	2.9	26:74	23.2 (1.70)	100
9	0.89	1.61	76.6	2.8	28:72	24.3 (1.75)	100
10 ^[h]	1.00	1.02	48.8	4.0	40:60	23.4 (1.19)	93

^[a]Reaction conditions: $n_{\text{Pd}} = 2.1 \cdot 10^{-5}$ mol, $V_{\text{sol}} = 21$ mL, $V_{\text{MA}} = 2.26$ mL, $[\text{MA}]/[\text{Pd}] = 1188$, $T = 308$ K, $P_E = 5$ bar, $t = 6$ h; ^[b] $\chi_{\text{TFE}} = n_{\text{TFE}}/(n_{\text{DCM}} + n_{\text{TFE}})$; ^[c]productivity as kg CP/mol Pd = kilograms of copolymer per mol of palladium; ^[d]calculated by ¹H NMR spectroscopy on isolated product; ^[e]calculated by ¹³C NMR spectroscopy on isolated product; ^[f]molecular weight (M_n and M_w) and molecular weight distribution (M_w/M_n) were measured by GPC; ^[g]Bd = branching degree as branches per 1000 carbon atoms, calculated by ¹H NMR spectroscopy on isolated product; ^[h]from reference 4.