

Versatile 2-Methoxyethylaminobis(phenolate)yttrium Catalysts: Catalytic Precision Polymerization of Polar Monomers via Rare Earth Metal-Mediated Group Transfer Polymerization

Peter T. Altenbuchner[†], Benedikt S. Soller[†], Stefan Kissling[†], Thomas Bachmann[†], Alexander Kronast[†], Sergei I. Vagin[†], Bernhard Rieger^{†*}

[†]WACKER-Lehrstuhl für Makromolekulare Chemie, Technische Universität München, Lichtenbergstraße 4, 85748 Garching bei München, Germany

Table of Contents

1. General Information	2
2. Analytical Data	4
2.1 Nuclear Magnetic Resonance Spectroscopy (NMR)	4
2.2 Kinetic Data	9
2.3 Endgroup Analysis	13
2.4 LCST (Lower critical solution temperature)	14
2.5 Eyring-Plot Data	15
2.6 Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC)	16
2.7 Gel-permeation chromatography (GPC) Data	17
2.7.1 Homopolymerization	17
2.7.2 Block copolymerization	26

1. General Information

Activity Measurements and Kinetic Analysis in the *in situ* ATR-IR:

For activity measurements, the stated amount of catalyst (42 – 135 μmol) is dissolved in 5 mL of dichloromethane, and the reaction mixture is transferred into the *in situ* IR autoclave and thermostatted to the desired temperature. Then, the stated amount of monomer (4.3-27 mmol) is added. During the course of the experiment the temperature is kept at the desired temperature (± 1 K). In case of block copolymerization experiments, an aliquot sample is taken after complete conversion of the first monomer A for GPC-MALS analysis. Monomer B (4.3 mmol) is added subsequently and the reaction mixture is stirred until full conversion. After the stated reaction time, the reaction is quenched by addition of wet chloroform (0.5 mL) and an aliquot is taken to determine the conversion. The polymer is precipitated in excess hexane, filtered off and freeze dried from distilled H_2O .

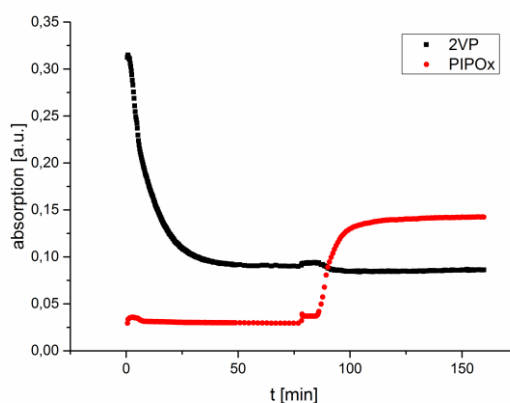


Figure S 1 ATR-IR block copolymerization experiment with block A P2VP (802 cm^{-1}) and block B PIPOx (1607 cm^{-1}).

The block copolymerization of 2VP and PIPOx was monitored in the ATR-IR (Figure S 1) through which the decrease of 2VP to complete conversion and the increase of PIPOx could be observed. The polymerization of IPOx was initiated immediately after the addition and preceded to full conversion within 30 minutes.

Sequential copolymerization

After dissolving the calculated amount of catalyst in dichloromethane at room temperature, the first monomer was added. The reaction mixture was stirred for 2 hours. One aliquot was taken and quenched by the addition of 0.5 mL MeOH while the calculated amount of a second monomer was added to the reaction solution and stirred for another 2 hours at room temperature (in case of DMAA: at $-78\text{ }^{\circ}\text{C}$) and quenched by addition of 0.5 mL MeOH. The polymers were precipitated by addition of the reaction mixtures to hexane (150 mL) and decanted from solution. Residual solvents were removed by drying the polymers under vacuum at $60\text{ }^{\circ}\text{C}$ overnight.

Molecular weight determination

GPC was carried out on a Varian LC-920 equipped with two PL Polargel columns. As eluent a mixture of 50% THF, 50% water, and 9 g L⁻¹ tetrabutylammonium bromide (TBAB) was used in the case of PDEVp, PIPOx, P2VP, P(2VP-b-PDEVp), P(2VP-b-PIPOx), P(2VP-b-PDMAA) and P(2VP-b-DEVp); for PDIVP analysis, the eluent was THF with 6 g L⁻¹ TBAB. Absolute molecular weights have been determined online by multiangle light scattering (MALS) analysis using a Wyatt Dawn Heleos II in combination with a Wyatt Optilab rEX as concentration source.

GPC for Polyhydroxybutyrate samples was carried on a Polymer Laboratories GPC50 Plus chromatograph. As eluent, chloroform with 1.5 g L⁻¹ tetrabutylammonium tetrafluoroborate was used. Polystyrene standards were used for calibration.

Kinetics by aliquots method

In the Glovebox the calculated amount of catalyst was dissolved in 20mL toluene at room temperature and the calculated amount of monomer was added in one injection. Aliquots were taken from the reaction solution at regular time intervals and quenched by addition to MeOH. For each aliquot, the conversion is determined by gravimetry or ¹H NMR spectroscopy and the molecular weight of the formed polymer by GPC-MALS analysis.

2. Analytical Data

2.1 Nuclear Magnetic Resonance Spectroscopy (NMR)

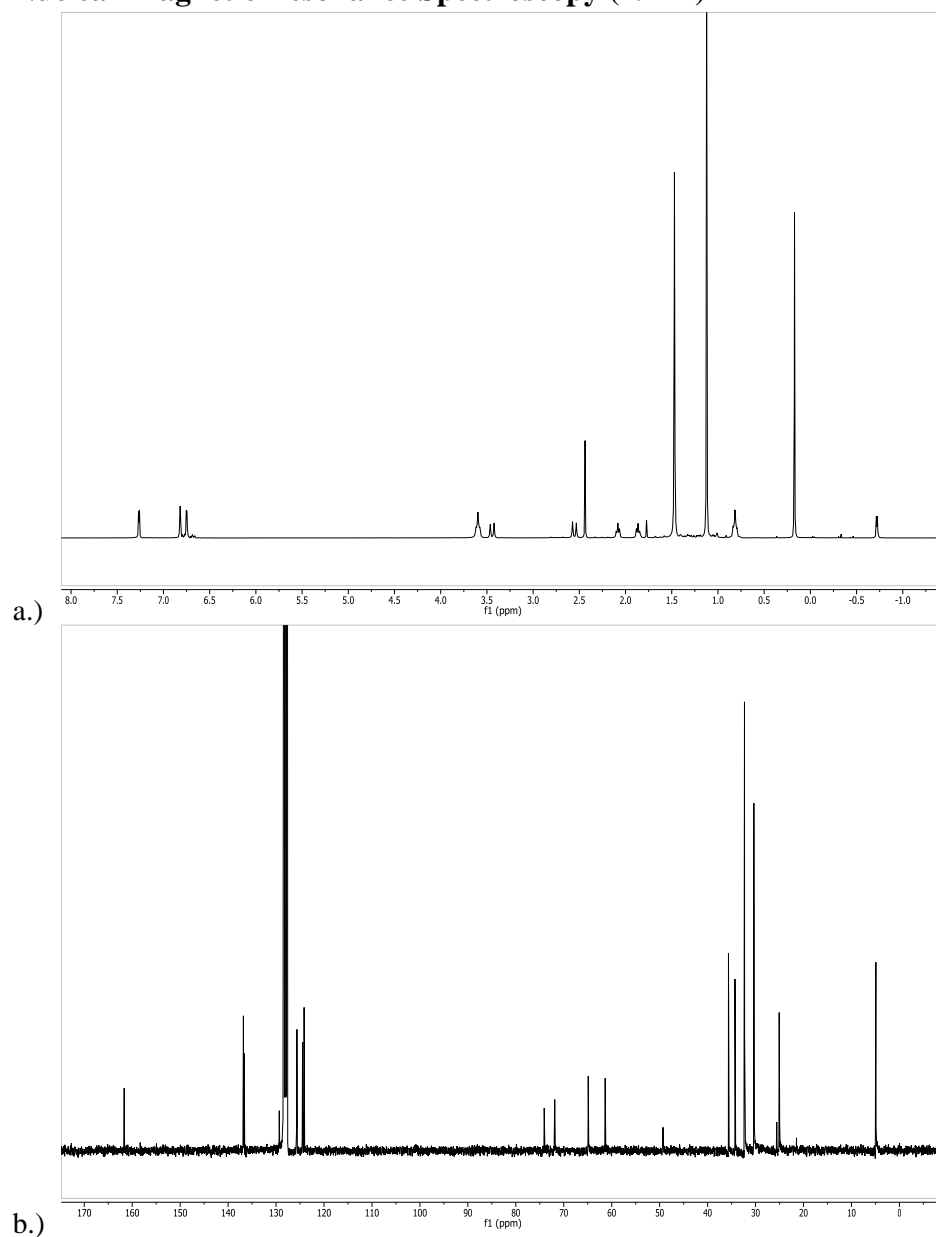


Figure S 2 a.) ^1H NMR spectrum b.) ^{13}C NMR spectrum of catalyst $(\text{ONOO})^t\text{BuY}(\text{CH}_2\text{Si}(\text{CH}_3)_3)(\text{thf})$ in C_6D_6 .

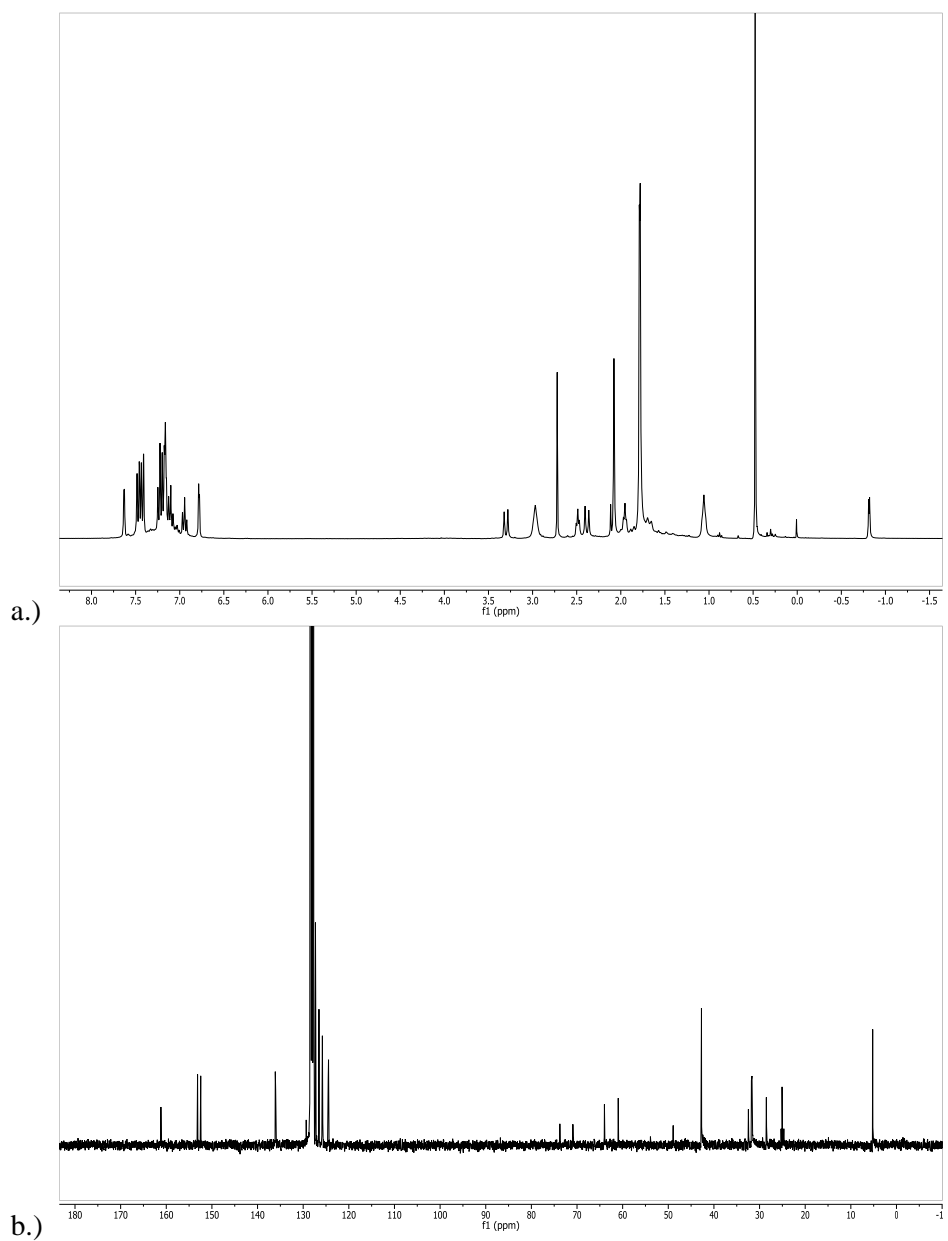


Figure S 3 a.) ^1H NMR spectrum b.) ^{13}C NMR spectrum of catalyst $(\text{ONOO})^{\text{CMe}_2\text{Ph}}\text{Y}(\text{CH}_2\text{Si}(\text{CH}_3)_3)(\text{thf})$ in C_6D_6 .

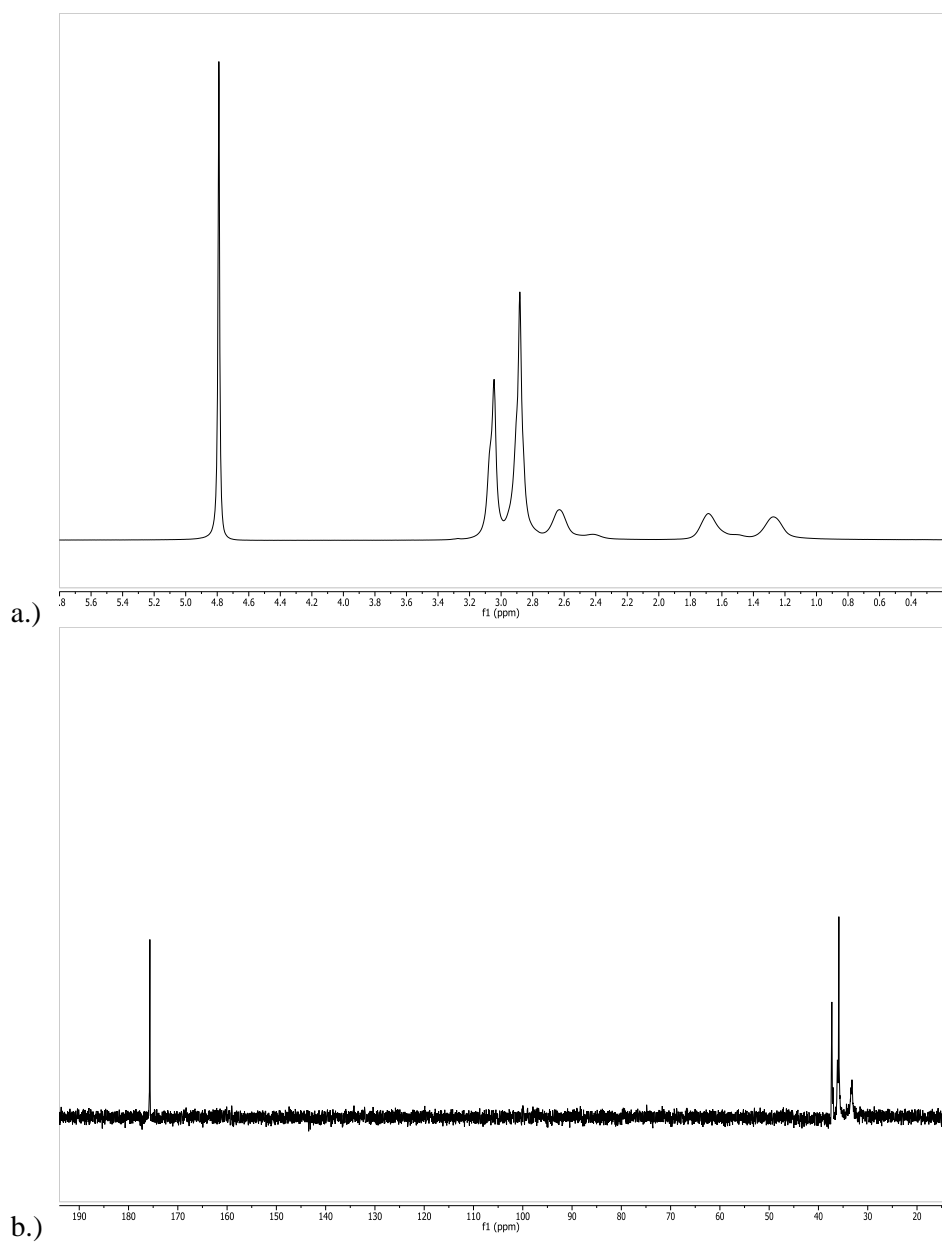


Figure S 4 ^1H a.) and ^{13}C b.) NMR spectra of PDMAA in D_2O .

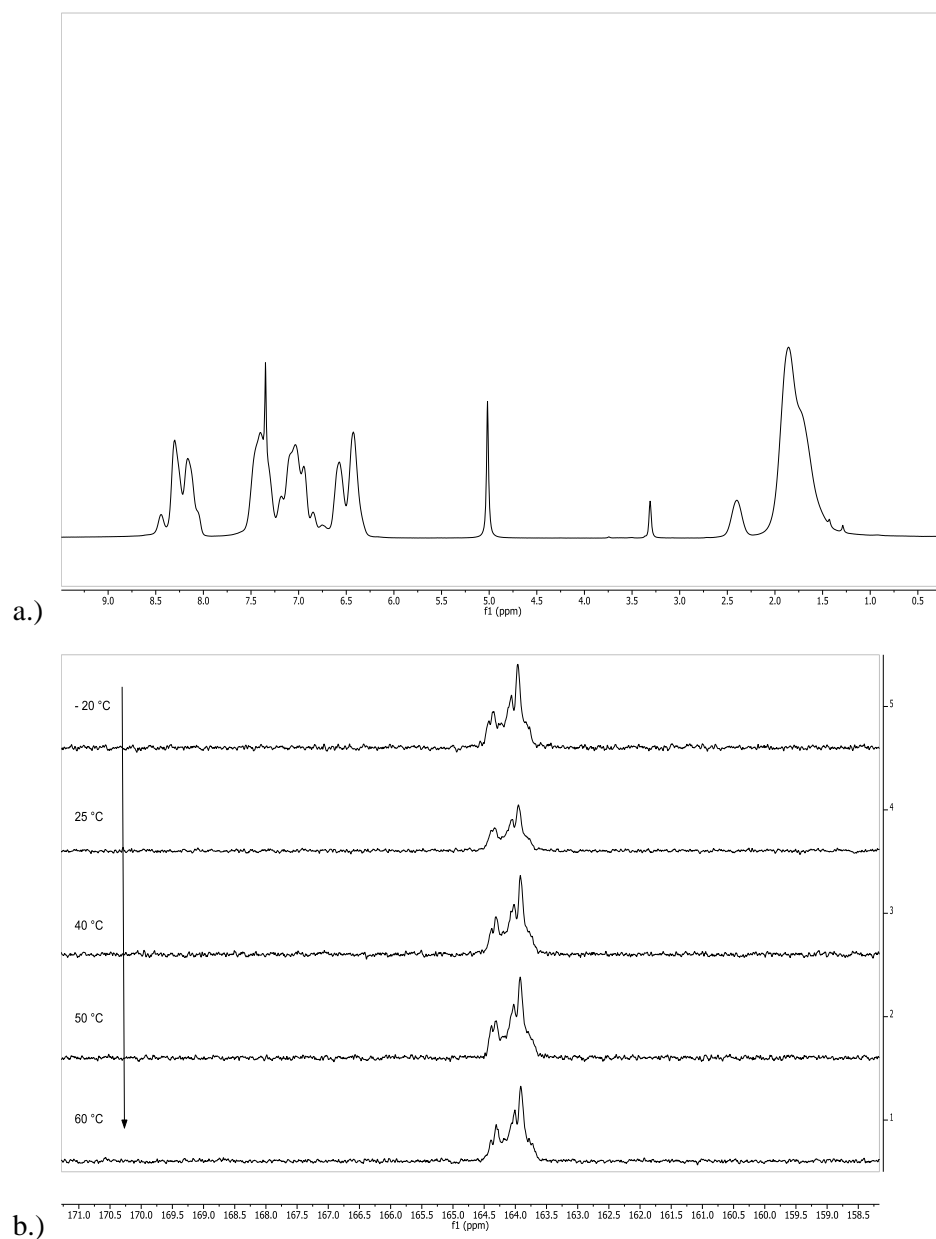


Figure S 5 a.) ^1H NMR P2VP b.) Polymer samples synthesized at different temperatures. Aromatic quaternary ^{13}C NMR resonances of P2VP in CDCl_3 measured at 25 °C.¹

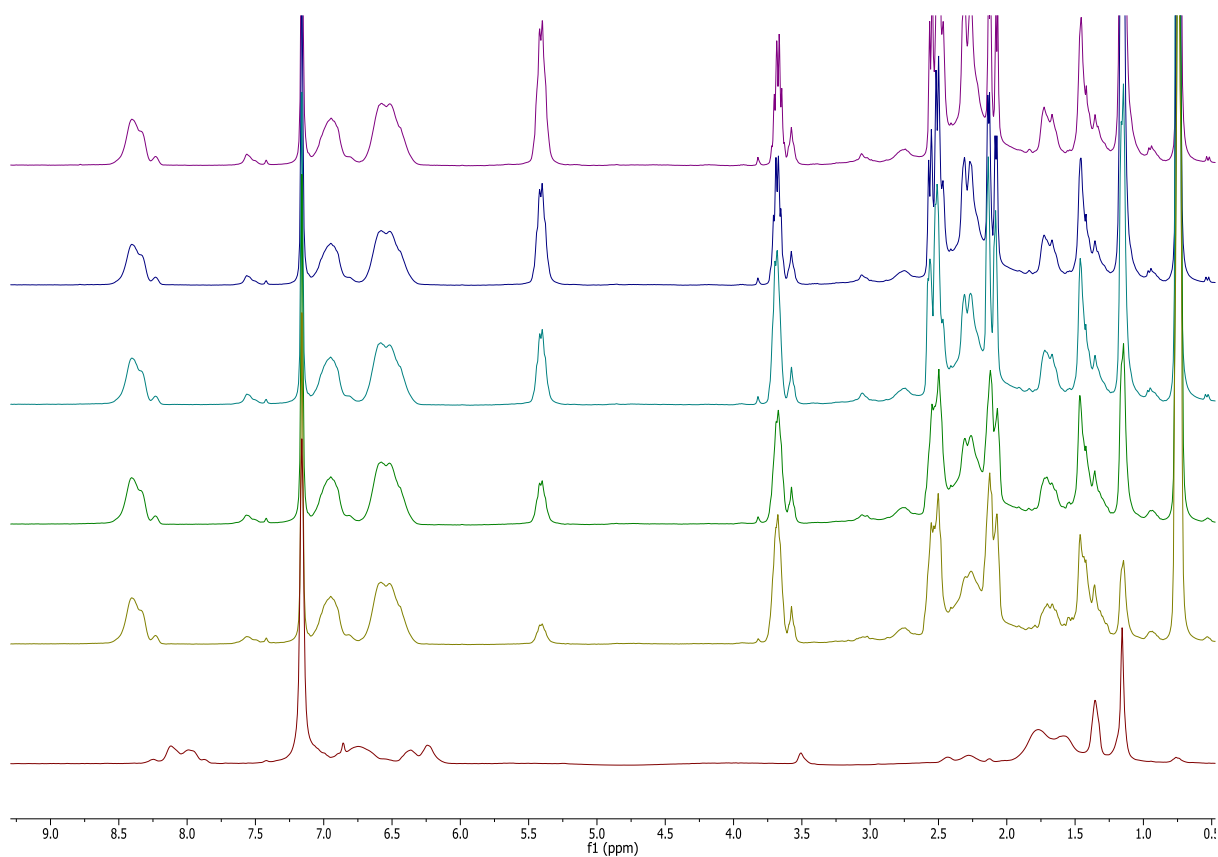


Figure S 6 ^1H NMR experiment with $(\text{ONOO})^{\text{tBu}}\text{Y}(\text{CH}_2\text{Si}(\text{CH}_3)_3)(\text{thf})$ (catalyst 13 μmol , 2VP 0.14 mmol, BL 0.14 mmol, C_6D_6 0.5 mL, $T = 25^\circ\text{C}$): Polymerization of monomer A (P2VP) and subsequent polymerization of monomer B (BL).

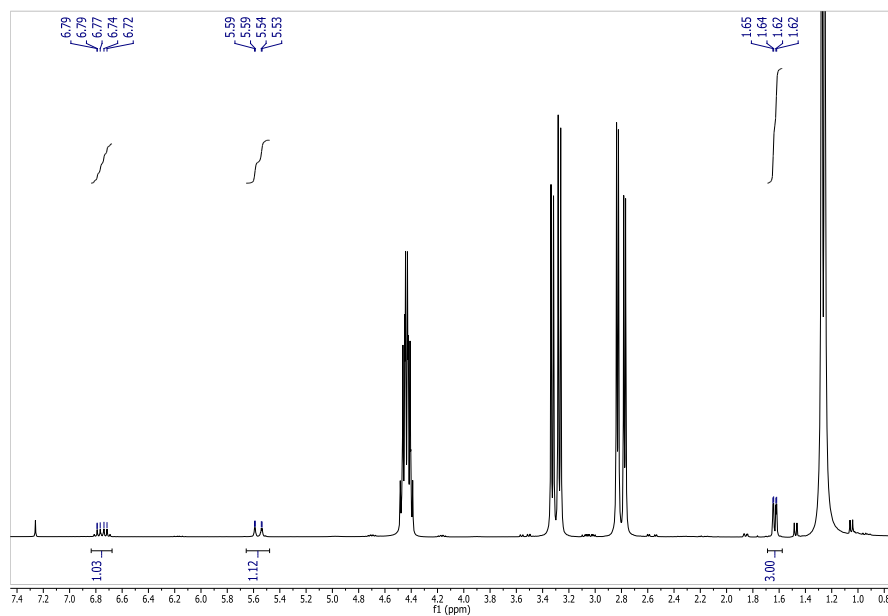


Figure S 7 ^1H NMR of BL with traces of crotonic acid in CDCl_3 .

2.2 Kinetic Data

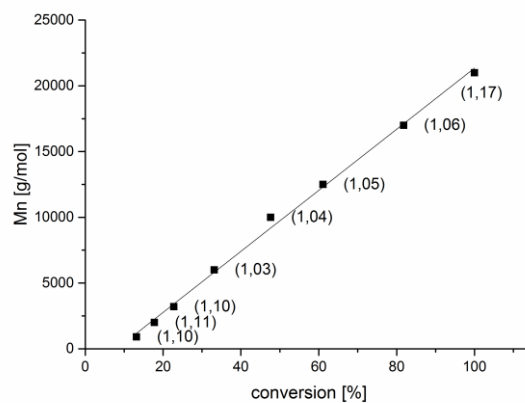


Figure S 8 Growth of the absolute molecular weight (M_n) determined by GPC-MALS as a function of monomer conversion (determined gravimetrically), respective PDI values shown in brackets: catalyst 1, 135 μmol , IPOx 27 mmol, toluene 20 mL, 25 $^{\circ}\text{C}$.

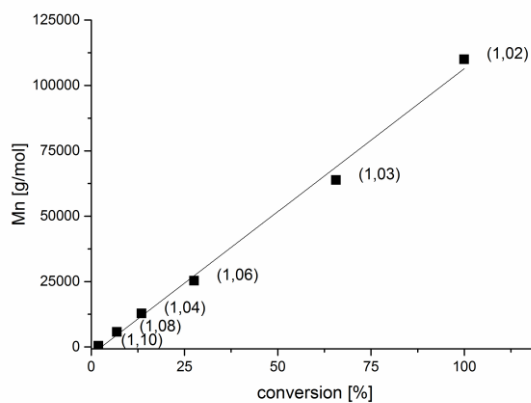


Figure S 9 Growth of the absolute molecular weight (M_n) determined by GPC-MALS as a function of monomer conversion (determined gravimetrically), respective PDI values shown in brackets: catalyst 1, 43 μmol , 2VP 27 mmol, toluene 20 mL, 25 $^{\circ}\text{C}$.

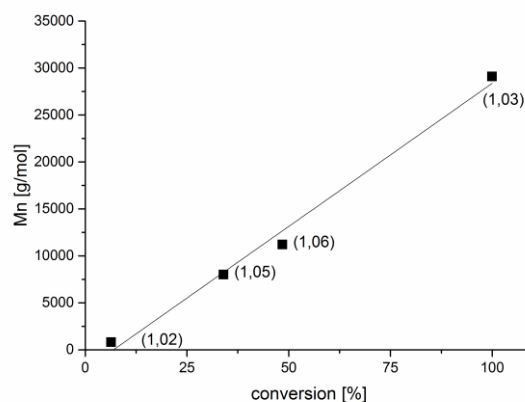


Figure S 10 Growth of the absolute molecular weight (M_n) determined by GPC-MALS as a function of monomer conversion (determined gravimetrically), respective PDI values shown in brackets: catalyst 2, 43 μmol , 2VP 135 mmol, toluene 20 mL, 25 $^{\circ}\text{C}$.

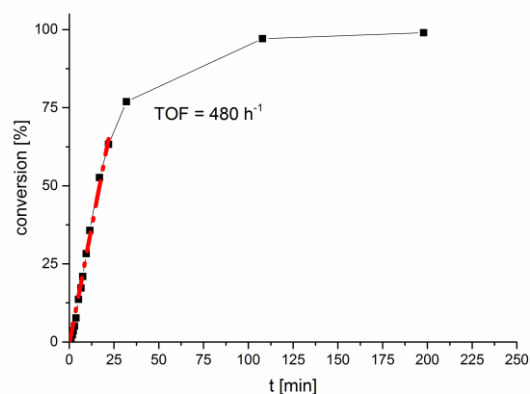


Figure S 11 Determination of catalytic activity of $(\text{ONOO})^{\text{tBu}}\text{Y}(\text{CH}_2\text{Si}(\text{CH}_3)_3)(\text{thf})$ (catalyst 135 μmol , DEVP 27 mmol, toluene 20 mL, $T = 25\text{ }^\circ\text{C}$).

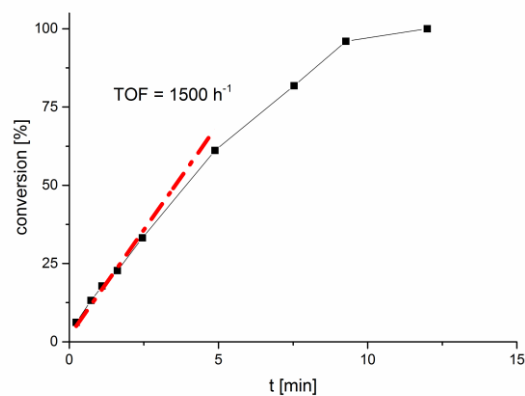


Figure S 12 Determination of catalytic activity of $(\text{ONOO})^{\text{tBu}}\text{Y}(\text{CH}_2\text{Si}(\text{CH}_3)_3)(\text{thf})$ (catalyst 135 μmol , IPOx 27 mmol, toluene 20 mL, $T = 25\text{ }^\circ\text{C}$).

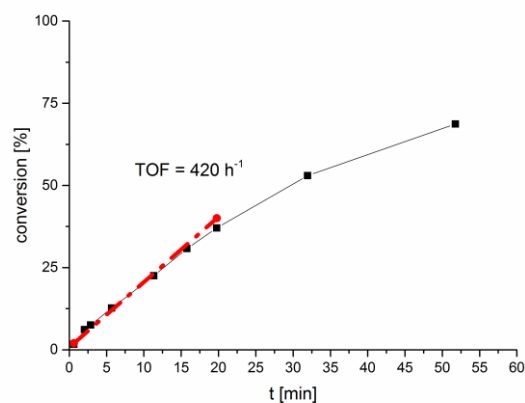


Figure S 13 Determination of catalytic activity of $(\text{ONOO})^{\text{tBu}}\text{Y}(\text{CH}_2\text{Si}(\text{CH}_3)_3)(\text{thf})$ (catalyst 43 μmol , 2VP 27 mmol, toluene 20 mL, $T = 25\text{ }^\circ\text{C}$).

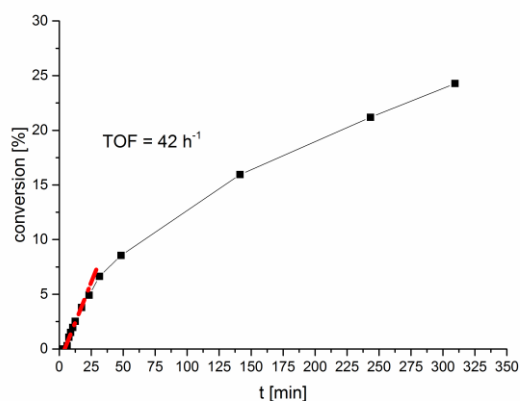


Figure S 14 Determination of catalytic activity of $(\text{ONOO})^{\text{tBu}}\text{Y}(\text{CH}_2\text{Si}(\text{CH}_3)_3)(\text{thf})$ (catalyst 135 μmol , DIVP 27 mmol, toluene 20 mL, $T = 25^\circ\text{C}$).

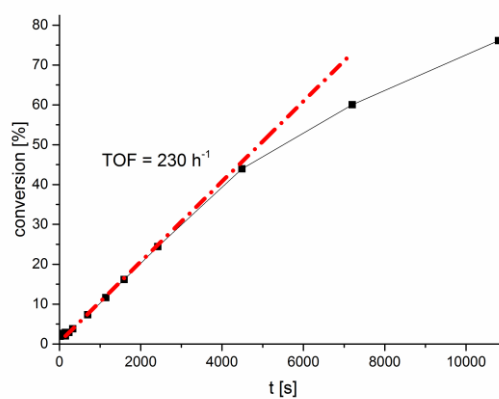


Figure S 15 Determination of catalytic activity of $(\text{ONOO})^{\text{CMe}_2\text{Ph}}\text{Y}(\text{CH}_2\text{Si}(\text{CH}_3)_3)(\text{thf})$ (catalyst 43 μmol , 2VP 27 mmol, toluene 20 mL, $T = 25^\circ\text{C}$).

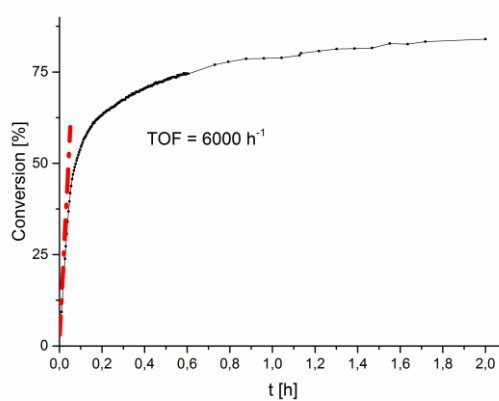


Figure S 16 Determination of catalytic activity of $(\text{ONOO})^{\text{tBu}}\text{Y}(\text{CH}_2\text{Si}(\text{CH}_3)_3)(\text{thf})$ (catalyst 14.3 μmol , BL 9 mmol, dichloromethane 5 mL, $T = 25^\circ\text{C}$).

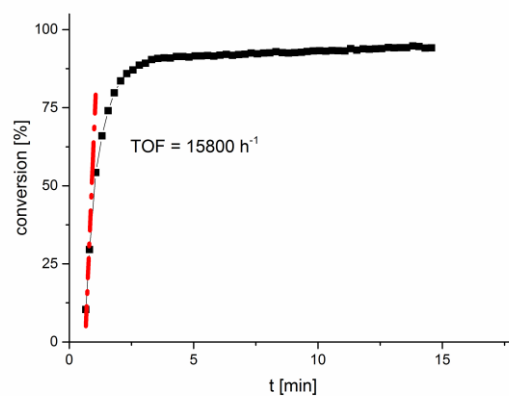


Figure S 17 Determination of catalytic activity of $(\text{ONOO})^{\text{CMe}_2\text{Ph}}\text{Y}(\text{CH}_2\text{Si}(\text{CH}_3)_3)(\text{thf})$ (catalyst $14.3\ \mu\text{mol}$, BL $9\ \text{mmol}$, dichloromethane $5\ \text{mL}$, $T = 25\ ^\circ\text{C}$).

2.3 Endgroup Analysis

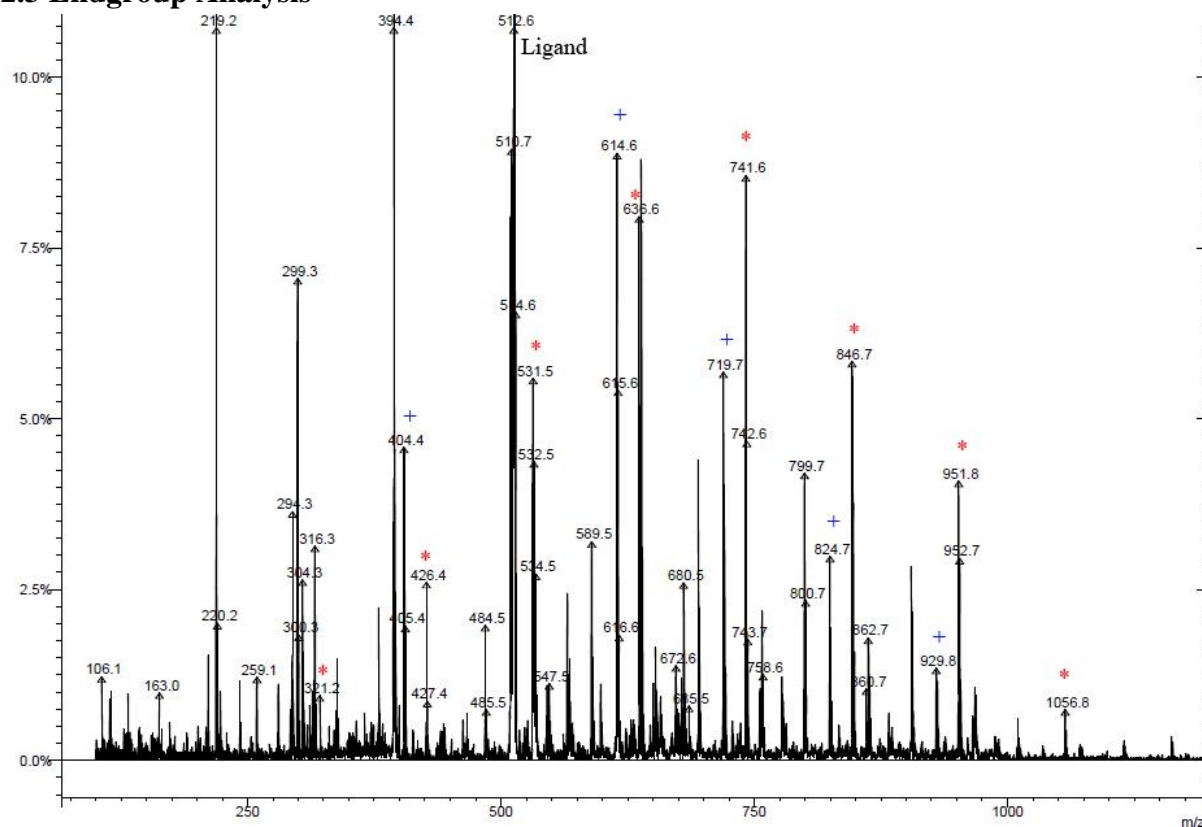


Figure S 18 Endgroup analysis ESI-MS measured in *i*PrOH; Catalyst 1 (40 μ mol of catalyst, 0.4 mmol 2VP, 0.5 mL C_6D_6 , 20 $^{\circ}C$): (*) $[(n \times M) + (CH_2TMS) + (Na)]^+$ (+) $[(n \times M) + (CH_2TMS) + H]^+$.

2.4 LCST (Lower critical solution temperature)

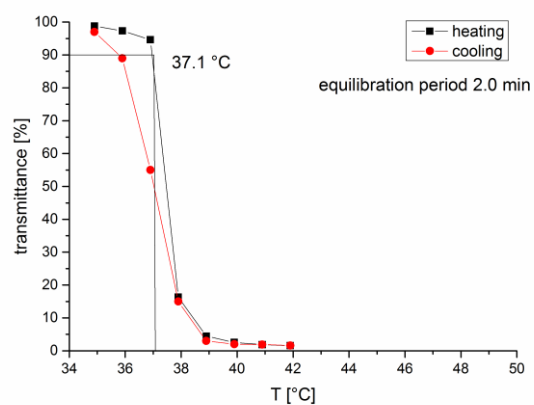


Figure S 19 Determination of the cloud point (lower critical solution temperature, LCST) of P2VP homopolymer. The cloud point was determined at 10% decrease of transmittance for a 5.0 wt % dest. H₂O:THF =1:1, $M_n = 2.2 \times 10^4$ g/mol, PDI = 1.01.

2.5 Eyring-Plot Data

Table S 1 Eyring plot for (ONOO)^{tBu}Y(CH₂Si(CH₃)₃)(thf) initiated 2VP (catalyst 42 µmol, 2VP 8.6 mmol, toluene 5.5 mL, temperature 298 – 331 K).

T [K]	v _{initial} [mol/L]	c(Mon) [mol/L]	n(Mon) [mol]	k (L/mols)	ln(k/T)	1/T
313	0,00215641	1,177845	0,008560015	0,31321527	-6,907067763	0,00319489
298	0,00043782	1,177845	0,008560015	0,06359269	-8,452350272	0,0033557
298	0,00046452	1,177845	0,008560015	0,06747082	-8,393153525	0,0033557
323	0,00557182	1,177845	0,008560015	0,80929836	-5,989239946	0,00309598
308	0,0014717	1,177845	0,008560015	0,21376218	-7,272990962	0,00324675
331	0,00997805	1,177845	0,008560015	1,44929656	-5,431040069	0,00302115

Table S 2 Eyring plot for (ONOO)^{CM₂Ph}Y(CH₂Si(CH₃)₃)(thf) initiated 2VP (catalyst 42 µmol, 2VP 8.6 mmol, toluene 5.5 mL, temperature 303 – 333 K).

T [K]	v _{initial} [mmol/mL]	c(Mon) [mol/L]	n(Mon) [mol]	k (L/mols)	ln(k/T)	1/T
333	0,00774761	1,177845	0,008560015	1,11611147	-5,698291743	0,003003
313	0,00108568	1,177845	0,008560015	0,15640177	-7,601530334	0,00319489
323	0,00198724	1,177845	0,008560015	0,28627943	-7,028439244	0,00309598
303	0,00026055	1,177845	0,008560015	0,03753452	-8,996226965	0,00330033
341	0,01309903	1,177845	0,008560015	1,88703067	-5,196877958	0,00293255

2.6 Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC)

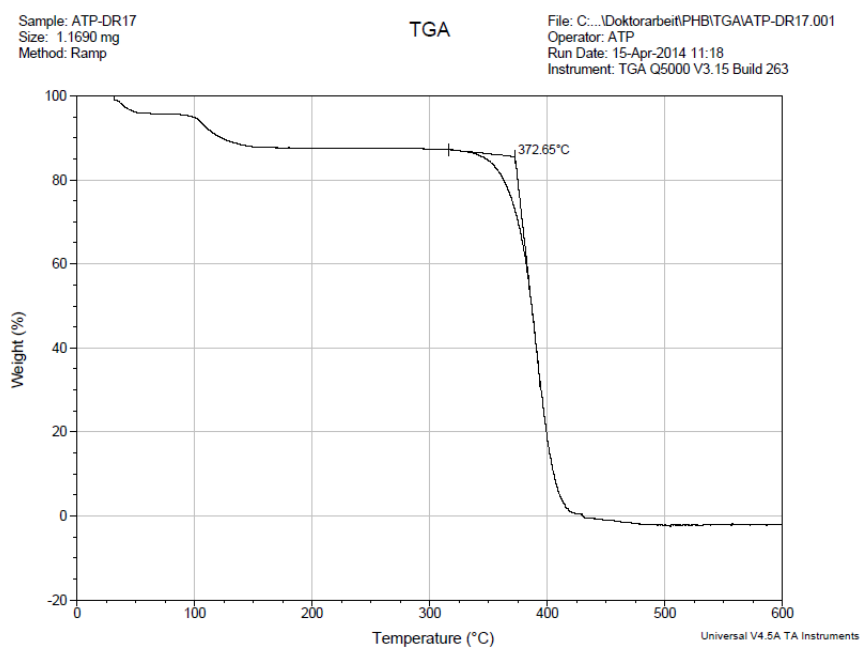


Figure S 20 TGA thermogram for P2VP reported in table 2, entry 2

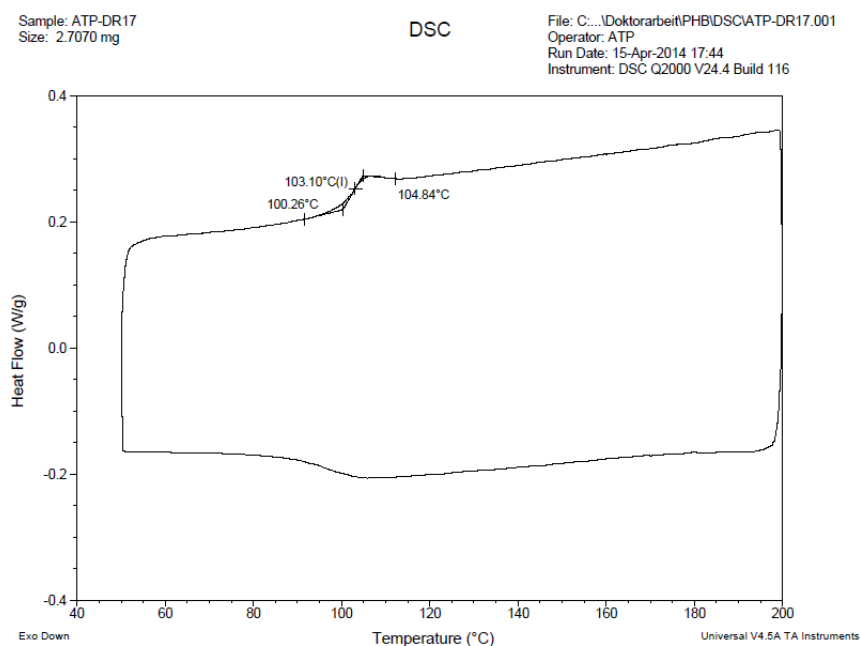


Figure S 21 DSC thermogram for P2VP reported in table 2, entry 2.

2.7 Gel-permeation chromatography (GPC) Data

2.7.1 Homopolymerization

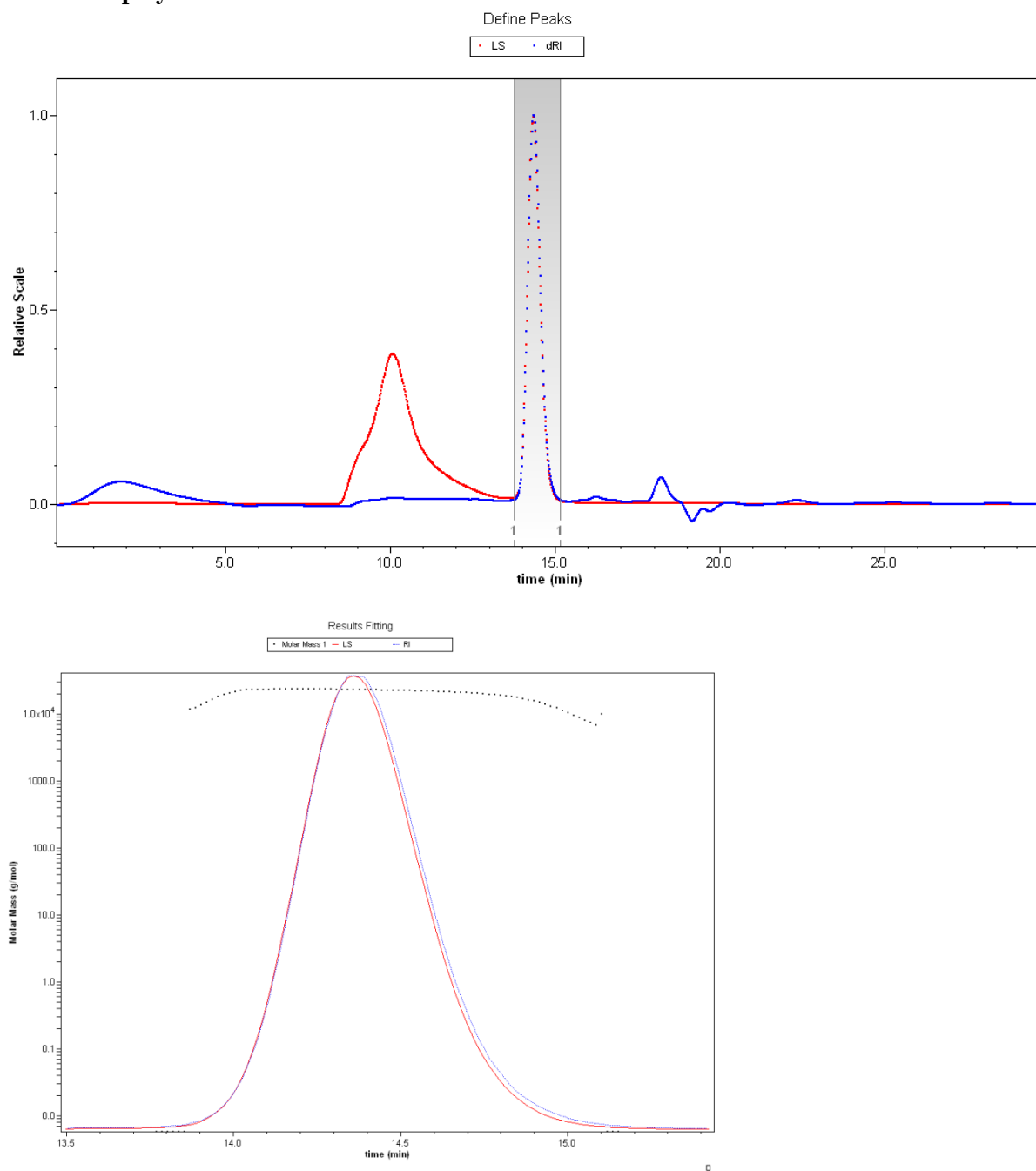


Figure S 22 REM-GTP (2VP), table 1, entry 1, conversion 99%.

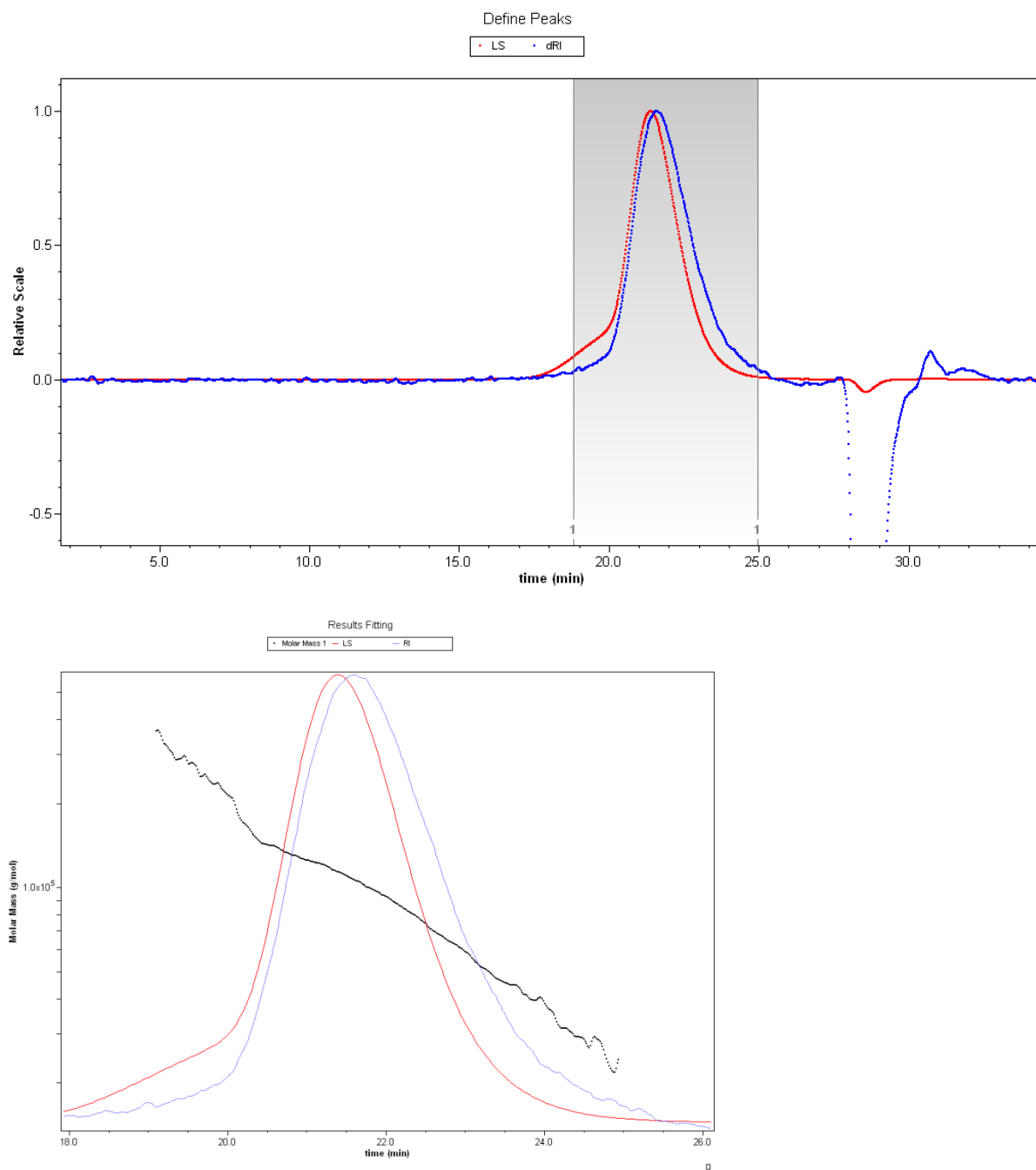


Figure S 23 REM-GTP (DEVP), table 1, entry 2, conversion 99%.

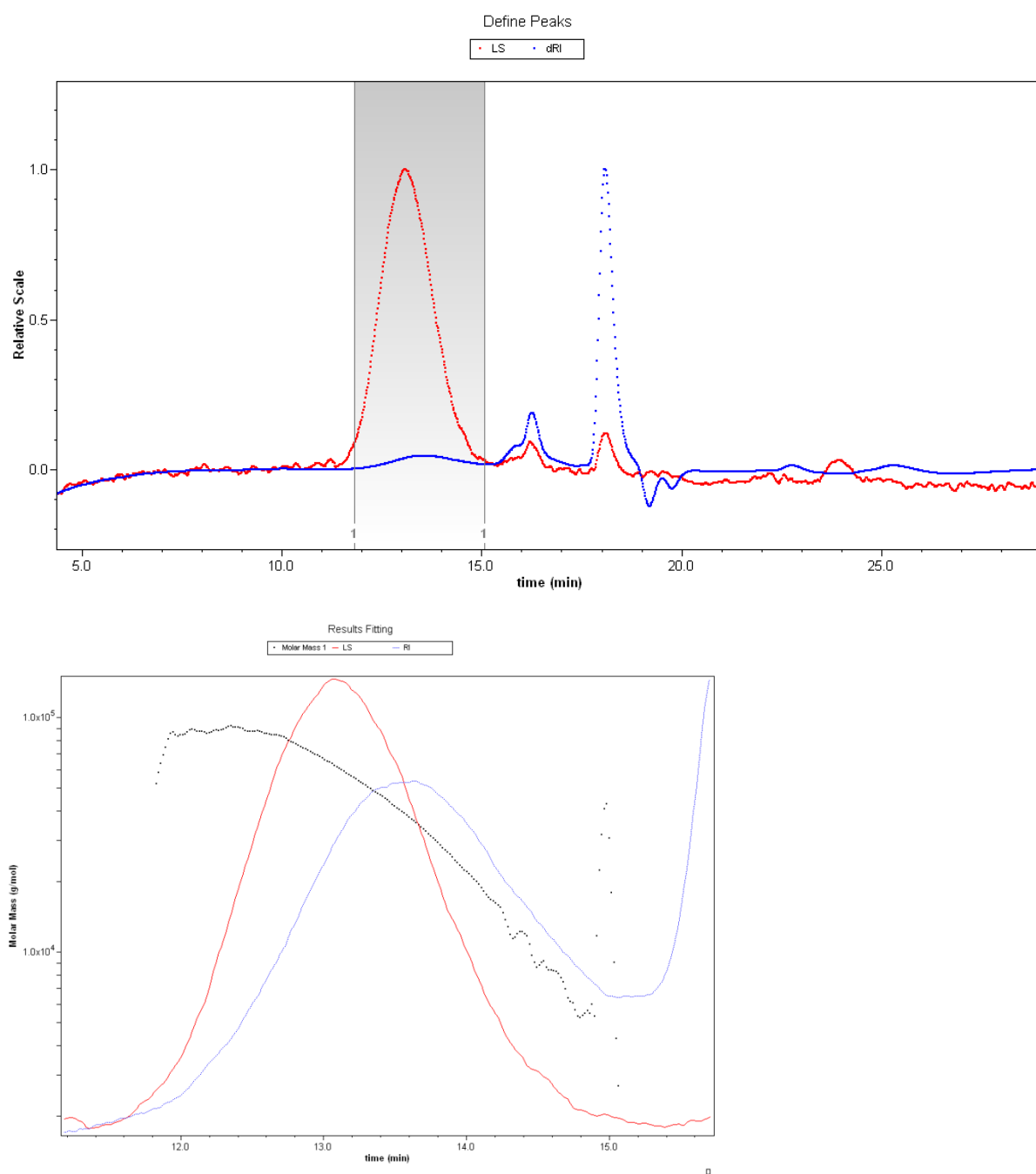


Figure S 24 REM-GTP (DIVP), table 1, entry 3, conversion 25%.

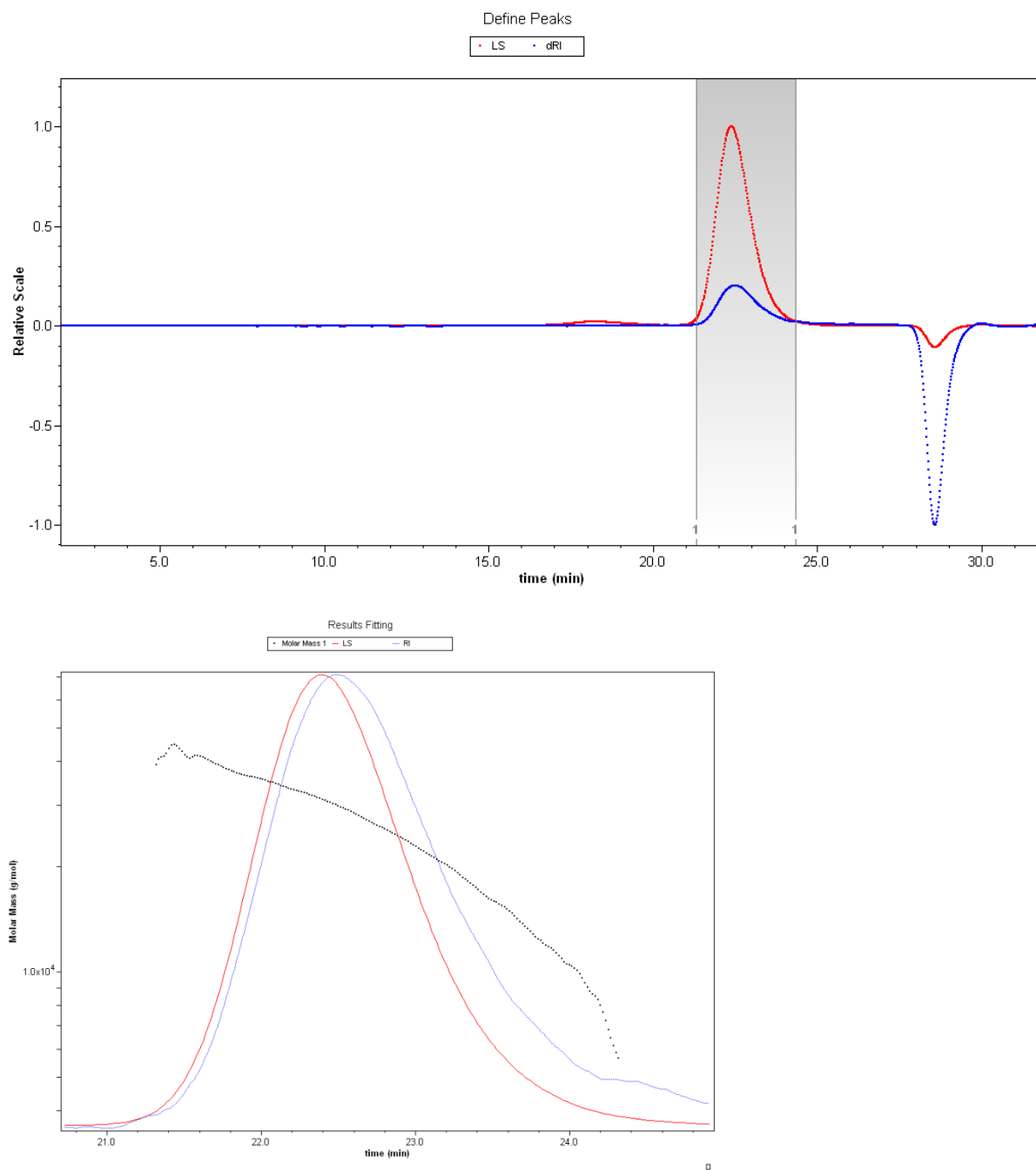


Figure S 25 REM-GTP (IPOx), table 1, entry 4, conversion 99%.

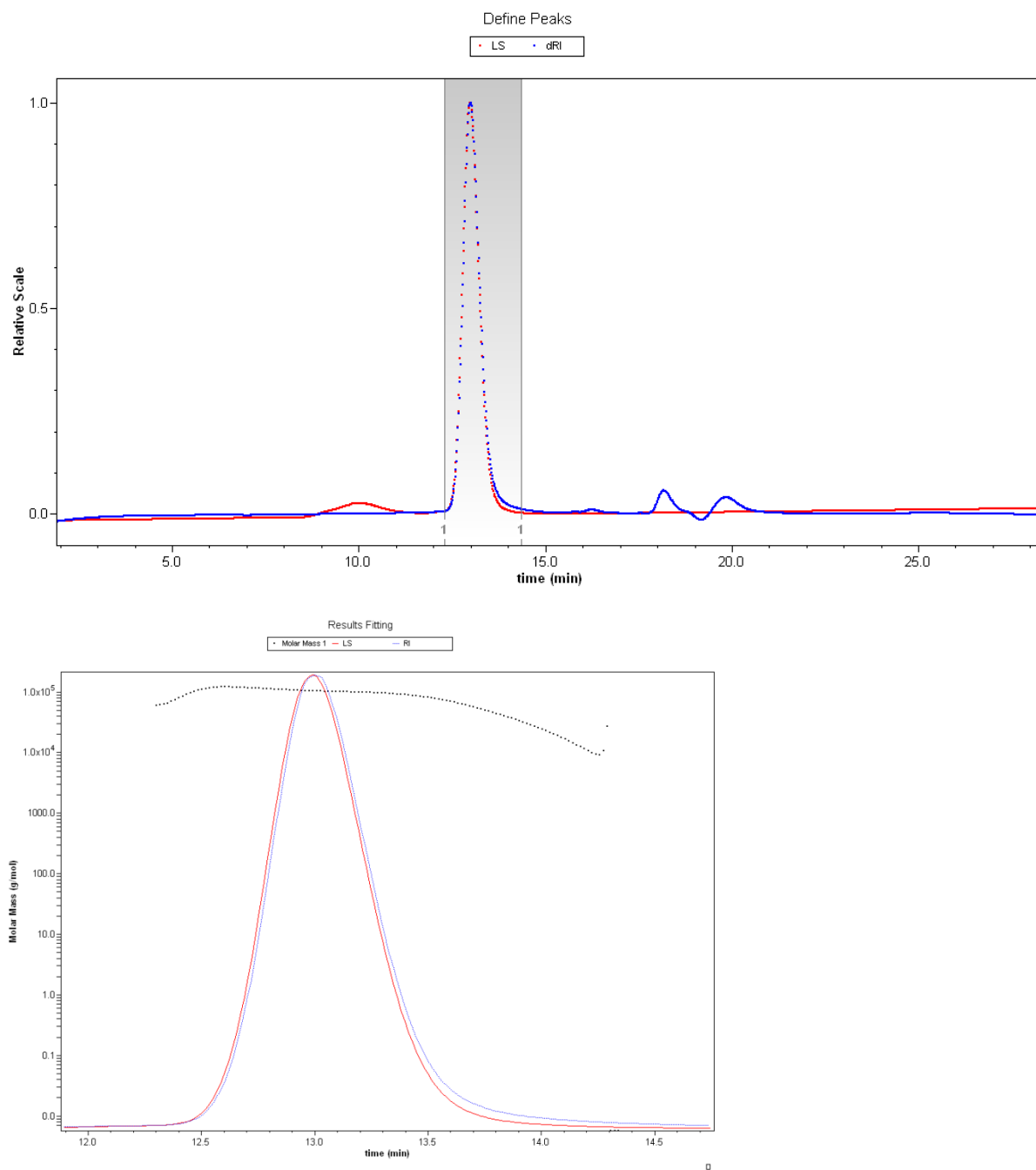


Figure S 26 REM-GTP (2VP), table 1, entry 5, conversion 99%.

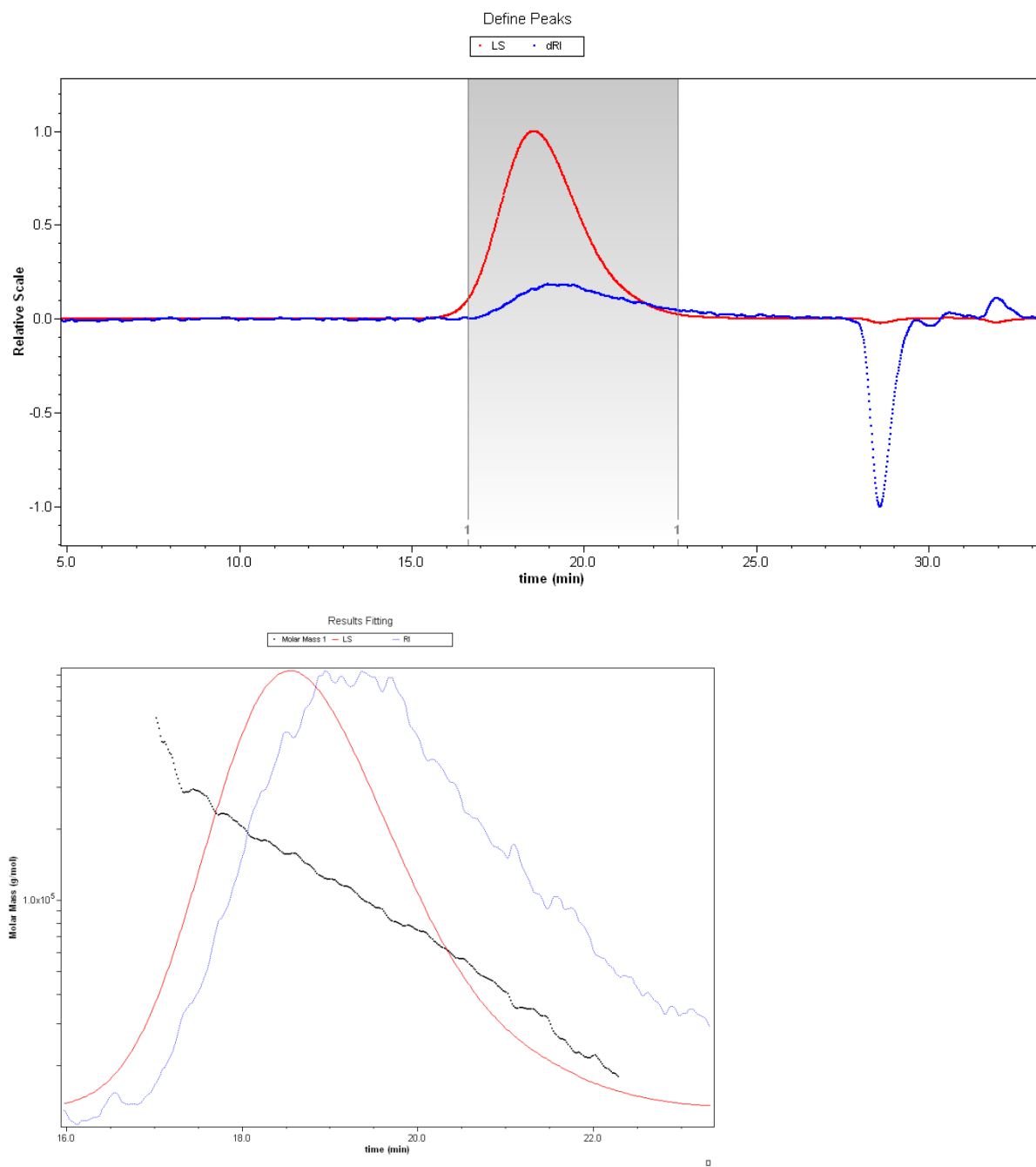
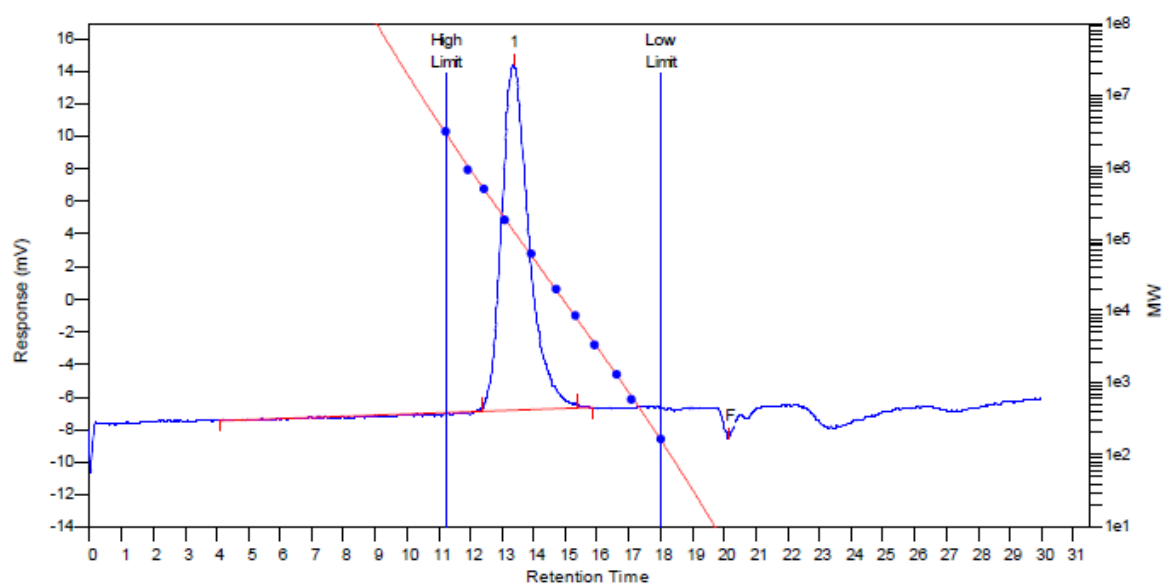


Figure S 27 REM-GTP (DMAA), table 1, entry 6, conversion 99%.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	129276	85510	130306	173311	216079	124085	1.52387
2	0	0	0	0	0	0	0

Figure S 28 ROP (BL), table 1, entry 7, conversion 89%.

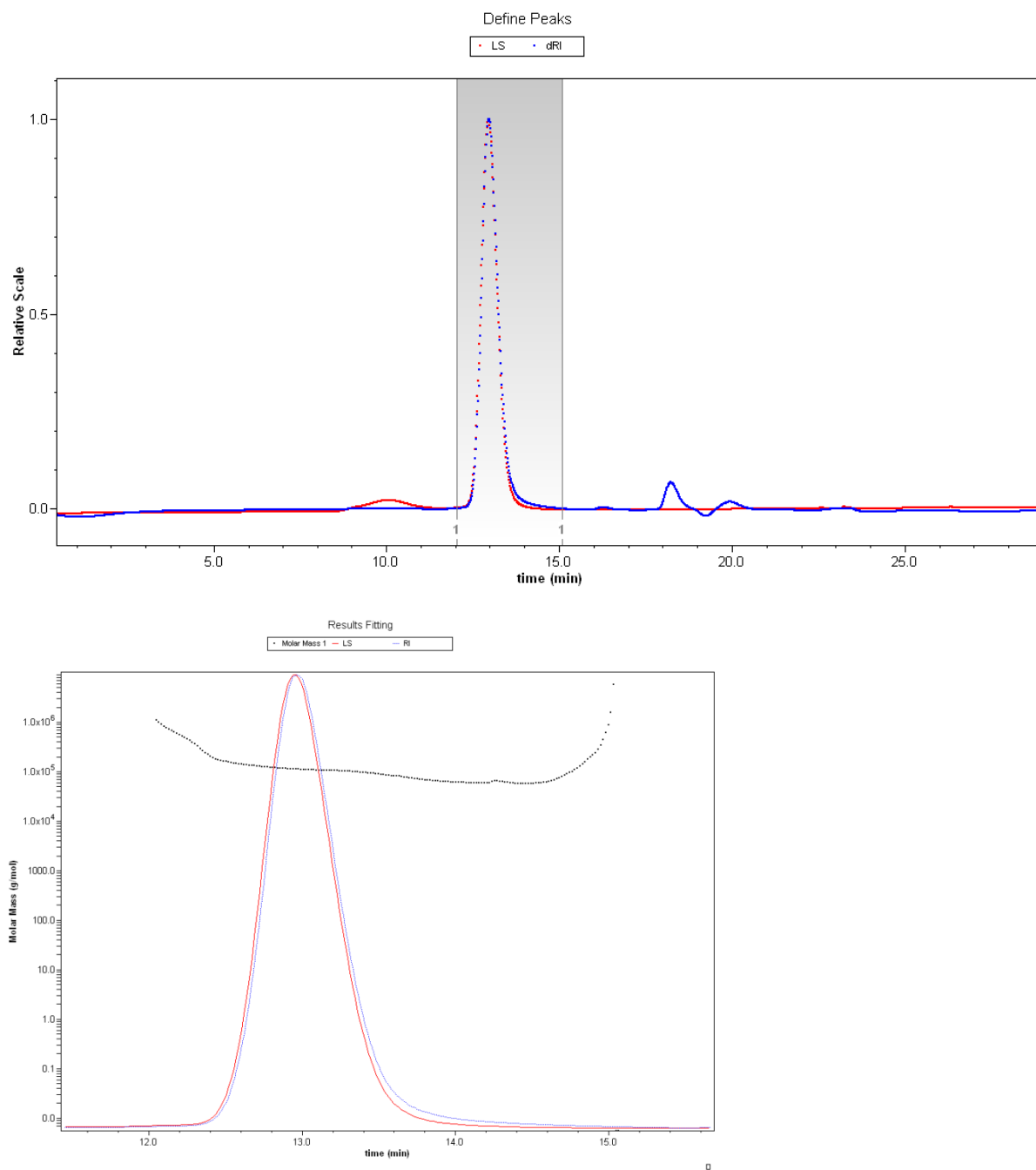


Figure S 29 REM-GTP (2VP), table 2, entry 1, conversion 99%.

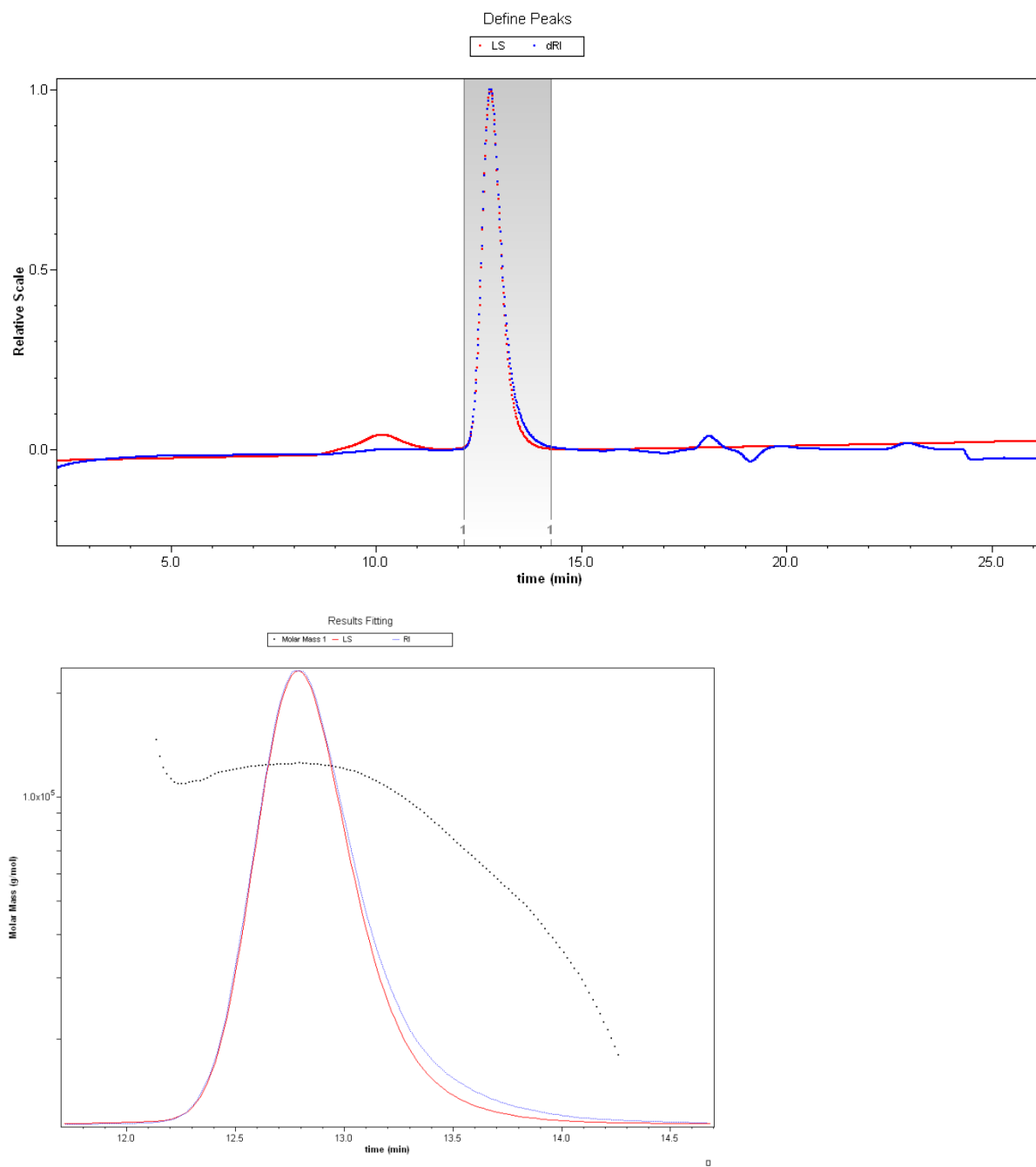
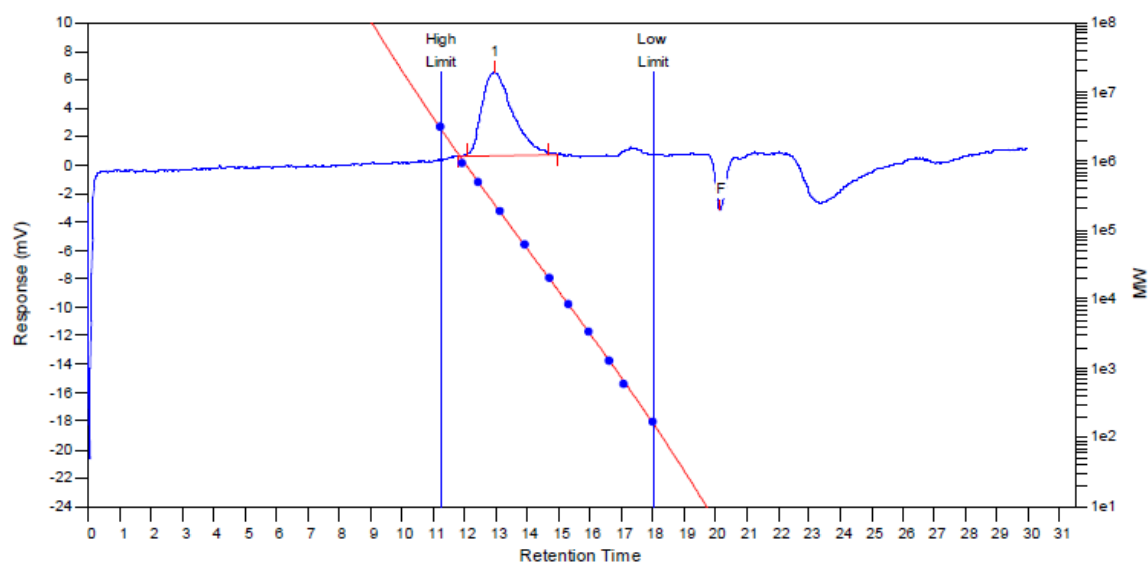


Figure S 30 REM-GTP (2VP), table 2, entry 2, conversion 82%.



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	232020	141585	222664	303406	374741	210730	1.57265
2	0	0	0	0	0	0	0

Figure S 31 ROP (BL), table 2, entry 3, conversion 99%.

2.7.2 Block copolymerization

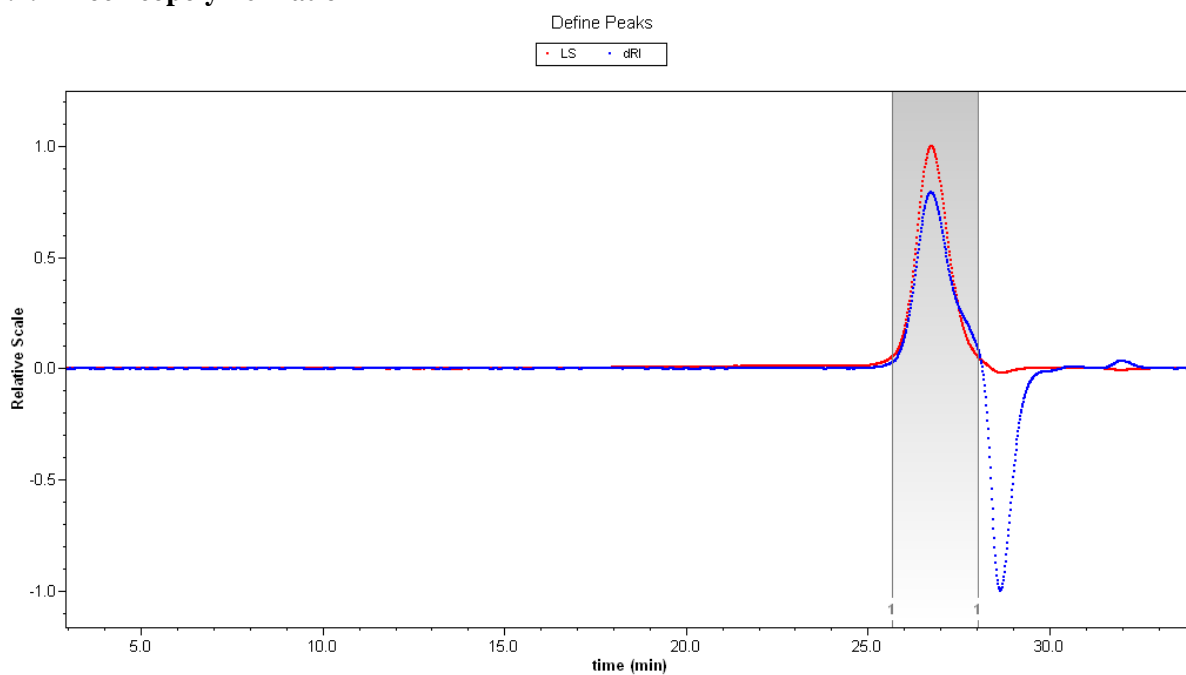


Figure S 32 REM-GTP (P2VP-b-PDEVp), table 4, entry 1.

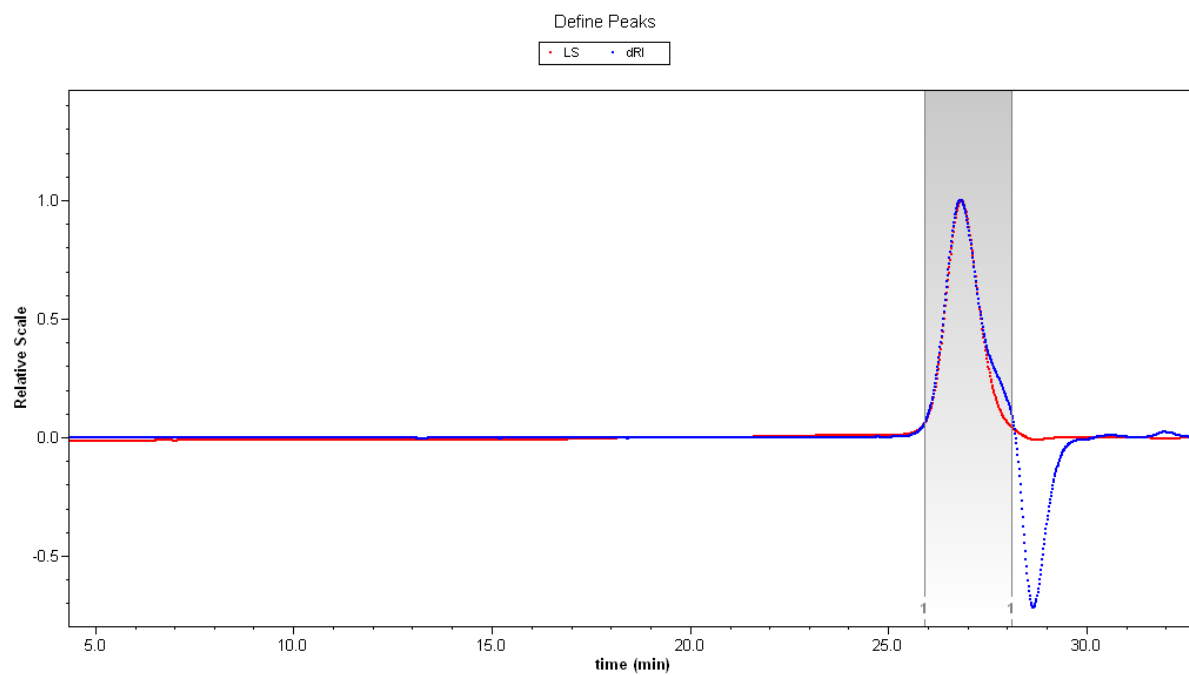


Figure S 33 REM-GTP (P2VP), table 4, entry 2 (aliquot sample).

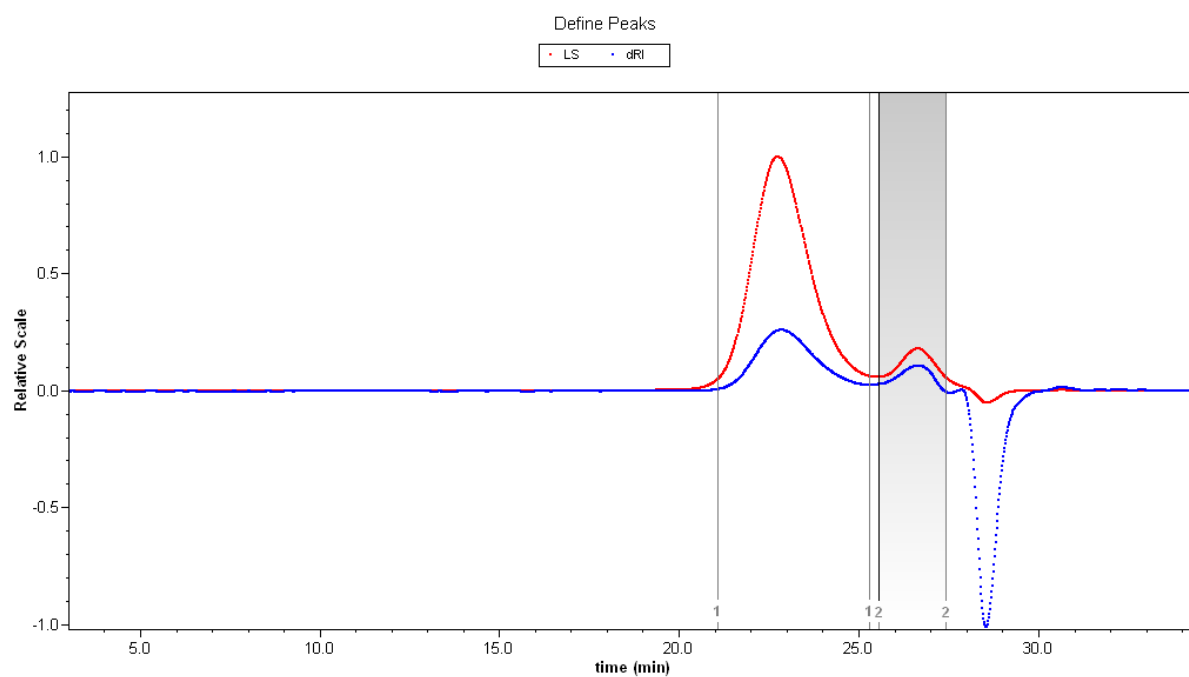


Figure S 34 REM-GTP (P2VP-b-PIPOx), table 4, entry 2.

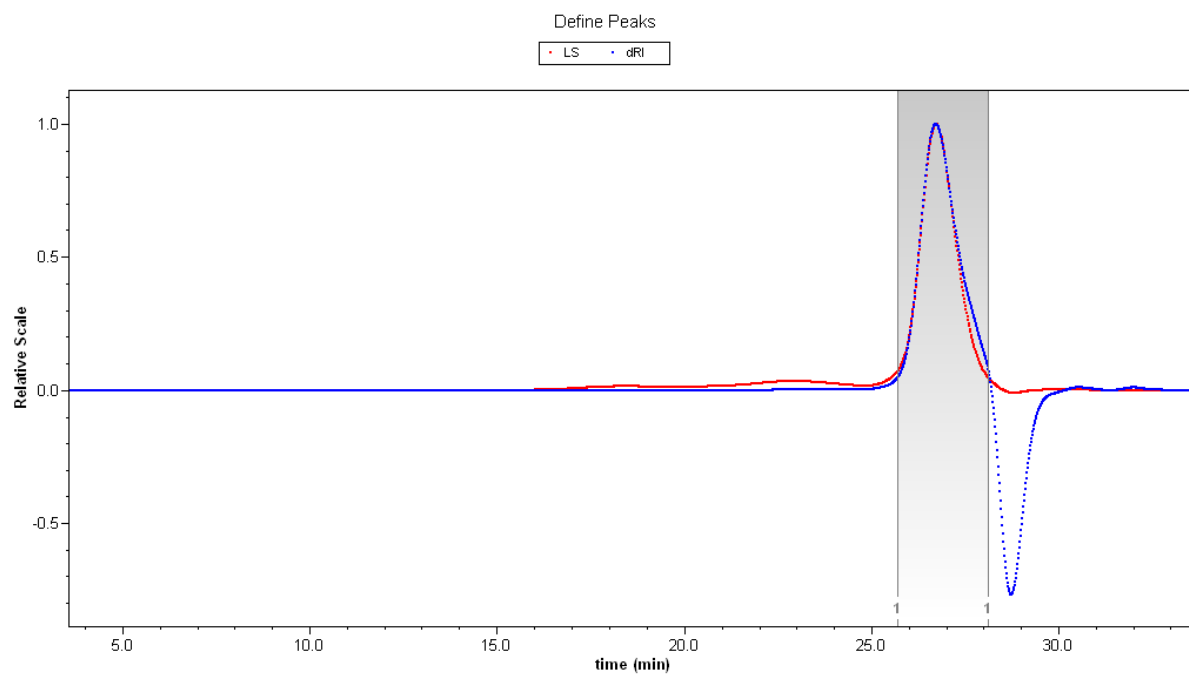


Figure S 35 REM-GTP (P2VP), table 4, entry 3 (aliquot sample).

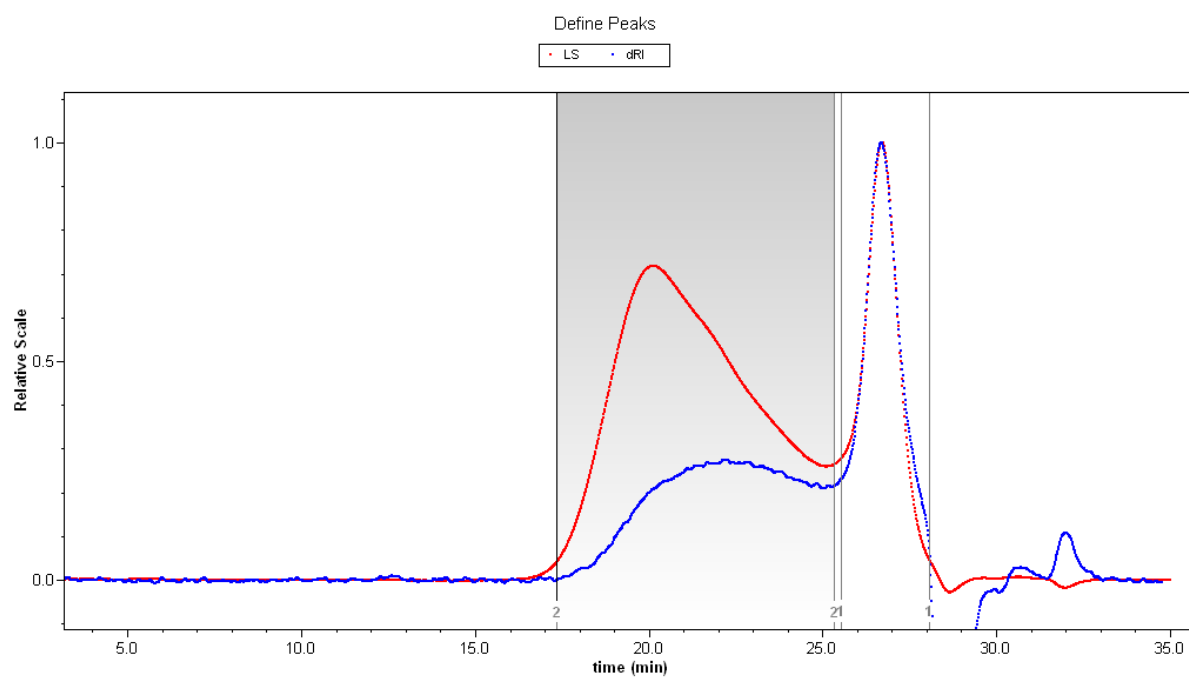


Figure S 36 REM-GTP (P2VP-b-PDMAA), table 4, entry 3.

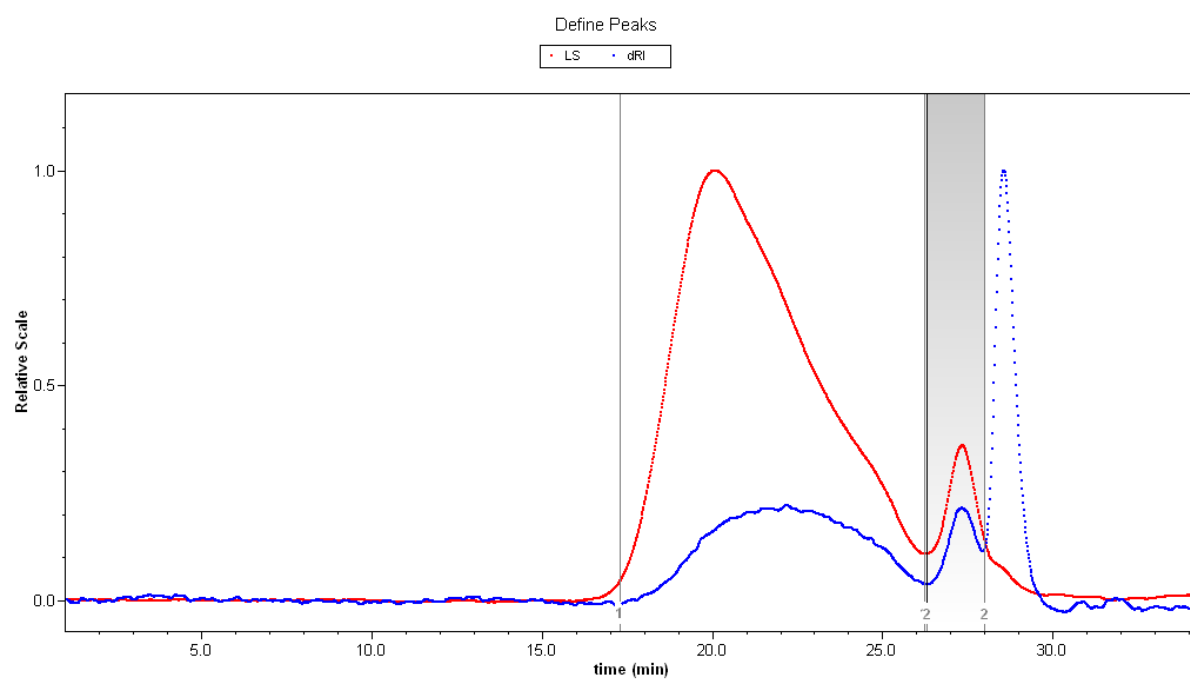


Figure S 37 REM-GTP (P2VP-b-PDMAA), table 4, entry 3: 2 hours washing with toluene.

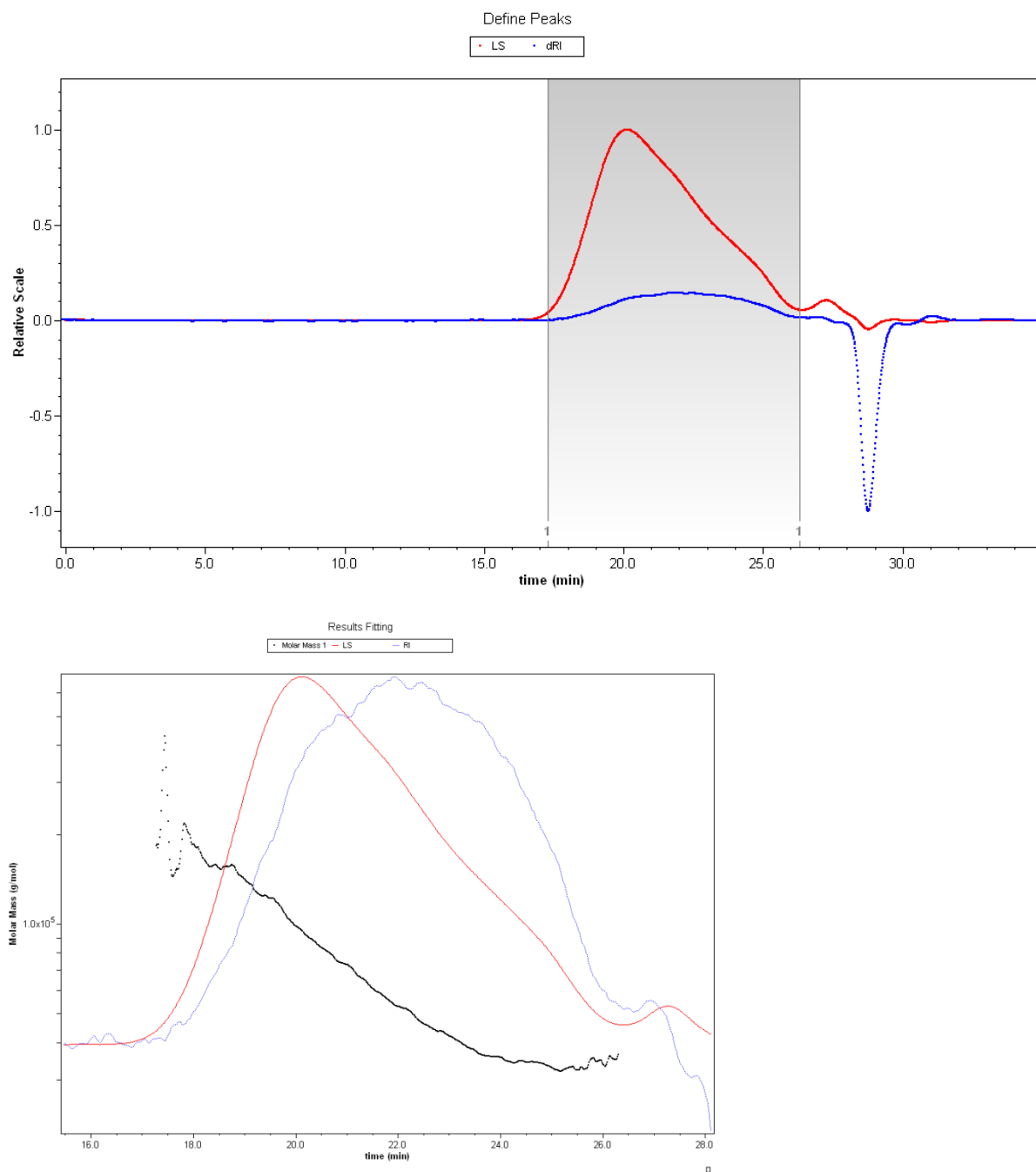


Figure S 38 REM-GTP (P2VP-b-PDMAA), table 4, entry 3: 48 hours washing with toluene.

1. Dimov, D. K.; Hogen-Esch, T. E. *Macromolecules* **1995**, 28, (22), 7394-400.