Electronic Supplementary Information for

Synthesis of High-Molecular-Weight Poly(ε-Caprolactone) Catalyzed by Highly Active Bis(amidinate) Tin(II) Complexes

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Experimental Section

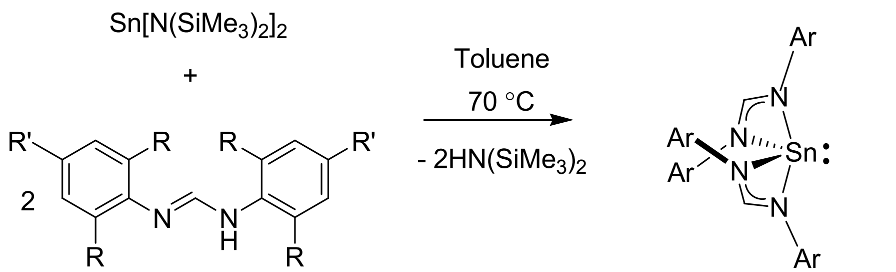
General Details. All operations were carried out under dry argon atmosphere using standard Schlenk techniques. Benzene, n-hexane, and toluene were dried using PURE SOLV MD-5 solvent purification system from Innovative Technology Inc. All amidine ligands, *N,N'*-diphenylformamidine (**1a**), *N,N'-bis*(4-methoxyphenyl)formamidine (**1b**), *N,N'-bis*(4-(trifluoromethyl)phenyl)formamidine (**1c**), *N,N'-bis*(2,6-dimethylphenyl)formamidine (**1d**), and *N,N'-bis*(2,6-diisopropylphenyl) formamidine (**1e**) were synthesized according to literature procedures.[1] $Sn[N(SiMe_3)_2]_2$ was synthesized according to literature procedure.[2] ε-Caprolactone (ε-CL) was purchased from Aldrich, dried over CaH_2 and distilled prior to use.

Measurements. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker DPX-300 or AVANCE 500 spectrometer and referenced to protio impurity of commercial chloroform-*d* ($CDCl_3$, δ 7.26 ppm) or benzene-d_6 (C_6D_6, δ 7.16 ppm) as internal standards. Elemental analyses were performed on a Perkin Elmer 2400 CHN. X-ray crystallography data was collected at 293K on a Bruker SMART CCD area-detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). MALDI-TOF mass spectrometry was carried out using a Bruker Daltonics flexAnalysis mass spectrometer. Spectra were recorded in reflector mode at an acceleration voltage of 19 kV and the delay time was 400 ns. The data was reprocessed using the Bruker XTOF software. Gel permeation chromatography (GPC) analyses were carried out on a Waters e2695 instrument equipped with Model 3580 refractive index detectors (Viscotek) and two 10 μm PL Gel columns. The GPC columns were eluted using tetrahydrofuran with flow rate of 1.0 mL/min at 35 °C. Molecular weights and molecular weight distributions were calibrated with polystyrene standards ranging from 500 to 10,000,000 amu. Water contact angles were measured using a home-made apparatus equipped with a syringe needle to dispense a water drop onto the surface. The average of at least three separate advancing contact angle measurements was determined. The contact angle of the water drop on the polymer surface was observed by CCD camera connected to a computer.

Synthesis of bis(amidinate)tin(II) complexes. A general synthetic procedure is described in Scheme S1. The following representative procedure is for complex **2a**. Other tin(II) complexes were synthesized similarly.

To a mixture of ligand **1a** (0.66 g, 3.36 mmol) and $Sn[N(SiMe_3)_2]_2$ (0.74 g, 1.68 mmol) was added 20 mL toluene. The reaction was allowed to stir at 70 °C overnight. After solvent removal, the product was obtained as a pale yellow microcrystalline (0.86 g, 1.68 mmol, >99%).

Scheme S1. Synthetic procedure for bis(amidinate) tin(II) complexes **2a–e**.



1a; R = H, R' = H
1b; R = H, R' = OCH_3
1c; R = H, R' = CF_3
1d; R = CH_3, R' = H
1e; R = ^{i}Pr, R' = H

2a; R = H, R' = H
2b; R = H, R' = OCH_3
2c; R = H, R' = CF_3
2d; R = CH_3, R' = H
2e; R = ^{i}Pr, R' = H

$[(C_6H_5)N)_2CH]_2Sn$ (2a) A pale yellow microcrystalline (>99%). ^1H NMR (300 MHz, C_6D_6): δ 8.69 (*s*, 2H, N=C*H*), 7.06 (*t*, $^3J_{HH}$ = 7.8 Hz, 8H, *m*-C_6H_5), 6.88 (*t*, $^3J_{HH}$ = 7.3 Hz, 4H, *p*-C_6H_5), 6.80 (*d*, $^3J_{HH}$ = 7.6 Hz, 8H, *o*-C_6H_5). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ 157.0 ($H\underline{C}(N(C_6H_3))_2$), 146.2 (*ipso-C*), 129.2 (*m-C*), 123.1 (*p-C*), 120.6 (*o-C*). Anal. Calcd for $C_{26}H_{22}N_4Sn$: C, 61.33; H, 4.35; N, 11.00. Found: C, 61.50; H, 4.63; N, 10.99.

[(((4-CH_3O)C_6H_4)N)$_2$CH]$_2$Sn (2b) A dark-green microcrystalline (81%). ^{1}H NMR (300 MHz, C_6D_6): δ 8.77 (*s*, 2H, N=C*H*), 6.83 (*d*, $^3J_{HH}$ = 8.7 Hz, 8H, C_6H_4), 6.74 (*d*, $^3J_{HH}$ = 8.8 Hz, 8H, C_6H_4), 3.32 (*s*, 12H, OCH_3). ^{13}C{^{1}H} NMR(75 MHz, $CDCl_3$): δ 157.3 (N=*C*H), 156.3 (*C*OCH_3), 140.0 (*ipso-C*), 121.6 (*o-C*), 114.7 (*m-C*), 55.0 (O*C*H_3). Anal. Calcd for $C_{30}H_{30}N_4O_4Sn$: C, 57.26; H, 4.81; N, 8.90. Found: C, 57.20; H, 4.60; N, 8.90.

[((4-$CF_3C_6H_4$)N)$_2$CH]$_2$Sn (2c) A pale yellow microcrystalline (83%). ^{1}H NMR (300 MHz, C_6D_6): δ 8.31 (*s*, 2H, N=C*H*), 7.28 (*d*, $^3J_{HH}$ = 8.4 Hz, 8H, C_6H_4), 6.45 (*d*, $^3J_{HH}$ = 8.0 Hz, 8H, C_6H_4). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 148.2 (N=*C*H), 129.3 (*ipso-C*), 126.6 (*o-C*), 125.7 (*C*CF_3), 123.2 (*C*F_3), 120.2 (*m-C*). Anal. Calcd for $C_{30}H_{18}F_{12}N_4Sn$: C, 46.13; H, 2.32; N, 7.17. Found: C, 46.23; H, 2.45; N, 7.14.

[((2,6-$Me_2C_6H_3$) N)$_2$CH]$_2$Sn (2d) A colorless microcrystalline (99%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (*s*, 2H, N=C*H*), 6.92 (*d*, $^3J_{HH}$ =7.4 Hz, 8H, *m*-C_6H_3), 6.84 (*t*, 4H, *p*-C_6H_3), 2.11 (*s*, 24H, CH_3). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 162.3 (N=*C*H), 144.6 (*ipso-C*), 132.2 (*o-C*), 128.1 (*m-C*), 123.4 (*p-C*), 19.3 (*C*H_3). Anal. Calcd for $C_{34}H_{38}N_4Sn$: C, 66.72; H, 6.16; N, 9.02. Found: C, 66.87; H, 5.94; N, 9.14.

[((2,6-^{i}Pr$_2C_6H_3$)N)$_2$CH]$_2$Sn (2e) A colorless microcrystalline (90%). ^{1}H NMR (300 MHz, C_6D_6,): δ 8.06 (*s*, 2H, N=C*H*), 7.06 (*m*, 12H, C_6H_3), 3.50 (*sep*, $^3J_{HH}$ = 6.7 Hz, 8H, C*H*(CH_3)$_2$), 1.12 (*m*, 48H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 163.0 (N=*C*H), 143.8 (*o-C*), 142.2 (*i-C*), 125.3 (*p-C*), 123.6 (*m-C*), 28.9 (*C*H(CH_3)$_2$), 23.9 (CH(*C*H_3)$_2$). Anal. Calcd for $C_{50}H_{70}N_4Sn$: C, 71.00; H, 8.34; N, 6.62. Found: C, 71.27; H, 8.06; N, 6.54.

Polymerization of ε-caprolactone. The following representative polymerization is for ε-CL:**2e** molar ratio of 500:1. The amount of tin(II) complex can be adjusted accordingly for ε-CL:Sn molar ratios of 10:1, 100:1, 1000:1, 5000:1 and 10000:1.

Polymerization without the addition of benzyl alcohol: Complex **2e** (0.100 g, 0.118 mmol, 1 equiv) and ε-CL (6.743 g, 59.15 mmol, 500 equiv) were added to a Schlenk flask. The flask was then submerged with continuous stirring into a preheated oil bath at 110°C. After 2 min, the flask was taken out of the oil bath and then submerged into a cold water bath. A small amount of sample was taken for NMR analysis. The rest of the polymer was dissolved in CH_2Cl_2 (20 mL) and precipitated with excess methanol. The solid polymer was collected and dried under vacuum.

Polymerization with addition of benzyl alcohol: The polymerization was carried out similarly as described above except that 1 equiv of benzyl alcohol was added to the reaction along with the tin complex and ε-caprolactone.

X-ray crystallography The single crystal X-ray analyses were carried out at the Mahidol crystallographic facility. Diffraction measurements were made on a 4 K Bruker SMART[3] CCD area detector diffractometer using graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å). The crystals were mounted in paratone oil and held in a low-temperature N_2 stream during data collection. Cell constants and an orientation matrix for data collection were obtained from a least-square refinement using the measured positions of reflections in the range $4.14° < 2\theta < 54.9°$ for complex **2e**. The frame data were integrated by the program SAINT[4] and corrected for Lorentz and polarization effects. The structure was solved by the maXus crystallographic software package,[5] using direct methods (SIR97)[6] and refined by full-matrix least-squares method on $(F_{obs})^2$ using the SHELXTL-PC V 6.12 software package.[7] Note that, for complex **2e**, the methine carbons of the isopropyl groups (C7, C23, C32, and C48) are surrounded by methyl carbons with high thermal motion (*i.e.*, large thermal ellipsoids) resulting in lower U_{eq} values as compared to those of the surrounding carbons.

References:

1) E. K. Kelly, D. E. Gary, P. Masood, R. Roland, *J. Am. Chem. Soc.* 2005, **127**, 4142- 4143.

2) C. D. Jr. Schaeffer, L. K. Myers, S. M. Coley, J. C. Otter, C. H. Yoder, *J. Chem. Educ.* 1990, **67**, 347-349.

3) *SMART v.5.6*, Bruker AXS Inc., Madison, WI, USA 2000.

4) *SAINT v.4*, Siemens Analytical X-ray systems, Inc., Madison, WI, USA 1996.

5) S. Mackay, C. J. Gilmore, C. Edwards, N. Stewart and K. Shankland, *maXus Computer Program for the Solution and Refinement of Crystal Structures*, Bruker Nonius, The Netherlands, MacScience, Japan & The University of Glasgow.

6) A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. App. Crystallogr.*, 1999, **32**, 115.

7) G. M. Sheldrick, *SHELXTL v.6.12*, Siemens Analytical X-ray Systems, Inc., Madison, WI, USA 1997.

Table S1. Experimental Details for X-ray Crystallography of complex **2e**.

	2e
empirical formula	$C_{50}H_{70}N_4Sn$
FW	845.83
cryst color, habit	Colorless, cube
cryst system	monoclinic
space group	$P2_1/c$
a (Å)	14.9195(4)
b (Å)	16.3981(5)
c (Å)	21.0942(6)
α(deg)	90
β(deg)	110.127(2)
γ(deg)	90
volume (Å^3)	4845.6(2)
2θ range (deg)	4.14 – 54.9
Z	4
T/K	298
D_{calc} (g/cm^3)	1.159
μ (mm^{-1})	0.562
no. of params refined	10680
refln/param ratio	496
final residuals R; R_{all}[a]	5.54; 8.62
goodness of fit indicator[b]	1.047
max. shift/error in final LS cycle	0

[a] $R = \Sigma| |F_o| - |F_c| | / \Sigma|F_o|$. [b] GOF = $[\Sigma w(|F_o| - |F_c|)^2 / (N_{obs} - N_{param})]^{1/2}$.

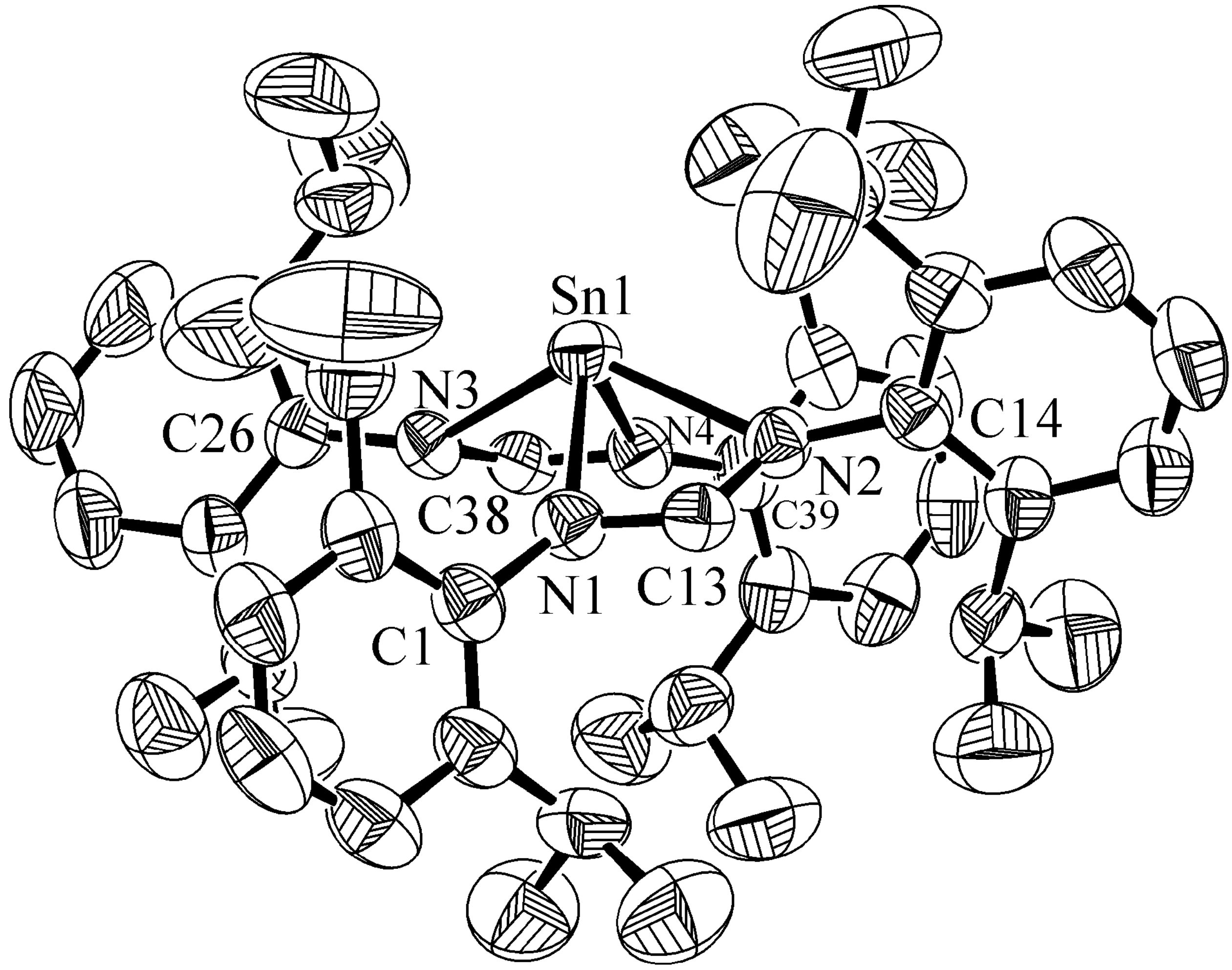


Figure S1. ORTEP drawing of complex **2e** with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

Selected bond lengths (Å) and bond angles (°).

Sn1−N1	2.221(3)	Sn1−N4	2.241(3)	Sn1−N3	2.371(3)
Sn1−N2	2.379(3)	N2−C13	1.301(5)	N1−C13	1.321(5)
N4−C38	1.316(5)	N3−C38	1.304(5)		
N1−Sn1−N4	102.4(1)	N1−Sn1−N3	92.7(1)	N3−Sn1−N4	57.8(1)
N1−Sn1−N2	57.9(1)	N2−Sn1−N4	91.2(1)	N2−Sn1−N3	133.2(1)

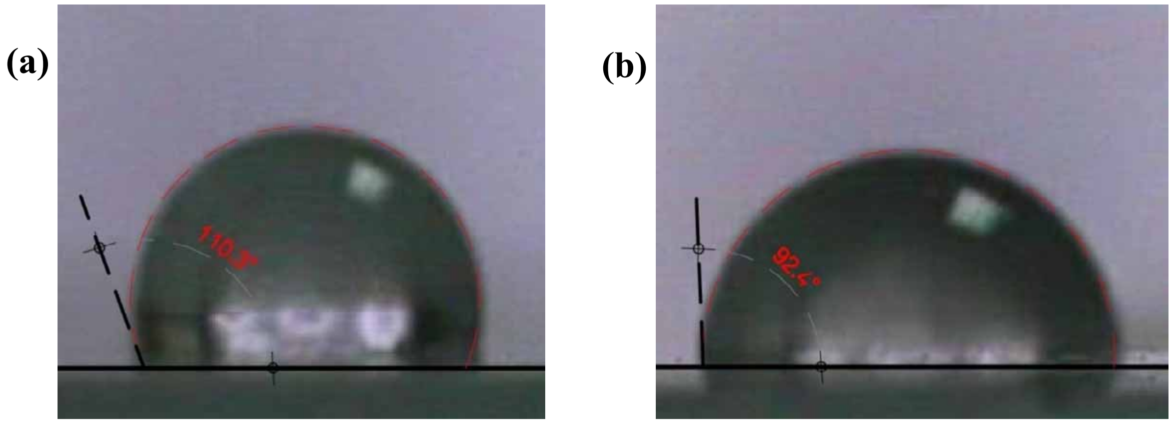


Figure S2. Water contact angle of poly(ε-caprolactone) synthesized from complex **2e** with ε-CL:**2e** molar ratio of 500:1 (a) without the addition of BnOH and (b) with the addition of 1equiv of BnOH.

Table S2. Water contact angles of poly(ε-caprolactone) synthesized from complex **2e** with ε-CL:**2e** molar ratio of 500:1.

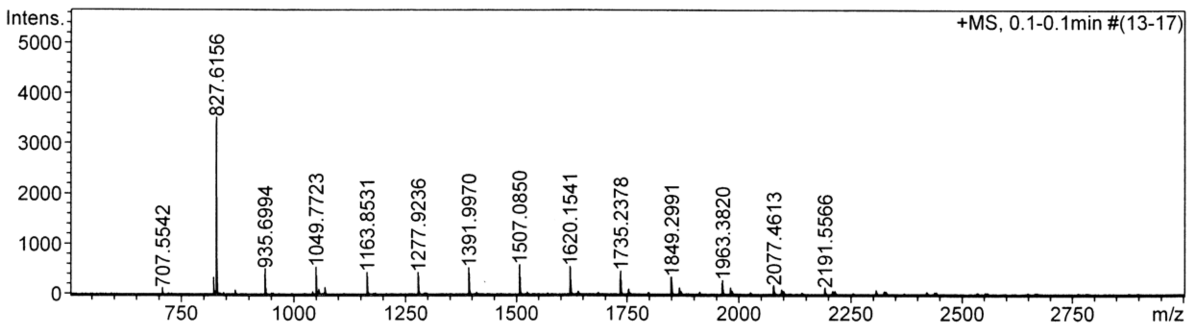
No BnOH

Run	**Degree (°)**
1	104.5
2	105.0
3	107.9
4	110.3
5	109.1
Average	**107.4**
SD	**2.5**

Add 1 equiv of BnOH

Run	**Degree (°)**
1	93.5
2	92.4
3	92.6
Average	**92.8**
SD	**0.6**

Mass spectrum of the polymerization of ε-CL at 110°C for 1 min using ε-CL:**2e** = 10:1. The repeating major mass is assigned to cyclic $[\varepsilon\text{-CL}]_n + Na^+$. The peaks with much lower intensities observed at 1600-2200 Dalton (e.g. 1753.3, 1867.2, 1981.4, 2098.5, 2209.5) are assigned to linear $H[CL]_nOH+Na^+$.

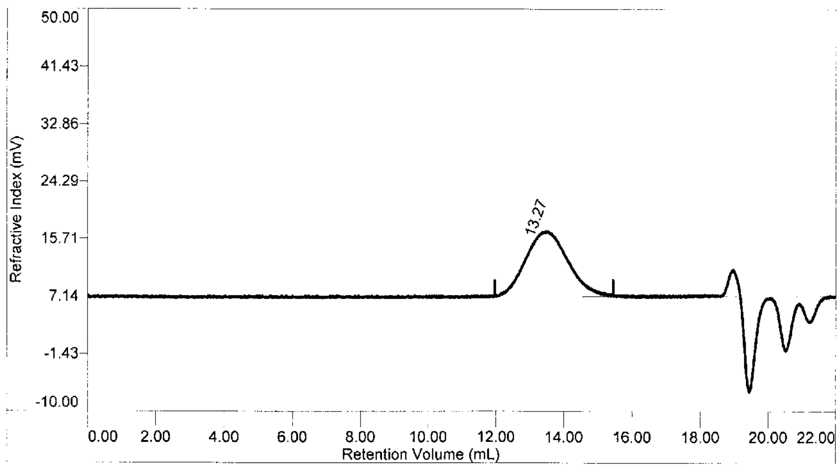


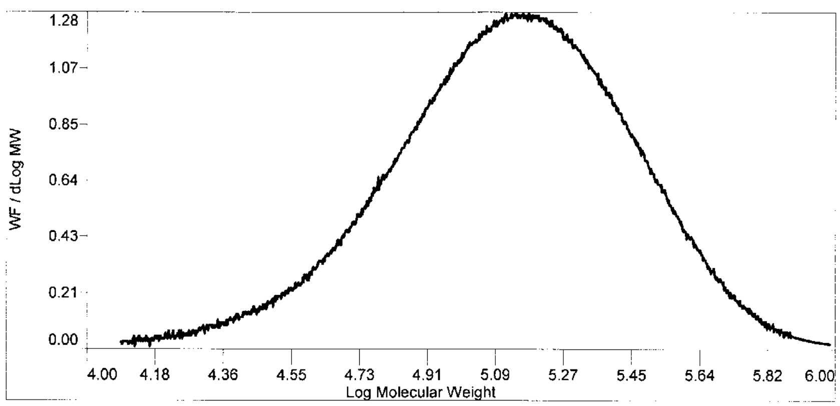
#	m/z	Res.	S/N	I	FWHM
1	821.6324	8184	309.7	337	0.1004
2	827.6156	8295	3210.3	3517	0.0998
3	828.6157	8348	1757.1	1928	0.0993
4	829.6175	7826	631.9	694	0.1060
5	830.6162	8729	194.7	214	0.0952
6	935.6994	8050	404.8	511	0.1162
7	936.7051	8324	240.9	305	0.1125
8	1049.7723	8959	431.8	543	0.1172
9	1050.7762	9209	292.1	367	0.1141
10	1163.8531	7893	375.0	441	0.1475
11	1164.8476	7866	293.5	345	0.1481
12	1277.9236	7643	371.1	437	0.1672
13	1278.9332	8144	301.1	355	0.1570
14	1391.9970	8302	407.7	531	0.1677
15	1393.0029	7422	317.8	415	0.1877
16	1394.0090	8383	177.4	232	0.1663
17	1506.0758	7883	391.8	559	0.1911
18	1507.0850	8309	413.8	591	0.1814
19	1508.0888	9457	233.7	334	0.1595
20	1620.1541	7596	360.7	553	0.2133
21	1621.1597	7725	339.1	521	0.2099
22	1622.1547	7828	187.9	289	0.2072
23	1734.2371	7872	255.6	420	0.2203
24	1735.2378	7809	283.3	465	0.2222
25	1736.2283	7713	161.9	266	0.2251
26	1848.3129	8333	209.6	347	0.2218
27	1849.2991	7246	209.9	348	0.2552
28	1850.3221	9592	161.1	267	0.1929
29	1962.3830	7437	139.4	229	0.2639
30	1963.3820	8397	169.2	278	0.2338

Sample Information

ID	Am-H+BnOH 1_500
Method	Conventional
Acq.	Sep 08, 2009 - 22:12:44
Solvent	THF

Flow	1.0000
Inj Vol	100.0
Col	35.00
Det	35.00





Sample	Mn	Mw	Mp	Mz	Mw/Mn
08-09-2009_22;12;44_Am-H+BnOl	101,593	172,932	189,090	265,905	1.702

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Table 1, Entry 1.

Sample Information

ID	Am-OMe+BnOH 1_500	Flow	1.0000
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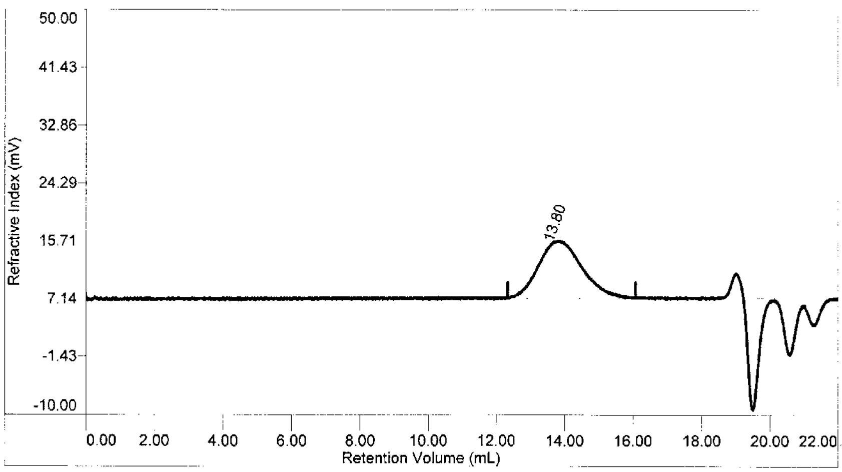
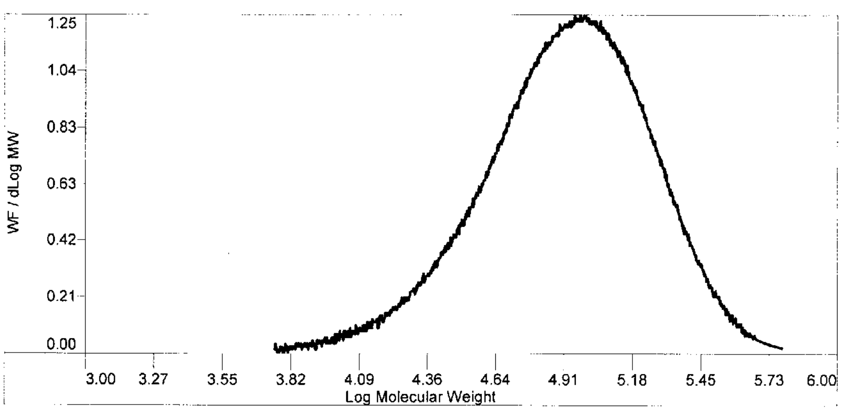
Solvent	THF	Det	35.00





Sample	Mn	Mw	Mp	Mz	Mw/Mn
08-09-2009_23;08;17_Am-OMe+B	60,224	107,708	97,616	167,510	1.788

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Table 1, Entry 2.

Sample Information

ID	Am-CF3+BnOH 1_500	**Flow**	1.0000
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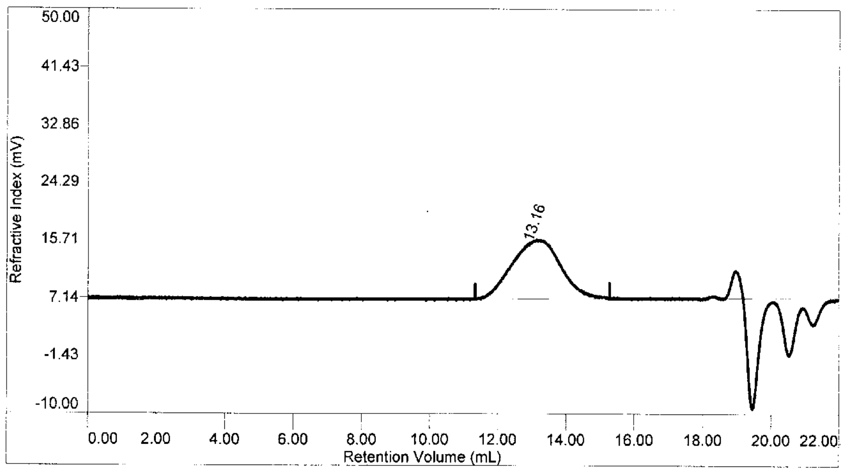
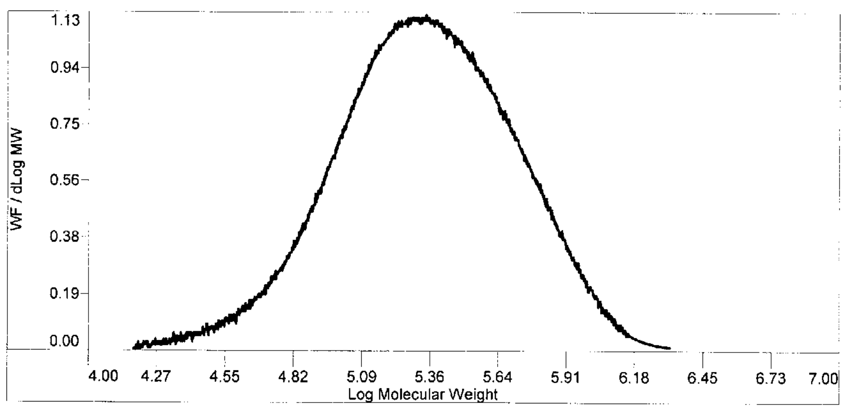
Solvent	THF	**Det**	35.00





Sample	Mn	Mw	Mp	Mz	Mw/Mn
09-09-2009_00;03;49_Am-CF3+Br	157,923	300,214	217,885	511,631	1.901

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Table 1, Entry 3.

Sample Information

ID	Am-CH3+BnOH 1_500
Method	Conventional
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Solvent	THF

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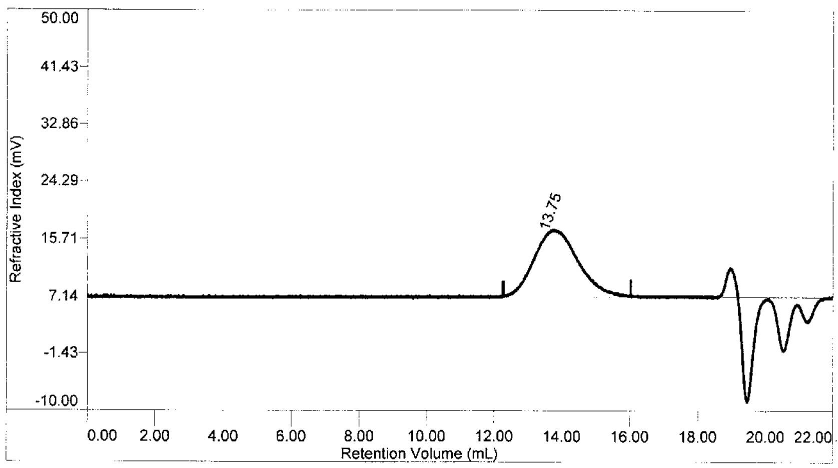
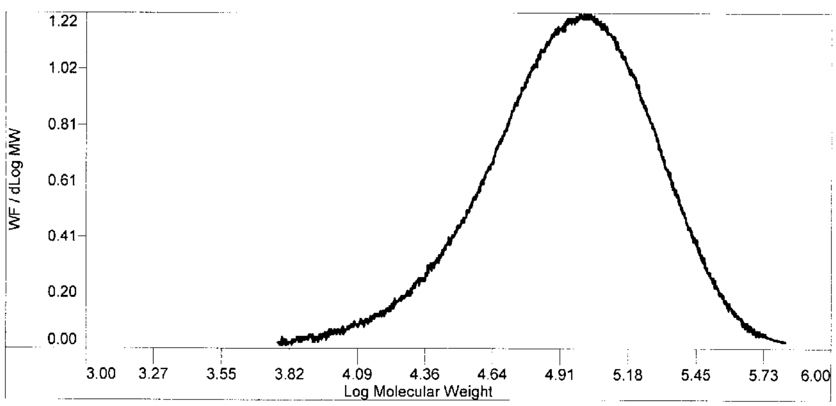
Inj Vol	100.0
Col	35.00
Det	35.00





Sample	Mn	Mw	Mp	Mz	Mw/Mn
08-09-2009_21;17;11_Am-CH3+Br	62,004	114,263	103,932	180,690	1.843

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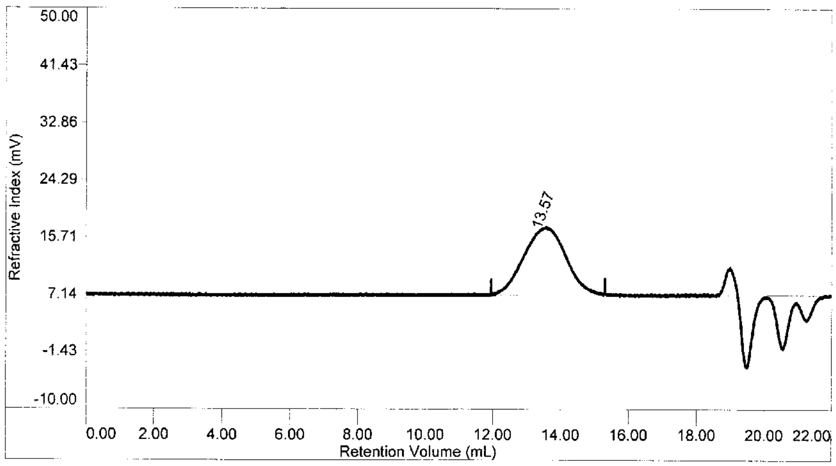
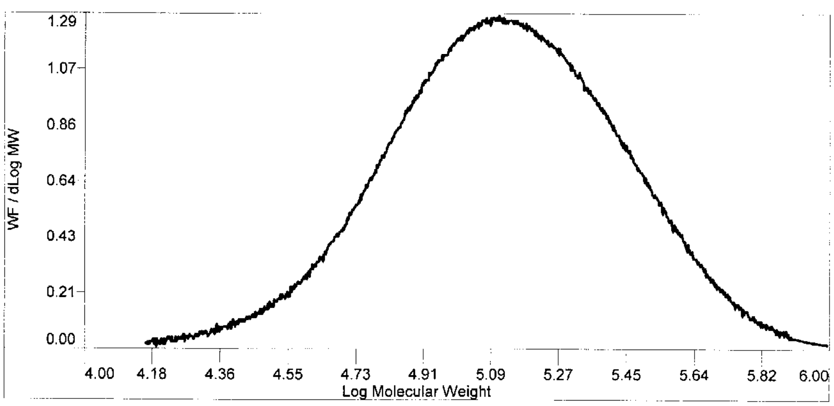
Table 1, Entry 4.

Sample Information

ID	Am-iPr+BnOH 1_500
Method	Conventional
Acq.	Sep 08, 2009 - 20:21:39
Solvent	THF

Flow	1.0000
Inj Vol	100.0
Col	35.00
Det	35.00





Sample	Mn	Mw	Mp	Mz	Mw/Mn
08-09-2009_20;21;39_Am-iPr+BnC	103,645	170,502	130,361	265,040	1.645

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Table 1, Entry 5.

Sample Information

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Solvent	THF

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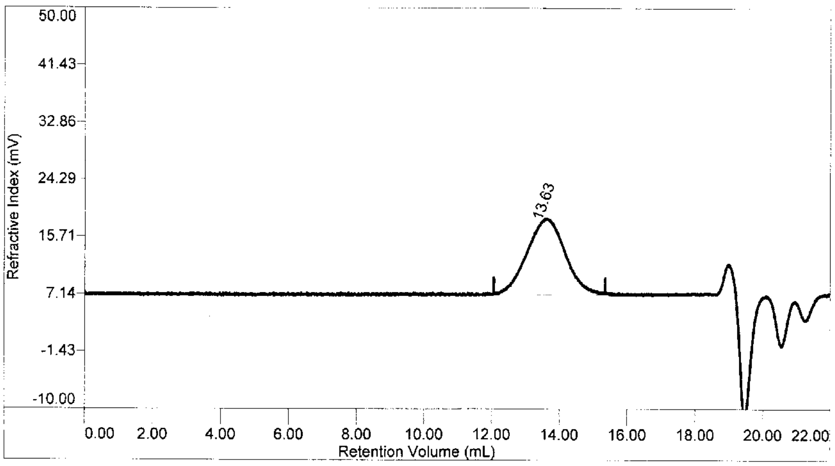
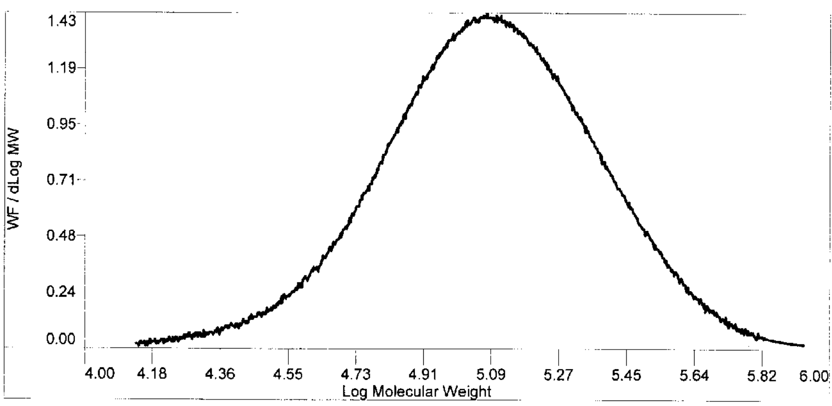
Det	35.00





Sample	Mn	Mw	Mp	Mz	Mw/Mn
08-09-2009_17;35;01_Am-H_1_50	97,455	151,300	120,649	225,604	1.553

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Table 1, Entry 6.

Sample Information

ID	Am-OMe 1_500
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Acq.	Sep 08, 2009 - 18:30:33
Solvent	THF

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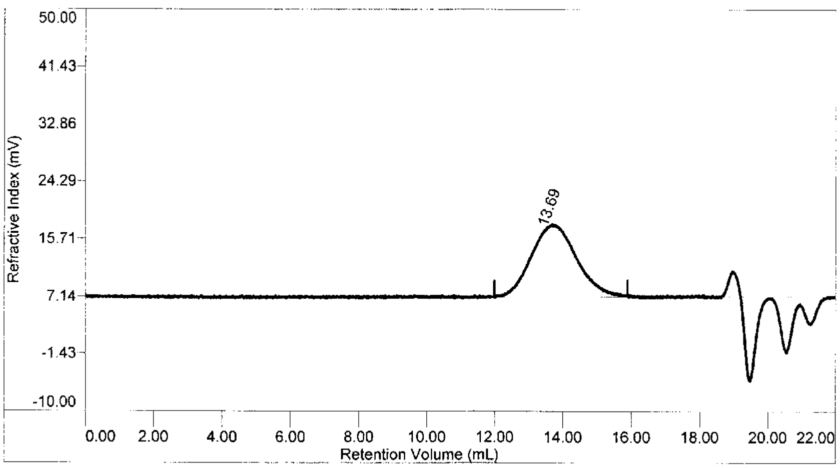
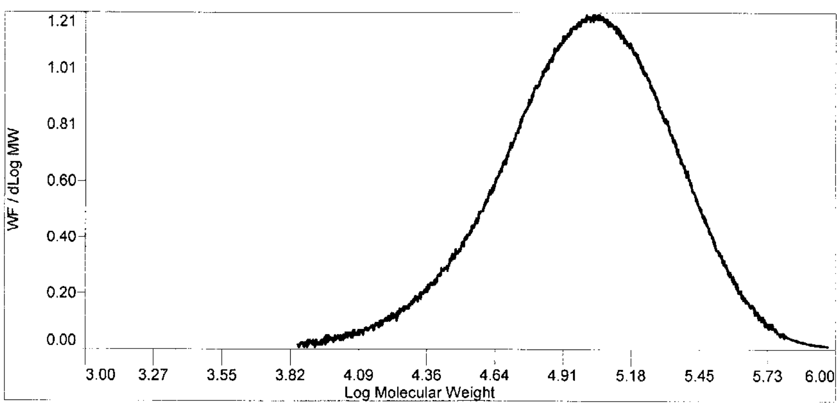
Inj Vol	100.0
Col	35.00
Det	35.00





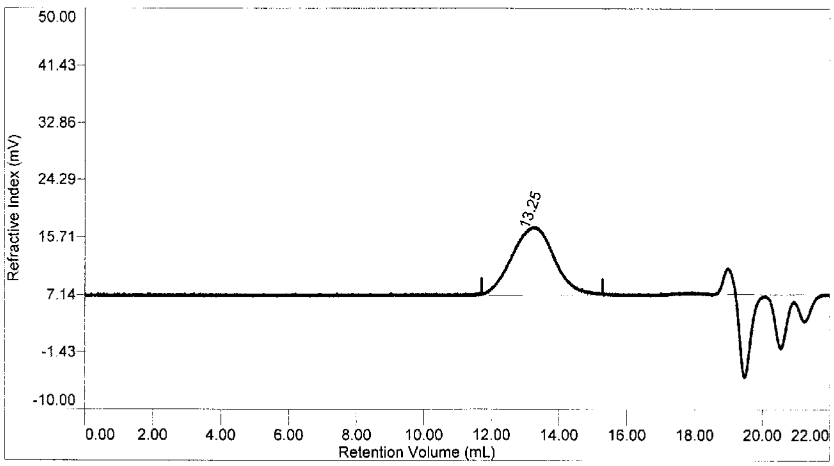
Sample	Mn	Mw	Mp	Mz	Mw/Mn
08-09-2009_18;30;33_Am-OMe_1_	71,426	132,225	112,153	216,549	1.851

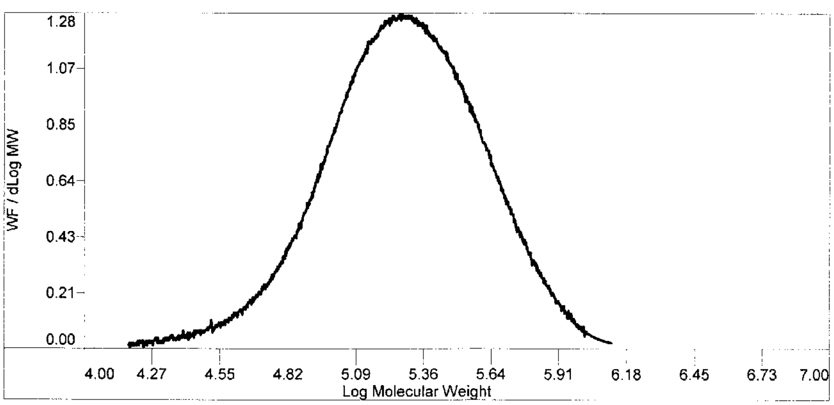
OmniSEC www.viscotek.com

Table 1, Entry 7.

Sample Information

ID	Am-CF3 1_500	Flow	1.0000
Method	Conventional	Inj Vol	100.0
Acq.	Sep 08, 2009 - 19:26:06	Col	35.00
Solvent	THF	Det	35.00





Sample	Mn	Mw	Mp	Mz	Mw/Mn
08-09-2009_19;26;06_Am-CF3_1_	145,802	245,882	194,239	379,466	1.686

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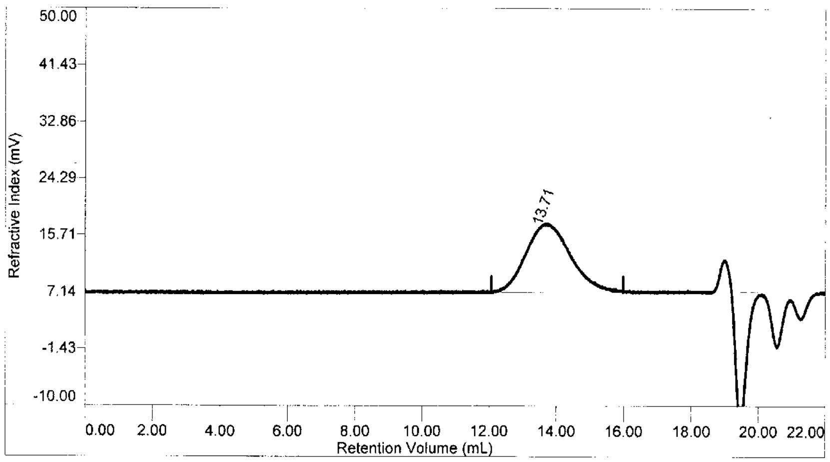
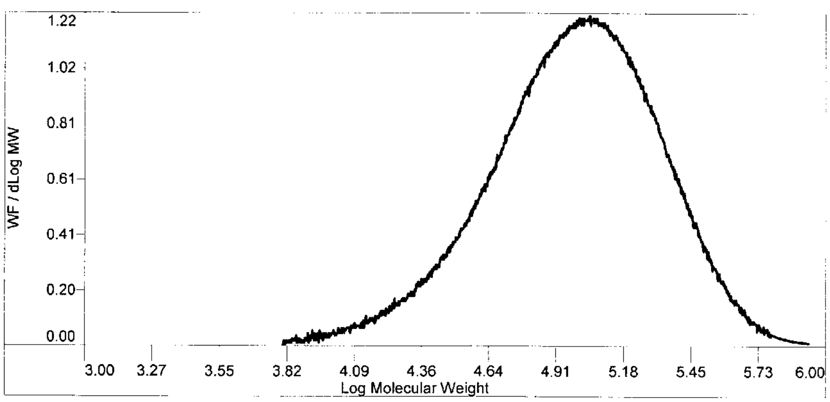
Table 1, Entry 8.

Sample Information

ID	Am-CH3 1_500	**Flow**	1.0000
Method	Conventional	**Inj Vol**	100.0
Acq.	Sep 08, 2009 - 16:39:28	**Col**	35.00
Solvent	THF	**Det**	35.00





Sample	Mn	Mw	Mp	Mz	Mw/Mn
08-09-2009_16;39;28_Am-CH3_1_	68,555	126,807	109,834	204,133	1.850

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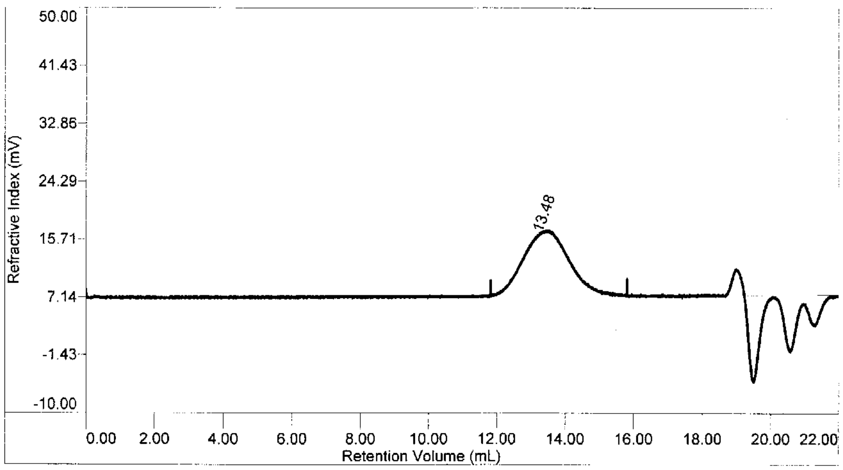
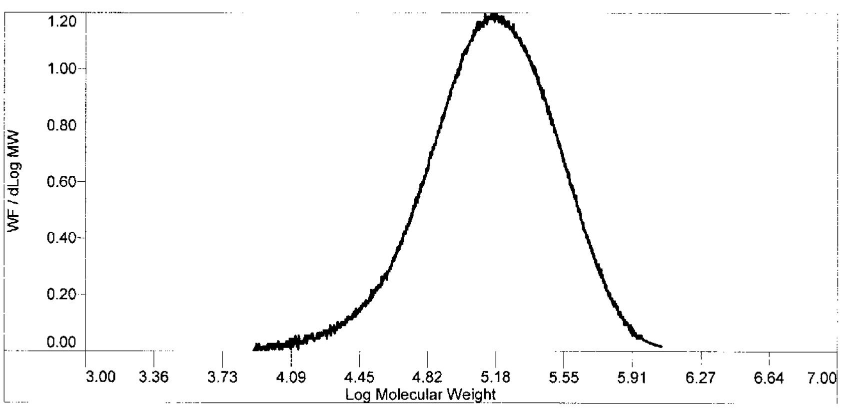
Table 1, Entry 9.

Sample Information

ID	Am-iPr 1_500	Flow	1.0000
Method	Conventional	Inj Vol	100.0
Acq.	Sep 08, 2009 - 12:01:45	Col	35.00
Solvent	THF	Det	35.00





Sample	Mn	Mw	Mp	Mz	Mw/Mn
08-09-2009_12;01;45_Am-iPr_1_5	102,634	190,278	146,184	307,217	1.854

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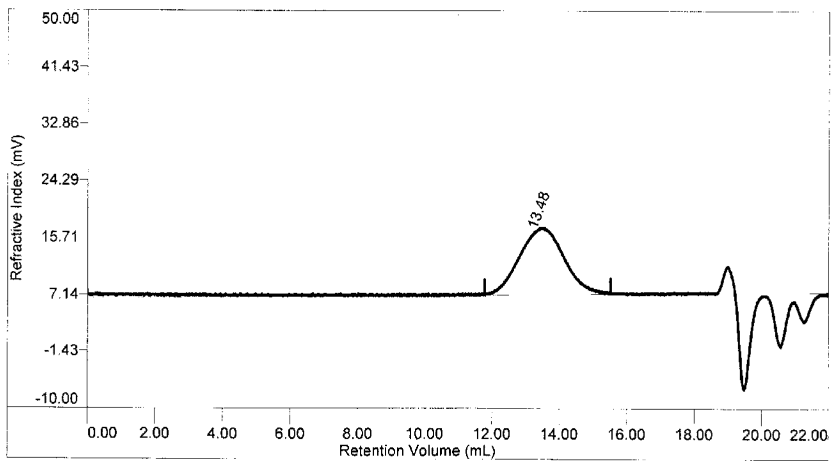
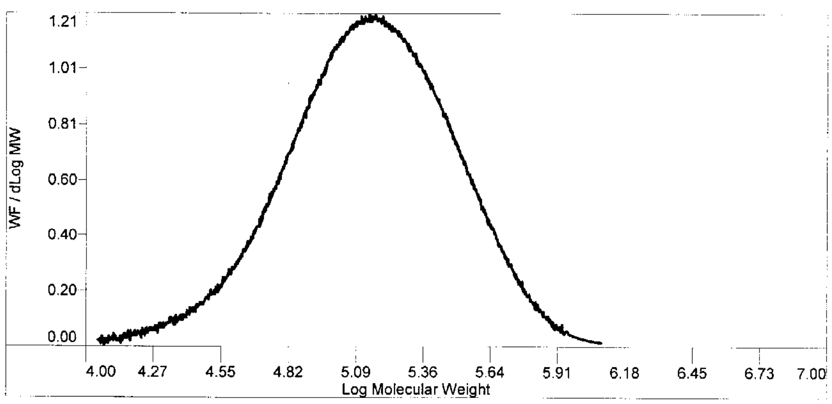
Table 1, Entry 10.

Sample Information

ID	Am-iPr 1_1000
Method	Conventional
Acq.	Sep 08, 2009 - 12:57:17
Solvent	THF

Flow	1.0000
Inj Vol	100.0
Col	35.00
Det	35.00





Sample	Mn	Mw	Mp	Mz	Mw/Mn
08-09-2009_12;57;17_Am-iPr_1_1	103,121	185,582	145,931	302,822	1.800

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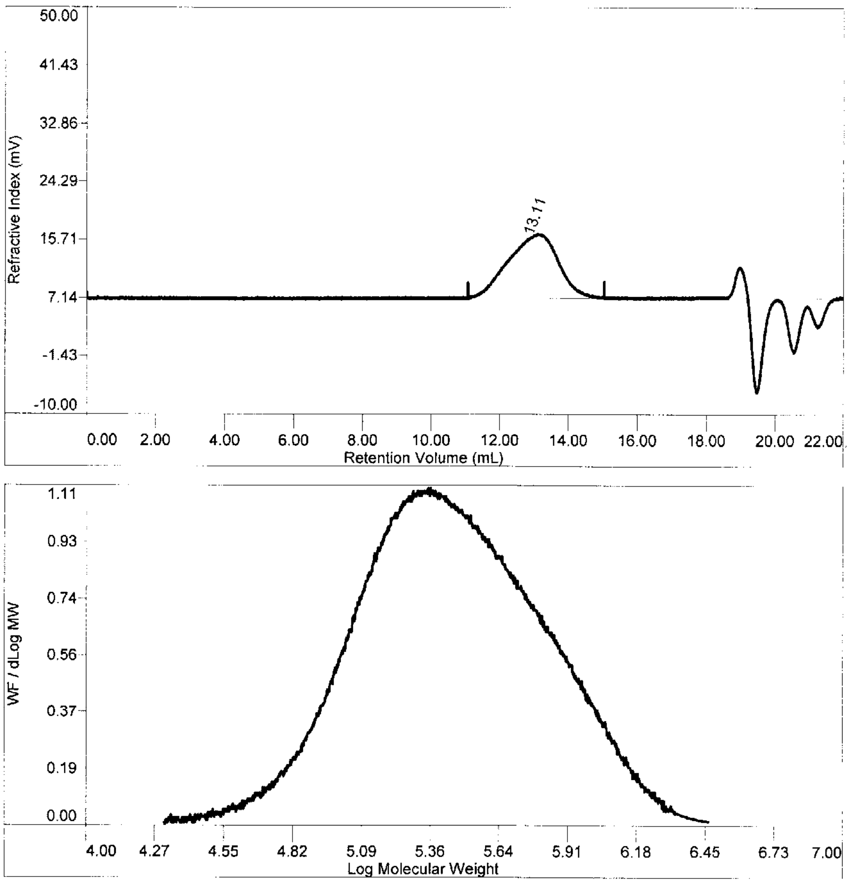
Table 1, Entry 11.

Sample Information

ID	Am-iPr 1_5000	Flow	1.0000
Method	Conventional	Inj Vol	100.0
Acq.	Sep 08, 2009 - 13:52:50	Col	35.00
Solvent	THF	Det	35.00



Sample	Mn	Mw	Mp	Mz	Mw/Mn
08-09-2009_13;52;50_Am-iPr_1_5	202,045	392,610	230,151	712,476	1.943

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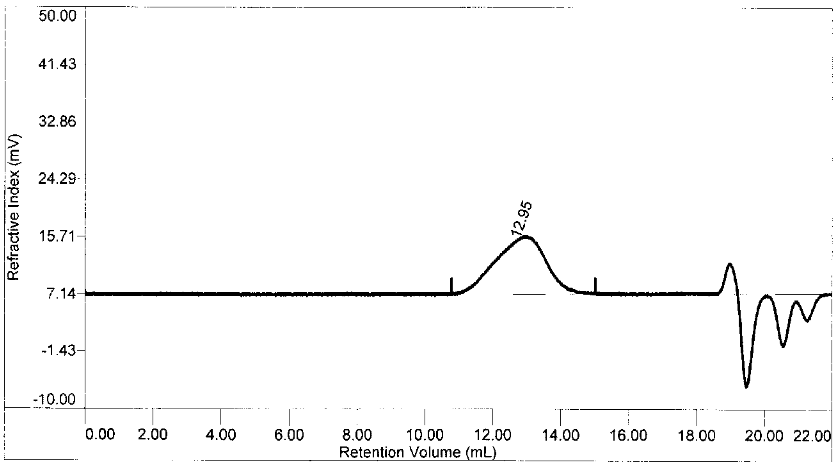
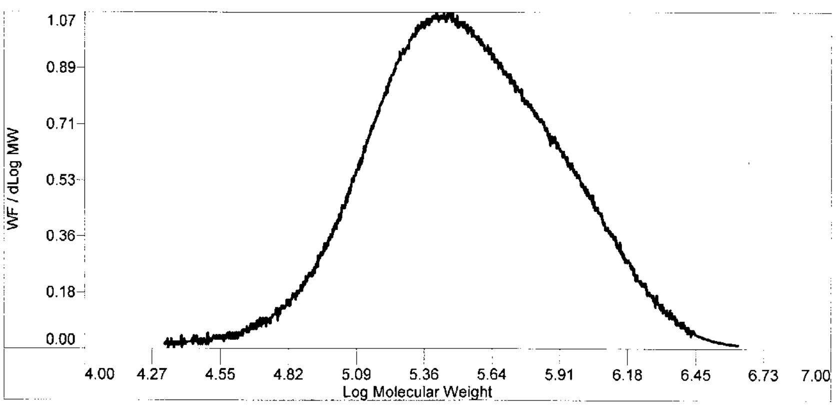
Table 1, Entry 12.

Sample Information

ID	Am-iPr 1_10000	Flow	1.0000
Method	Conventional	Inj Vol	100.0
Acq.	Sep 08, 2009 - 14:48:22	Col	35.00
Solvent	THF	Det	35.00





Sample	Mn	Mw	Mp	Mz	Mw/Mn
08-09-2009_14;48;22_Am-iPr_1_1	236,166	489,442	284,205	942,472	2.072

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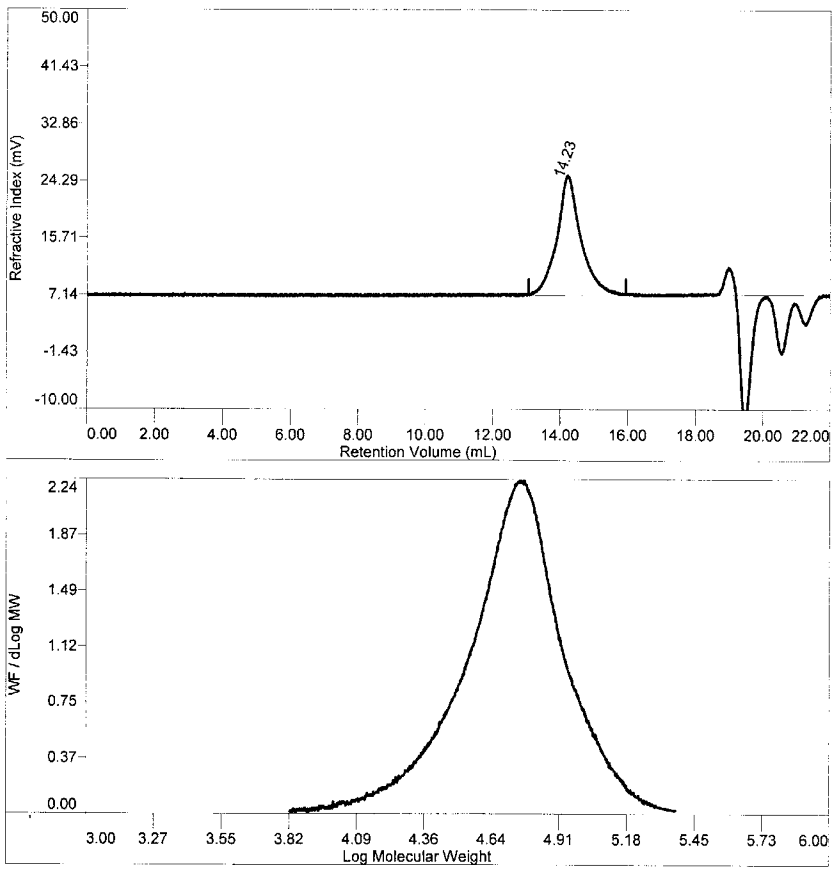
Table 1, Entry 13.

Sample Information

ID	M-Sn(Oct)	Flow	1.0000
Method	Conventional	Inj Vol	100.0
Acq.	Sep 08, 2009 - 15:43:55	Col	35.00
Solvent	THF	Det	35.00



Sample	Mn	Mw	Mp	Mz	Mw/Mn
08-09-2009_15;43;55_M-Sn(Oct)_	45,087	59,288	56,991	74,702	1.315

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Table 1, Entry 14.