

Supplementary Information

Mechanochemical synthesis of poly(lactic Acid) block copolymers: overcoming the miscibility of the macroinitiator, monomer and catalyst under solvent-free conditions

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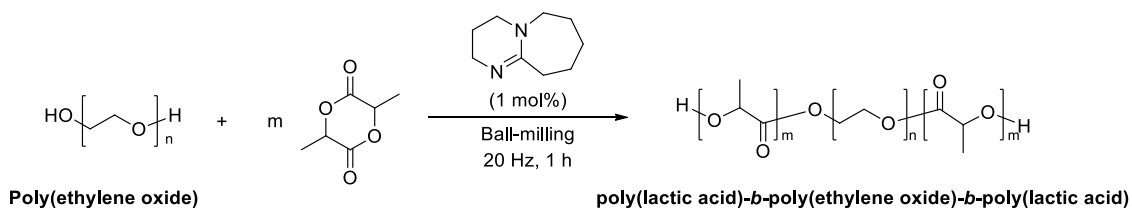
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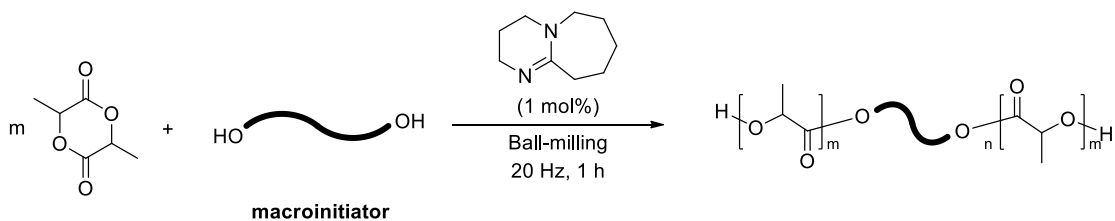
A. Raw data for Table 1 and Table 2.

Table S1. Data of PLA-*b*-PEG-*b*-PLA Synthesis (table 1)^a



Entry	Macroinitiator	Lactide (equiv)	Product (targeted)	Conv (%) ^b	M_n (kg/mol) ^c	M_w/M_n ^c	Condition
1-1	PEO1000	14	PLA1000-PEO1000-PLA1000	93	2.78	1.25	7 mm ball x 3 ea
1-2				99	3.32	1.18	
2-1	PEO1000	28	PLA2000-PEO1000-PLA2000	99	4.64	1.30	7 mm ball x 3 ea
2-2				>99	4.59	1.28	
3-1	PEO1000	42	PLA3000-PEO1000-PLA3000	97	6.76	1.29	7 mm ball x 3 ea
3-2				98	6.90	1.40	
4-1	PEO6000	42	PLA3000-PEO6000-PLA3000	>99	14.5	1.22	12 mm ball x 1 ea, THF 20 μ L
4-2				>99	14.7	1.18	
5-1	PEO6000	83	PLA6000-PEO6000-PLA6000	>99	17.7	1.33	12 mm ball x 1 ea
5-2				>99	18.1	1.33	
6-1	PEO6000	125	PLA9000-PEO6000-PLA9000	>99	21.2	1.48	12 mm ball x 1 ea
6-2				>99	21.1	1.46	
7-1	PEO6000	167	PLA12000-PEO6000-PLA12000	>99	20.1	1.67	12 mm ball x 1 ea
7-2				>99	19.7	1.64	
8-1	PEO6000	167	PLA12000-PEO6000-PLA12000	>99	25.4	1.47	12 mm ball x 1 ea, THF 20 μ L
8-2				>99	26.0	1.47	
9-1	PEO20000	69	PLA5000-PEO20000-PLA5000	>99	20.8	1.13	12 mm ball x 1 ea
9-2				>99	20.4	1.13	
10-1	PEO20000	139	PLA10000-PEO20000-PLA10000	>99	24.5	1.18	12mm ball x 1 ea
10-2				>99	23.3	1.23	
11-1	PEO20000	278	PLA20000-PEO20000-PLA20000	>99	32.0	1.23	12mm ball x 1 ea
11-2				>99	29.4	1.21	

a. Polymerization conditions: D-lactide (100 mg), DBU (1.0 μ L), and PEO in a 25 mL stainless-steel jar with stainless-steel balls; b. Determined by ¹H-NMR spectroscopy; c. Determined by GPC calibrated with polystyrene standards in tetrahydrofuran (THF) at 40 °C.

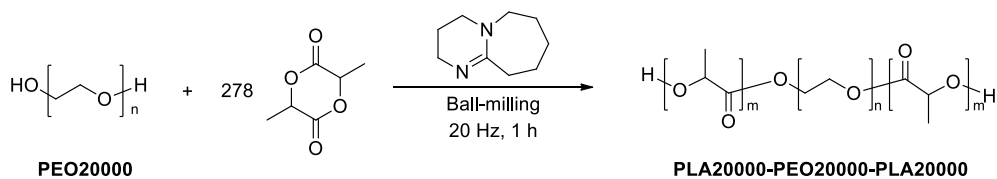
Table S2. Data of PLA block copolymer from various macroinitiators (table 2)^a

Entry	Macroinitiator	Lactide (equiv)	Product (targeted)	Conv (%) ^b	M_n (kg/mol) ^c	M_w/M_n ^c	Condition
1-1	HO-P ϵ DL-OH	56	PLA4000-P ϵ DL4600-PLA4000	98	10.8	1.53	7 mm ball x 3 ea, THF 20 μ L
1-2				85	9.04	1.50	
2-1	HO-P δ DL-OH	56	PLA4000-P δ DL4400-PLA4000	92	11.3	1.41	7 mm ball x 3 ea
2-2				84	10.1	1.41	
3-1	P ϵ CL-OH	56	P ϵ CL4800-PLA4000	95	12.1	1.21	7 mm ball x 3 ea, THF 20 μ L
3-2				83	10.5	1.20	
4-1	PTHF	28	PLA2000-PTHF2900-PLA2000	89	8.81	1.53	7 mm ball x 3 ea
4-2				98	8.97	1.57	
5-1				56	PLA4000-PTHF2900-PLA4000	74	
5-2	92	13.4	1.35				

a. Polymerization conditions: D-lactide (100 mg), DBU (1.0 μ L), and macroinitiator in a 25 mL stainless-steel jar with stainless-steel balls; b. Determined by ¹H-NMR spectroscopy; c. Determined by GPC calibrated with polystyrene standards in tetrahydrofuran (THF) at 40 °C.

B. LAG effect experiments for PLA20000-PEO20000-PLA20000 synthesis

Table S3. LAG effect tests on chain degradation protection.



Entry	LAG (equiv)	Conv (%) ^c	M_n (kg/mol) ^d	M_w/M_n ^d
1-1	Toluene 20 uL	>99	32.0	1.23
1-2		>99	29.4	1.21
2-1	THF 20 uL	>99	24.7	1.23
2-2		>99	25.0	1.21
3-1	DME 20 uL	>99	25.3	1.20
3-2		>99	24.4	1.25

a. Polymerization conditions: D-lactide (100 mg), DBU (1.0 uL), and PEO in a 25 mL stainless-steel jar with stainless-steel balls; b. Determined by ¹H-NMR spectroscopy; c. Determined by GPC calibrated with poly-styrene standards in tetrahydrofuran (THF) at 40 °C.

C. LAG effect experiments for PEO6000 initiator reactions.

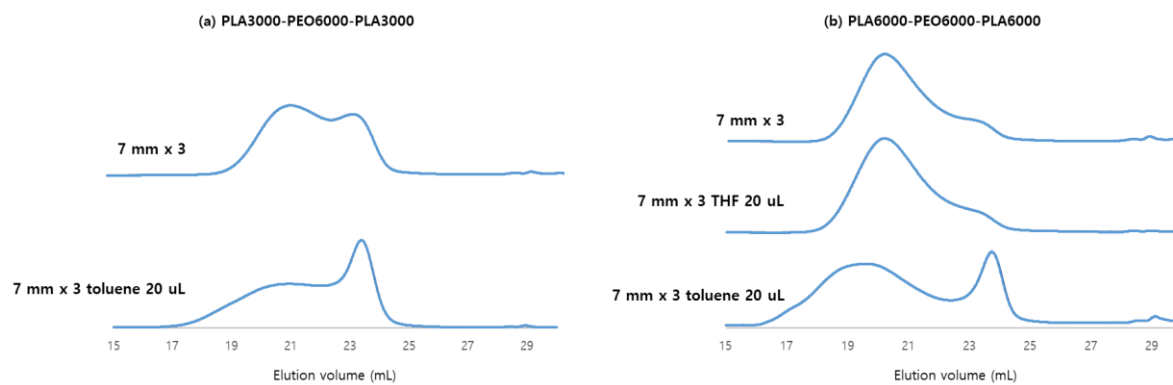


Figure S1. GPC spectra of liquid-additive effect tests on PEO6000 initiated lactide polymerization.

D. Different Scanning Calorimeter Analysis of PLA10000-PEO20000-PLA10000 (Table 1, entry 10).

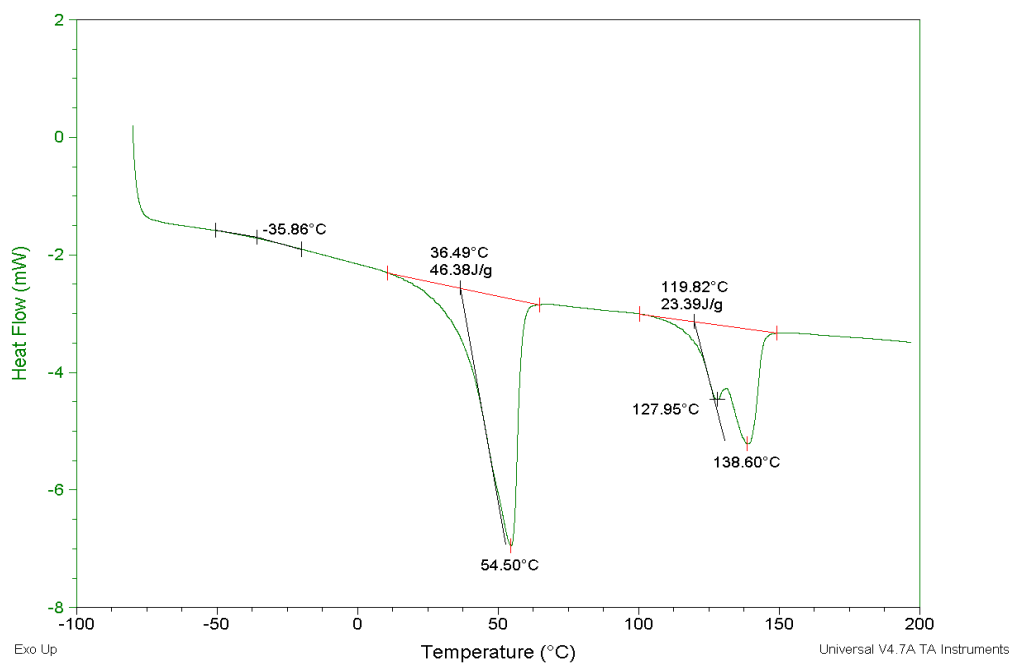


Figure S2. DSC spectra of liquid-additive effect tests on PEO20000 initiated lactide polymerization.

E. PEO recovery experiment after the degradation of PLA10000-PEO20000-PLA10000 (entry 10)

In a 4 mL vial, 1 M NaOH solution (MeOH, 0.2 mL) was added to the solution of PLA10000-PEO20000-PLA10000 (Table 1, entry 10) (10 mg) in THF (1 mL). The resulting solution was placed on 40 °C heating block. After 1 h, the complete degradation of PLA was confirmed by ¹H-NMR and an aliquot was taken for GPC analysis of the resulting PEO (Figure S3, top). The authentic PEO was dissolved in the mixture of THF (1 mL) and 1 M NaOH (MeOH, 0.2 mL), then an aliquot was subjected to GPC analysis (Figure S3, bottom).

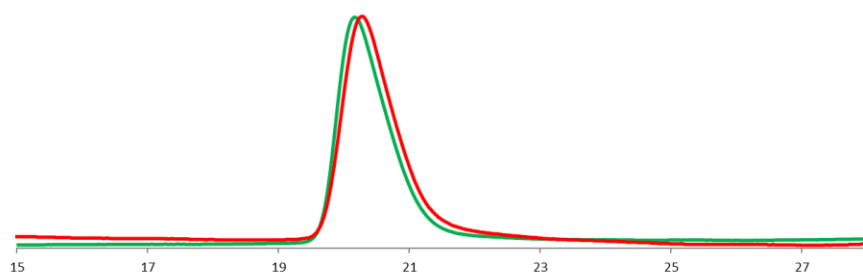


Figure S3. GPC spectra of the recovered PEO20000 after PLA10000-PEO20000-PLA10000 degradation (red) and the authentic PEO20000 (green).

F. Reactor temperature measurement after the reaction.

The temperature of the reaction was measured after immediate opening of the vessel by visual IR thermometer. The highest temperature 43.5 °C was recorded at the milling ball location.

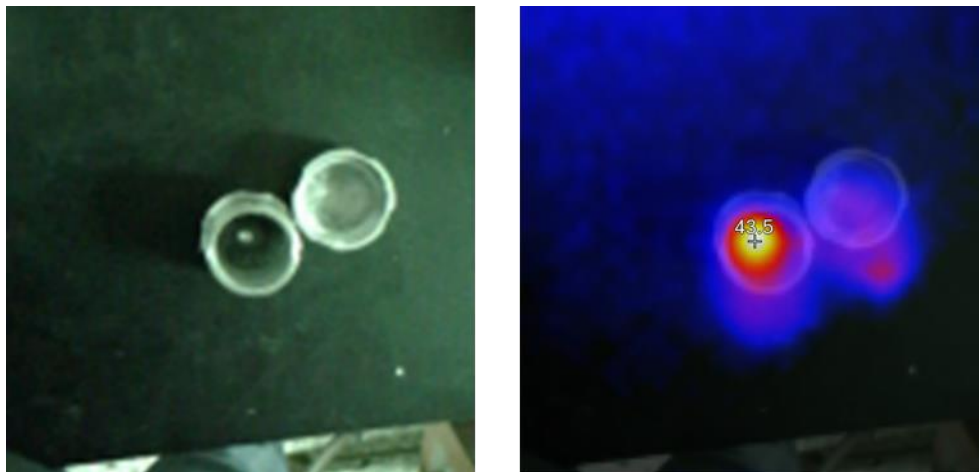
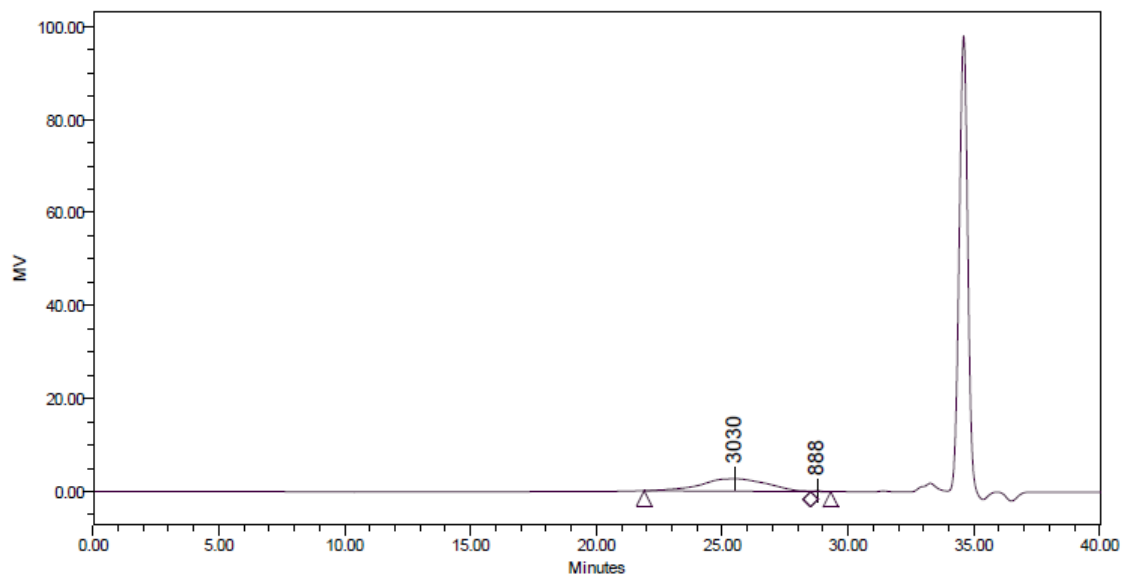


Figure S4. Visual IR thermometer images of the reaction vessel after the reaction.

G. GPC and NMR Spectra of table 1 and table 2

Table 1, entry 1-1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	2784	3503	3030	4505	5756	1.258623	1.285842	1.643037
2	880	883	888	886	889	1.003379	1.003294	1.006515

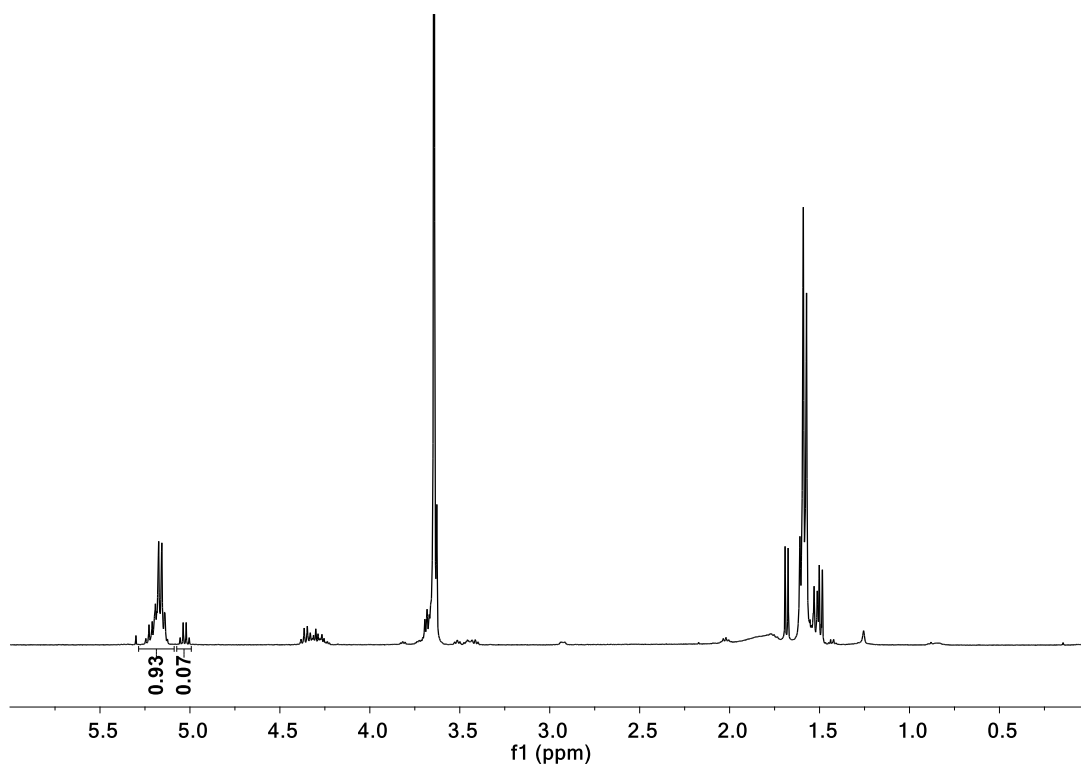
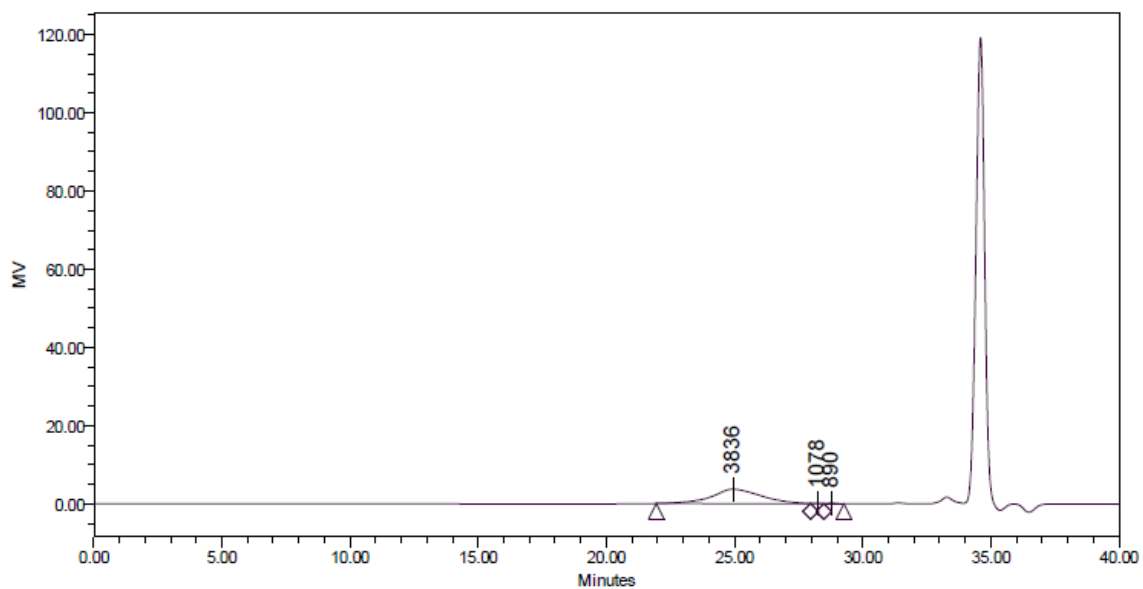


Table 1 entry 1-2



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		3319	3927	3836	4689	5622	1.183137	1.193981	1.431702
2		1095	1097	1078	1100	1103	1.002643	1.002619	1.005212

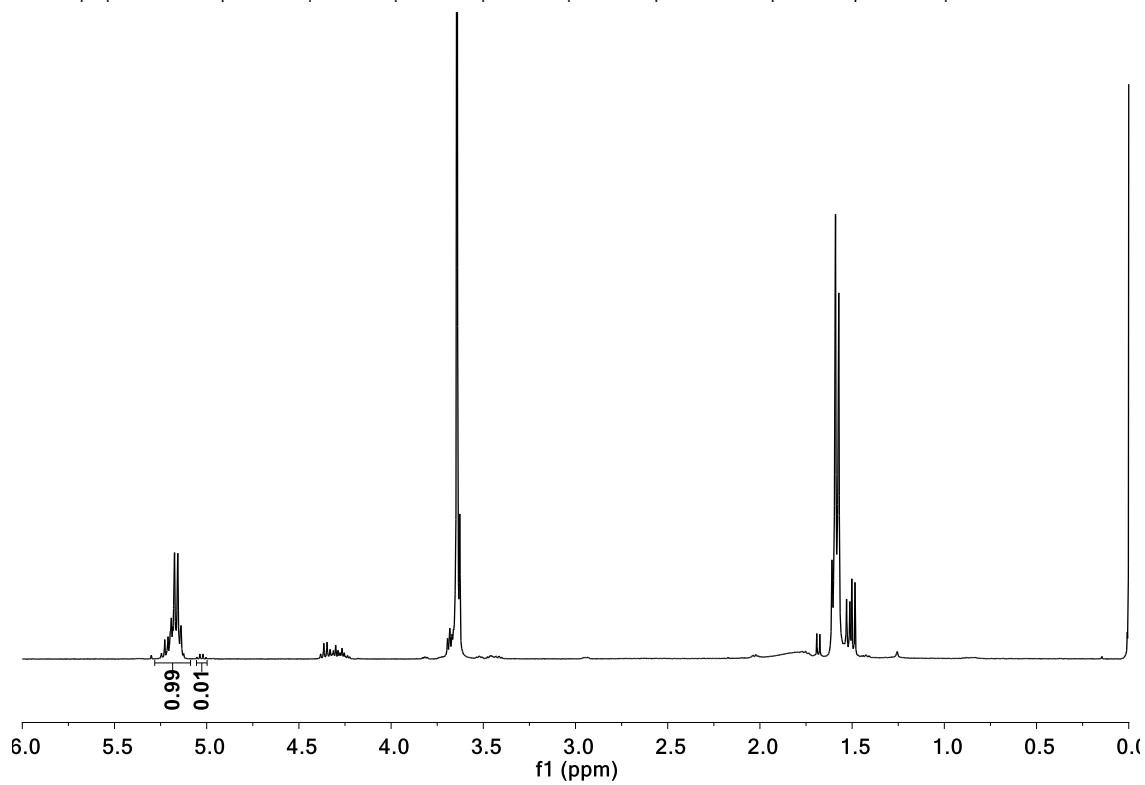
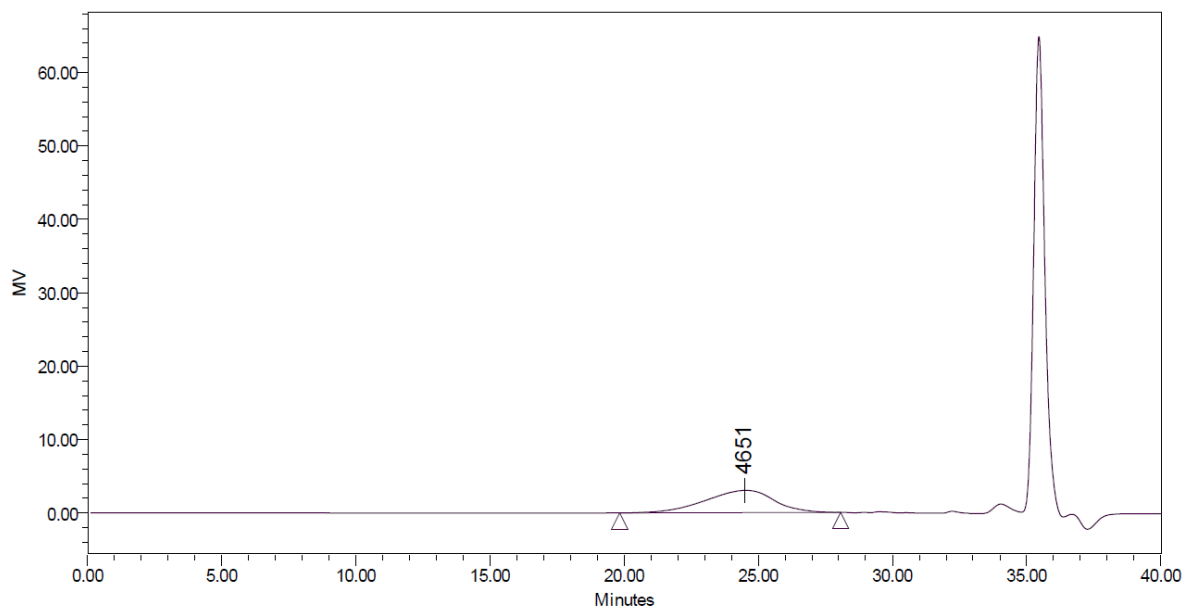


Table 1 entry 2-1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	4635	6063	4651	8124	10800	1.308173	1.339950	1.781216

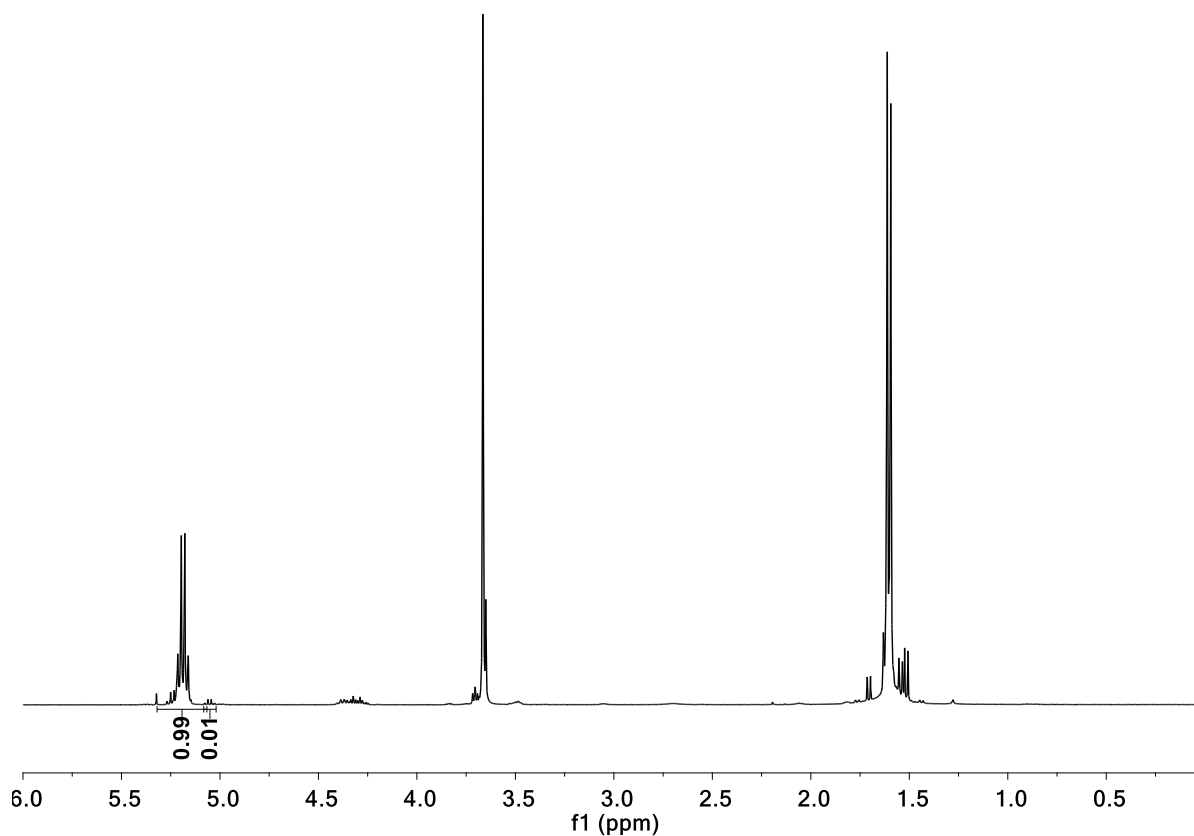
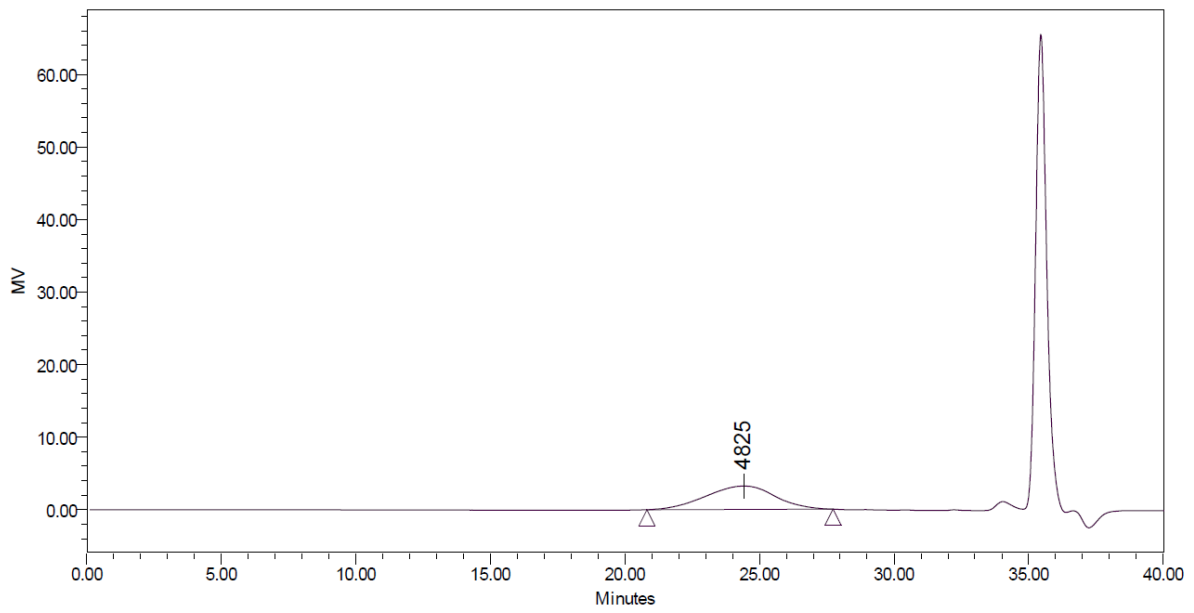


Table 1 entry 2-2



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	4592	5875	4825	7506	9333	1.279471	1.277517	1.588474

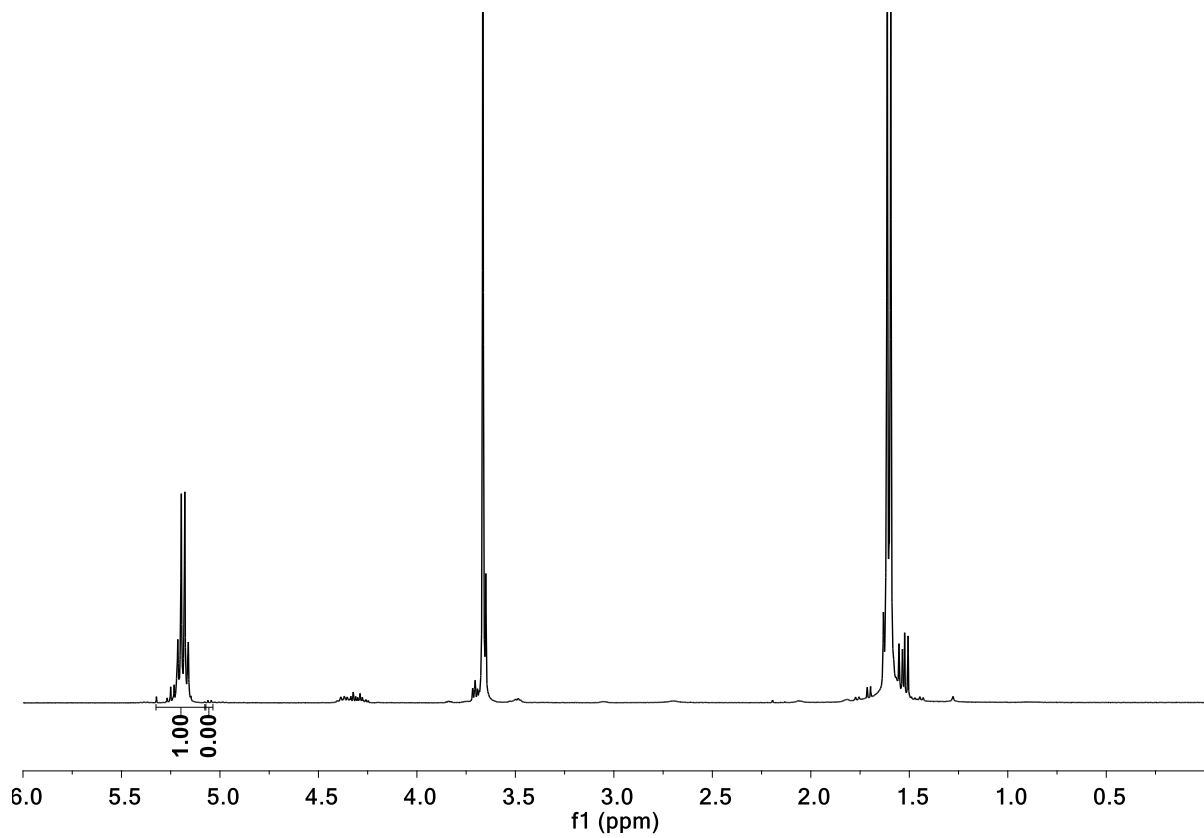
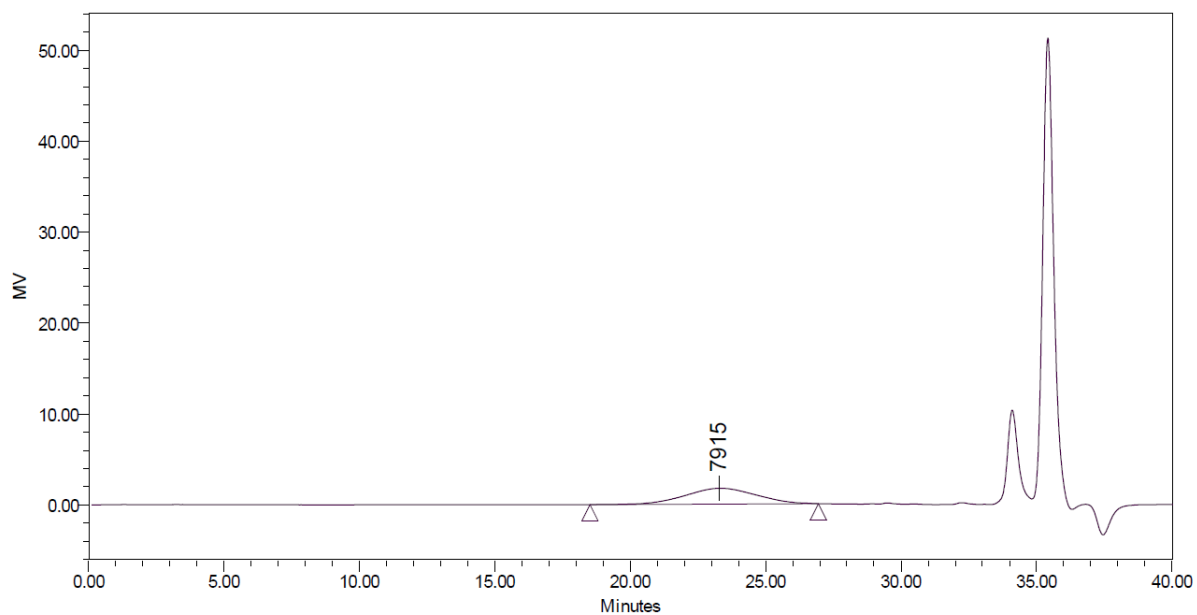


Table 1 entry 3-1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	6759	8817	7915	11402	14418	1.304433	1.293184	1.635148

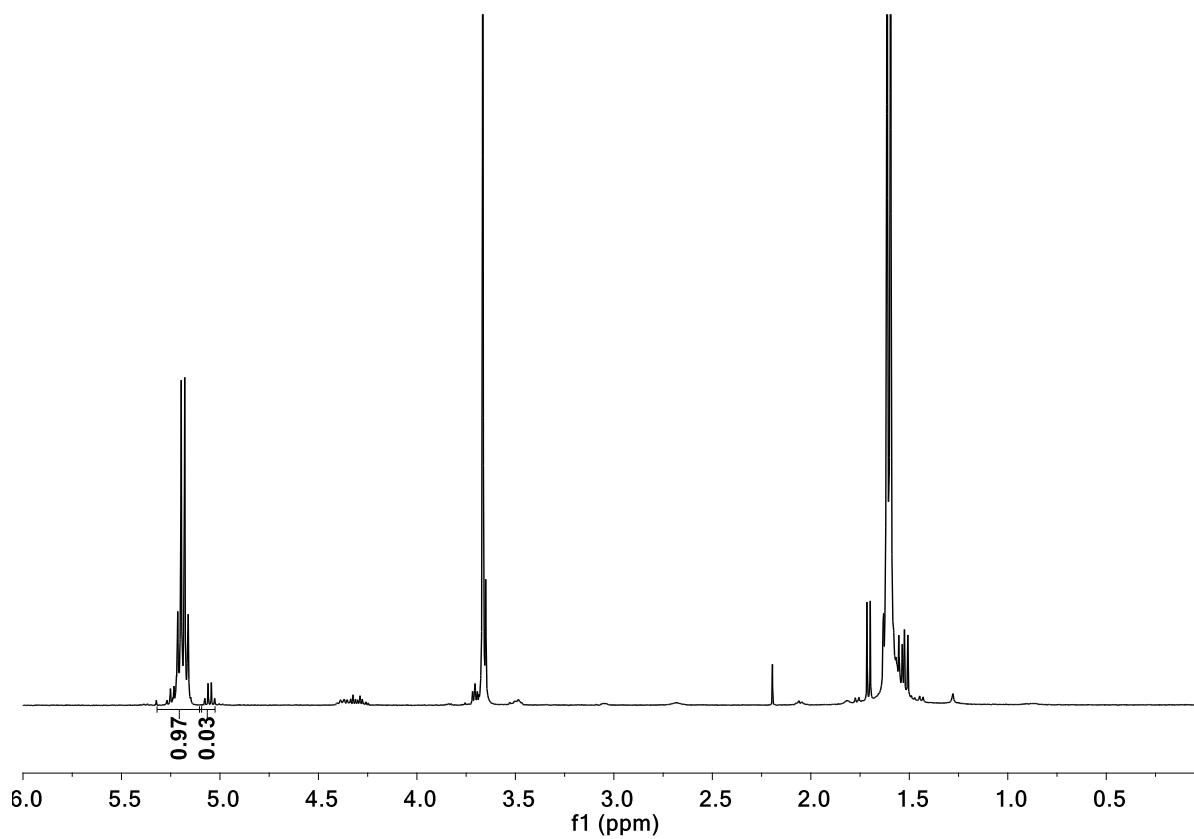
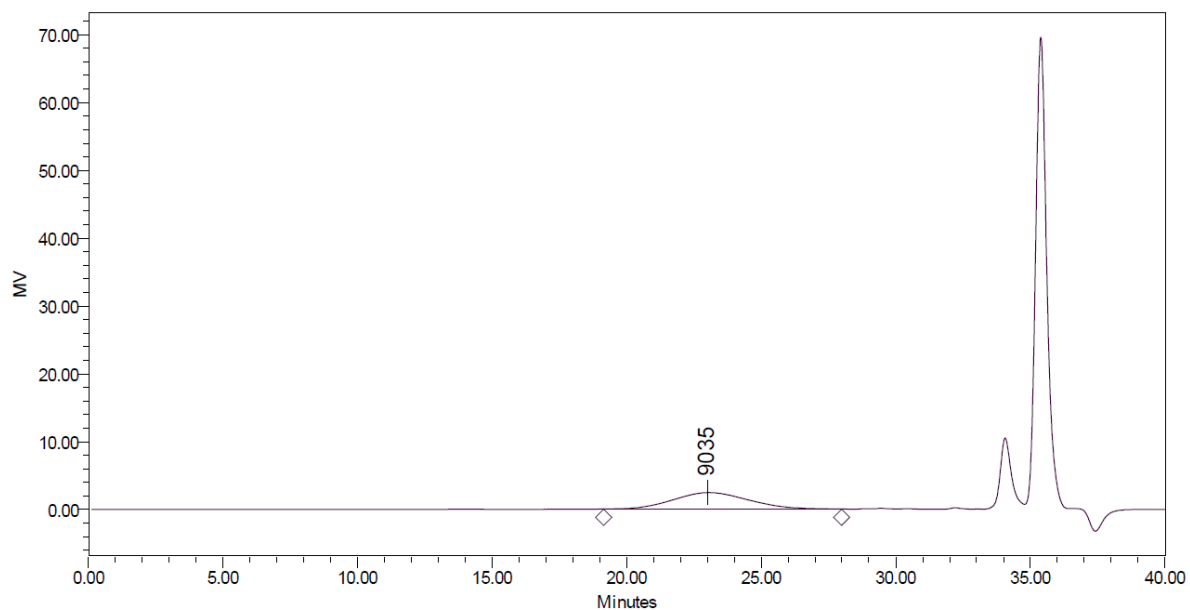


Table 1 entry 3-2



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		6895	9638	9035	12902	16580	1.397715	1.338694	1.720351

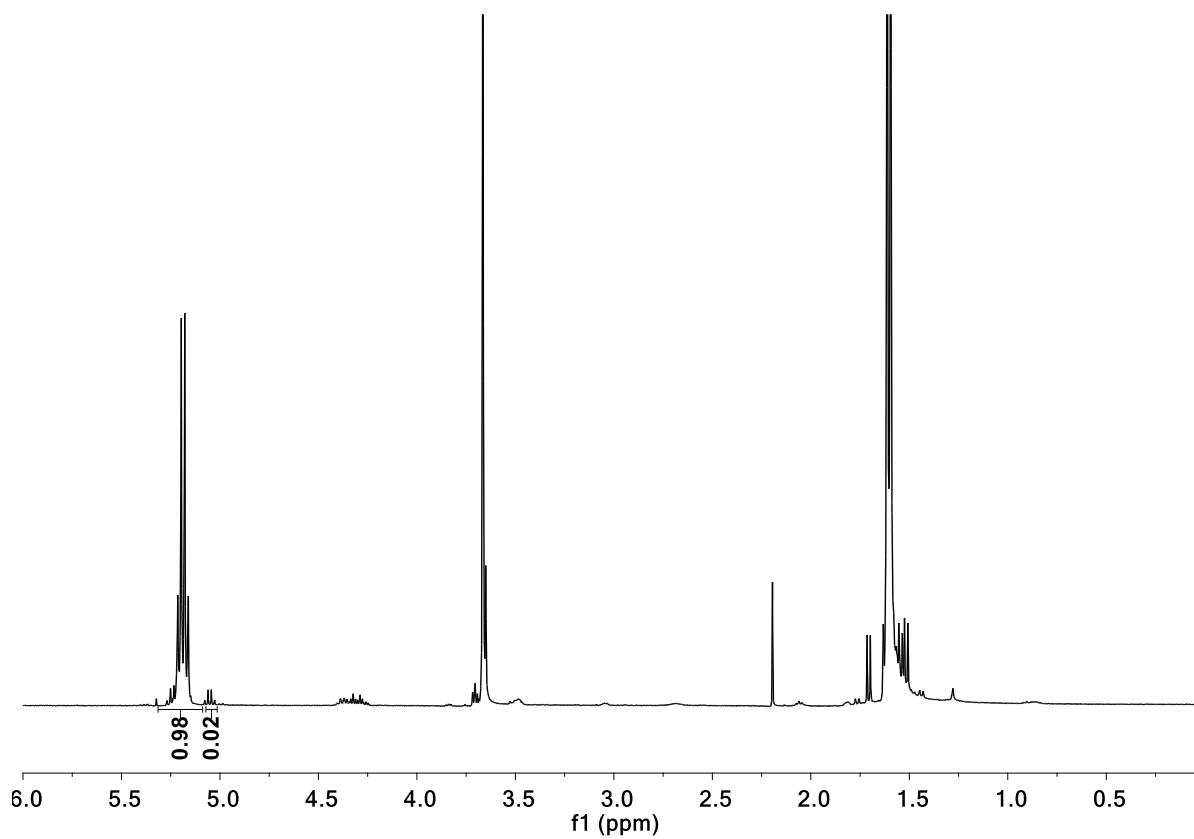
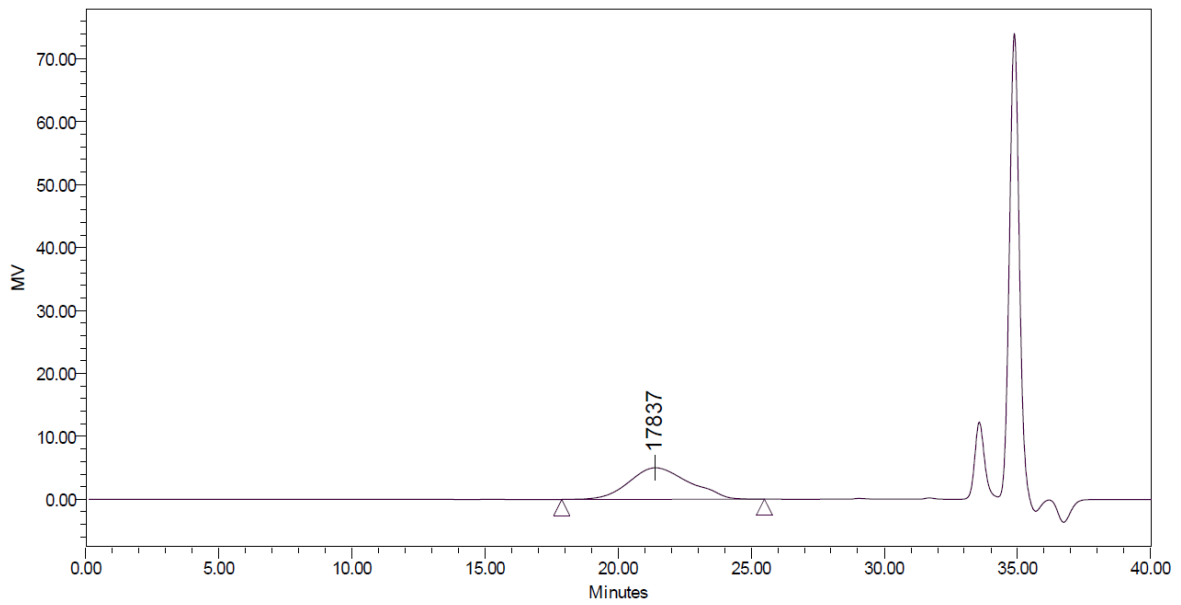


Table 1 entry 4-1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	14519	17686	17837	21151	24958	1.218087	1.195920	1.411175

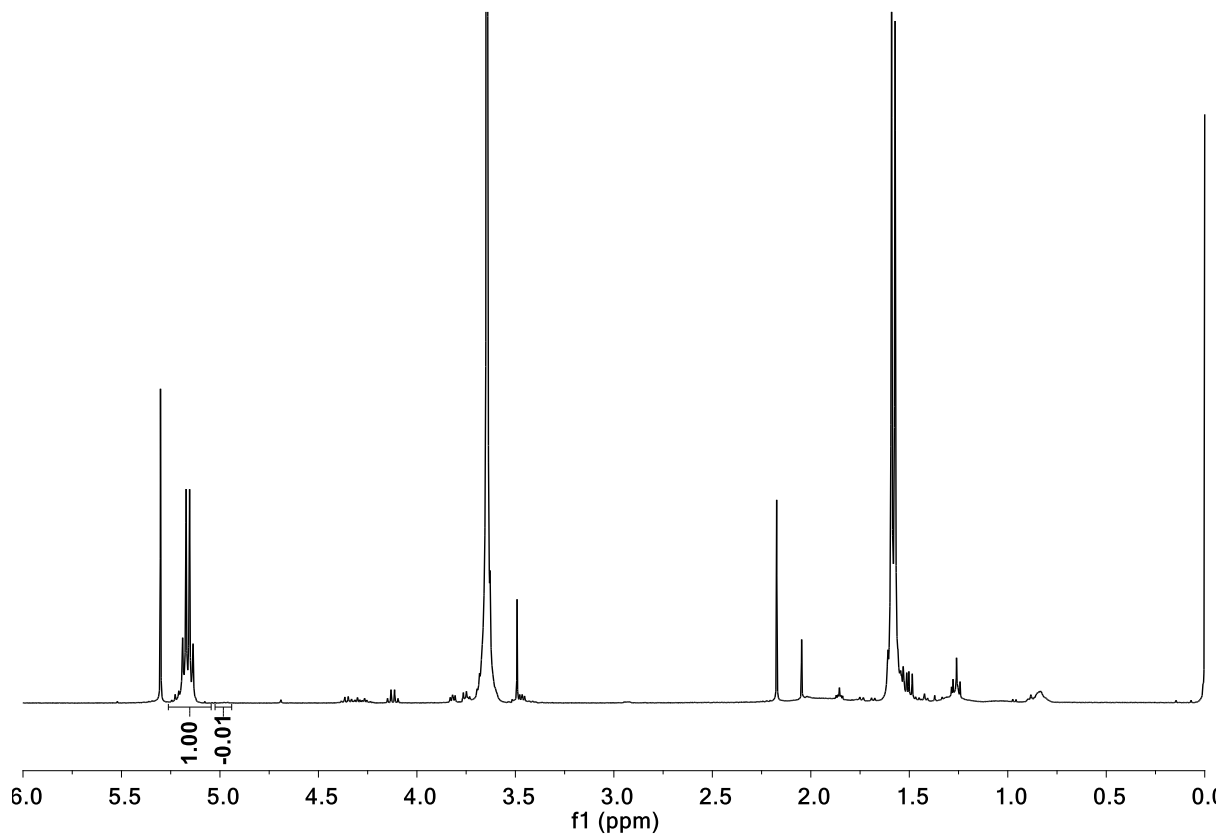
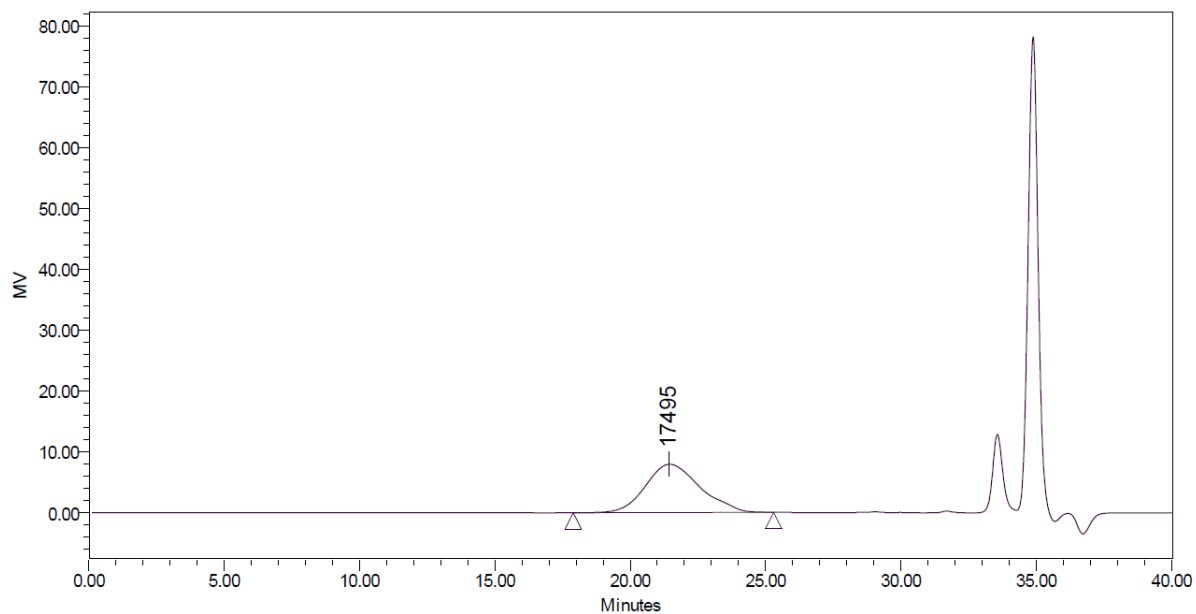


Table 1 entry 4-2



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	14658	17240	17495	19938	22833	1.176171	1.156484	1.324416

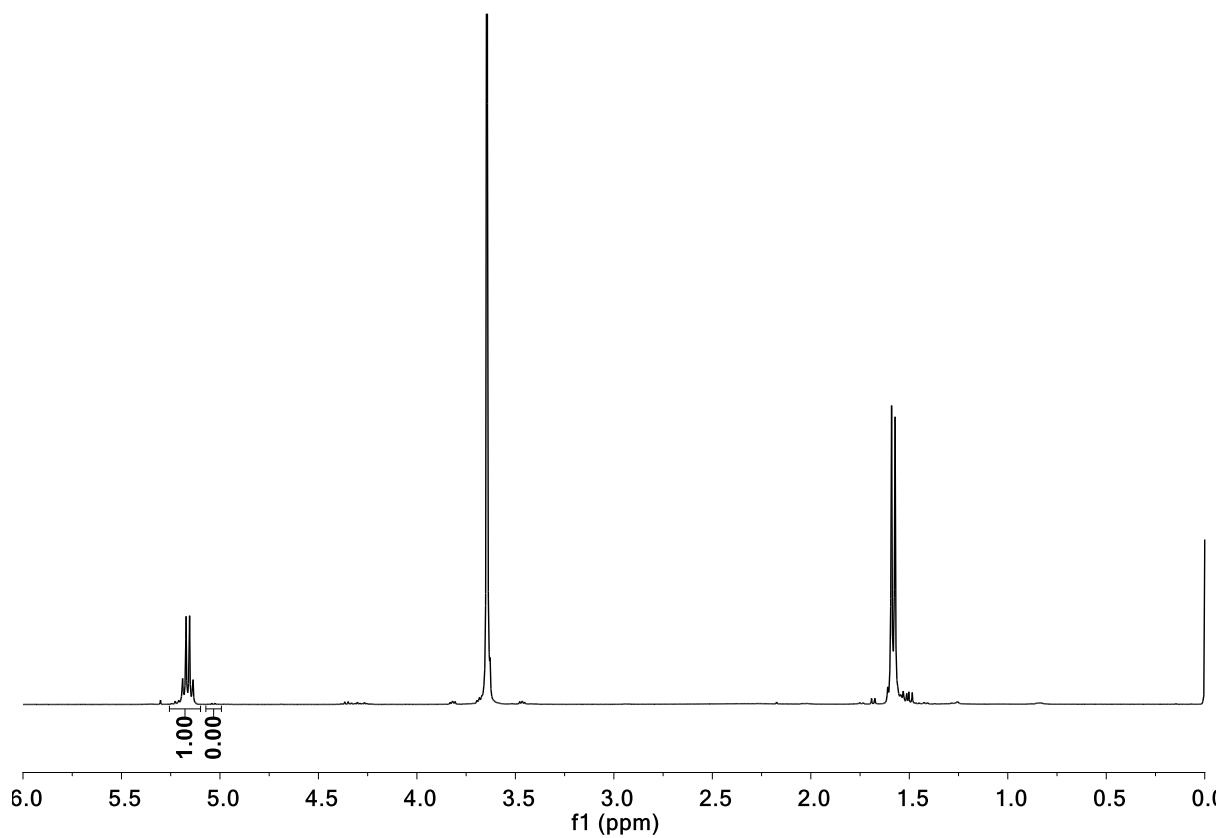
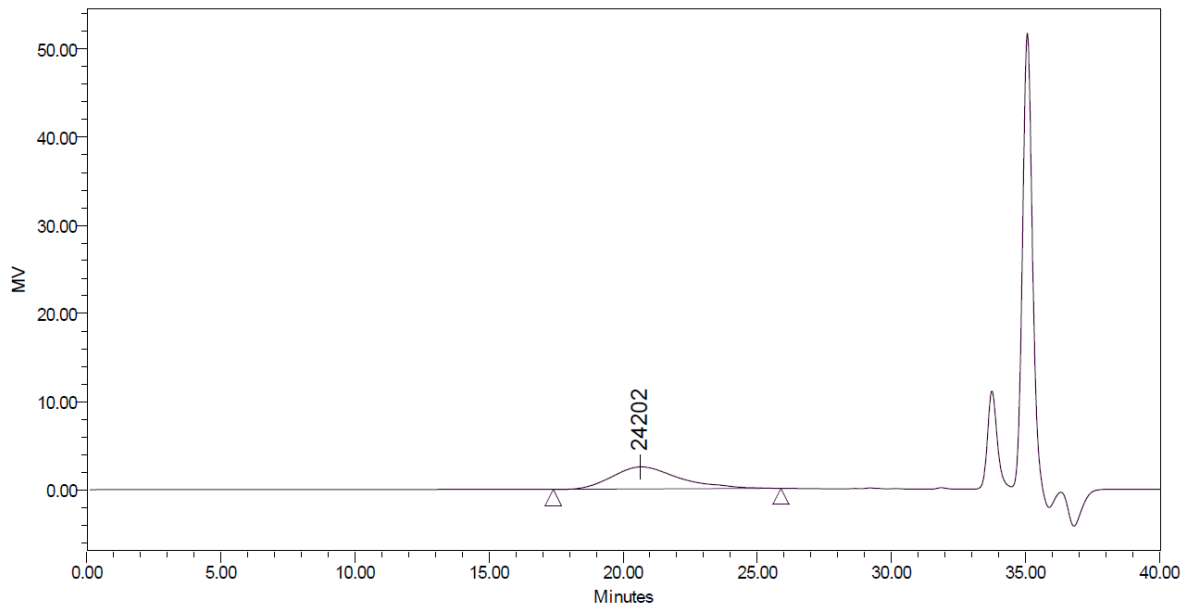


Table 1 entry 5-1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	17654	23457	24202	29032	34518	1.328726	1.237686	1.471546

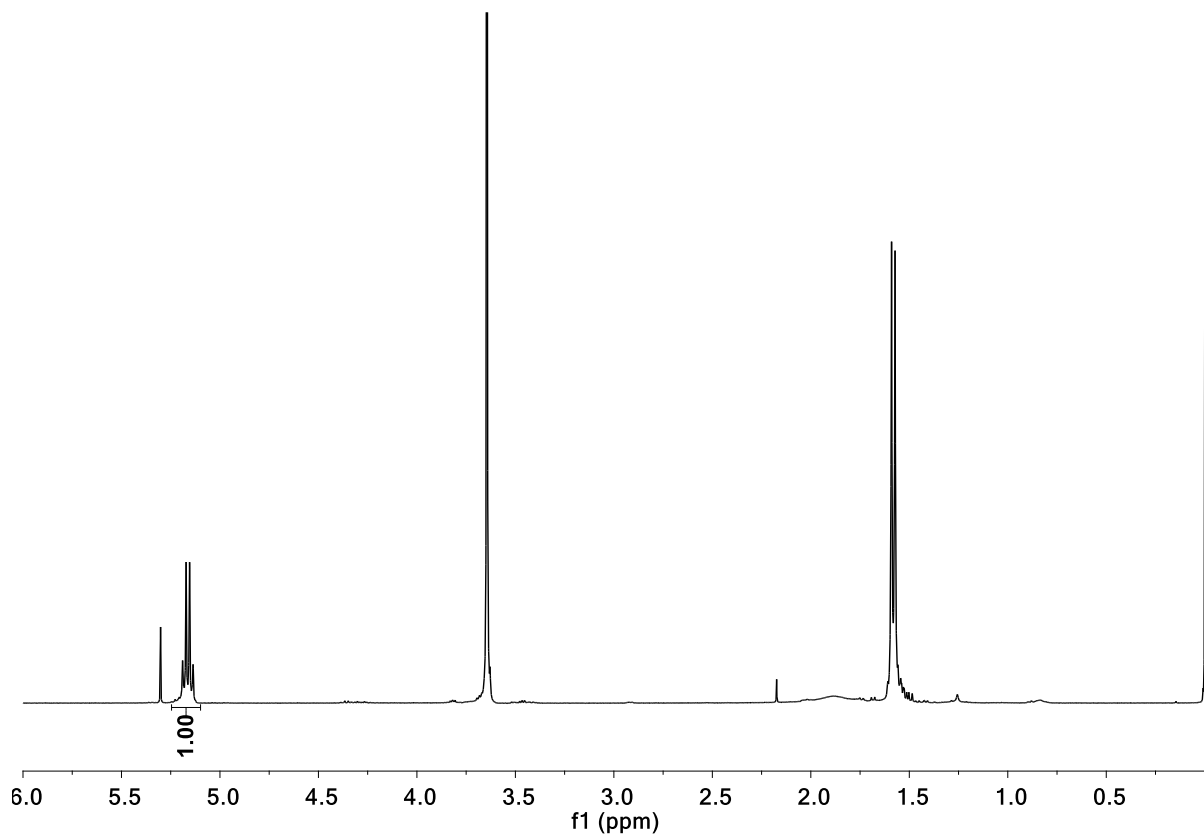
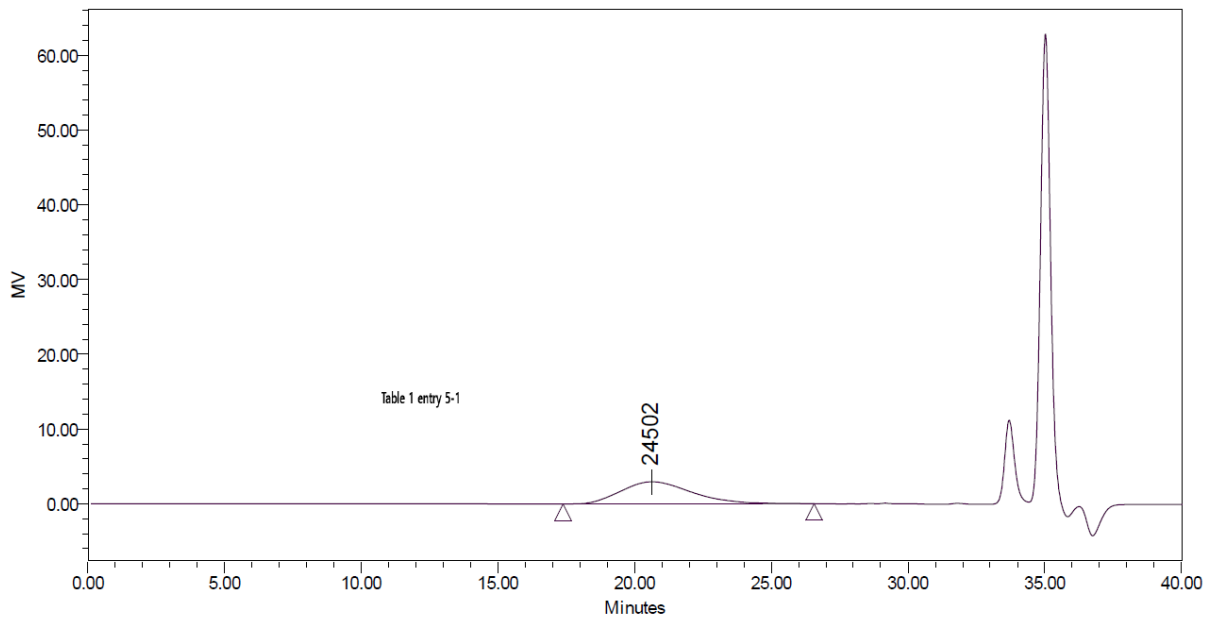


Table 1 entry 5-2



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		18116	24185	24502	30027	35835	1.334755	1.241544	1.481702

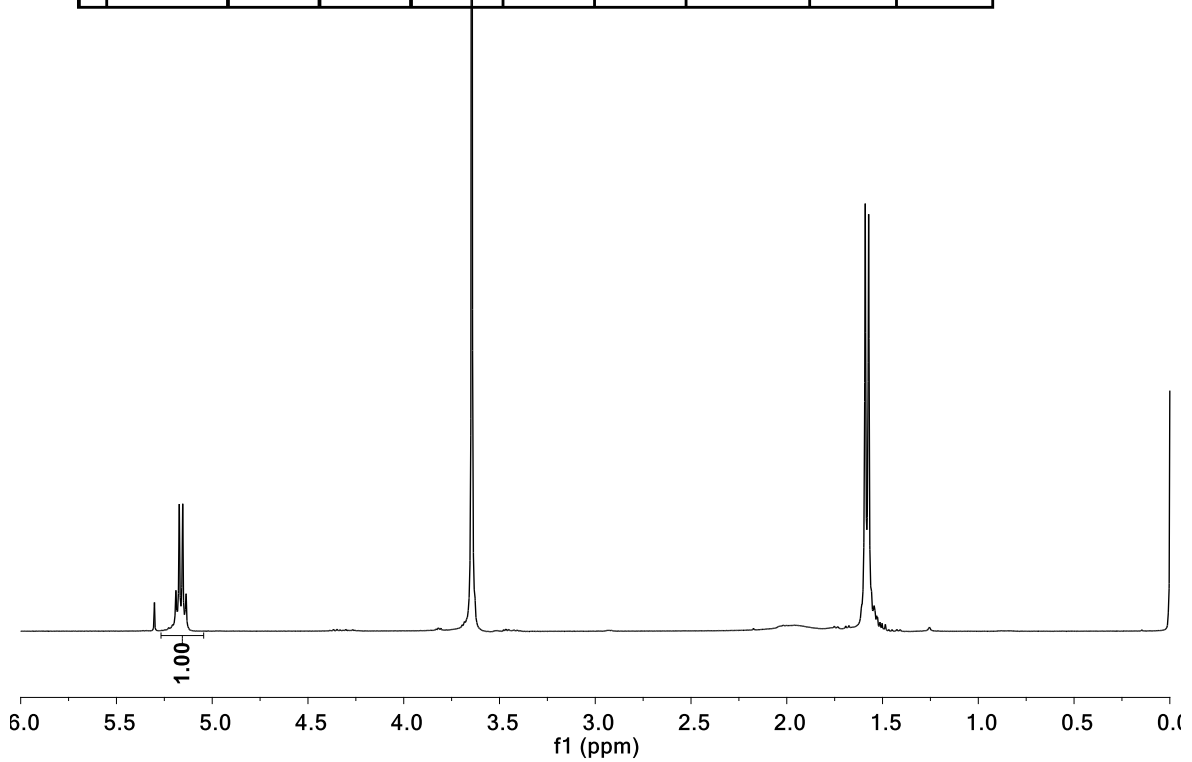
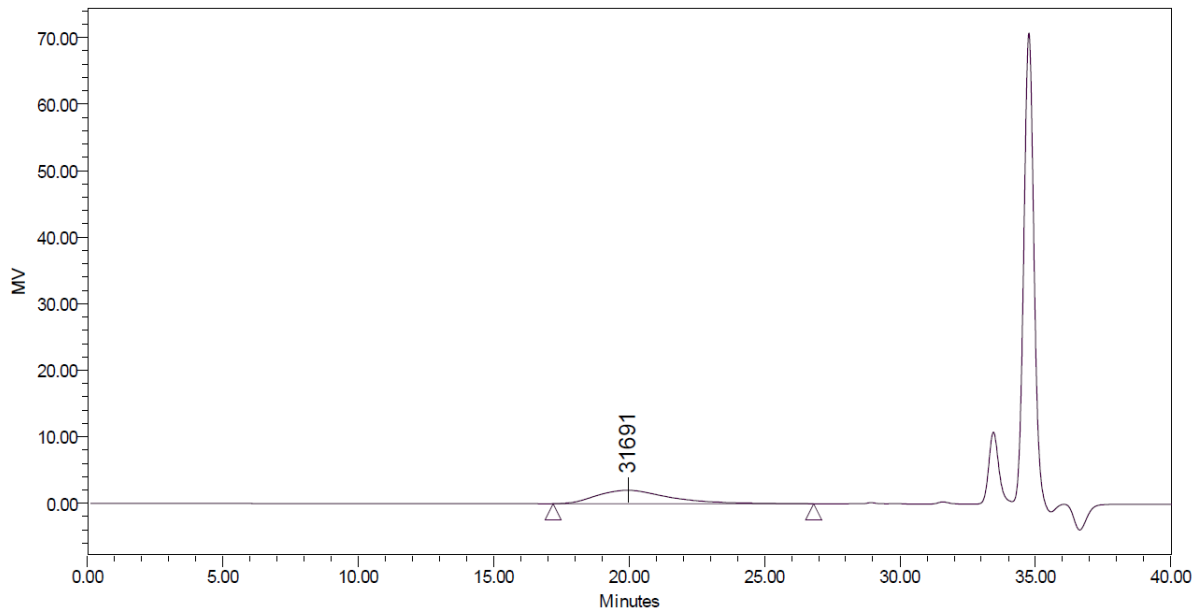


Table 1 entry 6-1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	21180	31356	31691	40616	49880	1.480433	1.295324	1.590751

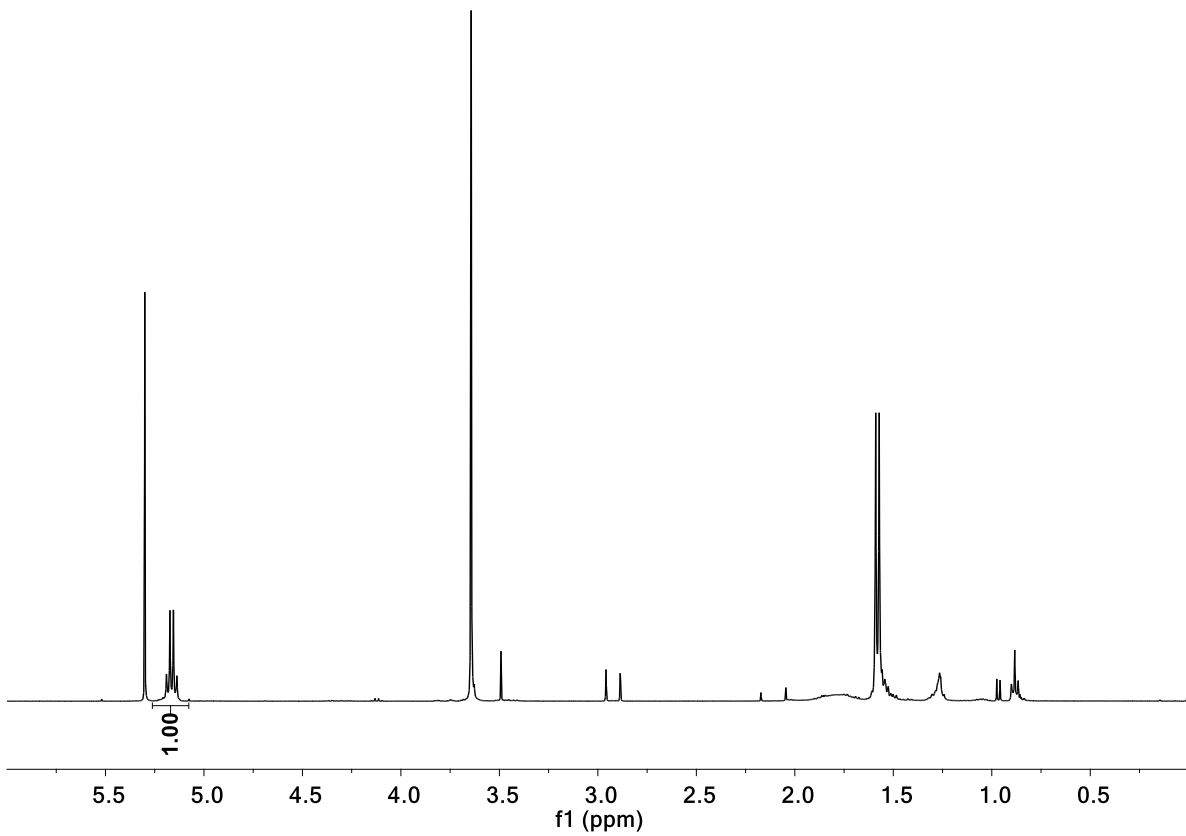
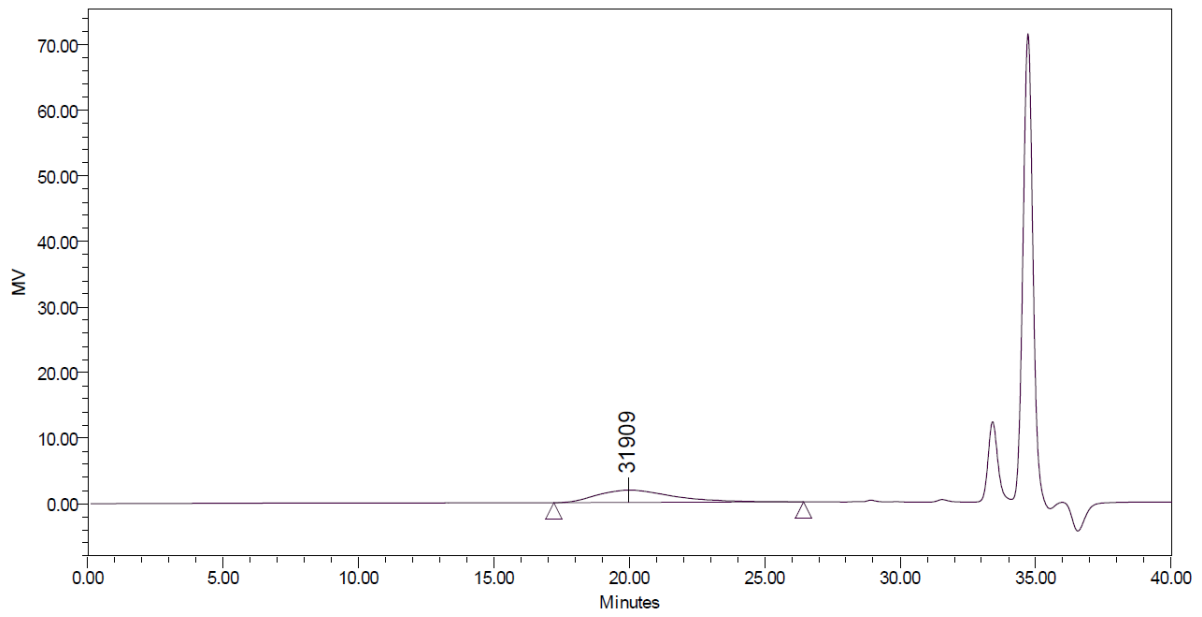


Table 1 entry 6-2



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	21152	30782	31909	39936	49009	1.455250	1.297404	1.592148

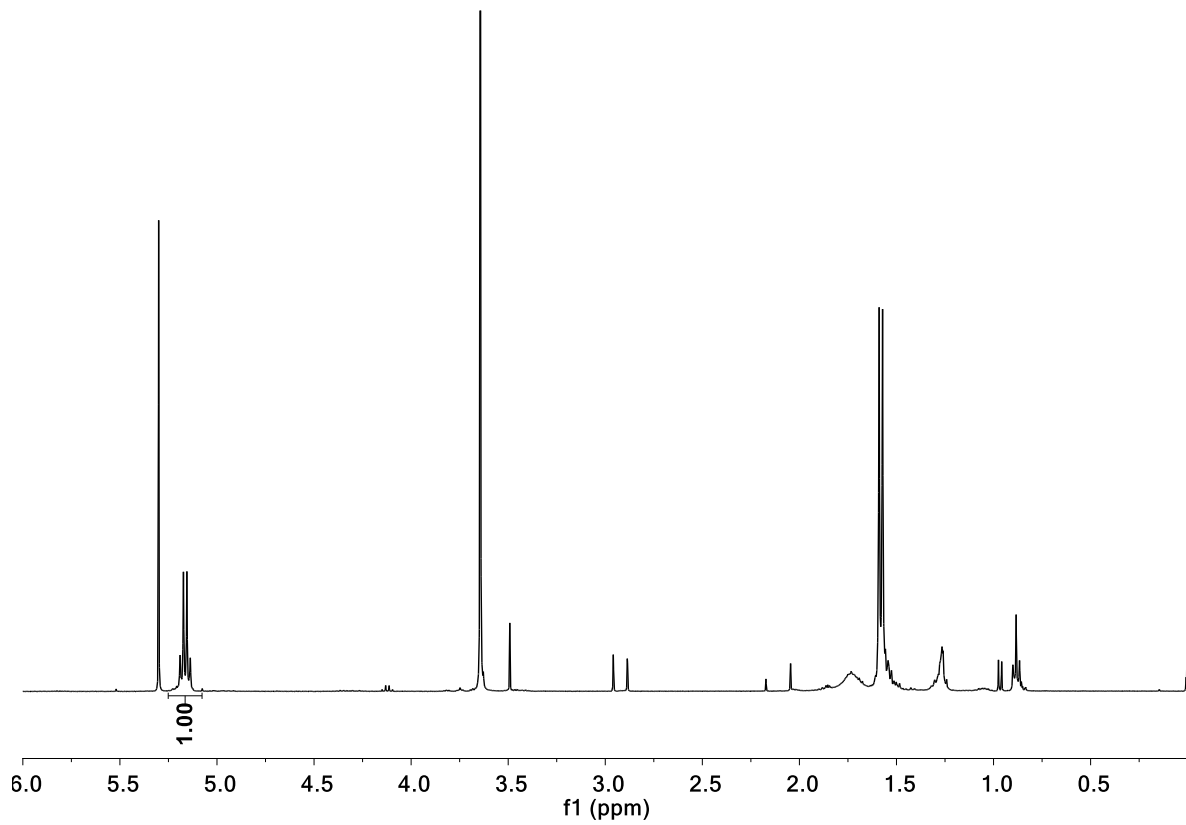
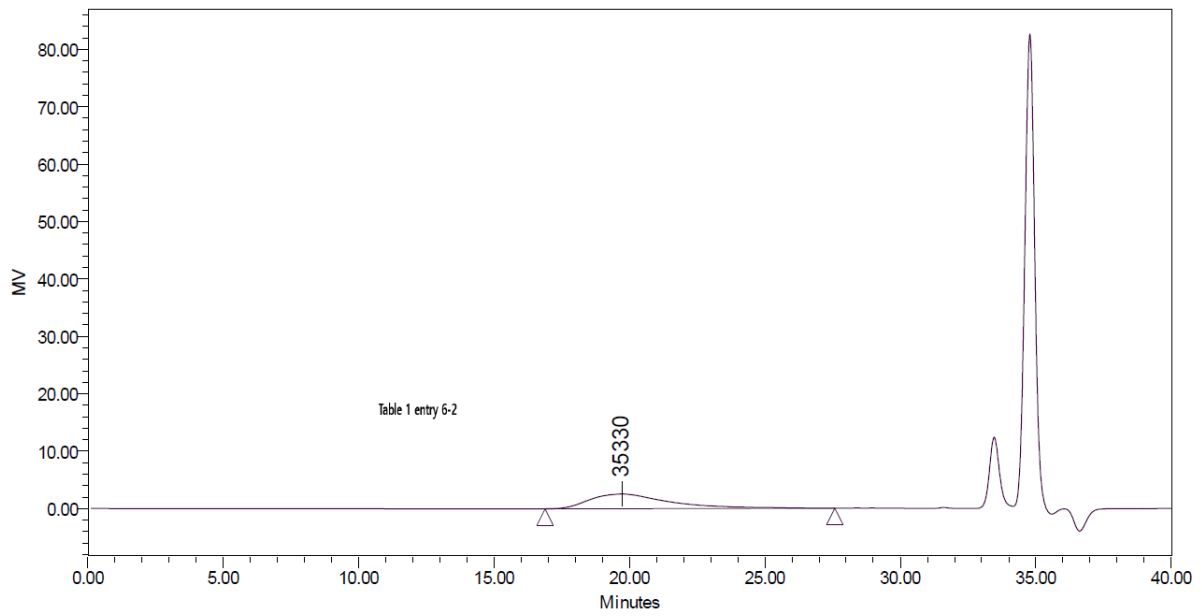


Table 1 entry 7-1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	20079	33579	35330	45400	56935	1.672342	1.352024	1.695541

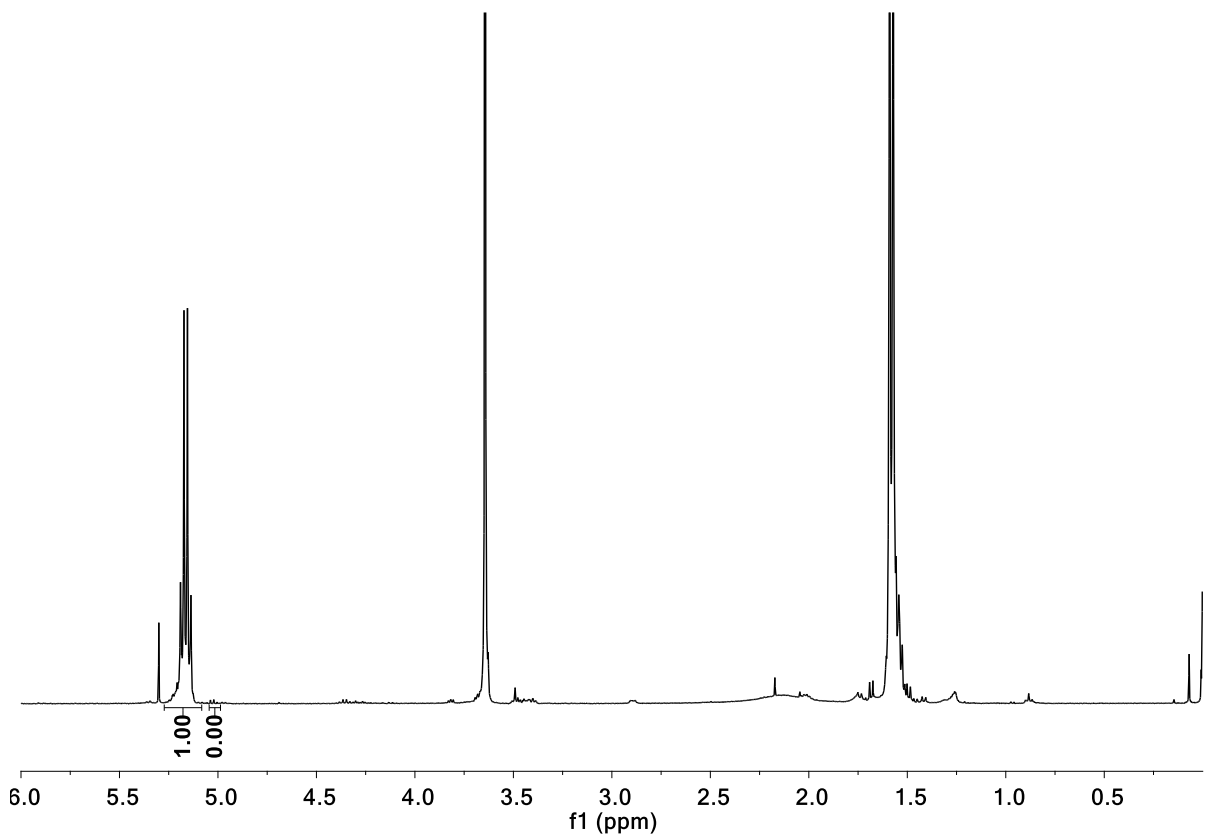
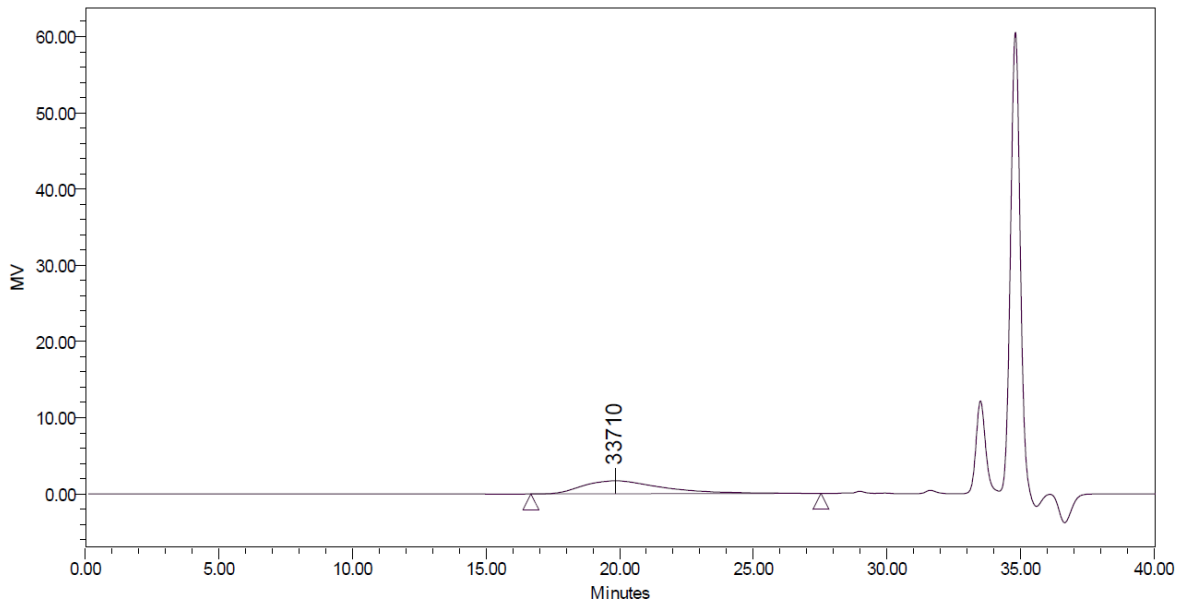


Table 1 entry 7-2



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	19673	32176	33710	43557	54827	1.635586	1.353704	1.703939

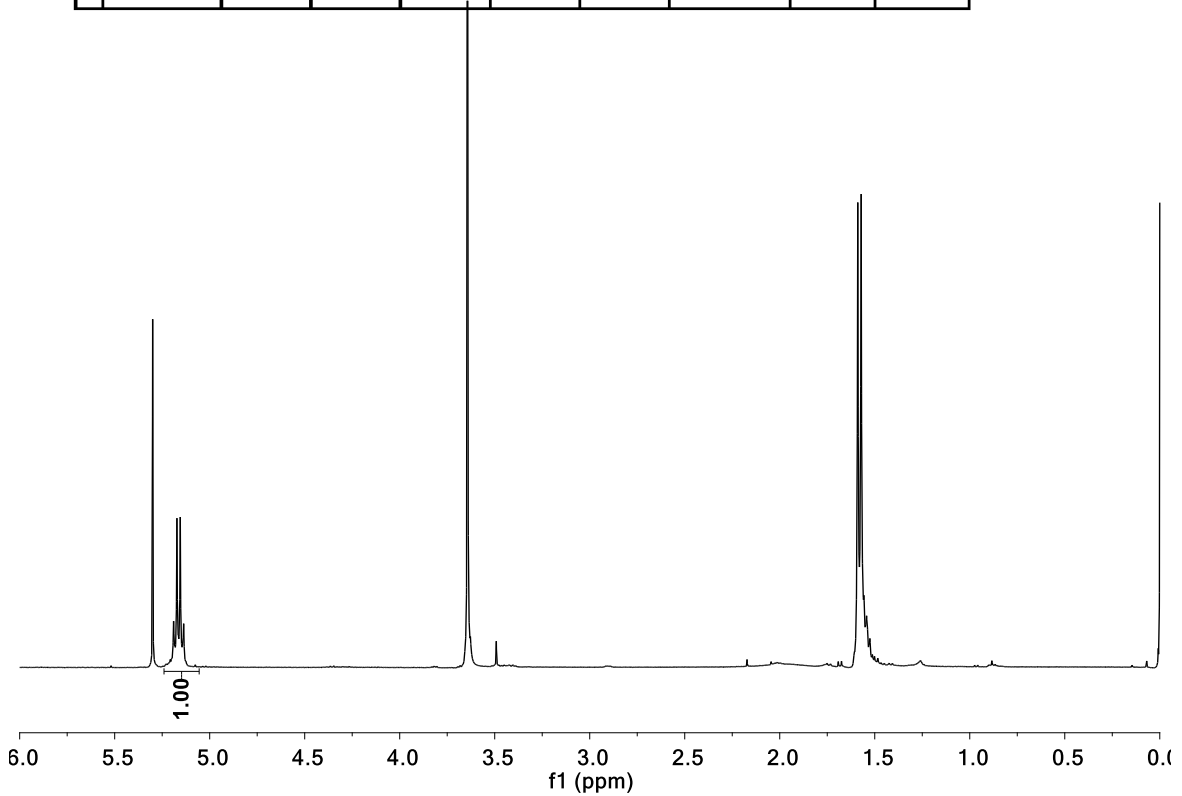
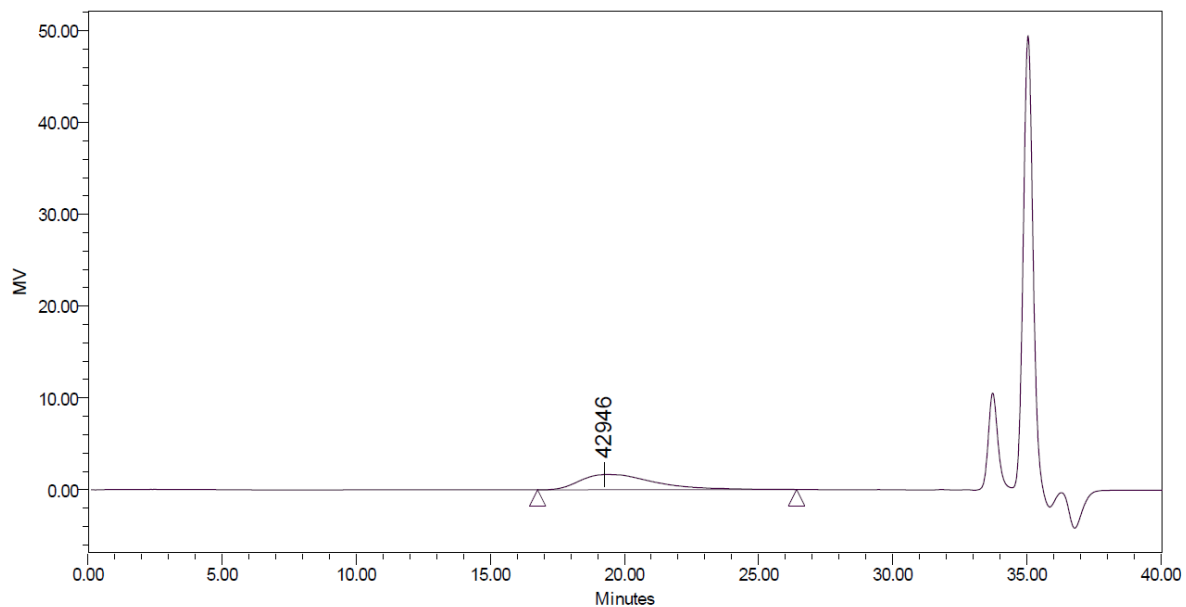


Table 1 entry 8-1



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		25420	37413	42946	48749	60354	1.471764	1.303013	1.613196

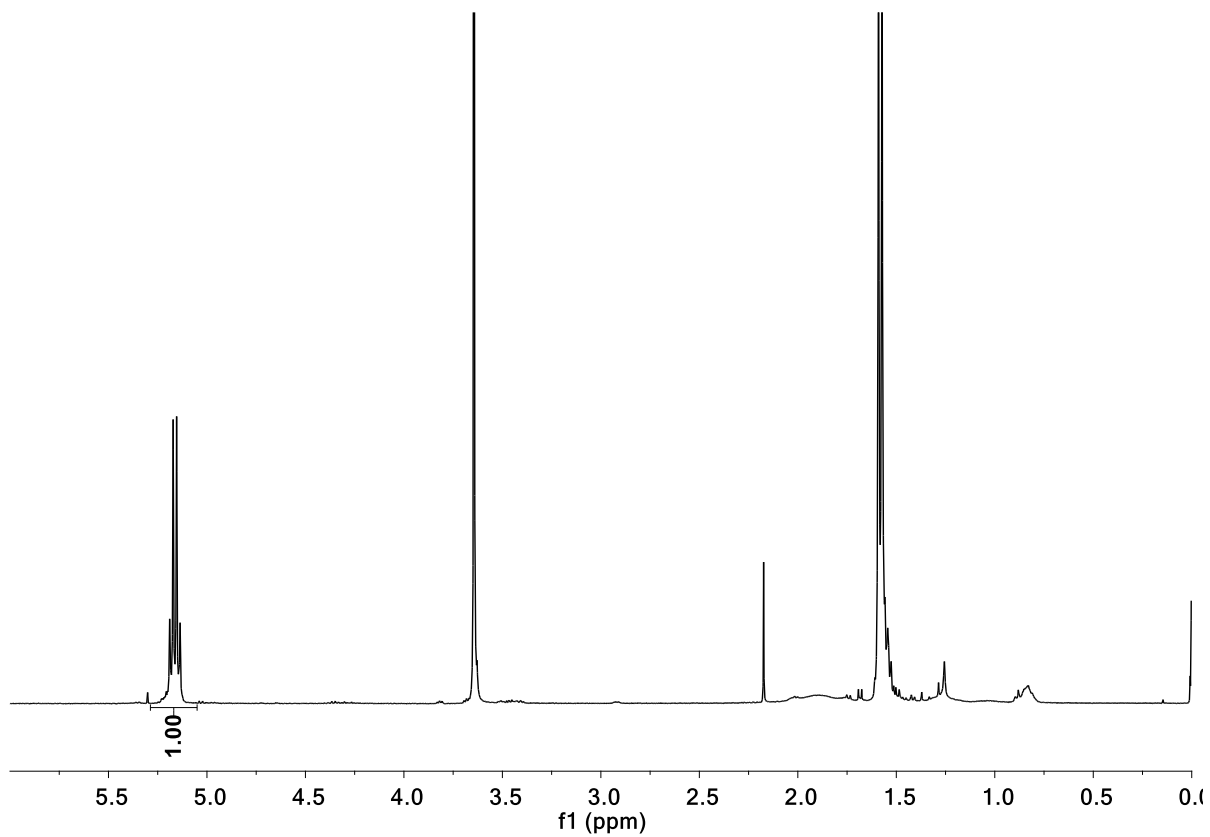
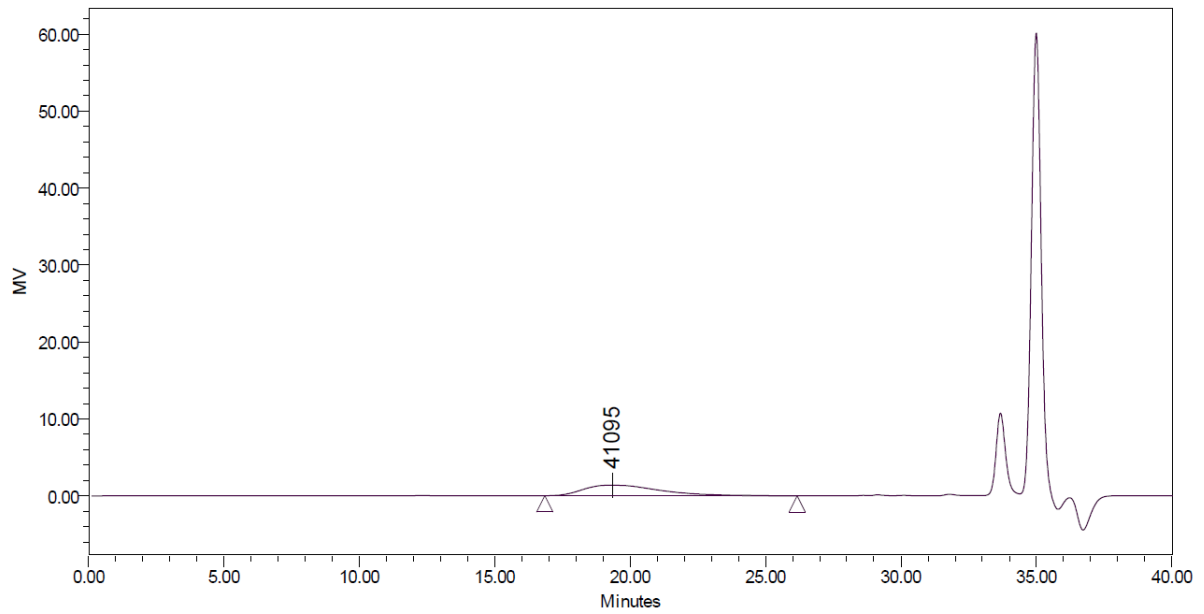


Table 1 entry 8-2



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	25990	38211	41095	50003	61945	1.470261	1.308589	1.621111

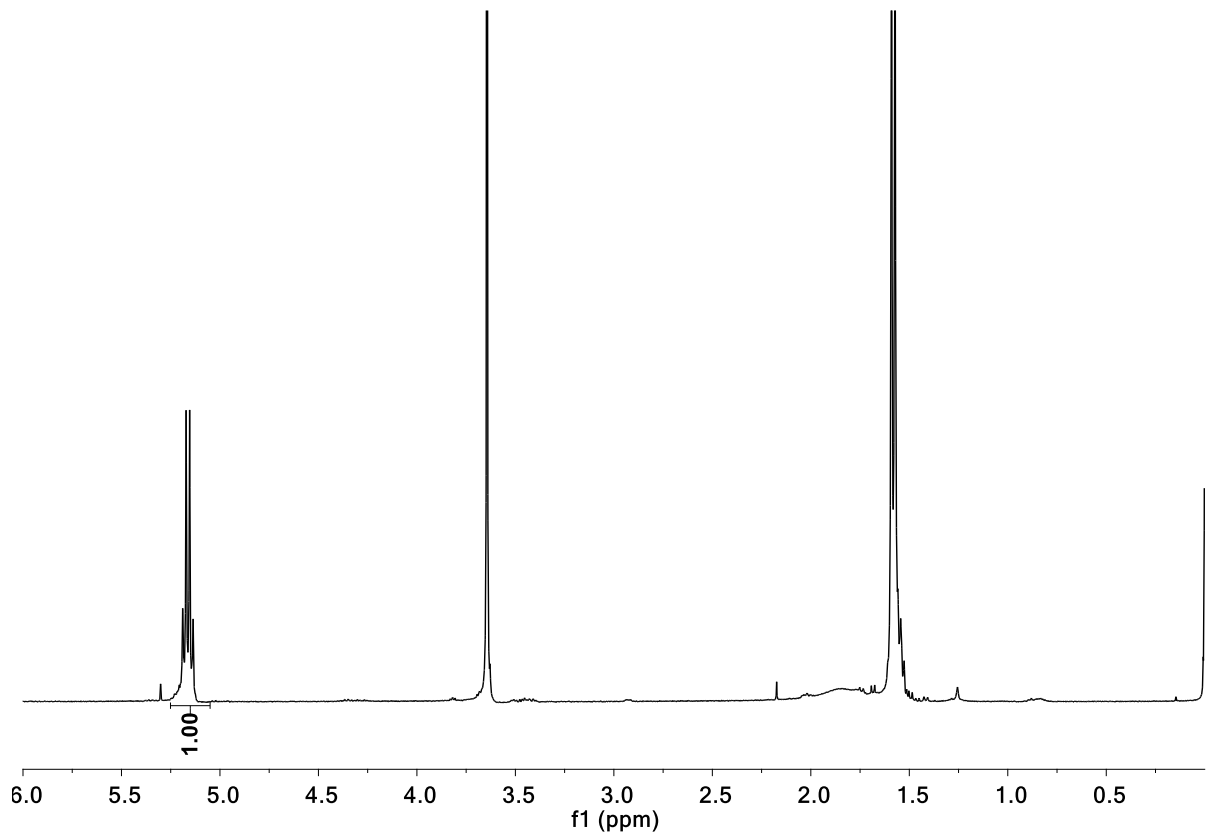
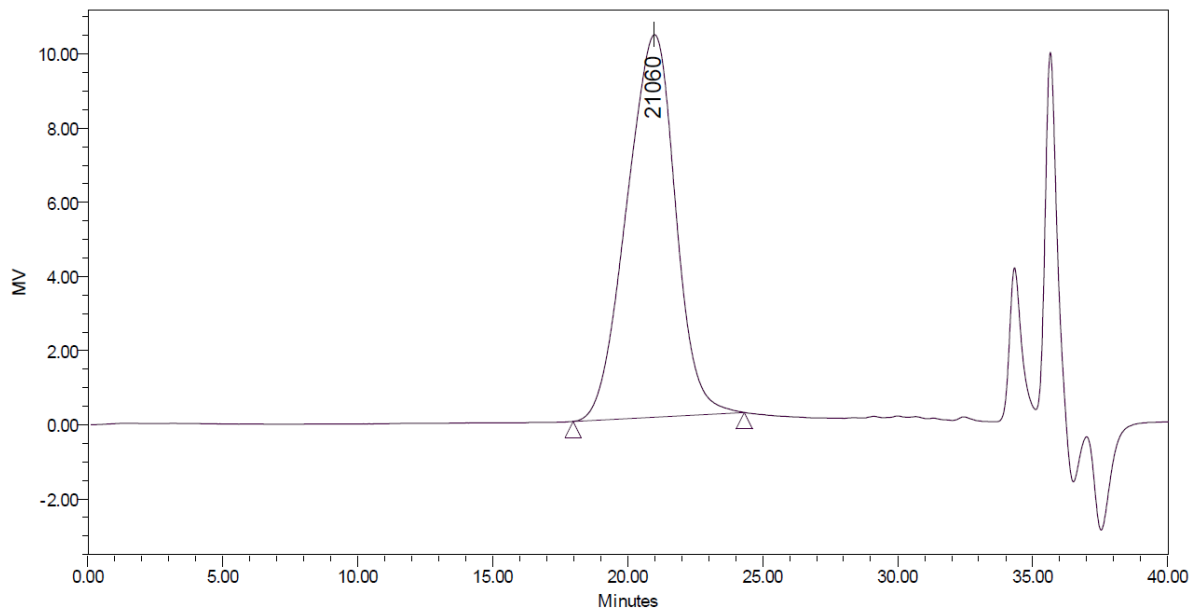


Table 1 entry 9-1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	20856	23589	21060	26605	29961	1.131045	1.127846	1.270107

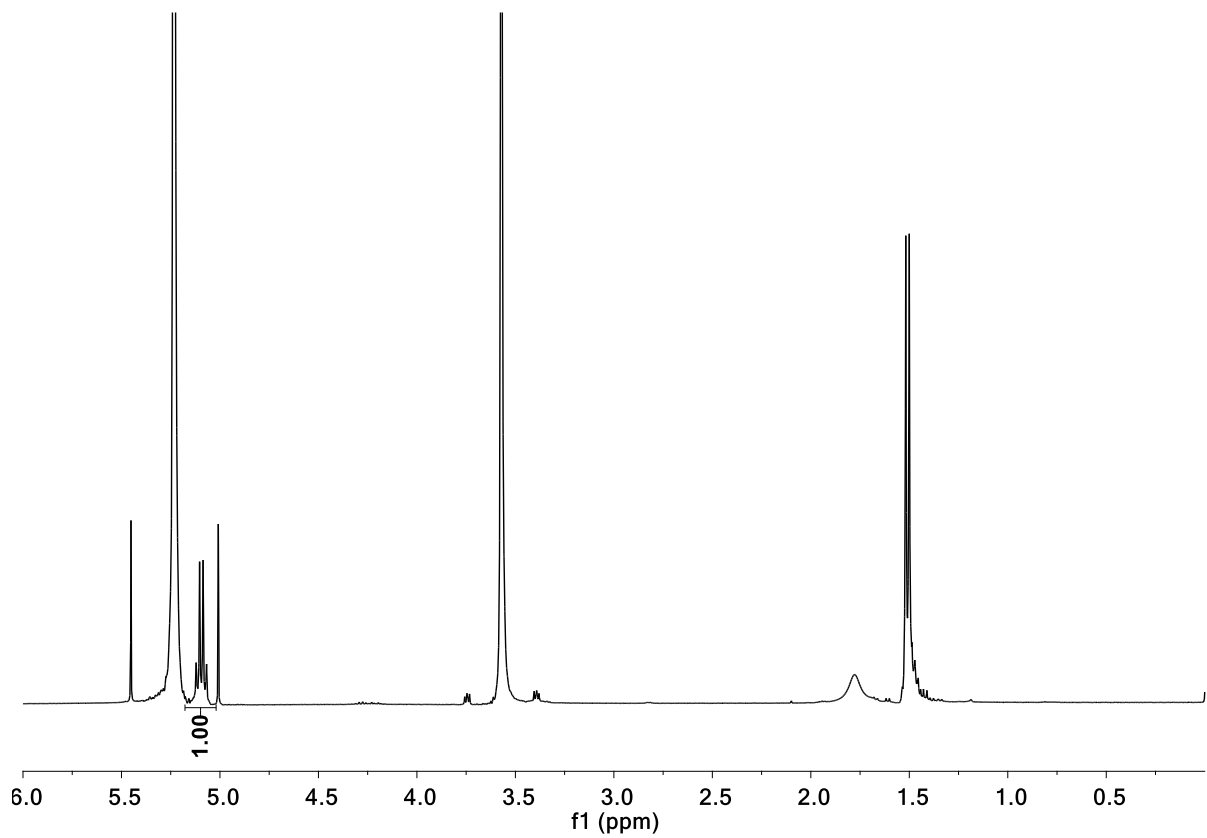
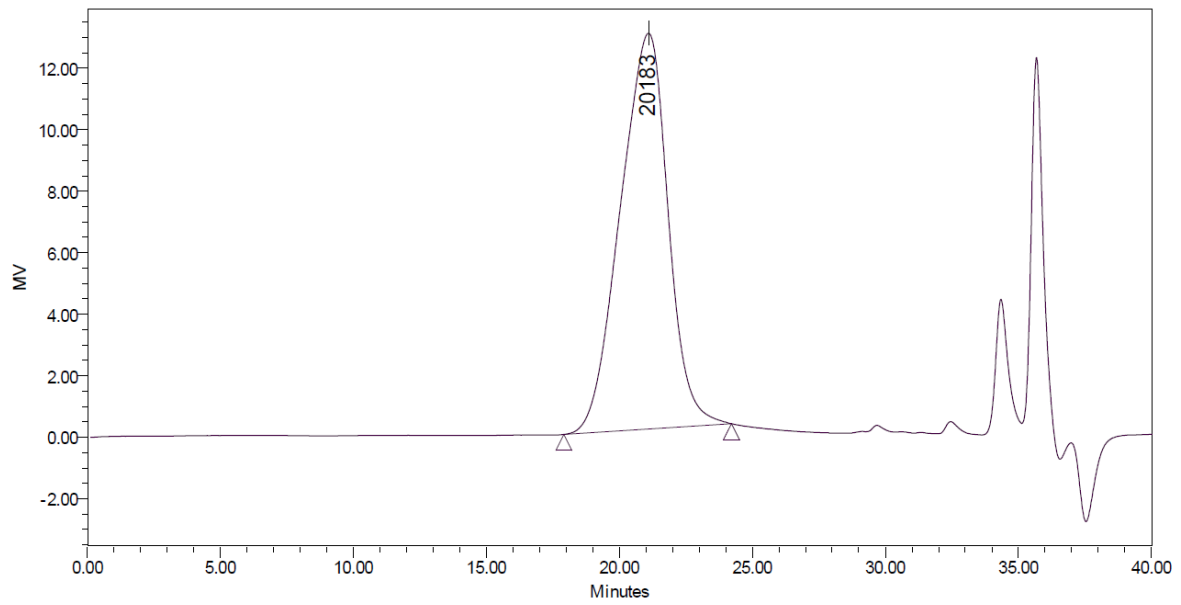


Table 1 entry 9-2



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	20447	23118	20183	26106	29468	1.130610	1.129288	1.274716

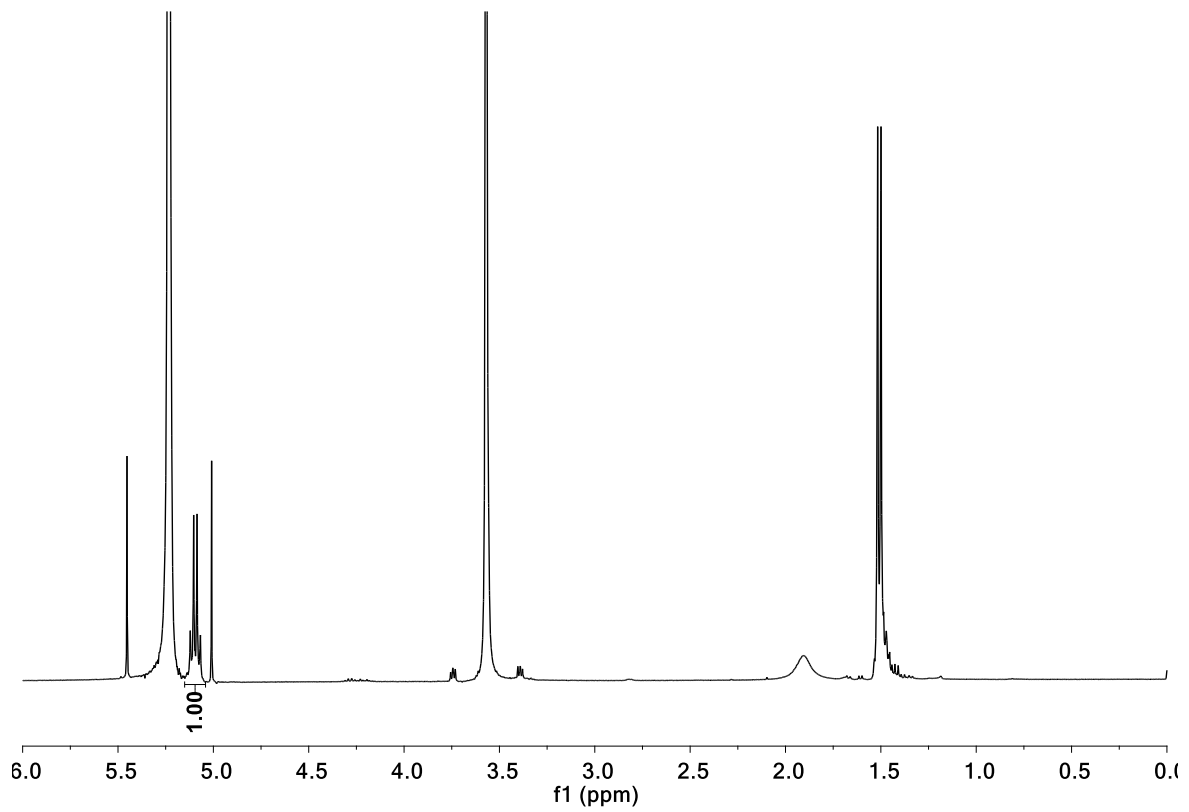
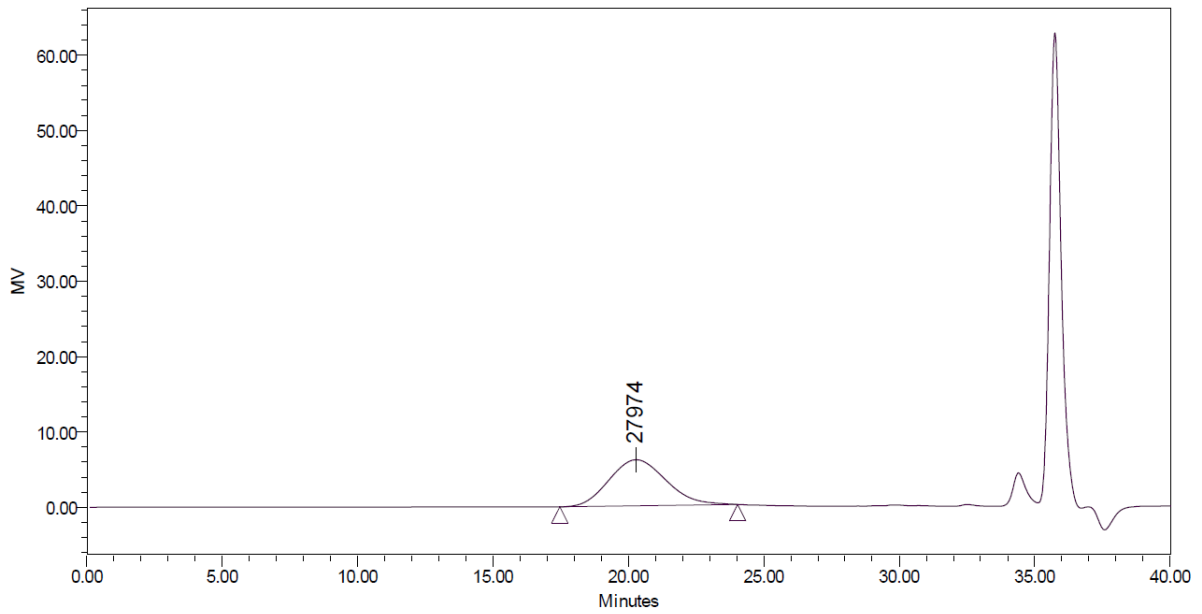


Table 1 entry 10-1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	24518	28984	27974	33791	39034	1.182145	1.165848	1.346714

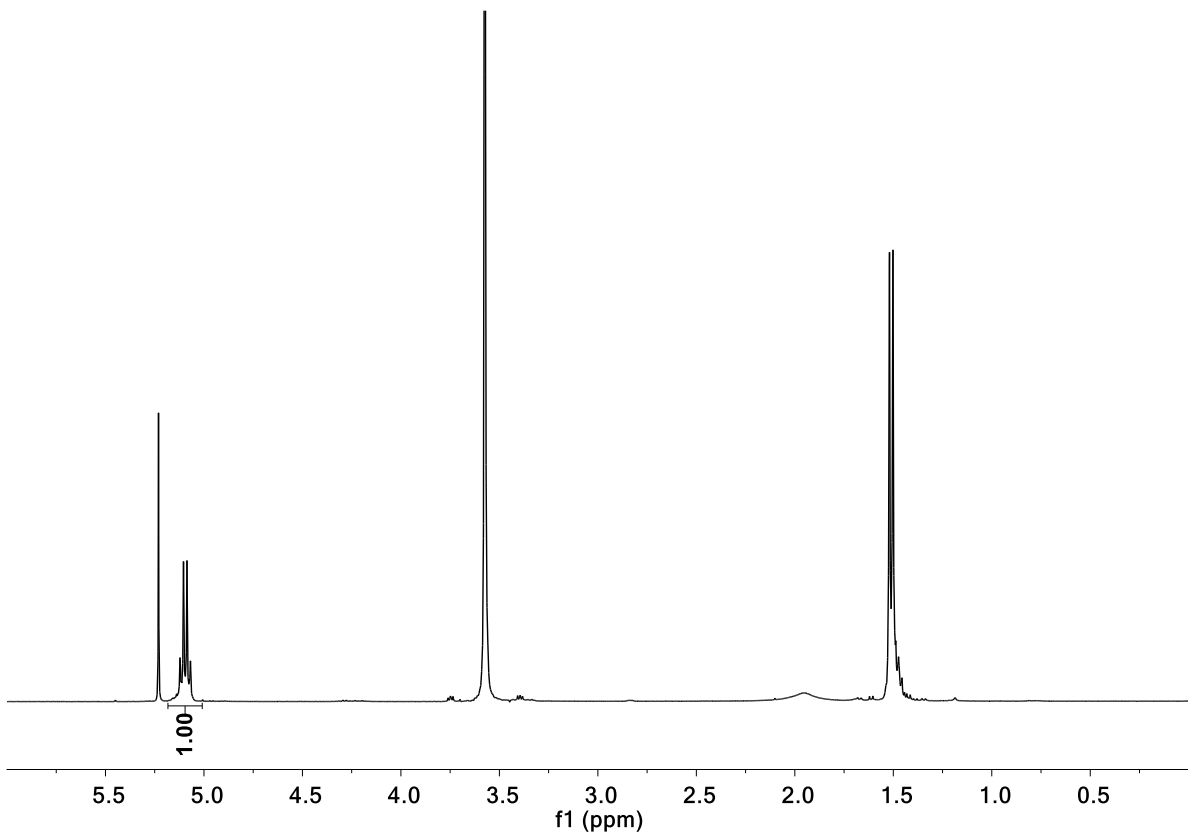
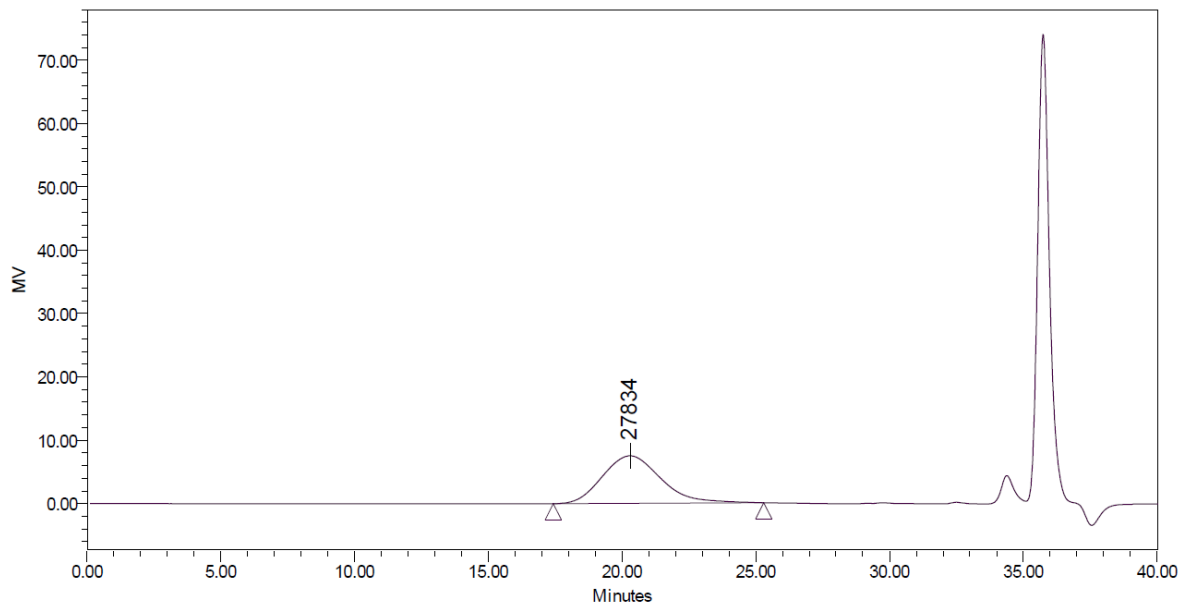


Table 1 entry 10-2



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	23260	28665	27834	33988	39627	1.232359	1.185695	1.382415

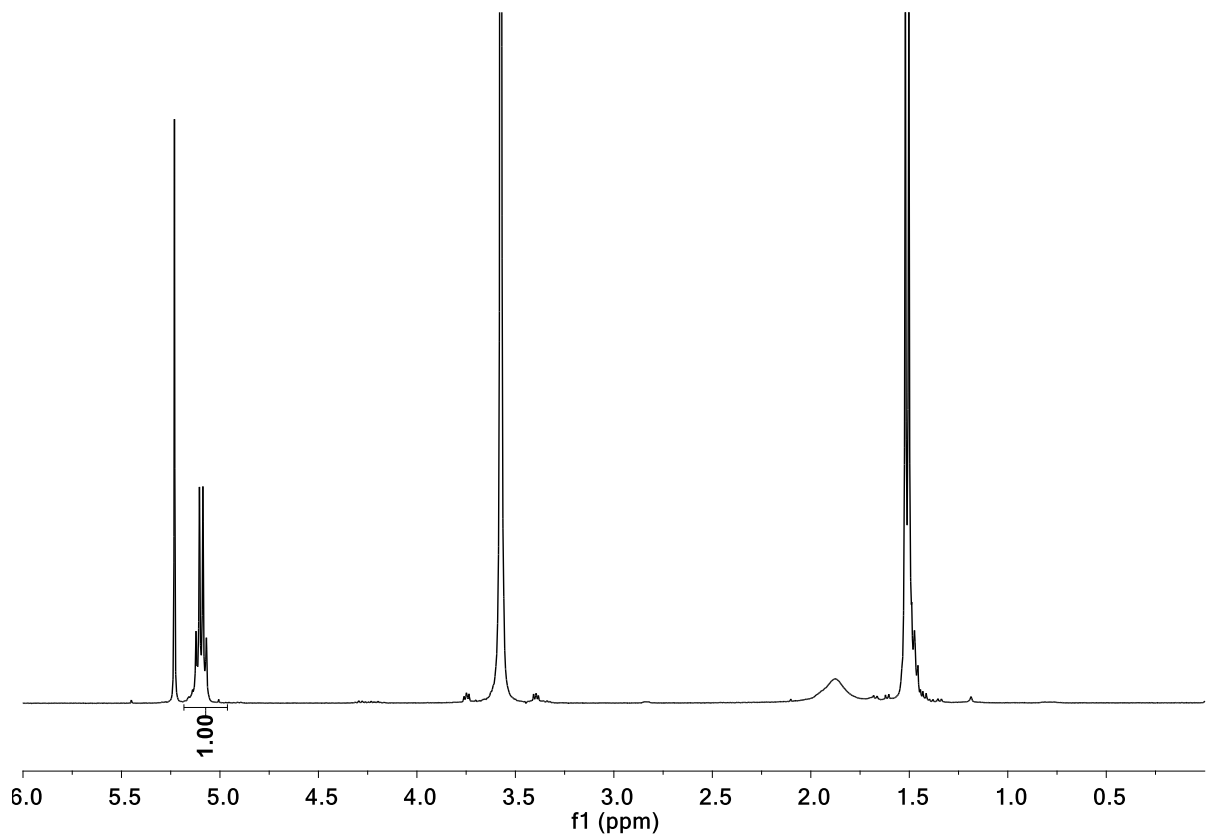
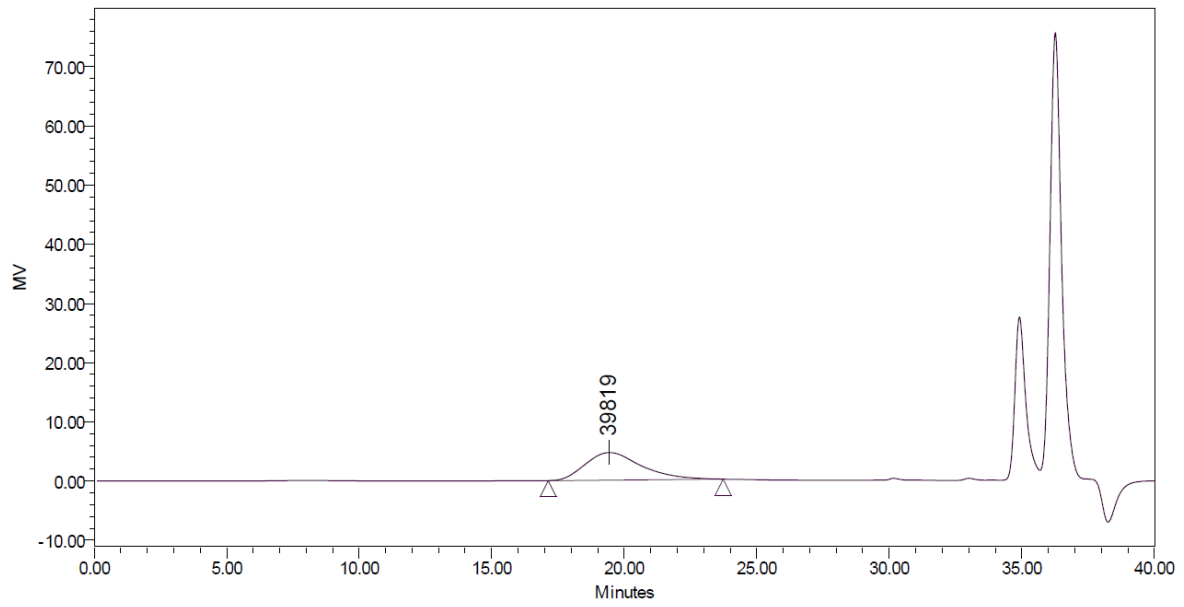


Table 1 entry 11-1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	31987	39227	39819	46763	54650	1.226329	1.192116	1.393182

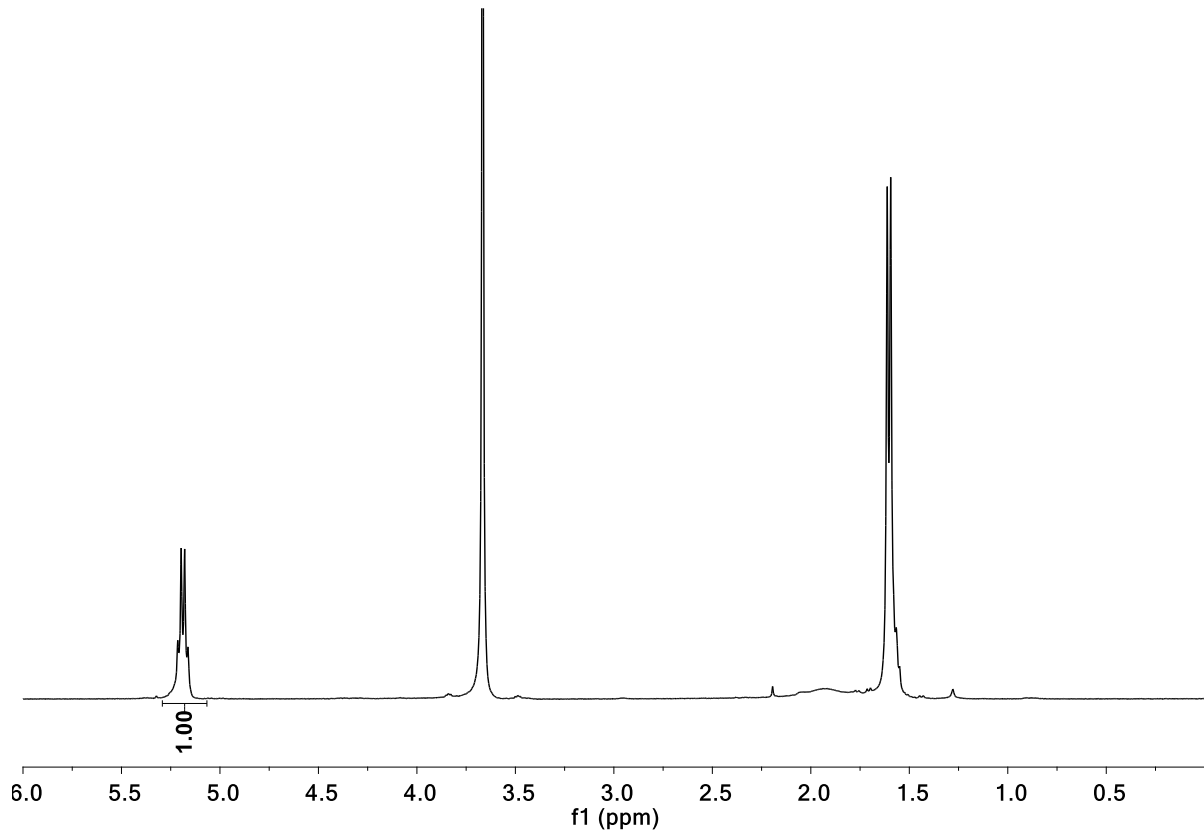
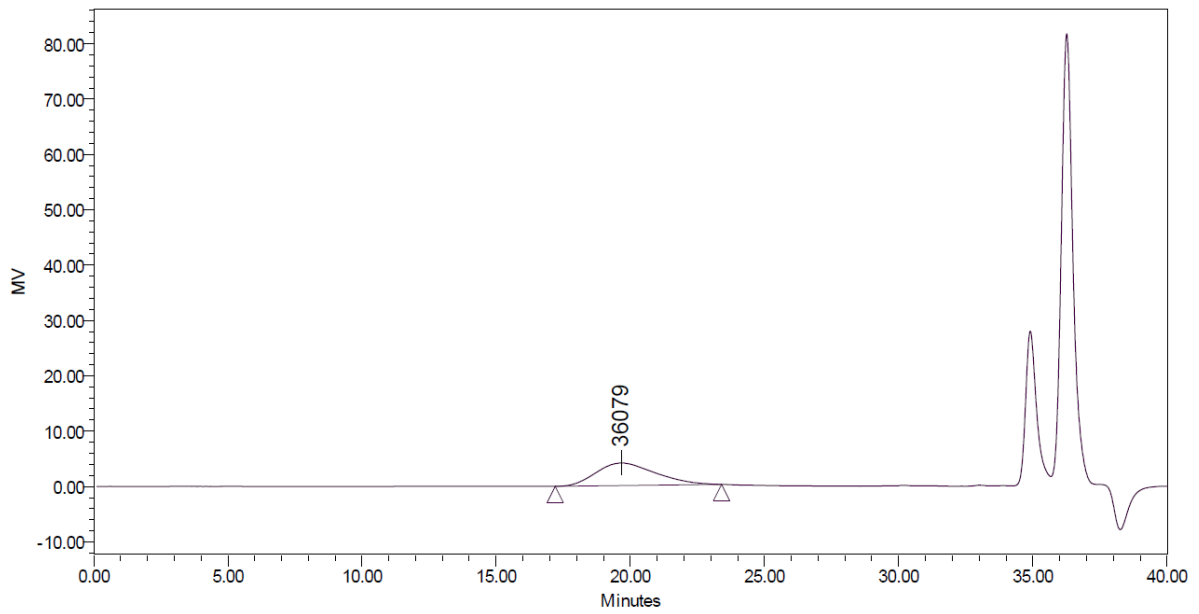


Table 1 entry 11-2



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	29403	35676	36079	42525	49835	1.213325	1.191968	1.396880

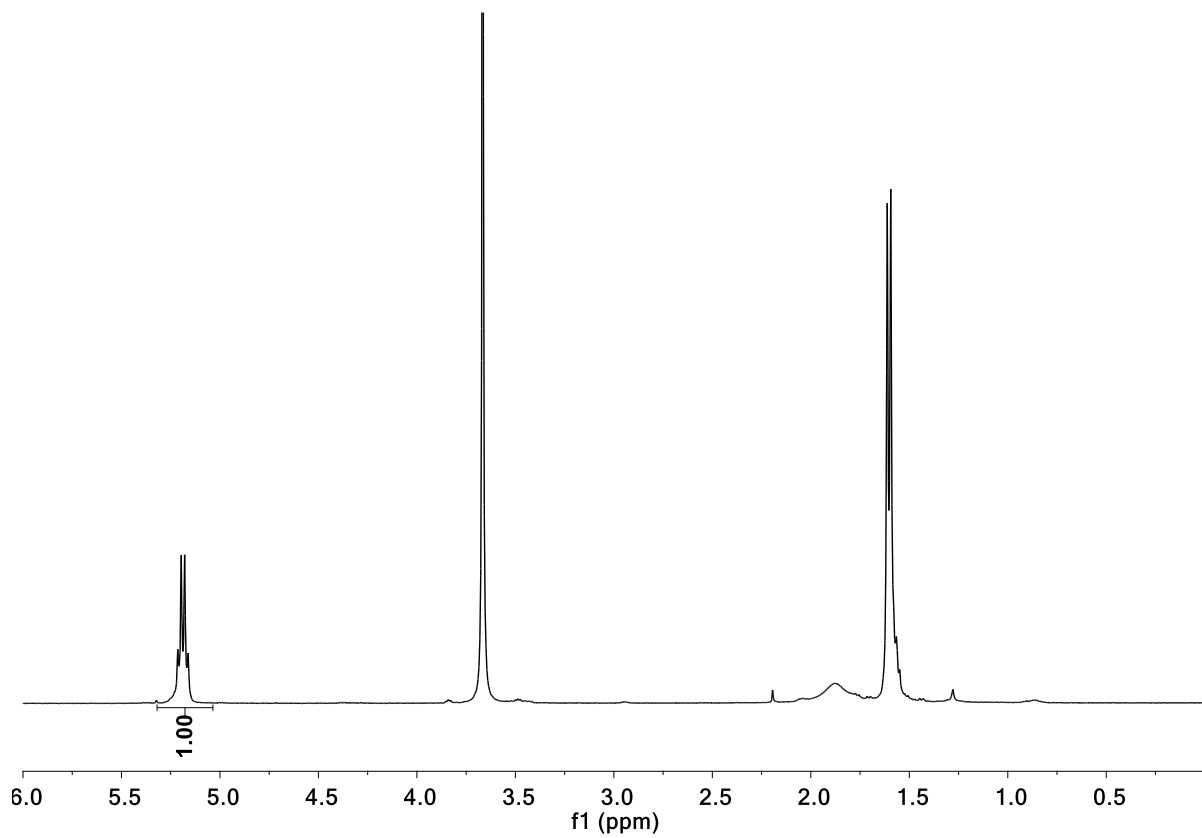
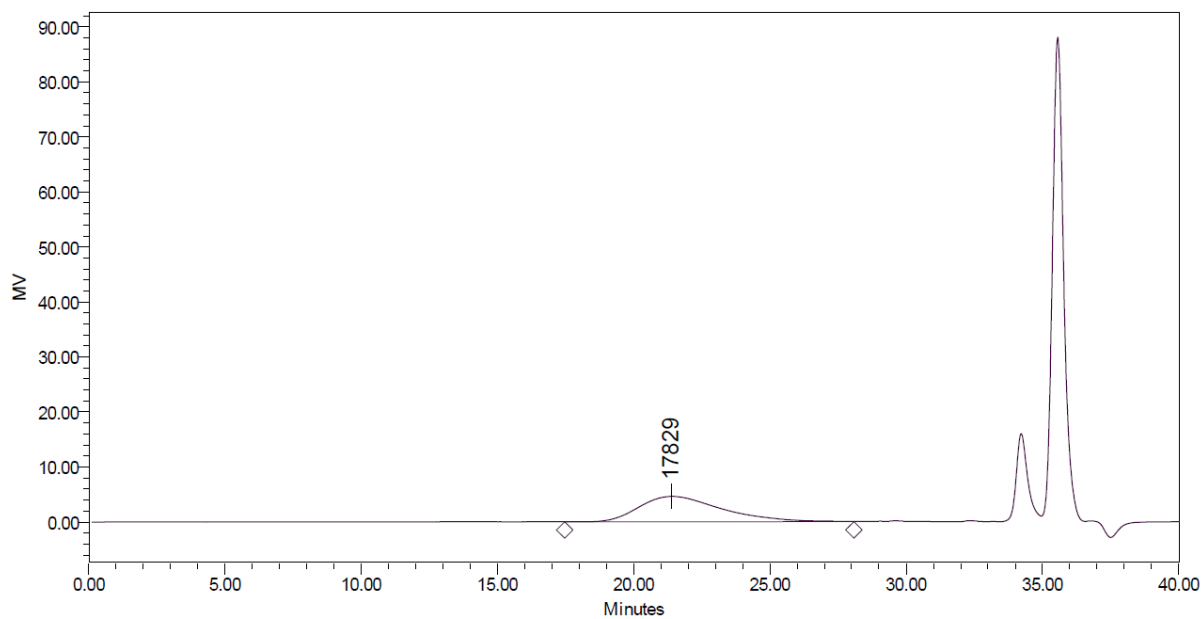


Table 2 entry 1-1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	10765	16524	17829	21871	27118	1.534957	1.323552	1.641068

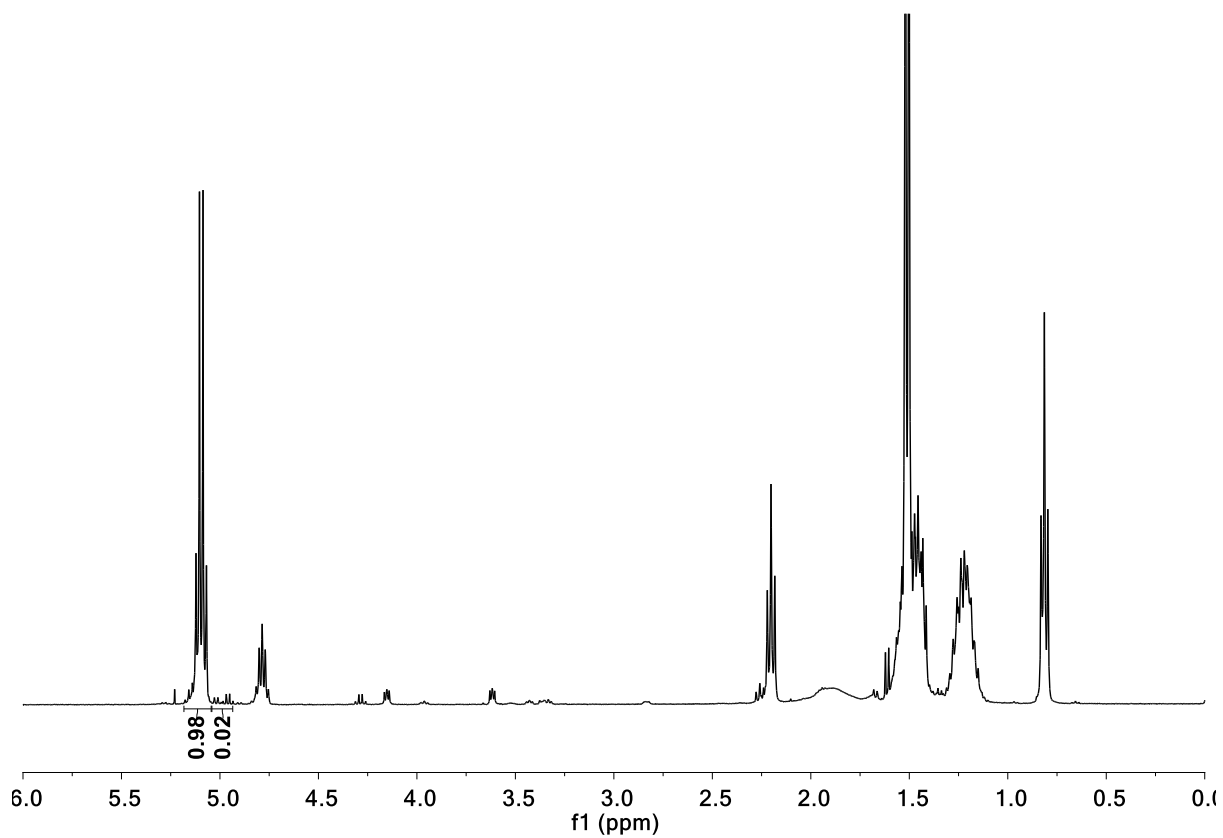
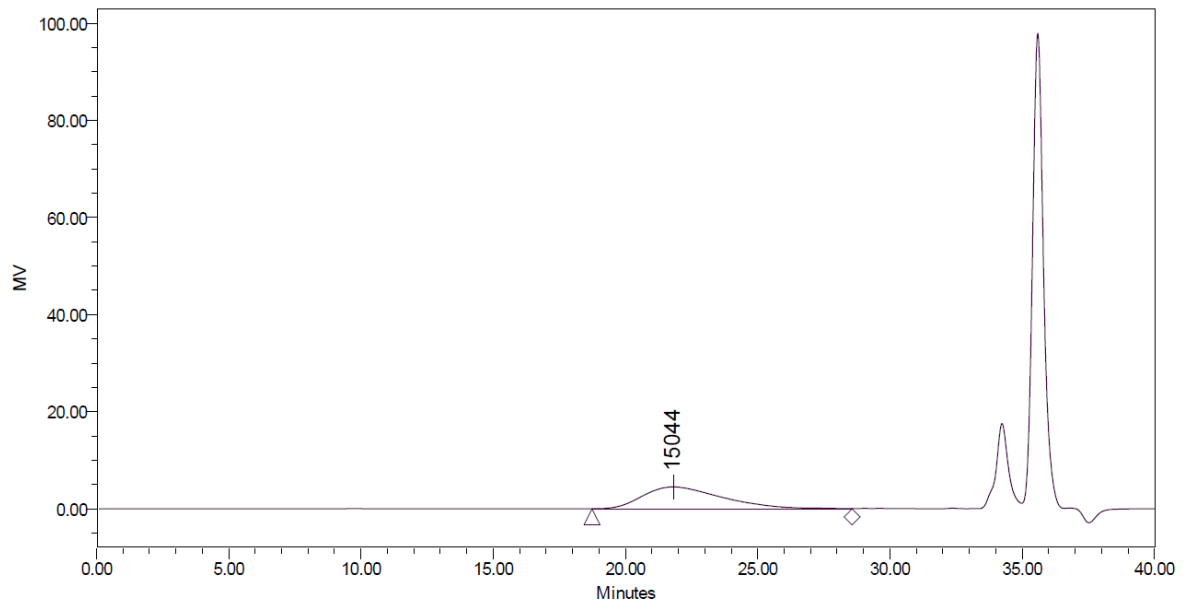


Table 2 entry 1-2



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	9040	13629	15044	17716	21212	1.507573	1.299868	1.556392

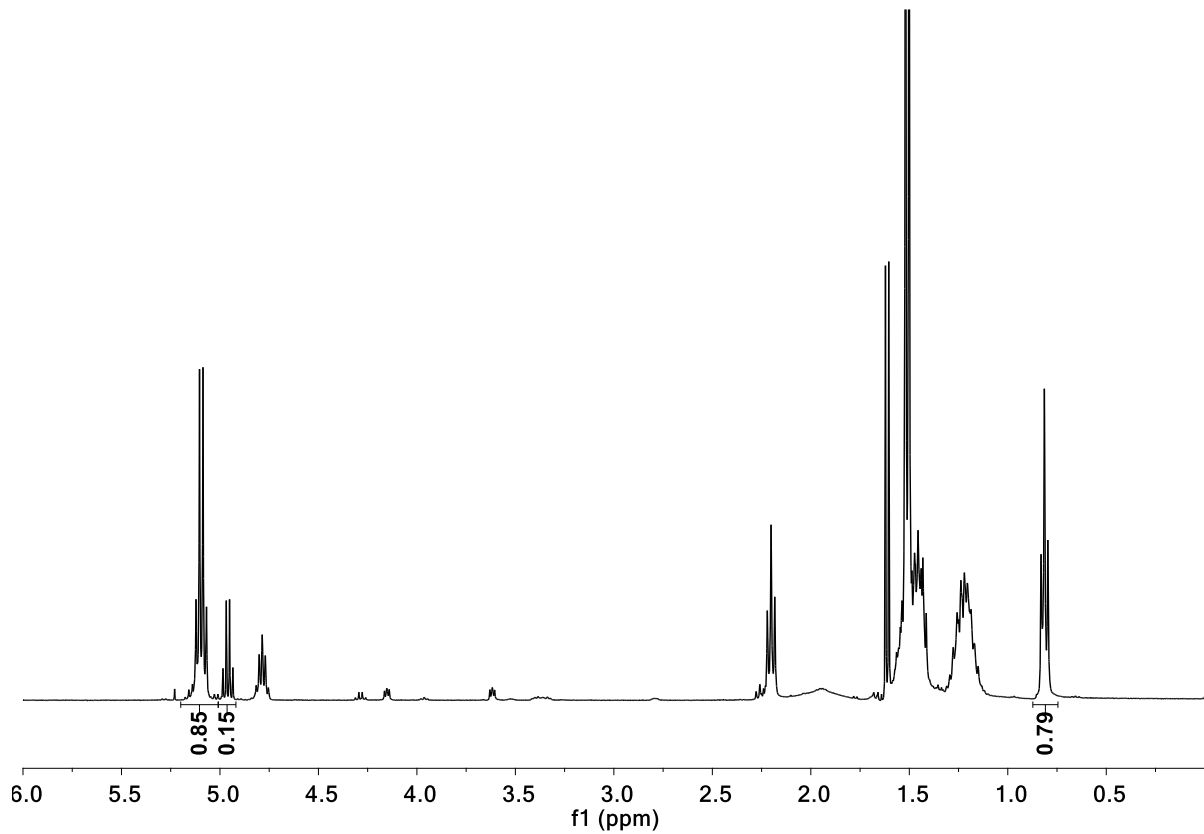
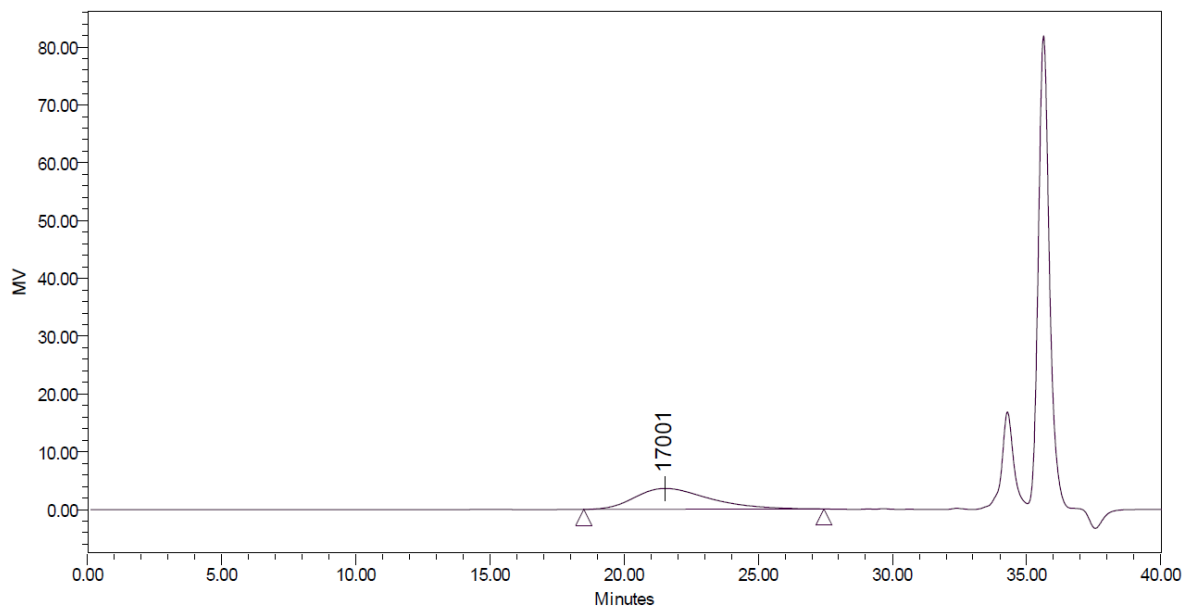


Table 2 entry 2-1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	11277	15848	17001	20066	23897	1.405396	1.266130	1.507844

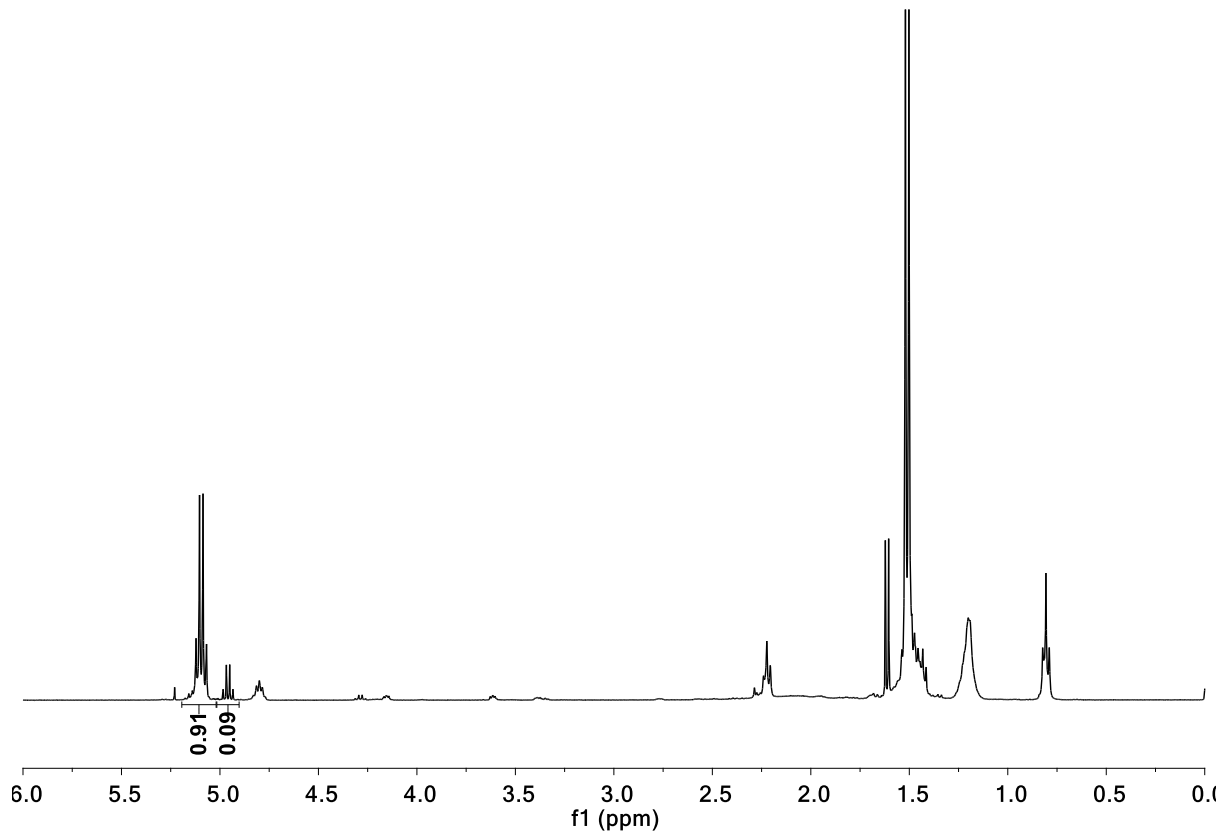
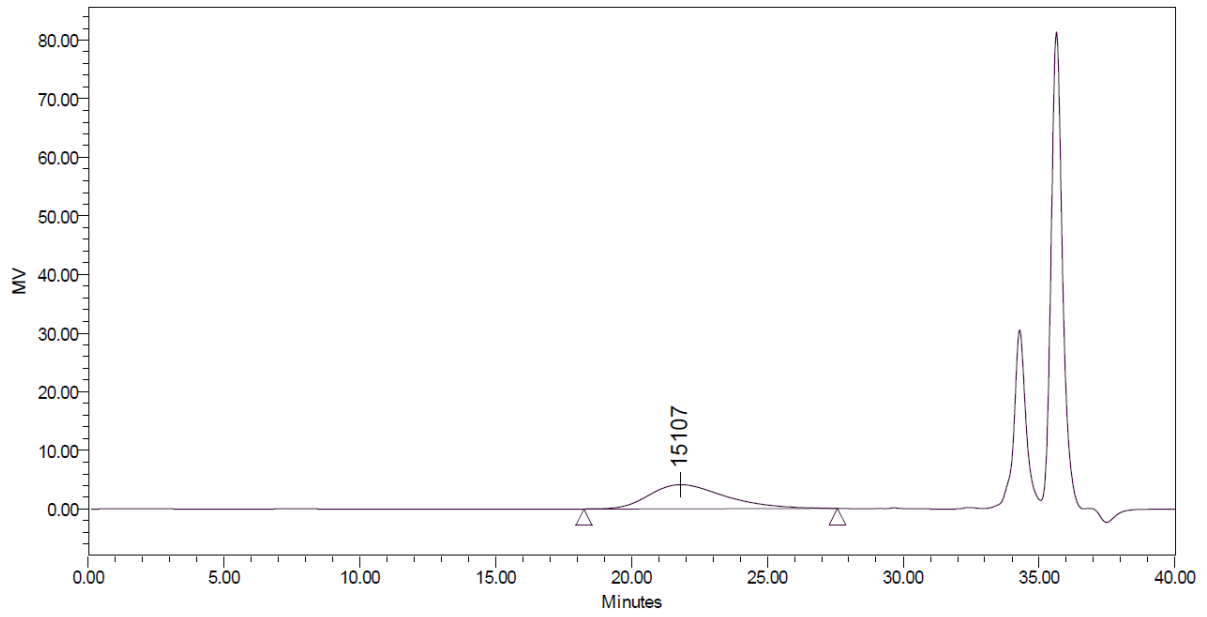


Table 2 entry 2-2



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	10137	14308	15107	18297	22074	1.411515	1.278794	1.542752

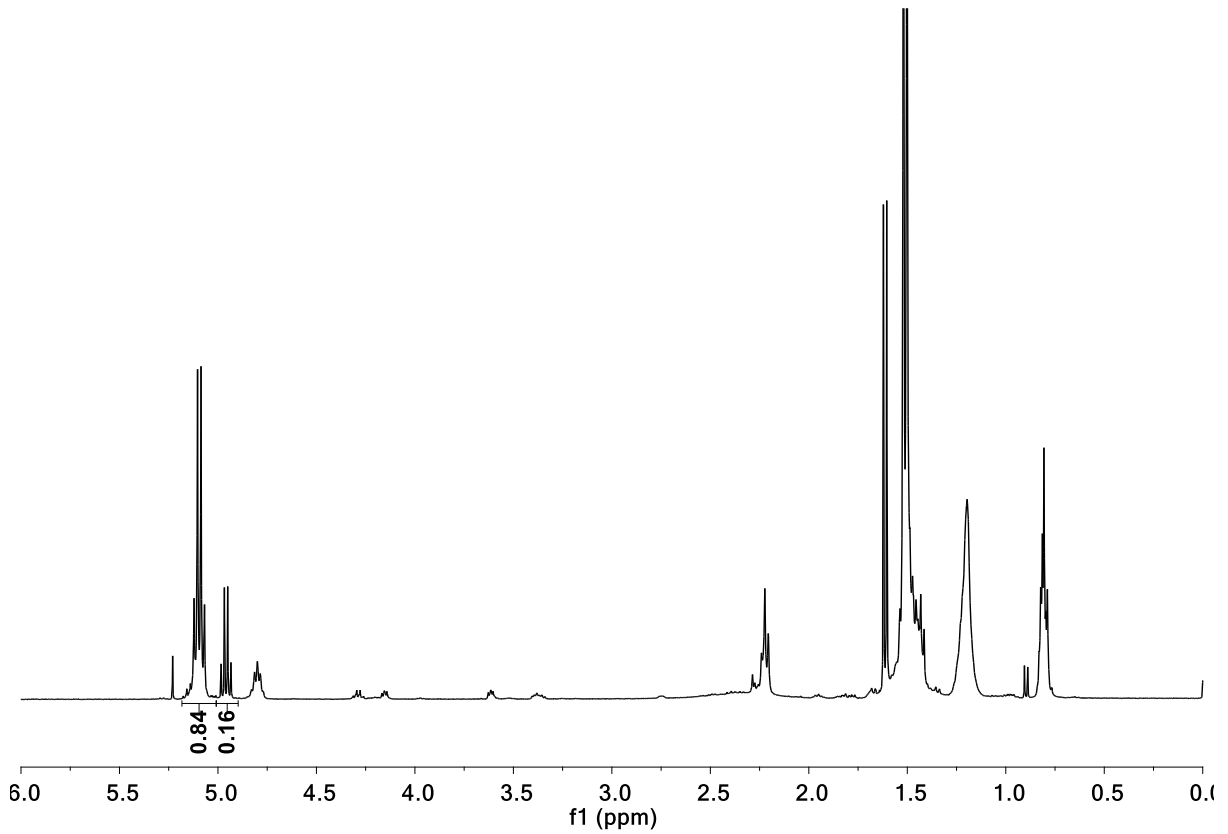
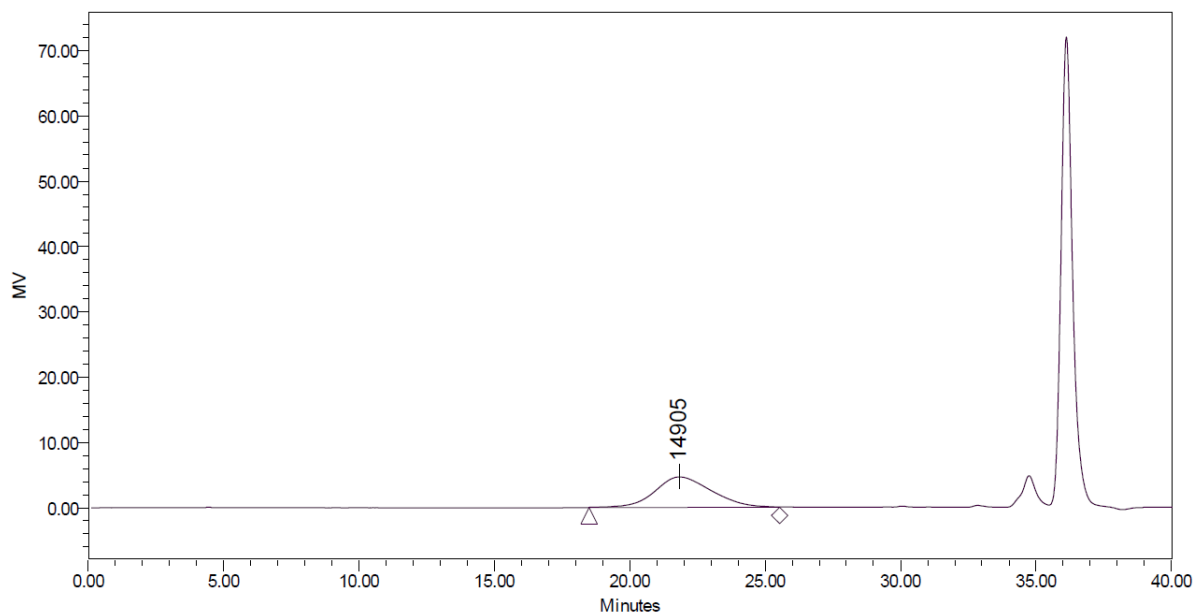


Table 2 entry 3-1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	12138	14701	14905	17493	20698	1.211146	1.189924	1.407957

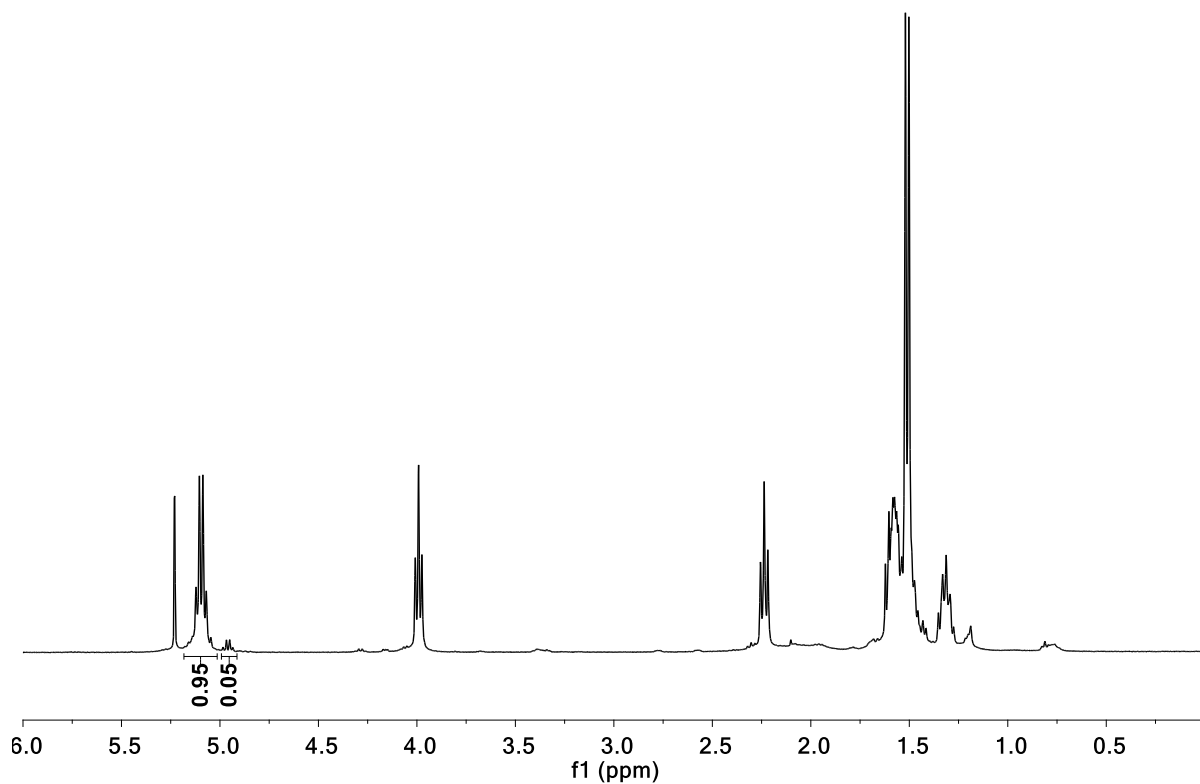
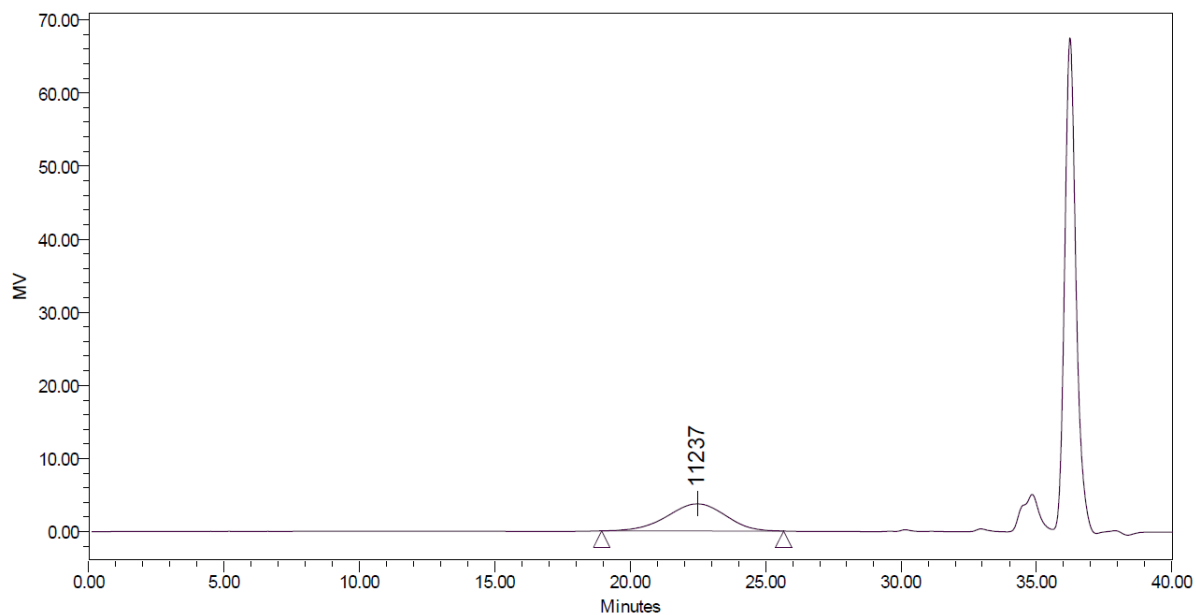


Table 2 entry 3-2



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	10528	12637	11237	15175	18133	1.200379	1.200813	1.434921

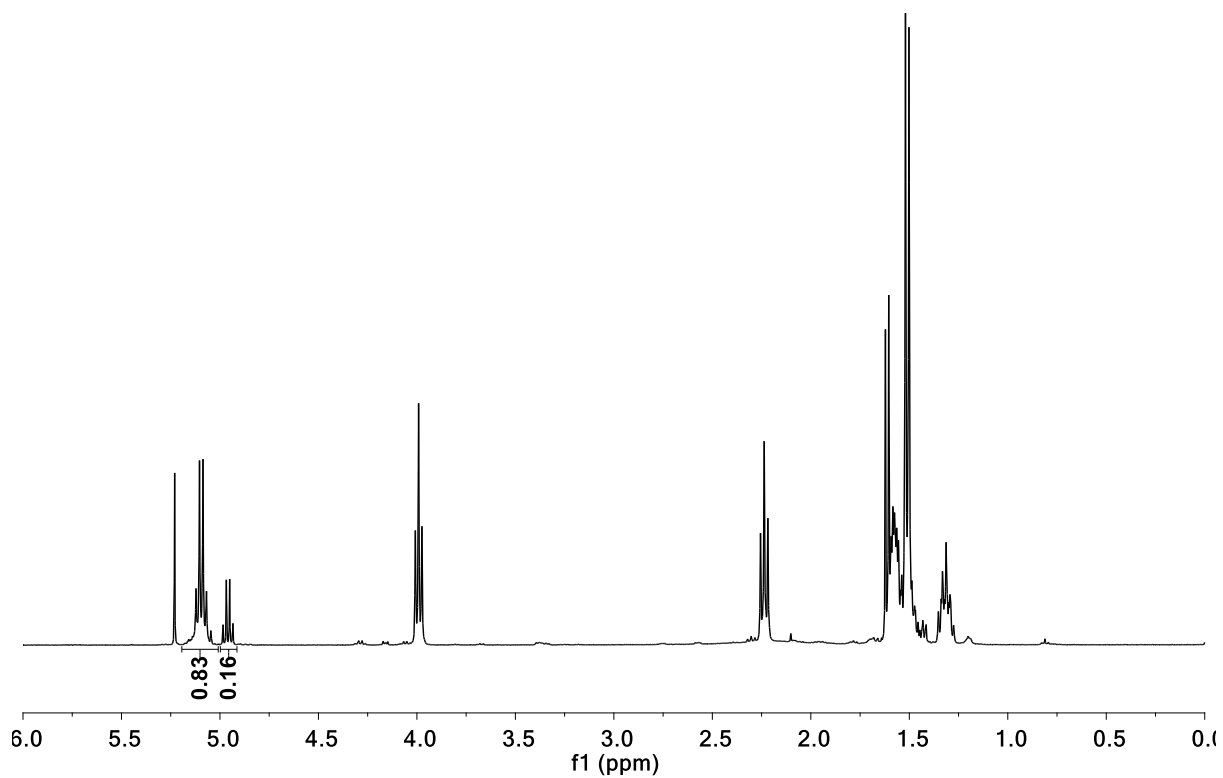
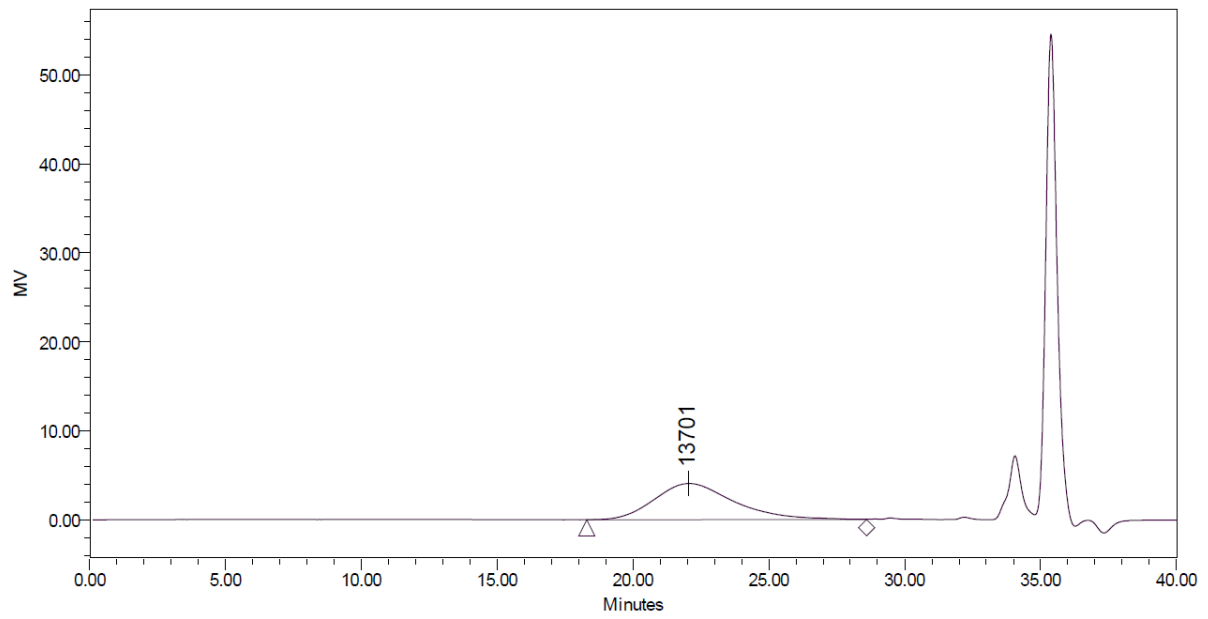


Table 2 entry 4-1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	8806	13446	13701	17880	22183	1.526905	1.329754	1.649801

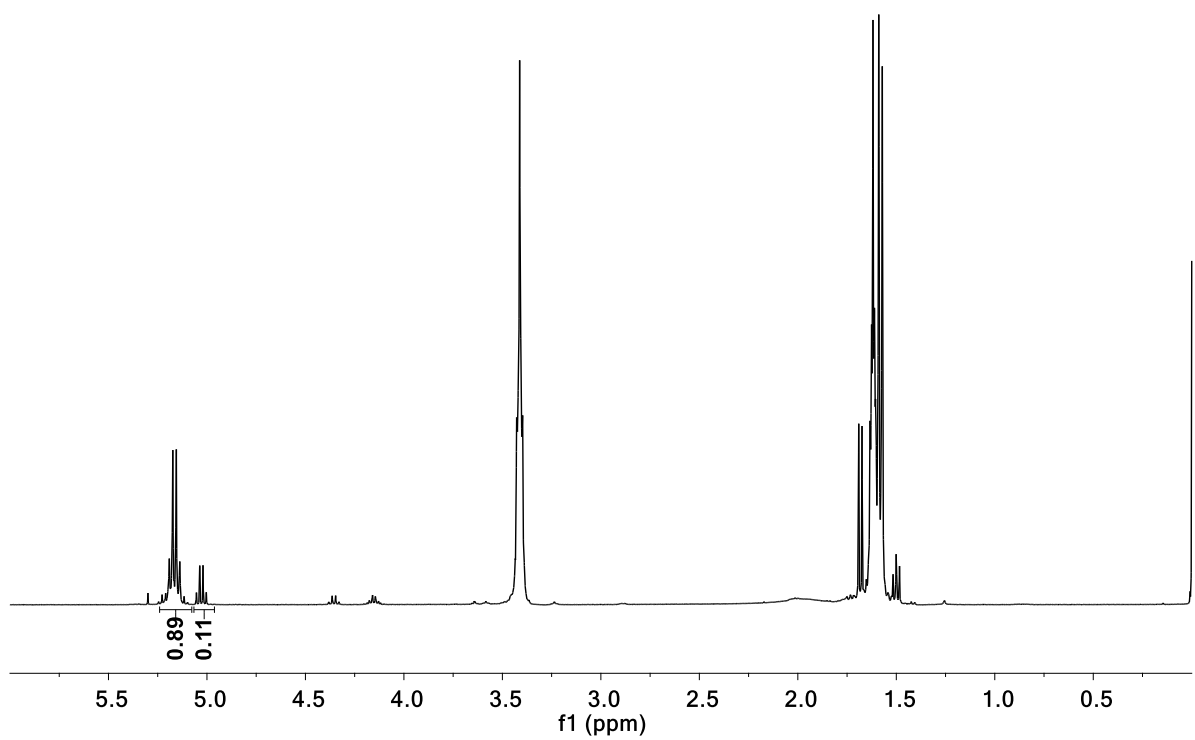
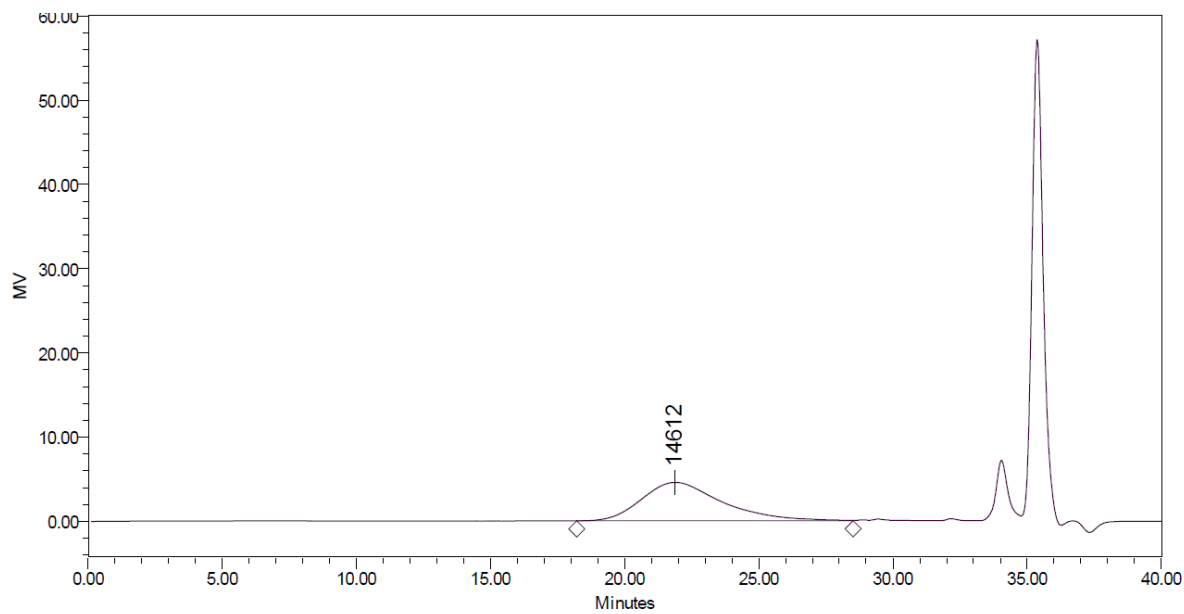


Table 2 entry 4-2



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	8972	14061	14612	18835	23390	1.567154	1.339554	1.663468

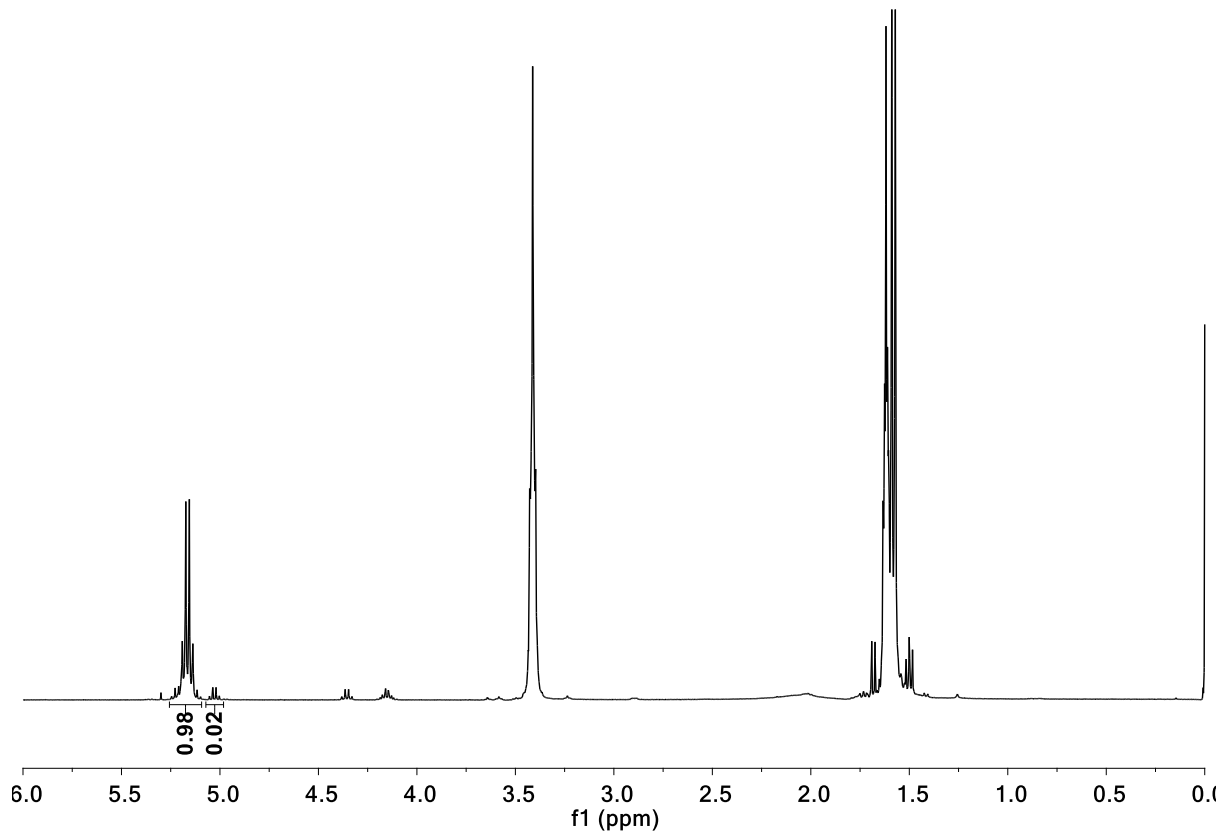
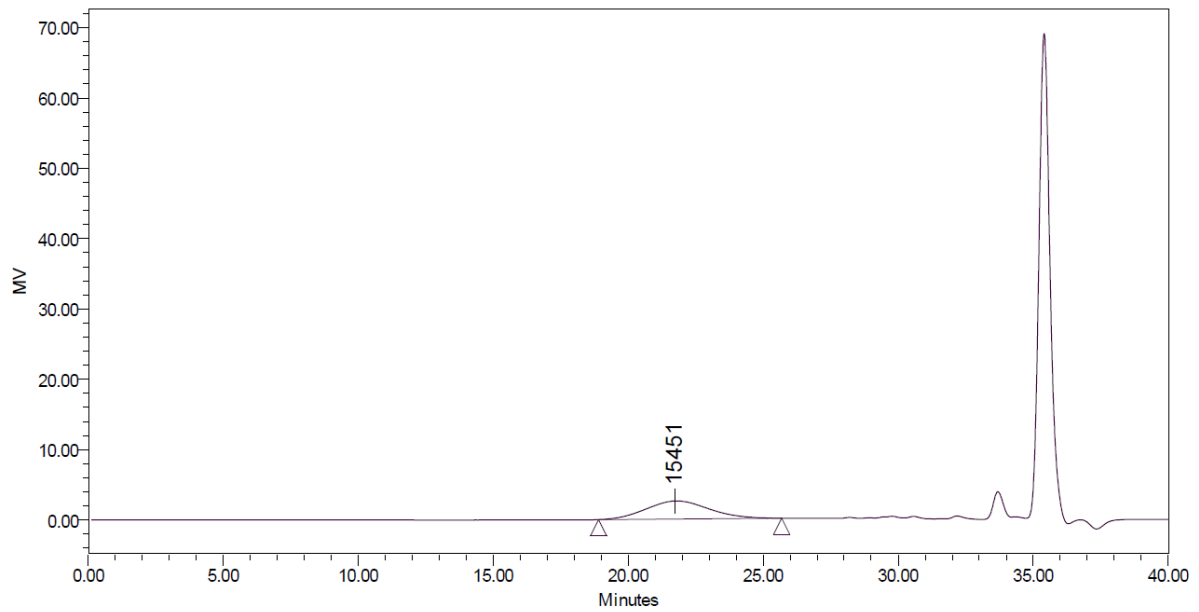


Table 2 entry 5-1



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+ 1 (Daltons)	Polydispersity	Mz/Mw	Mz+ 1/Mw
1	12973	15936	15451	19045	22169	1.228393	1.195037	1.391111

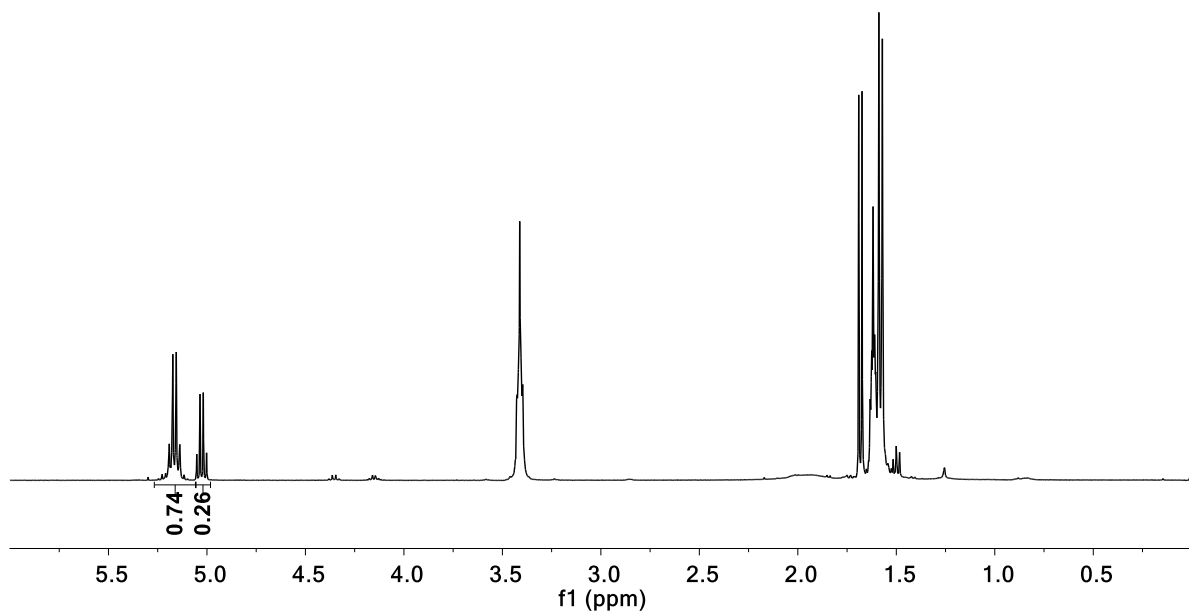
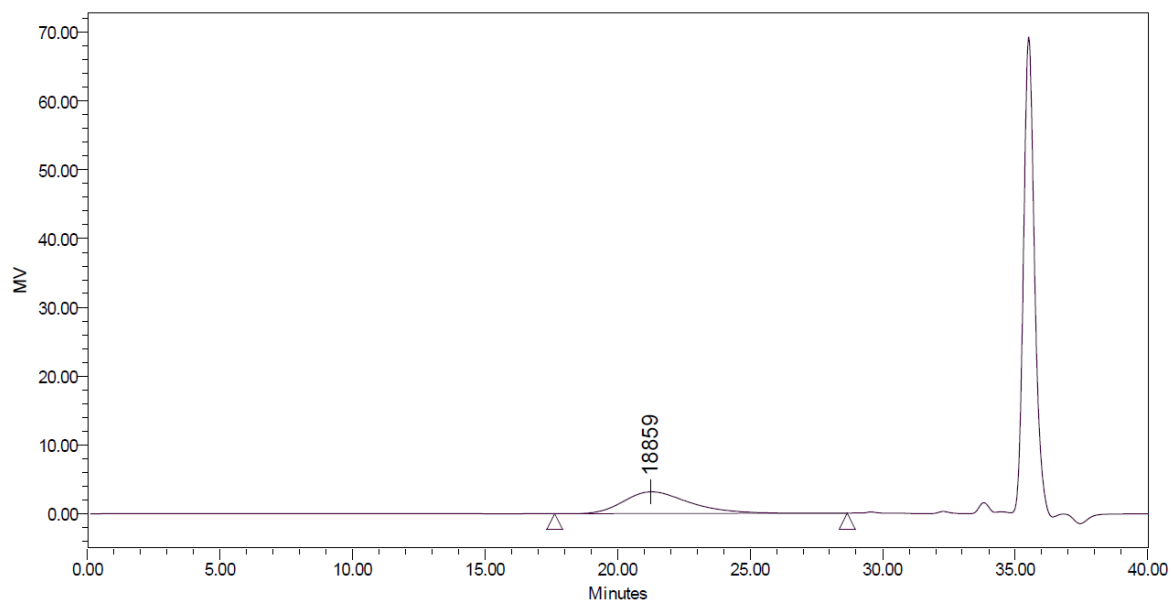


Table 2 entry 5-2



Broad Unknown Relative Peak Table

Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1	13354	17973	18859	22135	26153	1.345950	1.231542	1.455131

