

**Oligomerization of Styrenes Mediated by Cationic Allyl Nickel Complexes
Containing Triphenylstibine or Triphenylarsine**

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SPAIN*

Kurt Mereiter

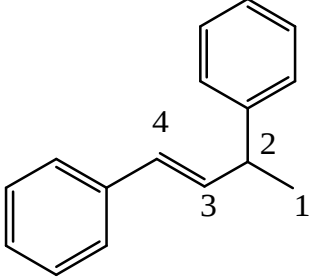
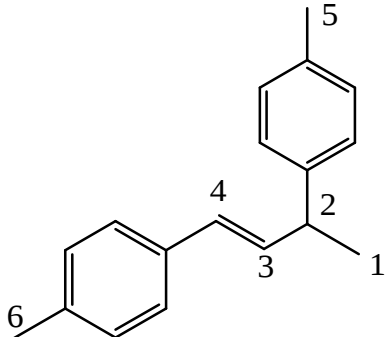
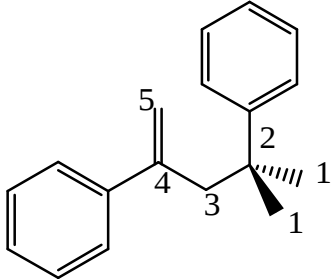
*Institute of Chemical Technologies and Analytics (E171), Vienna University of
Technology, Getreidemarkt 9, A-1060, AUSTRIA*

ELECTRONIC SUPPLEMENTARY MATERIAL

- **NMR data for the styrene, 4-methylstyrene and α -methylstyrene dimerization products**
- **Relevant GPC/SEC chromatograms for the oligomers**

NMR data for the styrene, 4-methylstyrene and α -methylstyrene dimerization products

Assignations by means of gCOSY, DEPT and gHSQC NMR spectra

 (E)-but-1-ene-1,3-diyl dibenzene	^1H NMR (CDCl_3) δ (ppm): 1.56 (d, $^3J_{\text{HH}} = 7.1$ Hz, 3 H, C^1H_3), 3.73 (pseudoquintet, 1 H, C^2H), 6.49 (second order multiplet, 2 H, C^3H, C^4H), 7.22-7.47 (m, 10 H, C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ (ppm): 21.5 (C^1), 42.9 (C^2), 128.9 (C^3), 135.6 (C^4), 126.5, 127.3, 127.7, 128.7, 128.8, 145.9 (C_6H_5).
 (E)-4,4'-(but-1-ene-1,3-diyl)bis(methylbenzene)	^1H NMR (CDCl_3) δ (ppm): 1.72 (d, $^3J_{\text{HH}} = 6.8$ Hz, 3 H, C^1H_3), 2.57, 2.59 (s, 3 H each, C^5H_3, C^6H_3), 3.85 (pseudoquintet, 1 H, C^2H), 6.64 (second order multiplet, 2 H, C^3H, C^4H), 7.3-7.5 (m, 8 H, C_6H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ (ppm): 21.25 (C^1), 20.9, 21.01 (C^5, C^6), 42.0 (C^2), 128.1 (C^3), 134.3 (C^4), 126.0, 127.0, 129.0, 129.1, 126.0, 142.7 (C_6H_4).
 (4-methylpent-1-ene-2,4-diyl) dibenzene	^1H NMR (CDCl_3) δ (ppm): 1.32 (s, 6 H, $(\text{C}^1\text{H}_3)_2$), 2.92 (s br, 2 H, C^3H_2), 4.87, 5.22 (br, 1 H each, $=\text{C}^5\text{H}_2$), 7.15-7.45 (m, 10 H, C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ (ppm): 28.7 (C^1), 38.6 (C^2), 49.6 (C^3), 116.8 (C^5), 149.3 (C^4), 125.4, 125.9, 126.5, 126.8, 127.9, 128.0, 143.4, 146.7 (C_6H_5).

Relevant GPC/SEC chromatograms for the oligomers

Run: Entry 5, Table 1 of the article

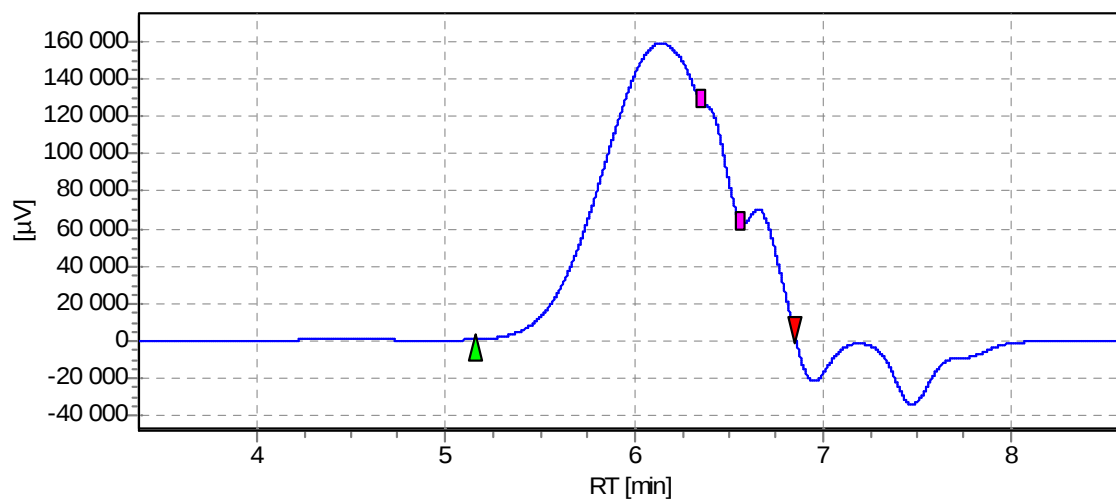
Catalyst: 0.05 % $[\text{Ni}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{PPh}_3)(\text{SbPh}_3)][\text{Ni}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{PPh}_3)_2][\text{BAR}'_4]_2$ (**3**)

Substrate: Styrene

Temperature: 25 °C

Reaction time: 45 minutes

Solvent: dichloromethane



Zone	Start [min]	Stop [min]	MW	Mn	Mz	Mz+1	Ip	Peak Area %
1 : Division 1 from peak # 1	5,16	6,35	854,01	725,72	1047,38	1321,67	1,18	71
2 : Division 2 from peak # 1	6,35	6,56	353,73	349,07	358,29	362,67	1,01	17
3 : Division 3 from peak # 1	6,56	6,86	222,78	218,33	227,09	231,18	1,02	12

Run: Entry 6, Table 1 of the article

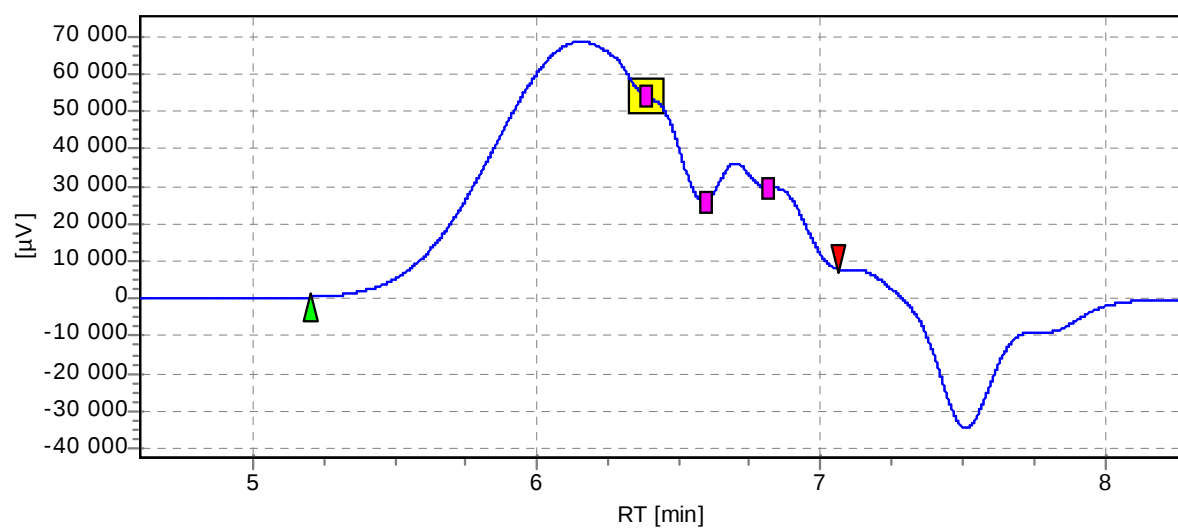
Catalyst: 0.05 % $[\text{Ni}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{PPh}_3)(\text{AsPh}_3)][\text{Ni}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{PPh}_3)_2][\text{BAr}'_4]_2$ (**4**)

Substrate: Styrene

Temperature: 25 °C

Reaction time: 45 minutes

Solvent: dichloromethane



Zone	Start [min]	Stop [min]	MW	Mn	Mz	Mz+1	Ip	Peak Area %
1 : Division 1 from peak # 1	5.21	6.38	829.71	699.72	1023.67	1291.05	1.19	65
2 : Division 2 from peak # 1	6.38	6.59	335.69	331.28	339.97	344.07	1.01	15
3 : Division 3 from peak # 1	6.59	6.81	211.82	208.72	214.95	218.06	1.01	12

Run: Entry 1, Table 2 of the article

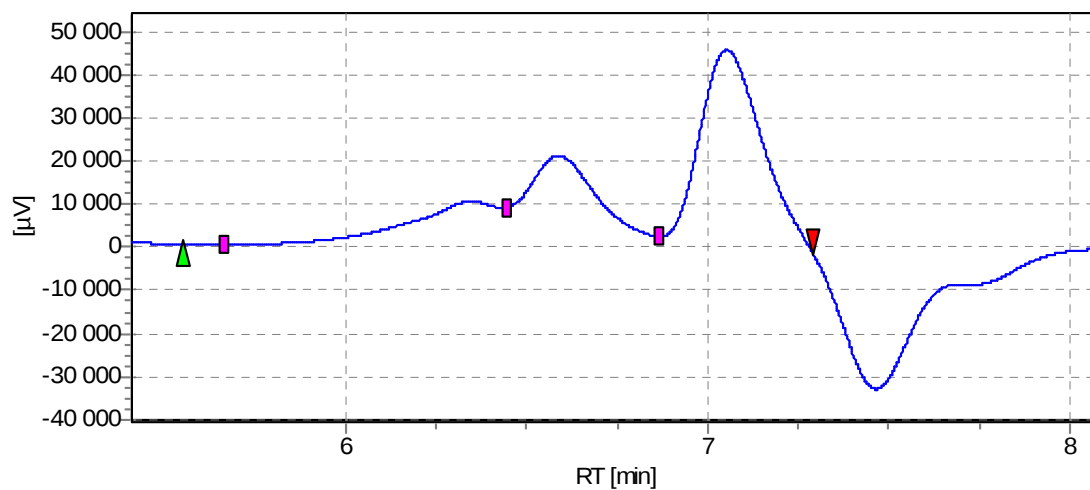
Catalyst: 0.05 % $[\text{Ni}(\eta^3\text{-CH}_2\text{C}(\text{CH}_3)\text{CH}_2)(\text{SbPh}_3)_3][\text{BAR}'_4]$ (**1a**)

Substrate: 4-methylstyrene

Temperature: 25 °C

Reaction time: 45 minutes

Solvent: dichloromethane



Zone	Start [min]	Stop [min]	MW	Mn	Mz	Mz+1	Ip	Peak Area %
1 : Division 1 from peak # 1	5,66	6,44	565,91	508,67	653,71	776,22	1,11	41
2 : Division 2 from peak # 1	6,44	6,86	254,85	245,98	263,23	271,00	1,04	59

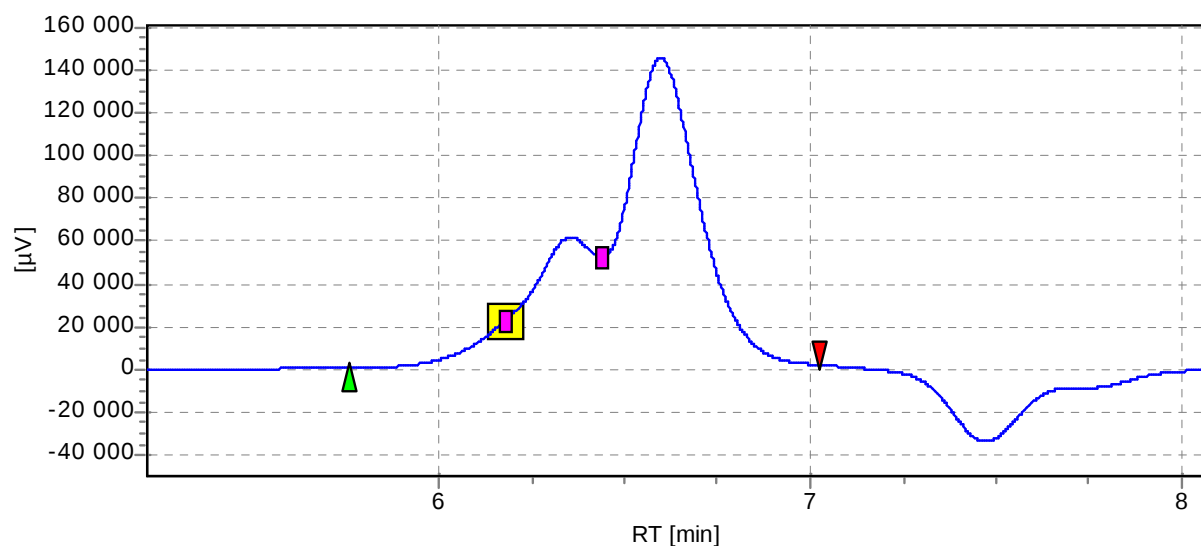
Run: Entry 2, Table 2 of the articleCatalyst: 0.05 % $[\text{Ni}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{SbPh}_3)_3][\text{BAr}'_4]$ (**1b**)

Substrate: 4-methylstyrene

Temperature: 25 °C

Reaction time: 45 minutes

Solvent: 1,2-dichloroethane



Zone	Start [min]	Stop [min]	MW	Mn	Mz	Mz+1	Ip	Peak Area %
1 : Division 1 from peak # 1	5.76	6.18	719.10	699.09	744.53	776.30	1.03	5
2 : Division 2 from peak # 1	6.18	6.43	445.45	437.74	453.56	461.92	1.02	25
3 : Division 3 from peak # 1	6.43	7.02	252.04	241.94	261.18	269.51	1.04	70

Run: Entry 3, Table 2 of the article

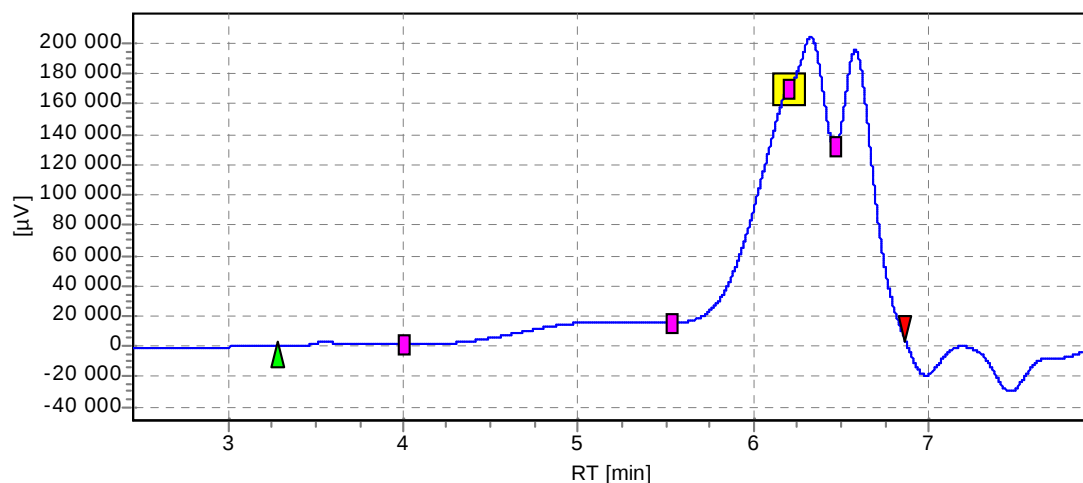
Catalyst: 0.05 % $[\text{Ni}(\eta^3\text{-CH}_2\text{C}(\text{CH}_3)\text{CH}_2)(\text{AsPh}_3)_2][\text{BAr}'_4]$ (**2a**)

Substrate: 4-methylstyrene

Temperature: 25 °C

Reaction time: 45 minutes

Solvent: dichloromethane



Zone	Start [min]	Stop [min]	MW	Mn	Mz	Mz+1	Ip	Peak Area %
1 : Division 2 from peak # 1	3.99	5.52	6708.03	4467.28	11138.81	17373.03	1.50	0.0
2 : Division 3 from peak # 1	5.52	6.20	854.20	777.87	965.86	1 113.18	1.10	0.0
3 : Division 4 from peak # 1	6.20	6.46	444.07	435.52	452.62	460.99	1.02	0.0
4 : Division 5 from peak # 1	6.46	6.86	257.84	250.24	264.96	271.54	1.03	0.0

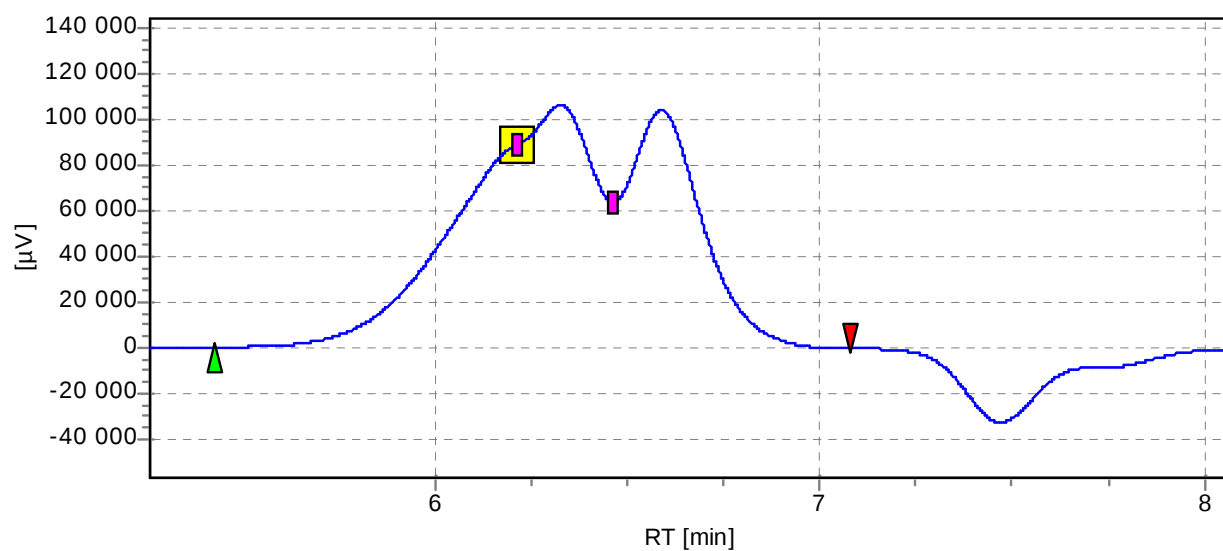
Run: Entry 4, Table 2 of the articleCatalyst: 0.05 % $[\text{Ni}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{AsPh}_3)_2][\text{BAr}'_4]$ (**2b**)

Substrate: 4-methylstyrene

Temperature: 25 °C

Reaction time: 45 minutes

Solvent: 1,2-dichloroethane



Zone	Start [min]	Stop [min]	MW	Mn	Mz	Mz+1	Ip	Peak Area %
1 : Division 1 from peak # 1	5.43	6.21	754.13	715.82	805.11	872.31	1.05	30
2 : Division 2 from peak # 1	6.21	6.46	438.39	430.69	446.04	453.51	1.02	34
3 : Division 3 from peak # 1	6.46	7.08	253.90	245.25	261.58	268.43	1.04	36

Run: Entry 5, Table 2 of the article

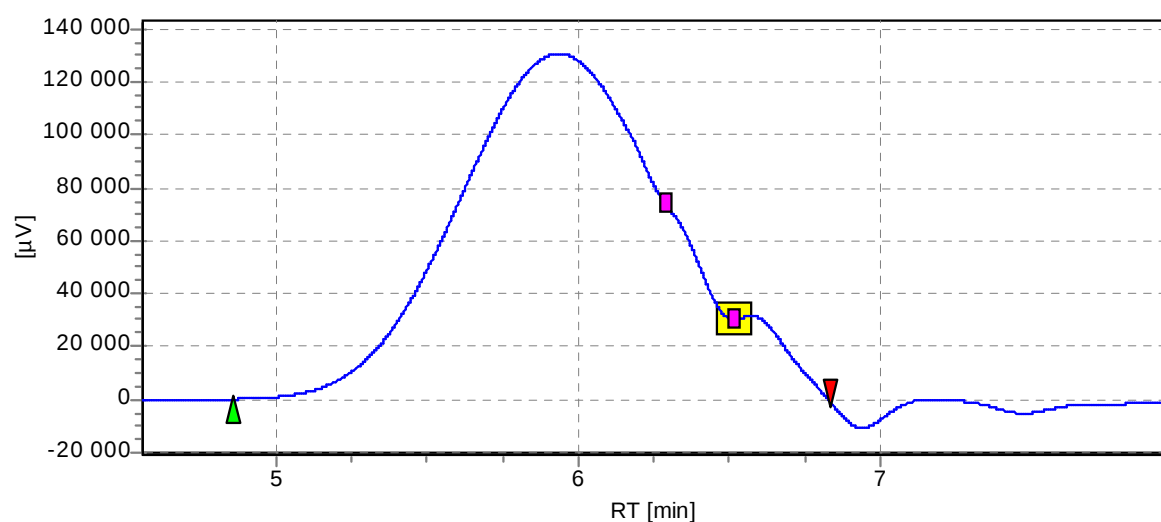
Catalyst: 0.05 % $[\text{Ni}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{PPh}_3)(\text{SbPh}_3)][\text{Ni}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{PPh}_3)_2][\text{BAR}'_4]_2$ (**3**)

Substrate: 4-methylstyrene

Temperature: 25 °C

Reaction time: 45 minutes

Solvent: dichloromethane



Zone	Start [min]	Stop [min]	MW	Mn	Mz	Mz+1	M visc	Ip	Peak Area %
1 : Division 1 from peak # 1	4.86	6.28	1198.66	960.08	1551.43	2020.34	0.00	1.25	83.2
2 : Division 2 from peak # 1	6.28	6.51	399.06	392.90	404.97	410.57	0.00	1.02	11
3 : Division 3 from peak # 1	6.51	6.84	246.83	241.68	251.66	256.12	0.00	1.02	6

Run: Entry 6, Table 2 of the article

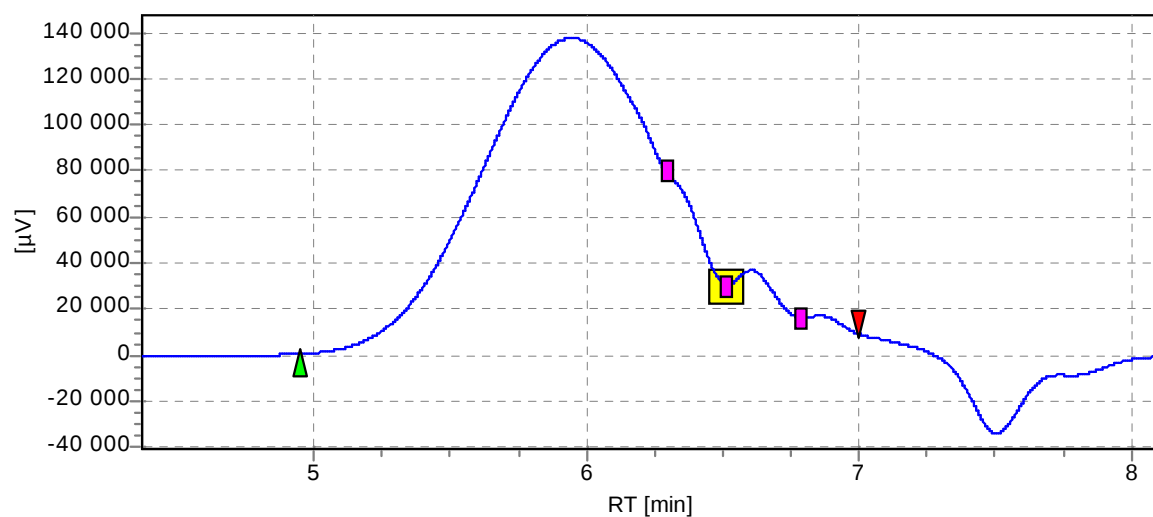
Catalyst: 0.05 % $[\text{Ni}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{PPh}_3)(\text{AsPh}_3)][\text{Ni}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{PPh}_3)_2][\text{BAR}'_4]_2$ (**4**)

Substrate: 4-methylstyrene

Temperature: 25 °C

Reaction time: 45 minutes

Solvent: dichloromethane



Zone	Start [min]	Stop [min]	MW	Mn	Mz	Mz+1	Ip	Peak Area %
1 : Division 1 from peak # 1	4.95	6.29	1179.16	943.99	1526.61	1984.26	1.25	82
2 : Division 2 from peak # 1	6.29	6.52	396.05	390.43	401.45	406.58	1.01	11
3 : Division 3 from peak # 1	6.52	6.78	242.86	238.06	247.53	252.00	1.02	7

Run: Entry 7, Table 2 of the article

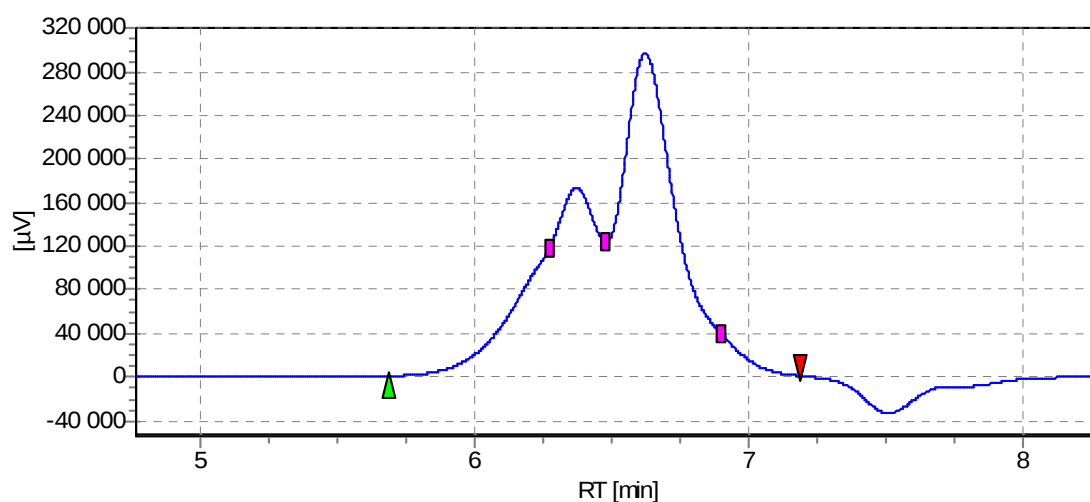
Catalyst: 0.05 % $[\text{Ni}(\eta^3\text{-CH}_2\text{C}(\text{CH}_3)\text{CH}_2)\text{Br}(\text{SbPh}_3)] + \text{NaBAr}'_4$ (**5a**)

Substrate: 4-methylstyrene

Temperature: 25 °C

Reaction time: 45 minutes

Solvent: fluorobenzene



Zone	Start [min]	Stop [min]	MW	Mn	Mz	Mz+1	Ip	Peak Area %
2 : Division 1 from peak # 1	5,69	6,27	636,44	611,07	670,30	715,11	1,04	16
3 : Division 2 from peak # 1	6,27	6,48	402,79	398,05	407,54	412,26	1,01	26
4 : Division 3 from peak # 1	6,48	6,90	236,87	228,32	244,91	252,35	1,04	58

Run: Entry 8, Table 2 of the article

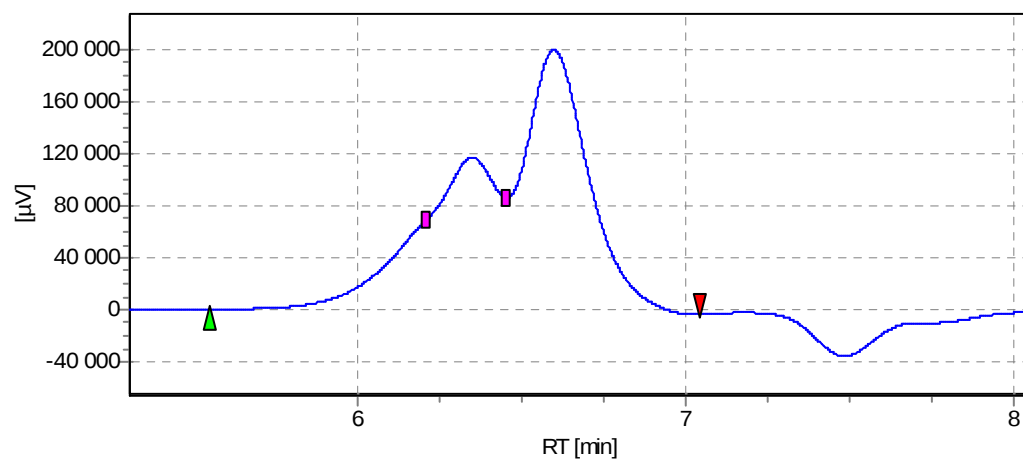
Catalyst: 0.05 % $[\text{Ni}(\eta^3\text{-CH}_2\text{CHCH}_2)\text{Br}(\text{SbPh}_3)] + \text{NaBAr}'_4$ (**5b**)

Substrate: 4-methylstyrene

Temperature: 25 °C

Reaction time: 45 minutes

Solvent: fluorobenzene



Zone	Start [min]	Stop [min]	MW	Mn	Mz	Mz+1	Ip	Peak Area %
2 : Division 1 from peak # 1	5,55	6,21	726,85	690,24	781,96	864,20	1,05	14
3 : Division 2 from peak # 1	6,21	6,45	435,25	428,28	442,35	449,47	1,02	29
4 : Division 3 from peak # 1	6,45	7,04	251,28	242,25	259,47	266,92	1,04	57

Run: Entry 9, Table 2 of the article

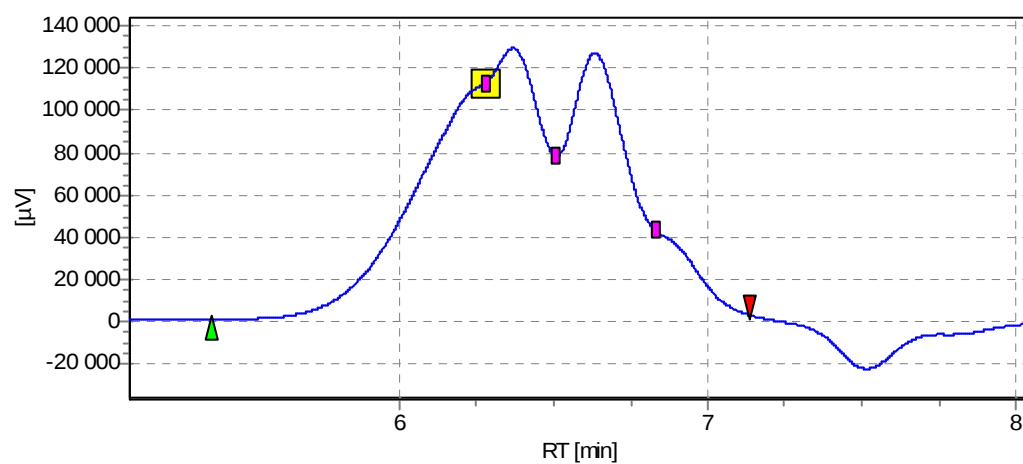
Catalyst: 0.05 % $[\text{Ni}(\eta^3\text{-CH}_2\text{C}(\text{CH}_3)\text{CH}_2)\text{Br}(\text{AsPh}_3)] + \text{NaBAr}'_4$ (**6a**)

Substrate: 4-methylstyrene

Temperature: 25 °C

Reaction time: 45 minutes

Solvent: fluorobenzene



Zone	Start [min]	Stop [min]	MW	Mn	Mz	Mz+1	Ip	Peak Area %
1 : Division 1 from peak # 1	5,39	6,28	721,18	665,84	808,59	948,95	1,08	36
2 : Division 2 from peak # 1	6,28	6,50	397,33	391,47	403,14	408,79	1,01	30
3 : Division 3 from peak # 1	6,50	6,83	235,49	229,14	241,71	247,65	1,03	34

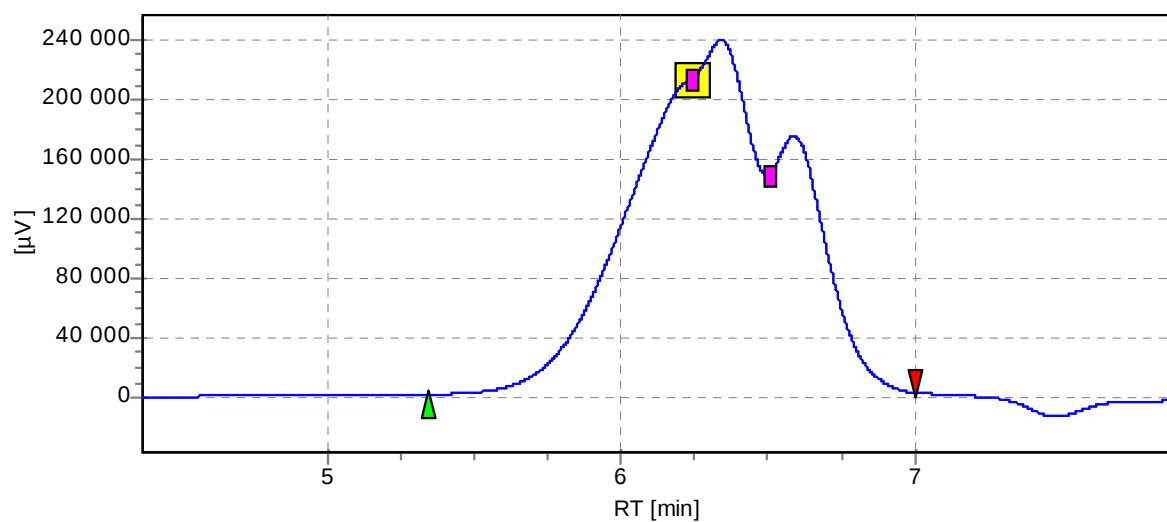
Run: Entry 10, Table 2 of the articleCatalyst: 0.05 % $[\text{Ni}(\eta^3\text{-CH}_2\text{CHCH}_2)\text{Br(AsPh}_3)] + \text{NaBAR}'_4$ (**6b**)

Substrate: 4-methylstyrene

Temperature: 25 °C

Reaction time: 45 minutes

Solvent: fluorobenzene



Zone	Start [min]	Stop [min]	MW	Mn	Mz	Mz+1	Ip	Peak Area %
1 : Division 1 from peak # 1	5.34	6.24	786.04	723.86	883.30	1036.58	1.09	39
2 : Division 2 from peak # 1	6.24	6.50	416.95	408.67	425.13	433.05	1.02	36
3 : Division 3 from peak # 1	6.50	7.00	243.97	235.54	251.27	257.55	1.04	25

Run: Entry 1, Table 3 of the article

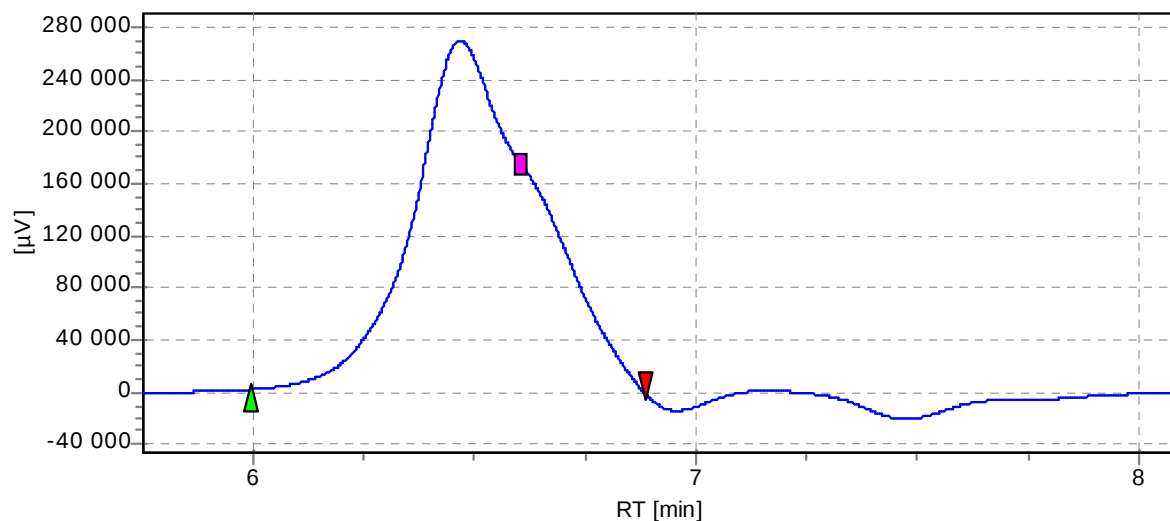
Catalyst: 0.05 % $[\text{Ni}(\eta^3\text{-CH}_2\text{C}(\text{CH}_3)\text{CH}_2)(\text{SbPh}_3)_3][\text{BAR}'_4]$ (**1a**)

Substrate: α -methylstyrene

Temperature: 50 °C

Reaction time: 24 hours

Solvent: 1,2-dichloroethane



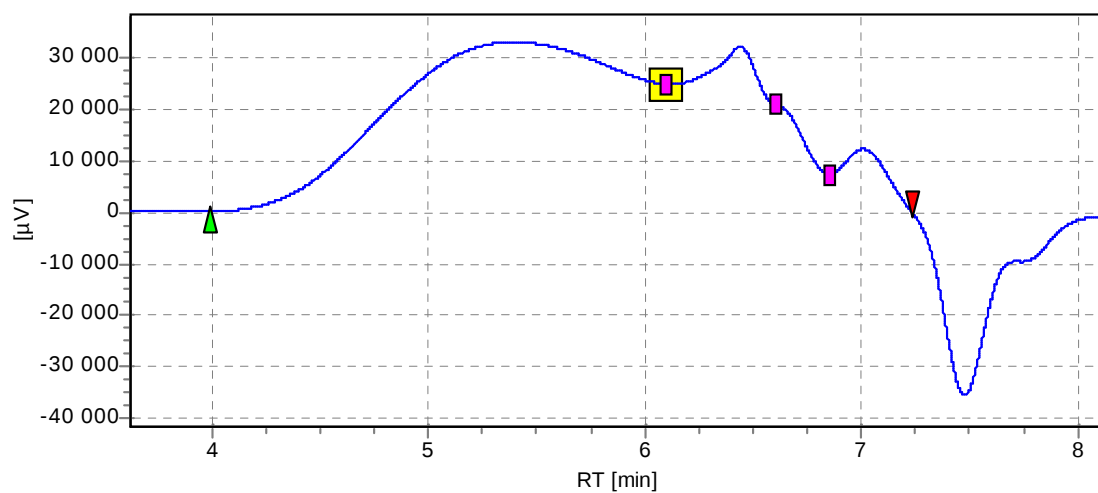
Zone	Start [min]	Stop [min]	MW	Mn	Mz	Mz+1	M visc	Ip	Peak Area %
1 : Division 1 from peak # 1	6.00	6.60	356.75	342.40	374.81	397.63	0.00	1.04	73
2 : Division 2 from peak # 1	6.60	6.89	216.69	213.25	219.87	222.78	0.00	1.02	27

Run: Entry 2, Table 3 of the articleCatalyst: 0.05 % $[\text{Ni}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{SbPh}_3)_3][\text{BAr}'_4]$ (**1b**)Substrate: α -methylstyrene

Temperature: 25 °C

Reaction time: 45 minutes

Solvent: dichloromethane



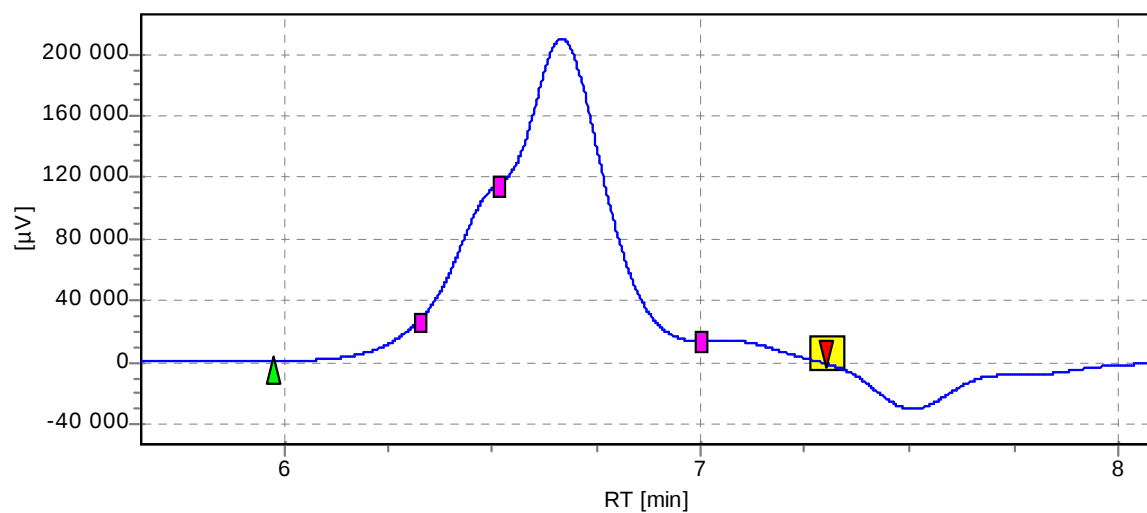
Zone	Start [min]	Stop [min]	MW	Mn	Mz	Mz+1	M visc	Ip	Peak Area %
1 : Division 1 from peak # 1	3.99	6.10	3944.39	2061.57	7515.92	12093.22	0.00	1.91	68
2 : Division 2 from peak # 1	6.10	6.60	433.72	402.90	466.01	497.14	0.00	1.08	21
3 : Division 3 from peak # 1	6.60	6.85	210.51	206.57	214.25	217.75	0.00	1.02	6
4 : Division 4 from peak # 1 (α -methylstyrene)	6.85	7.24	112.47	108.78	116.13	119.64	0.00	1.03	-

Run: Entry 3, Table 3 of the articleCatalyst: 0.05 % $[\text{Ni}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{SbPh}_3)_3][\text{BAr}'_4]$ (**1b**)Substrate: α -methylstyrene

Temperature: 50 °C

Reaction time: 24 hours

Solvent: 1,2-dichloroethane



Zone	Start [min]	Stop [min]	MW	Mn	Mz	Mz+1	M visc	Ip	Peak Area %
1 : Division 1 from peak # 1	5.97	6.32	524.52	513.47	538.05	554.38	0.00	1.02	3
2 : Division 2 from peak # 1	6.32	6.51	352.83	349.41	356.43	360.20	0.00	1.01	20
3 : Division 3 from peak # 1	6.51	7.00	221.09	212.33	229.14	236.43	0.00	1.04	73

Run: Entry 4, Table 3 of the article

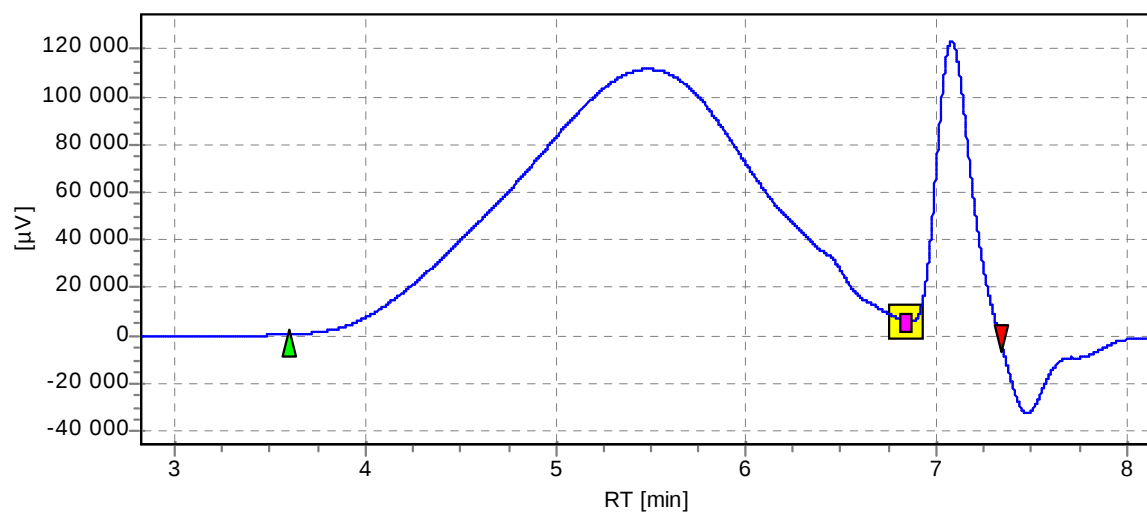
Catalyst: 0.05 % $[\text{Ni}(\eta^3\text{-CH}_2\text{C}(\text{CH}_3)\text{CH}_2)(\text{AsPh}_3)_2][\text{BAR}'_4]$ (**2a**)

Substrate: α -methylstyrene

Temperature: 25 °C

Reaction time: 45 minutes

Solvent: dichloromethane



Zone	Start [min]	Stop [min]	MW	Mn	Mz	Mz+1	M visc	Ip	Peak Area %
1 : Division 1 from peak # 1	3.60	6.84	4695.62	1398.27	13652.73	26525.63	0.00	3.36	100
2 : Division 2 from peak # 1 (α -methylstyrene)	6.84	7.34	95.56	92.52	98.64	101.78	0.00	1.03	-

Run: Entry 5, Table 3 of the article

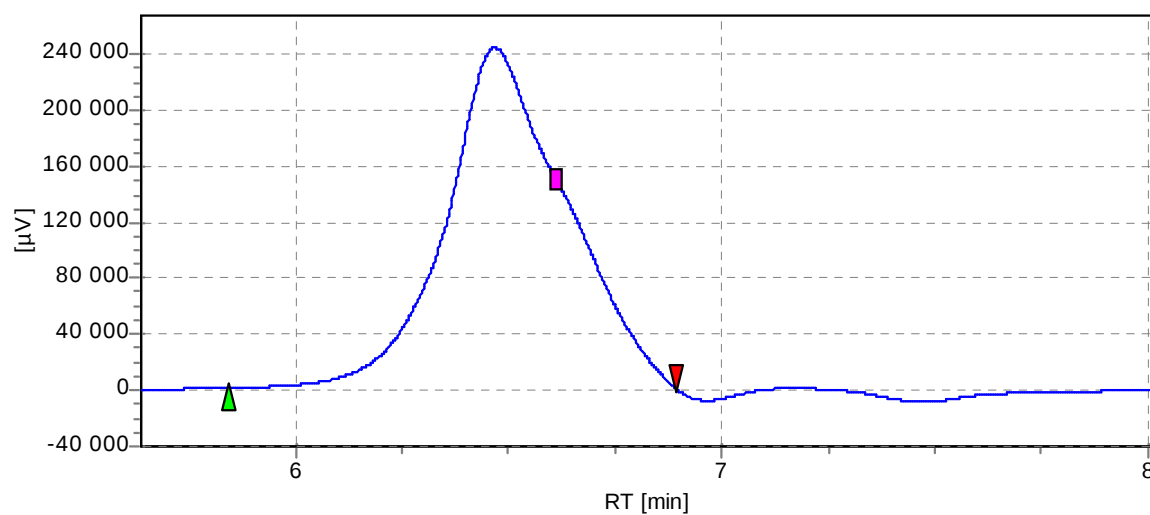
Catalyst: 0.05 % $[\text{Ni}(\eta^3\text{-CH}_2\text{C}(\text{CH}_3)\text{CH}_2)(\text{AsPh}_3)_2][\text{BAr}'_4]$ (**2a**)

Substrate: α -methylstyrene

Temperature: 50 °C

Reaction time: 24 hours

Solvent: 1,2-dichloroethane



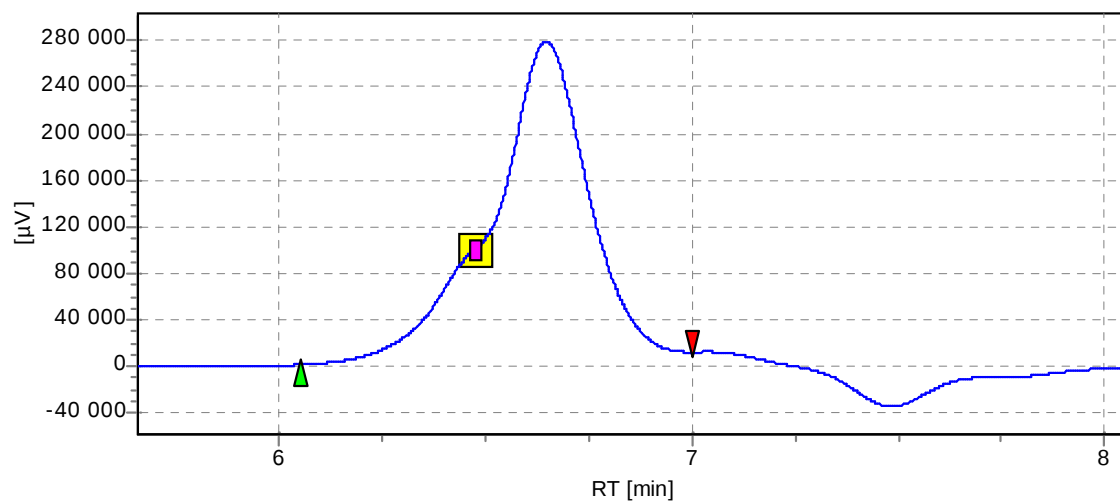
Zone	Start [min]	Stop [min]	MW	Mn	Mz	Mz+1	Ip	Peak Area %
2 : Division 1 from peak # 1	5,84	6,61	362,74	344,54	388,18	425,16	1,05	77
3 : Division 2 from peak # 1	6,61	6,89	213,92	210,51	217,06	219,91	1,02	33

Run: Entry 6, Table 3 of the articleCatalyst: 0.05 % $[\text{Ni}(\eta^3\text{-CH}_2\text{CHCH}_2)(\text{AsPh}_3)_2][\text{BAr}'_4]$ (**2b**)Substrate: α -methylstyrene

Temperature: 50 °C

Reaction time: 24 hours

Solvent: 1,2-dichloroethane



Zone	Start [min]	Stop [min]	MW	Mn	Mz	Mz+1	M visc	Ip	Peak Area %
1 : Division 1 from peak # 1	6.05	6.47	405.51	394.72	419.07	435.87	0.00	1.03	16
2 : Division 2 from peak # 1	6.47	7.00	230.91	221.41	239.74	247.91	0.00	1.04	83

Run: Entry 7, Table 3 of the article

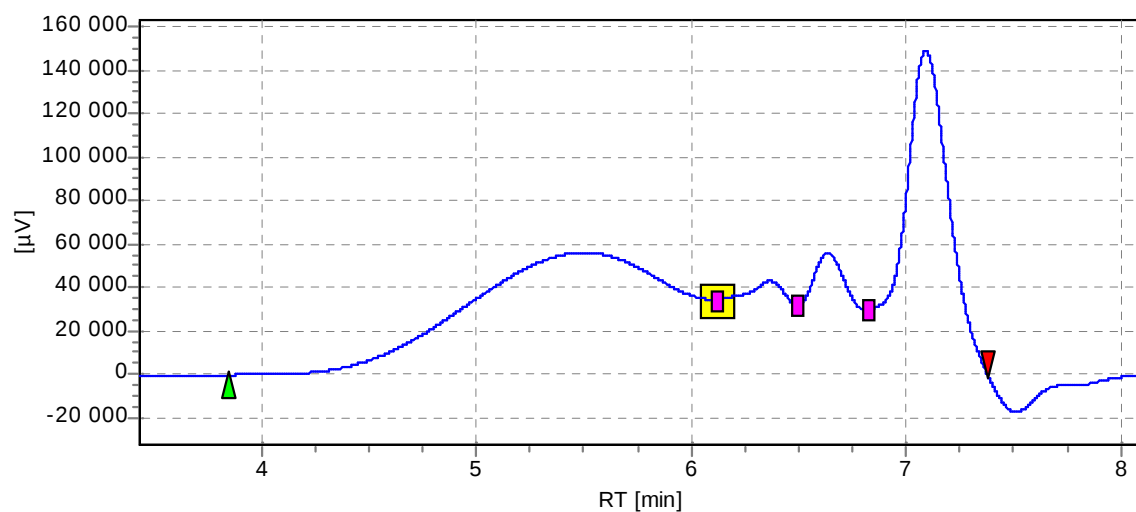
Catalyst: 0.05 % $[\text{Ni}(\eta^3\text{-CH}_2\text{C}(\text{CH}_3)\text{CH}_2)\text{Br}(\text{SbPh}_3)] + \text{NaBAR}'_4$ (**5a**)

Substrate: α -methylstyrene

Temperature: 25 °C

Reaction time: 45 minutes

Solvent: fluorobenzene



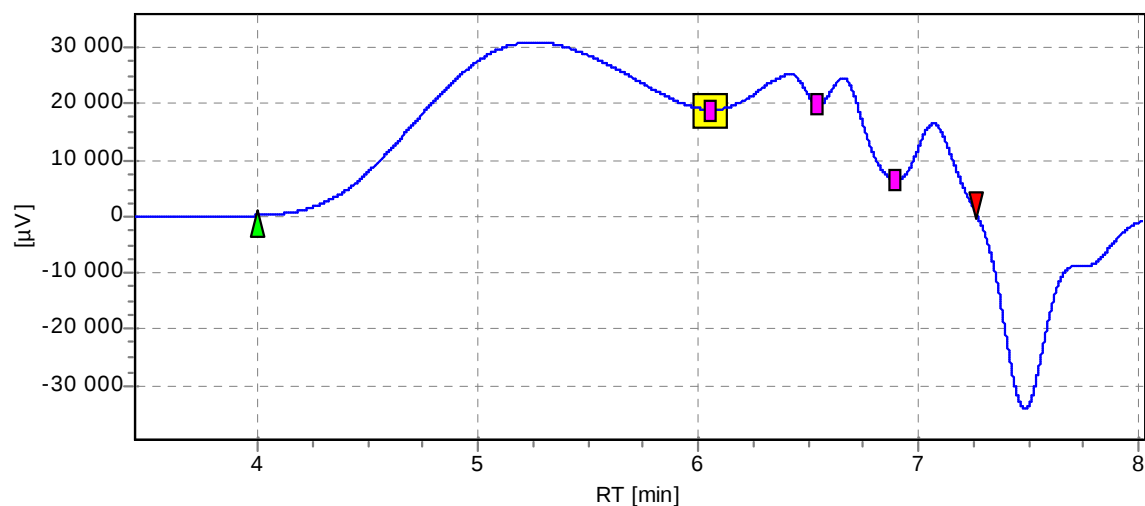
Zone	Start [min]	Stop [min]	MW	Mn	Mz	Mz+1	M visc	Ip	Peak Area %
1 : Division 1 from peak # 1	3.84	6.11	3400.22	1933.77	6280.51	10461.40	0.00	1.76	69
2 : Division 2 from peak # 1	6.11	6.49	470.55	451.42	490.26	509.61	0.00	1.04	15
3 : Division 3 from peak # 1	6.49	6.83	234.92	227.51	242.31	249.47	0.00	1.03	16
4 : Division 4 from peak # 1 (α -methylstyrene)	6.83	7.38	97.15	92.39	102.28	107.69	0.00	1.05	-

Run: Entry 8, Table 3 of the articleCatalyst: 0.05 % $[\text{Ni}(\eta^3\text{-CH}_2\text{CHCH}_2)\text{Br}(\text{SbPh}_3)] + \text{NaBAr}'_4$ (**5b**)Substrate: α -methylstyrene

Temperature: 25 °C

Reaction time: 45 minutes

Solvent: fluorobenzene



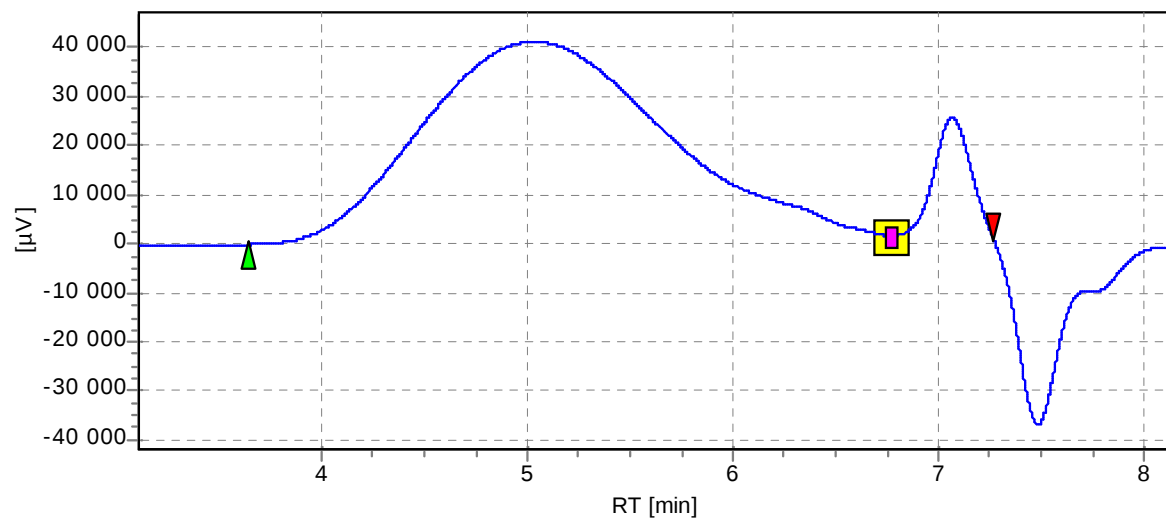
Zone	Start [min]	Stop [min]	MW	Mn	Mz	Mz+1	M visc	Ip	Peak Area %
1 : Division 1 from peak # 1	3.99	6.05	4385.45	2373.48	7840.19	12040.14	0.00	1.85	65
2 : Division 2 from peak # 1	6.05	6.54	473.85	441.58	508.06	541.50	0.00	1.07	19
3 : Division 3 from peak # 1	6.54	6.89	220.50	213.59	227.05	233.10	0.00	1.03	10
4 : Division 4 from peak # 1 (α -methylstyrene)	6.89	7.27	101.13	98.11	104.19	107.25	0.00	1.03	-

Run: Entry 9, Table 3 of the articleCatalyst: 0.05 % $[\text{Ni}(\eta^3\text{-CH}_2\text{CHCH}_2)\text{Br(AsPh}_3)] + \text{NaBAR}'_4$ (**6b**)Substrate: α -methylstyrene

Temperature: 25 °C

Reaction time: 16 hours

Solvent: fluorobenzene



Zone	Start [min]	Stop [min]	MW	Mn	Mz	Mz+1	Ip	Peak Area %
2 : Division 1 from peak # 1	3.65	6.76	6453.10	2204.18	13069.82	20517.07	2.93	100
3 : Division 2 from peak # 1 (α -methylstyrene)	6.76	7.26	102.43	98.64	106.70	111.49	1.04	-