Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supporting information:

Hydrophobe-free miniemulsion polymerization: towards high solid content of fatty acid-based poly(urethane-urea)s latexes

E. Rix, [ab] G. Ceglia,[ab] J. Bajt,[ab] G. Chollet,[c] V. Heroguez,[ab] E. Grau[ab] and H. Cramail*[ab]

Contents

S1: Polymerization protocols

Bulk polymerization:

Both monomers and the catalyst are introduced in a tubular schlenk. The polymerization is performed at 60°C under magnetic stirring for 4h. The stirring is no more efficient when the viscosity of the mixture increases. Then the oil bath is removed and samples are taken for analysis.

Miniemulsion polymerization:

Preparation of the aqueous phase:

Sodium dodecyl sulfate is dissolve in deionized water under magnetic stirring until complete dissolution.

Preparation of the organic phase and emulsification:

Both monomers and the catalyst are stirred manually with a spatula for about 10s. The organic phase is then introduced in the aqueous phase previously prepared. Sonication is applied to the system. During sonication, an ice bath is used to cool the system. An emulsion is obtained.

Polymerization:

Shortly after emulsification, the emulsion is inserted in a round-bottom flask equipped with a mechanic stirrer at 60°C. Polymerization is performed for 4h at this temperature with a stirring of 300rpm.

S2: Experimental data

^{1}H and ^{13}C-NMR spectra were recorded on Bruker Avance 400 spectrometer**.**

Size exclusion chromatography (SEC) analyses were performed in THF (40°C) on a PL-GPC 50 plus Integrated GPC from Polymer laboratories-Varian with a series of four columns from TOSOH (TSKgel TOSOH: HXL-L (guard column 6,0mm ID x 4,0cm L); G4000HXL (7,8mm ID x 30,0cm L) ;G3000HXL (7,8mm ID x 30,0cm L) and G2000HXL (7,8mm ID x 30,0cm L)). The elution of the filtered samples was monitored using simultaneous refractive index and UV detection. The elution times were converted to molar mass using a calibration curve based on low dispersity (M_w/M_n) polystyrene (PS) standards.

Differential scanning calorimetry (DSC) thermograms were measured using a DSC Q100 apparatus from TA instruments. For each sample, two cycles from -50 to 100 °C (or 120 °C for higher melting point polyurethanes) at 10 °C.min^{-1} were performed and then the glass transition temperatures were calculated from the second heating run.

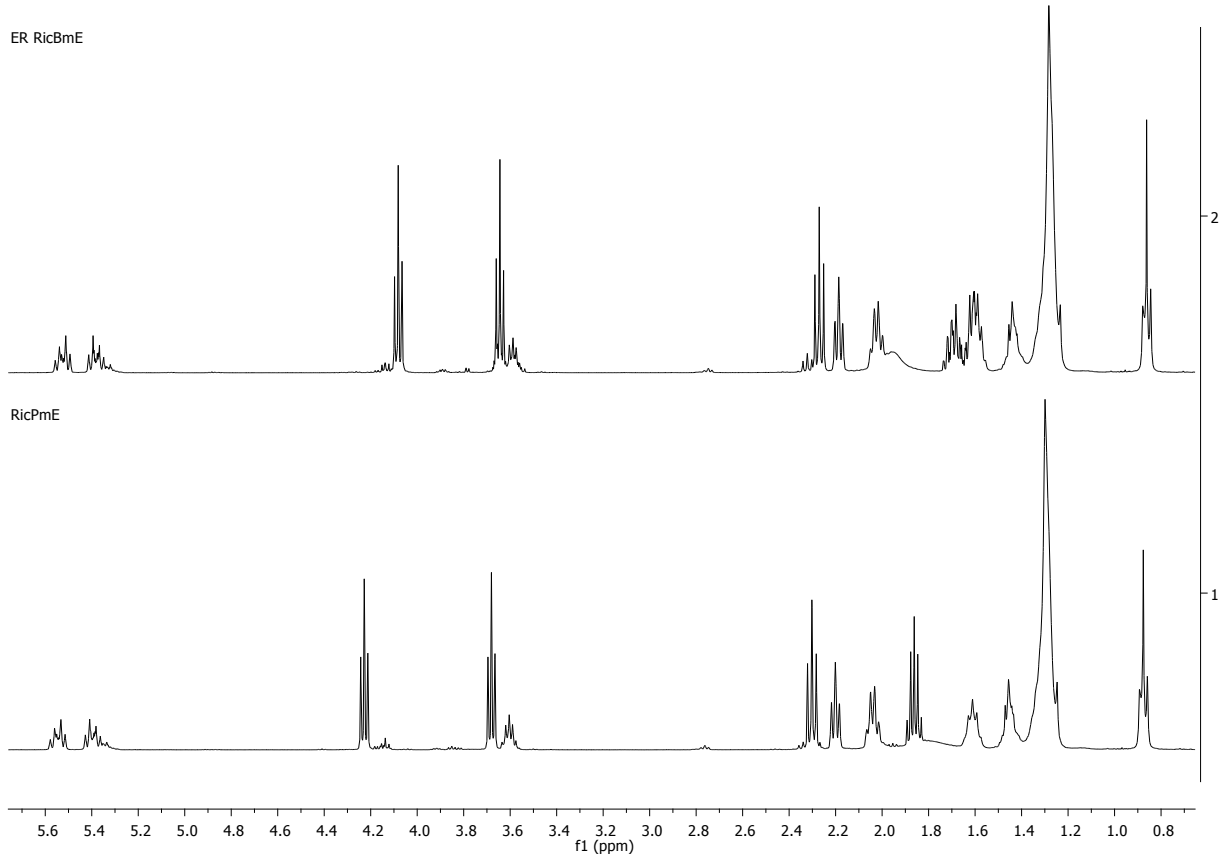
Table 1: Characteristics of PU latex and [bulk PU]

Entry	NCO/OH ratio	Mw [a,d] *(kg/mol)*	Đ [a,d]	Particle size [b] *(nm)*	Tg [c,d] *(°C)*	Urea content [d] *(%)*
ME0[YP40]	**0.8**	3.2 [9.6]	1.3 [1.1]	249±11	-16 [-12]	21 [5]
ME1[YP41]	**1**	3.7 [38.2]	1.4 [3.5]	238±19	-5 [14]	24 [-][e]
ME2[YP42]	**1.2**	4.8 [24.5]	1.5 [2.3]	243±7	9 [12]	30 [-][e]
ME3[YP43]	**1.5**	5.8 [9.6]	1.6 [1.7]	226±14	32 [-9]	34 [18]
ME4[YP44]	**1.8**	5.2 [2]	1.5 [1.4]	239±18	69 [-22]	43 [22]
ME5[YP45]	**2**	4.7 [2]	1.5 [1.4]	228±16	69 [-29]	55 [25]
ME8	**2.5**	4.2	1.4	232±14	*nd*	55
ME9	**3**	*nd*	*nd*	220±6	*nd*	55

RicPmE and IPDI were used as monomers, with 3.5 CMC of SDS. No hydrophobic agent was added. DBTDL concentration was 0.4wt% of the organic phase

[a] Measured by SEC in THF calibrated with polystyrene standards. [b] Measured by DLS with a 90° angle. The value given is the average value of three measurements. Dispersities are between 0.162 and 0.234. [c] Measured by differential scanning calorimetry. [d] Polymers insoluble in deuterated DMSO. *nd*: not determined

S3: ^{1}H NMR of RicBmE and RicPmE in $CDCl_3$



S4: Method to calculate the urea content

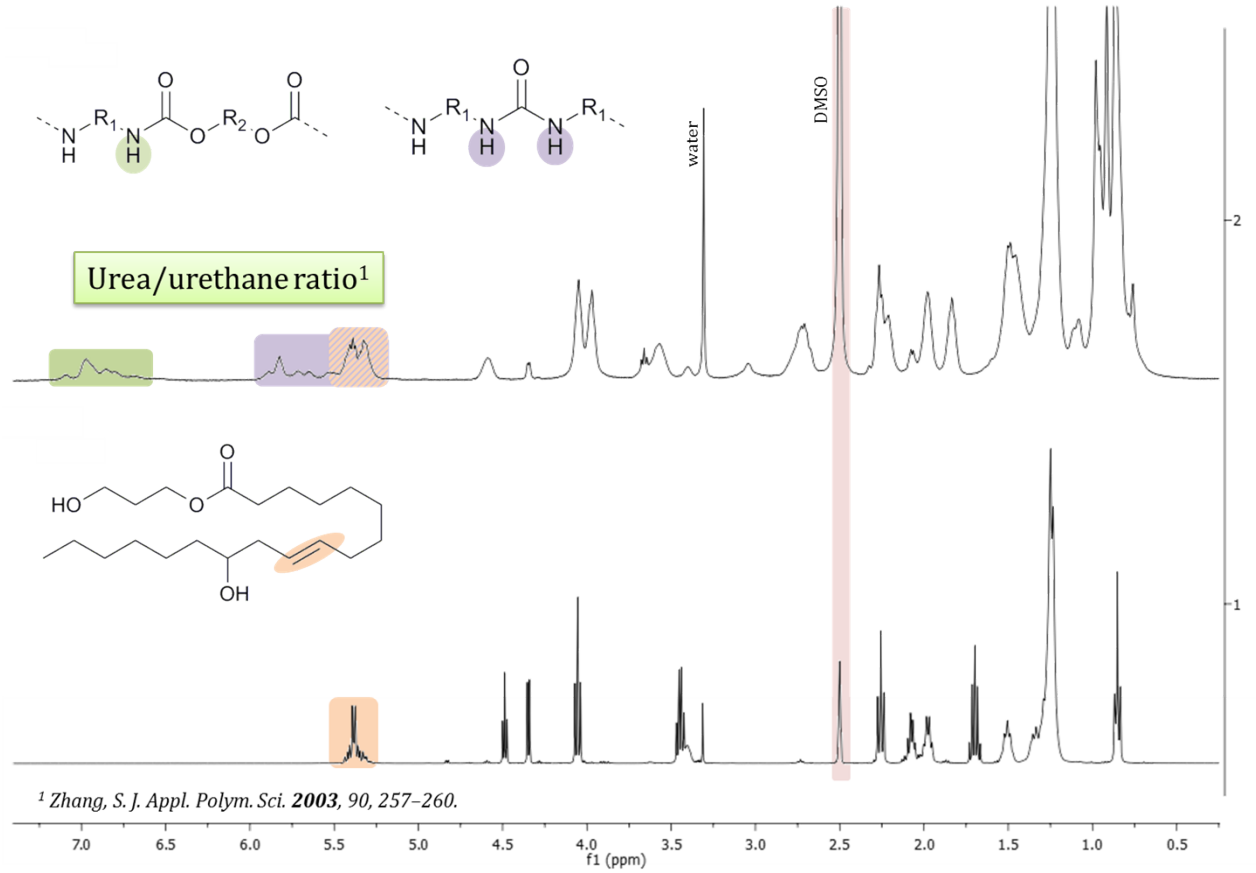


Figure 1: ^{1}H NMR Spectra in DMSO of a lyophilized latex and of RicPmE

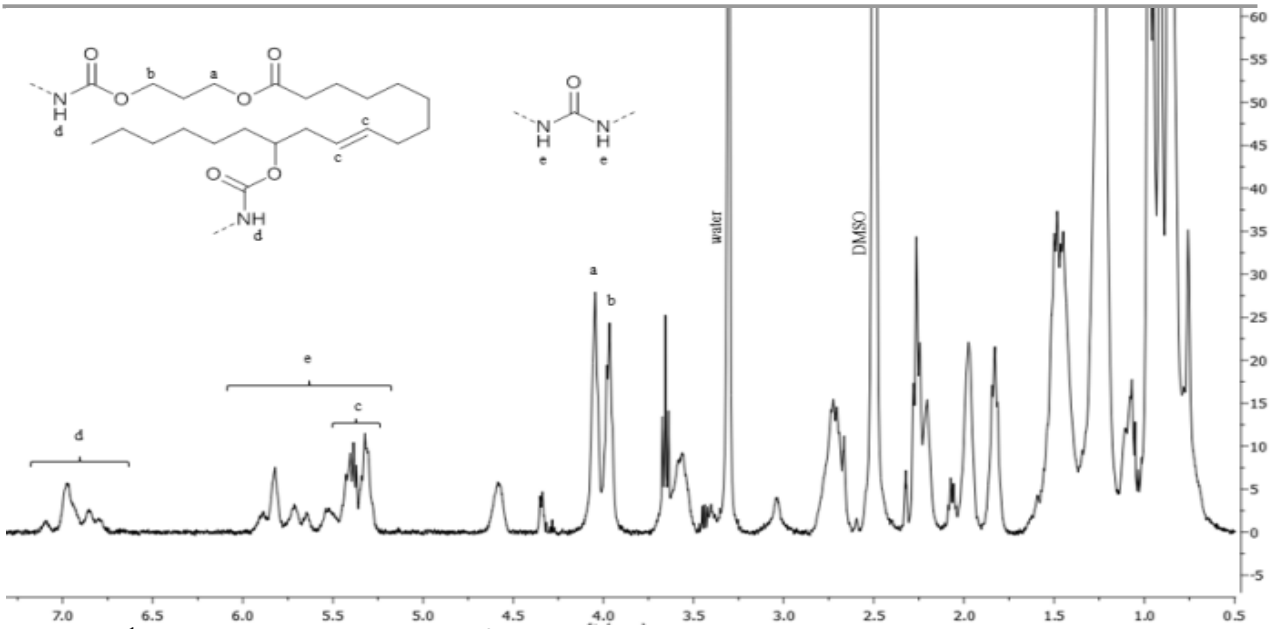


Figure 2: ^{1}H NMR Spectra in DMSO of a lyophilized latex

$$Urea\ content = \frac{urea}{urea + urethane}$$

Where:

- $urethane = d$
- $urea = \frac{(c + e) - (a + b + 2f)/2}{2}$

Equation 1: Definition of the urea content

a, b, c, d, e and f are the integrals corresponding to the following peaks: . f is the integral of the peak at 4.49ppm corresponding to the proton of the unreacted primary alcohol of RicPmE. f=0 when there is no more unreacted primary alcohol.
a + b is set to 4, as it corresponds to 4 protons.

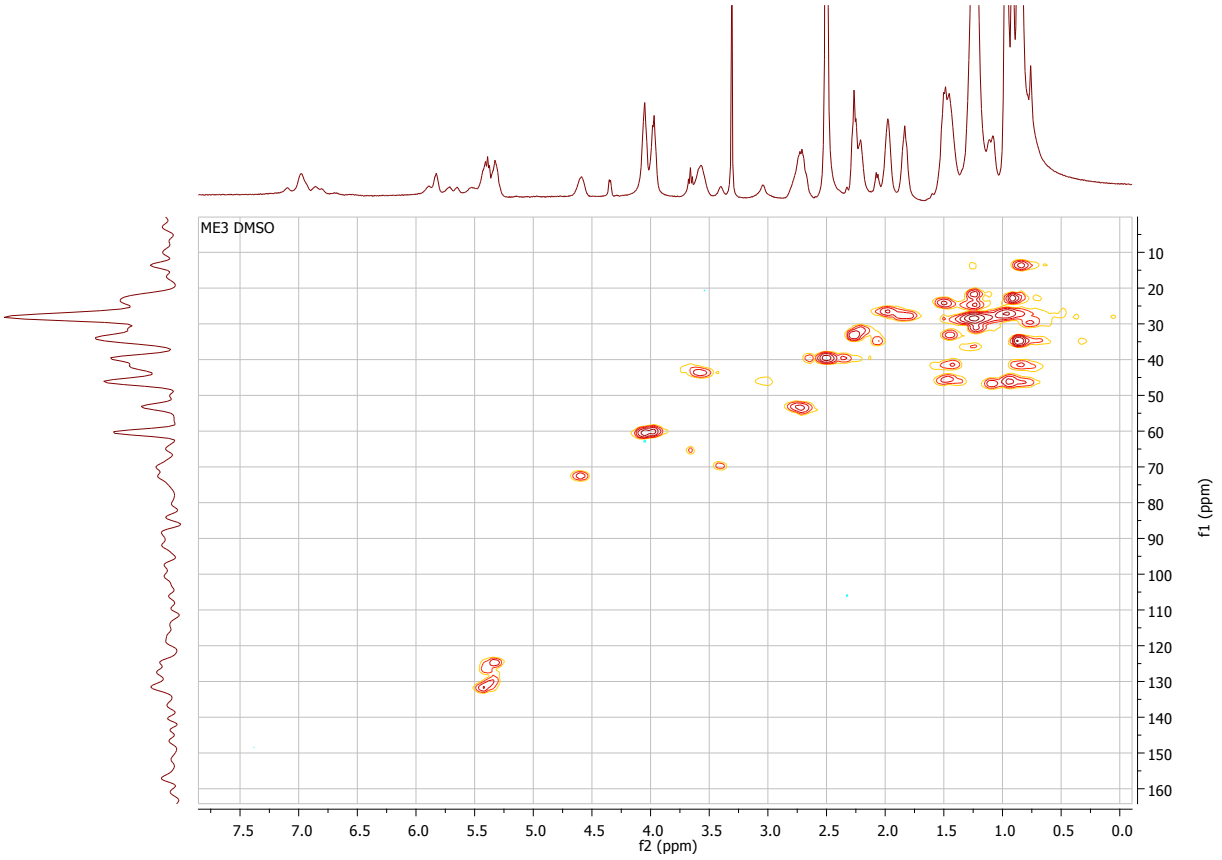


Figure 3: ^{13}C-^{1}H NMR of a lyophilized latex in DMSO.

It shows that the protons between 5 and 7.5ppm are not linked to a carbon atom. Only the protons of the double bond are visible in this range

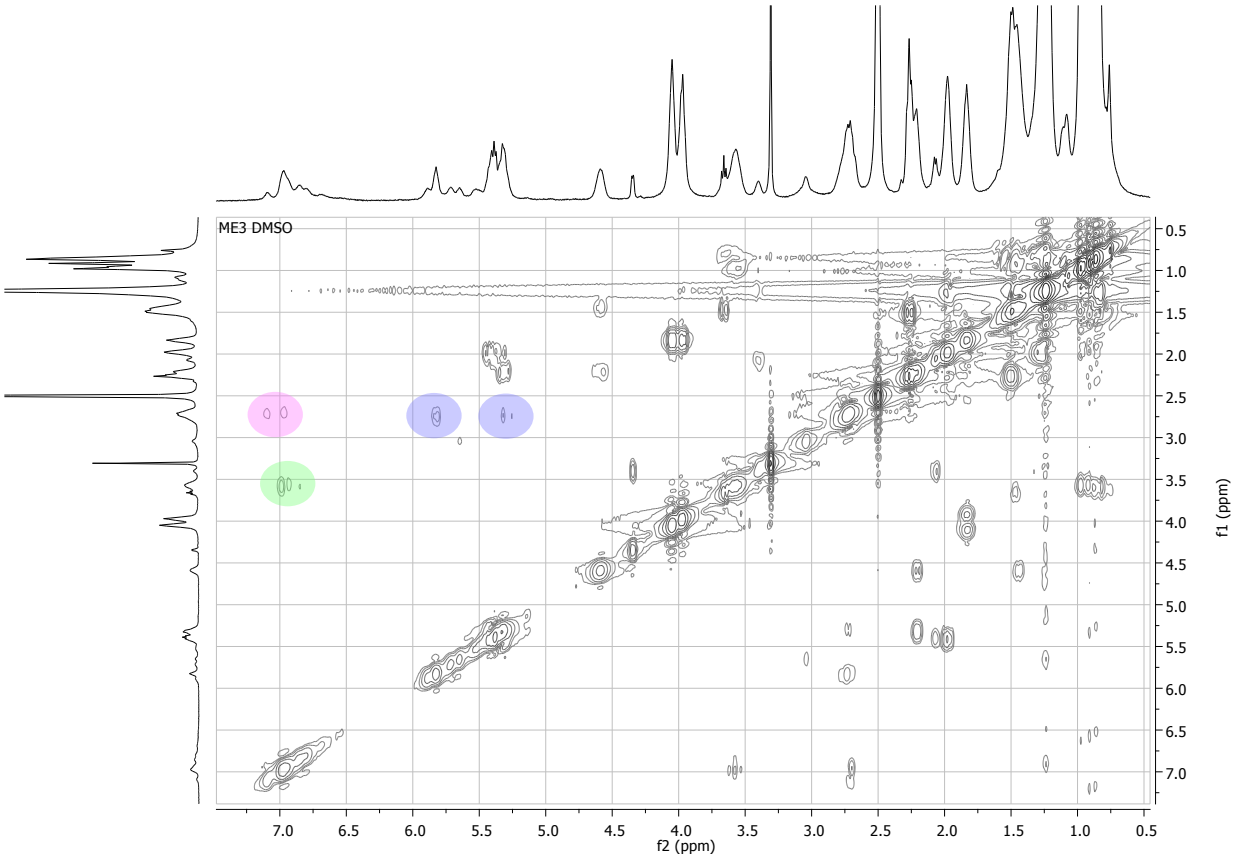
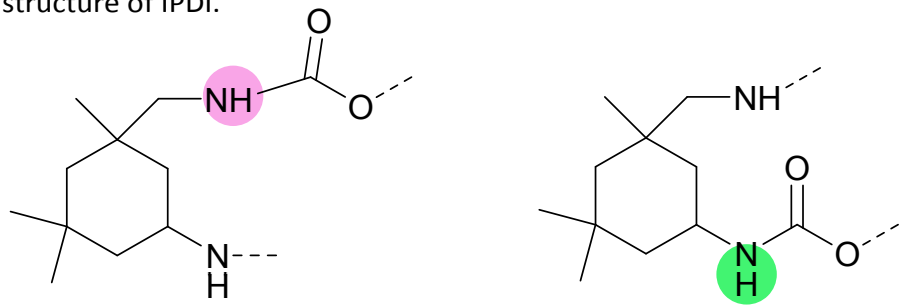
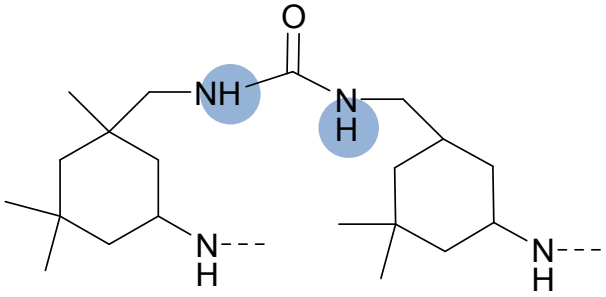


Figure 4: ^{1}H-^{1}H NMR spectrum in DMSO of a lyophilized latex

Around 7ppm (X axis), two correlation signals appear (in pink and green): they correspond to the proton of the NH of urethane functions. There are two signals because of the asymmetrical structure of IPDI.



Between 5 and 6ppm (X axis), signals corresponding to the double bond protons are visible. Two signals are visible (in blue), they correspond to the urea formed with the structure below.



Two other urea structures could be formed, but they are not visible on the NMR spectra. This can be explained by the different reactivity of the two isocyanate functions of the IPDI due to steric hindrance. The more reactive functions react with alcohols, then the less reactive with the alcohol functions remaining. Thus, when the side reaction of isocyanate and water occurs, the less reactive isocyanate function is the main one remaining.

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S5: NMR spectra of lyophilized latex and bulk polymers in DMSO

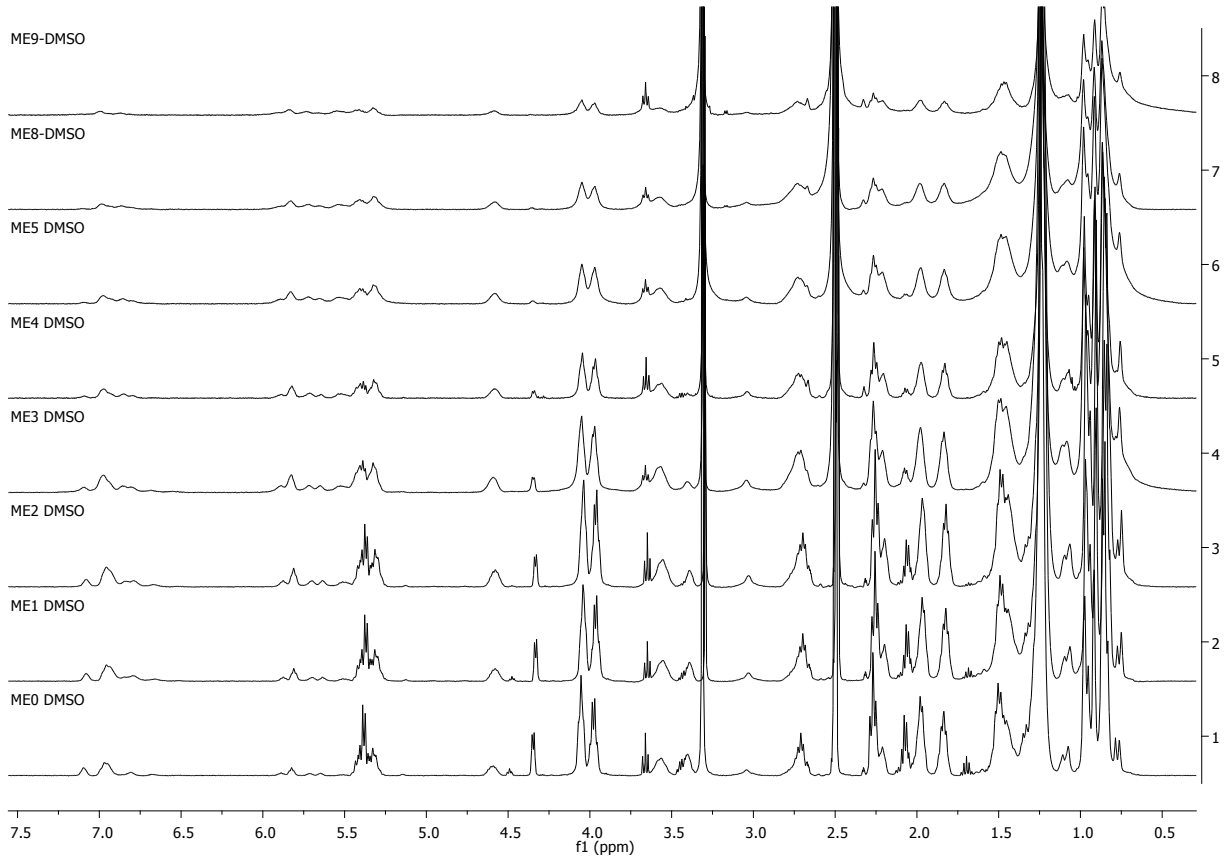


Figure 2: NMR spectra of lyophilized latex ME0 to ME9 in DMSO

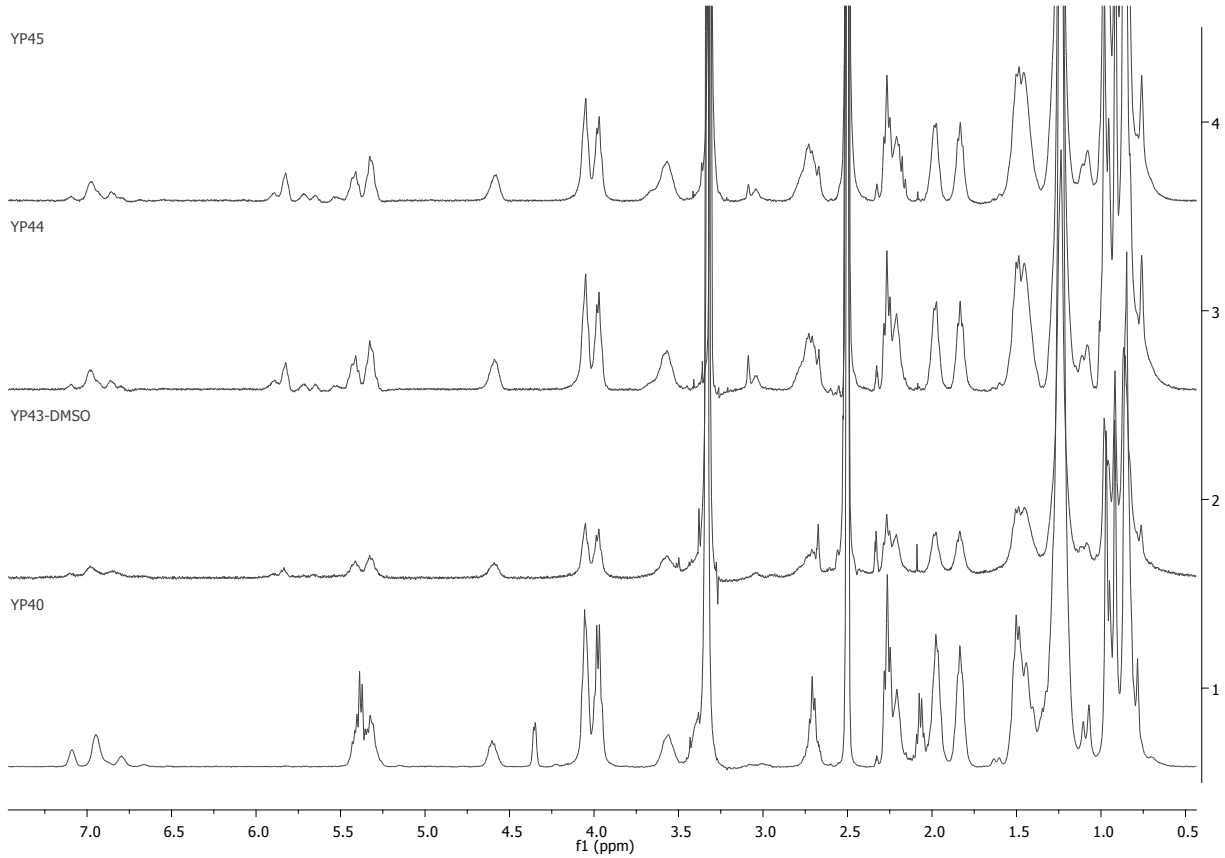
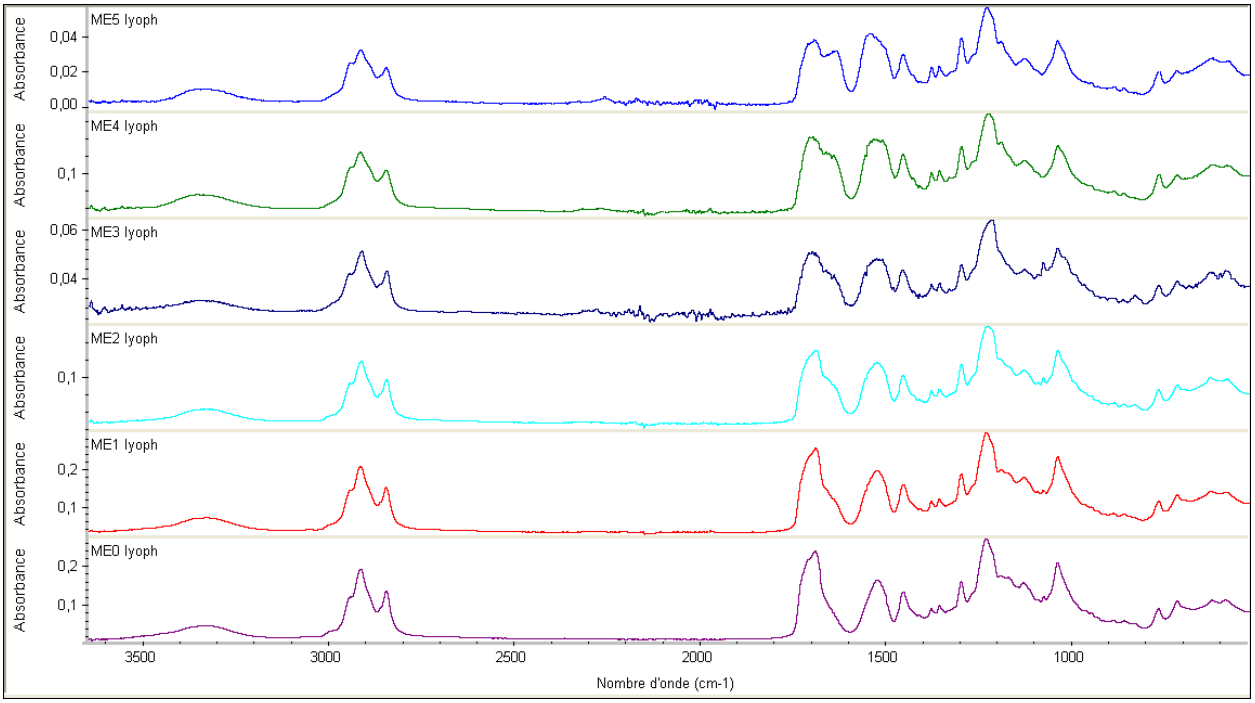


Figure 3: NMR spectra of bulk polymers in DMSO

S6: FTIR spectra of lyophilized latex



The peak at 1645cm^{-1} is due to the carbonyl group of urea. The peak at 1700cm^{-1} is due to the carbonyl group of urea. Urea increases with the amount of IPDI introduced which is in accordance with the urea contents calculated from ^{1}H NMR.

S7: ^{1}H NMR of lyophilized latex and bulk polymers in $CDCl_3$

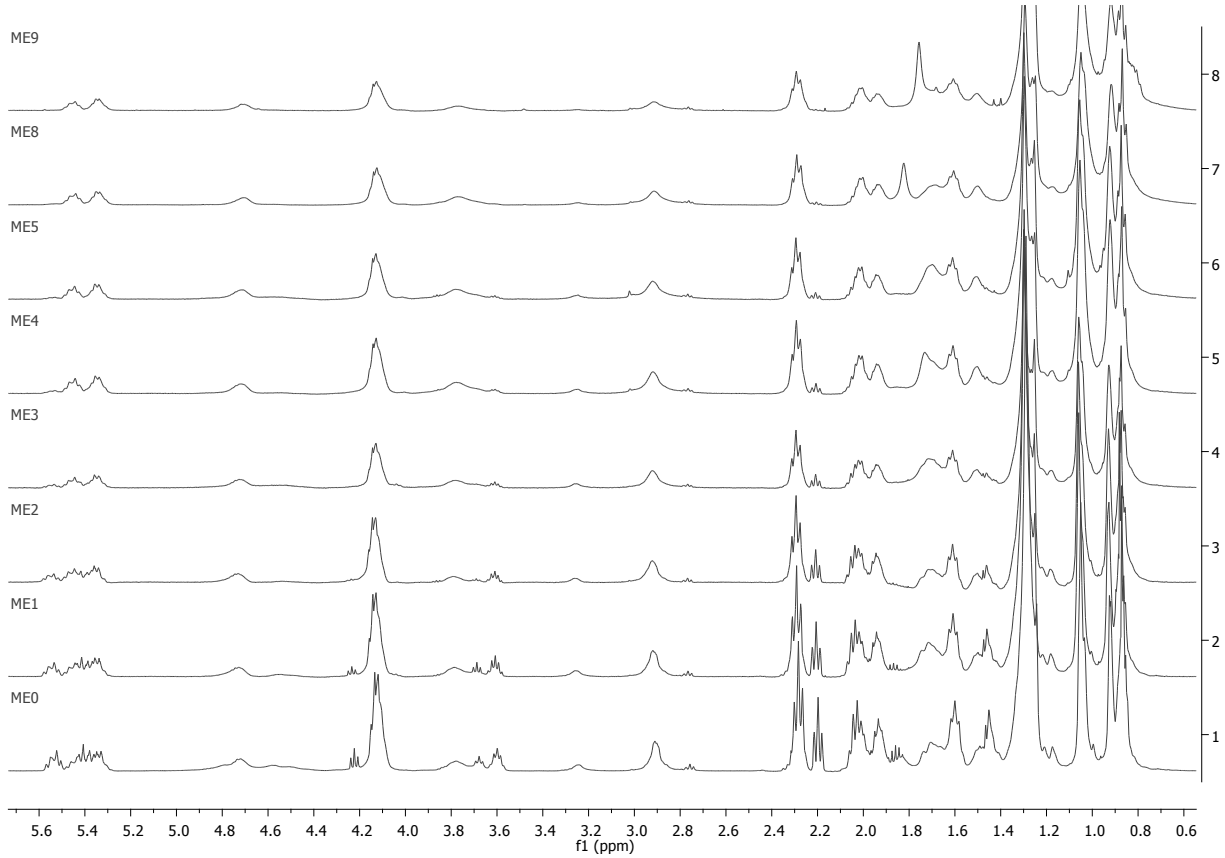


Figure 4: NMR spectra of lyophilized latex ME0 to ME9 in $CDCl_3$

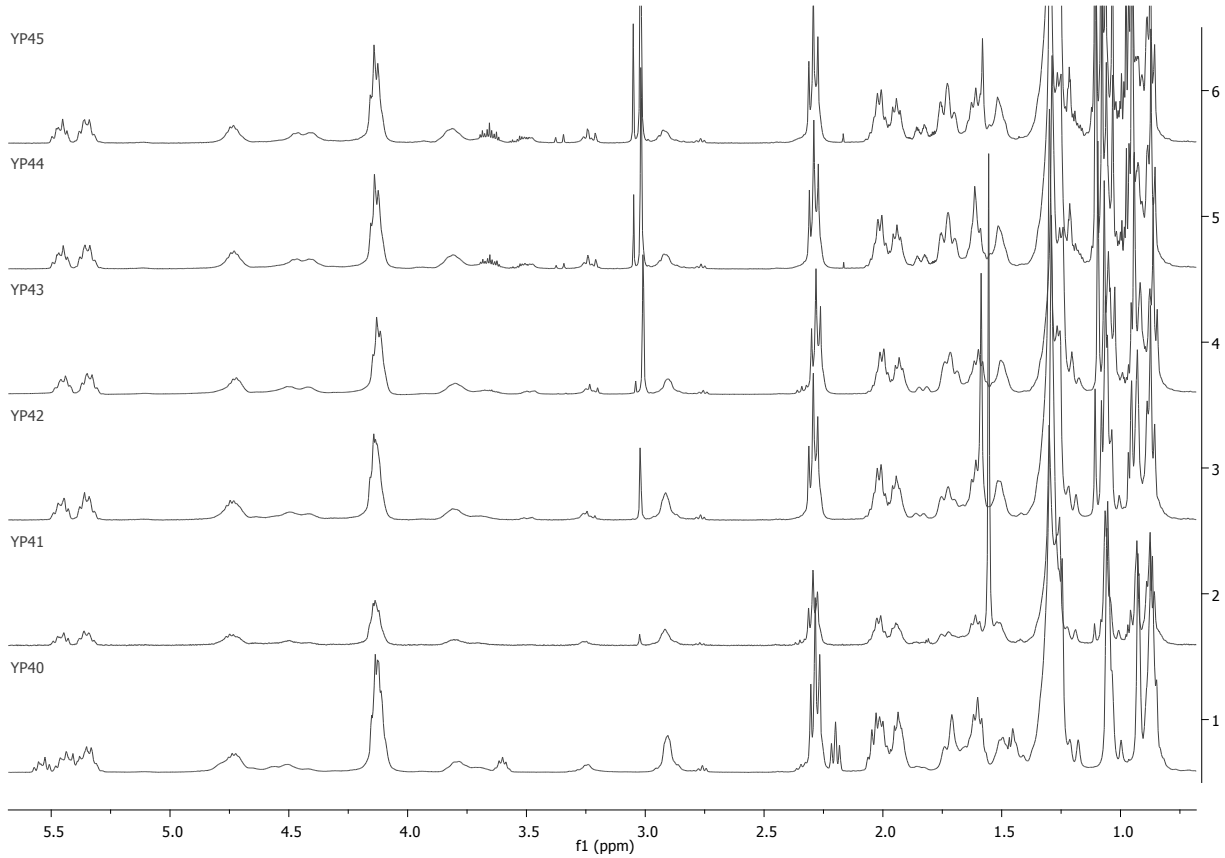
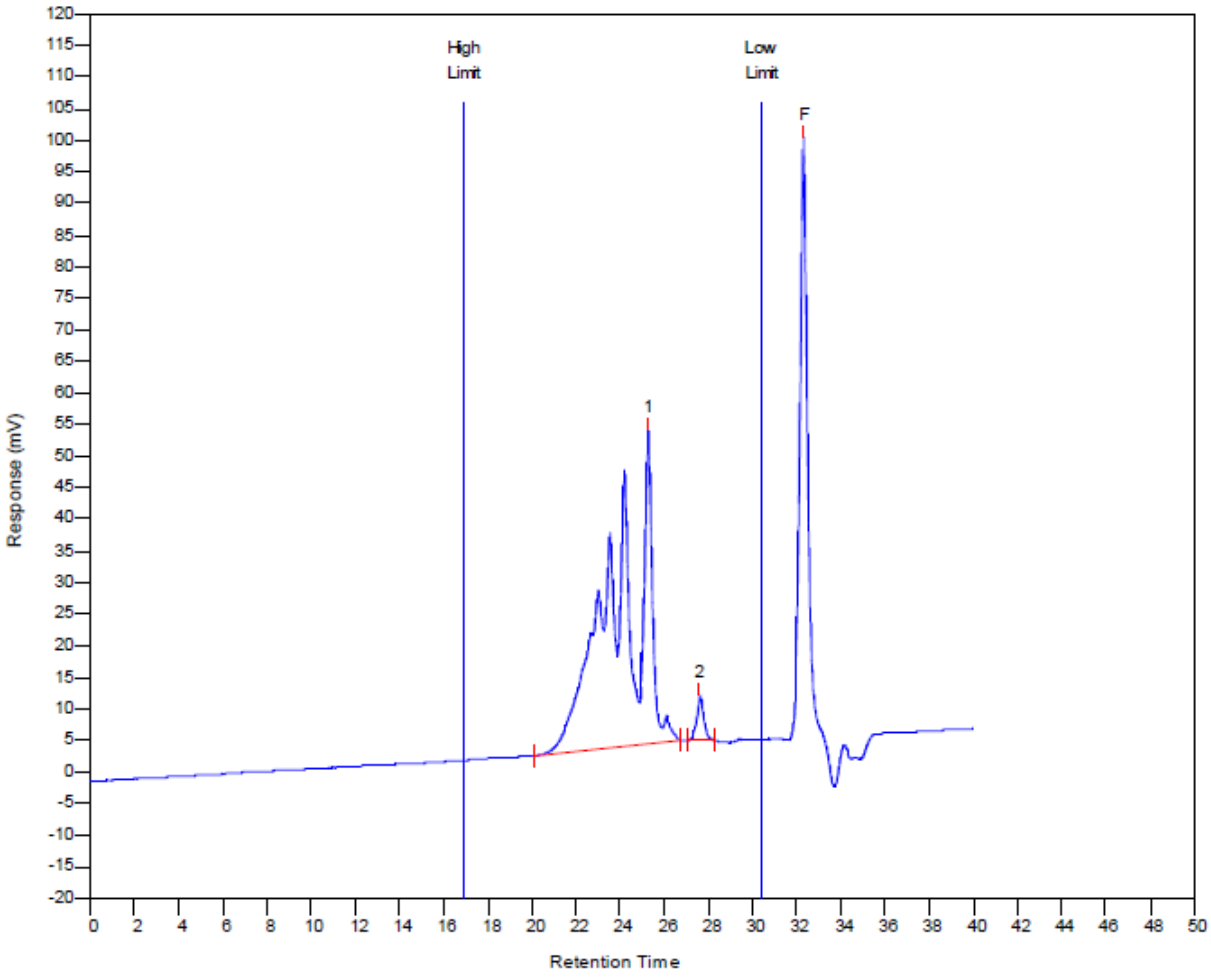


Figure 5: NMR spectra of bulk polymers in $CDCl_3$

S8: SEC graphs of lyophilized latex and bulk polymers

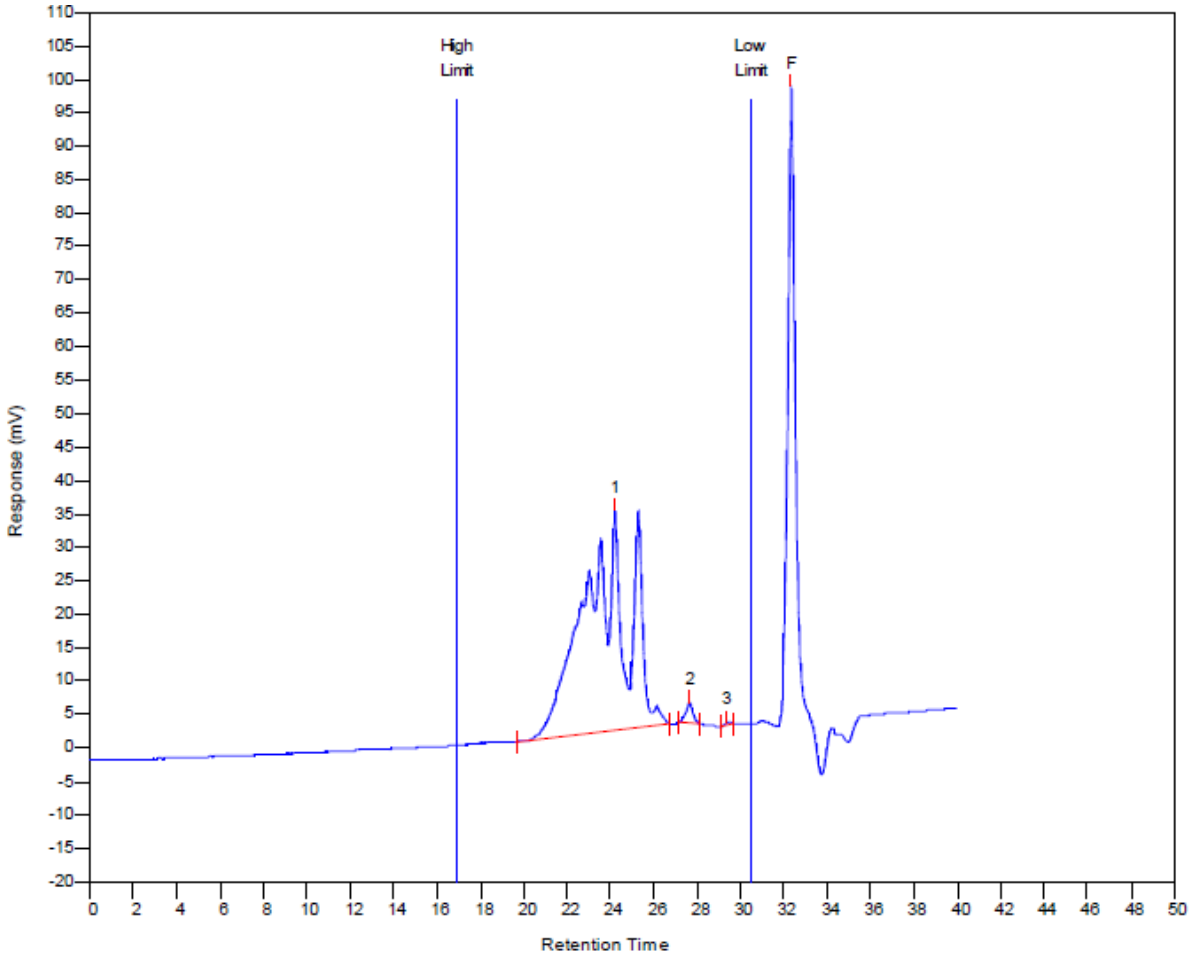
ME0



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1491	2406	3166	4282	5674	3027	1.31588
2	583	580	583	586	589	582	1.00517
3	0	0	0	0	0	0	0

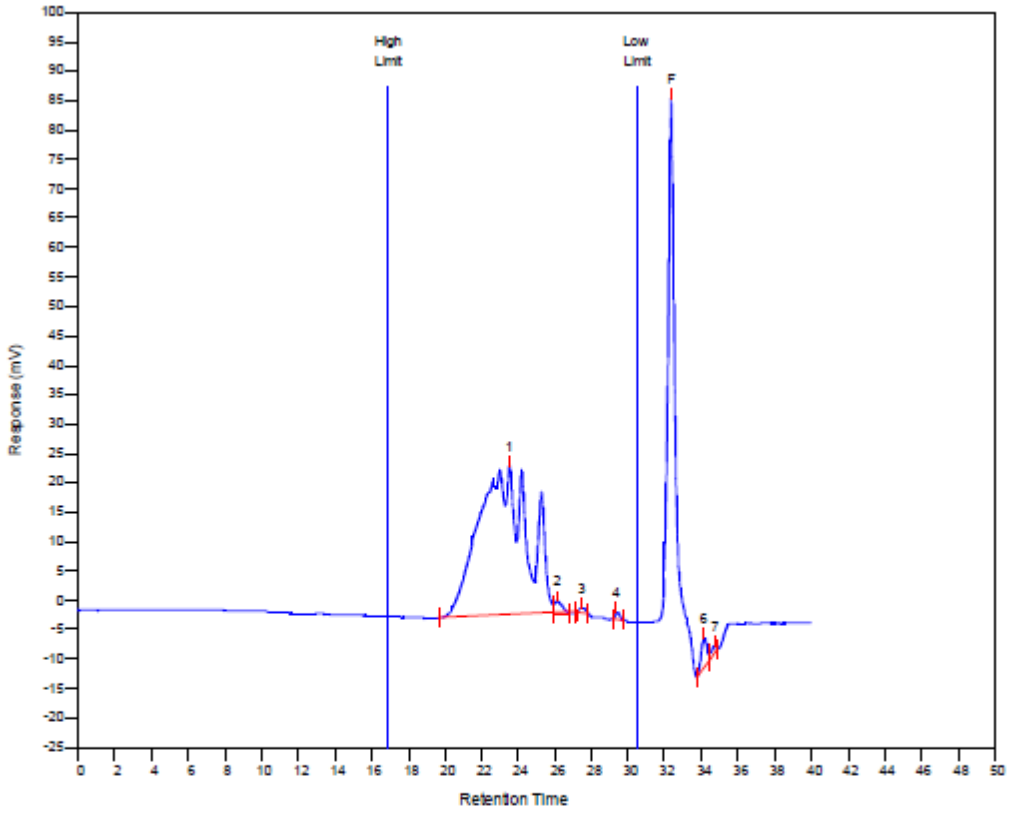
ME1



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2345	2681	3685	5136	6893	3503	1.37449
2	582	588	590	593	595	590	1.0034
3	271	273	272	273	274	271	0.996337
4	46	44	45	46	47	45	1.02273

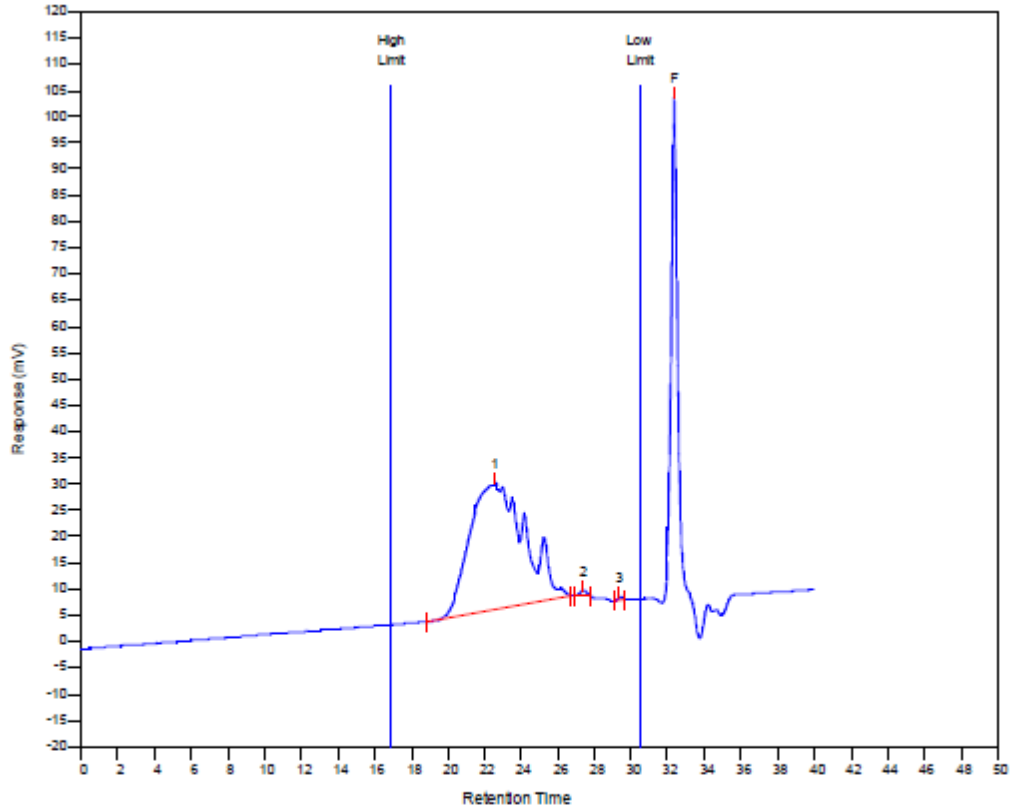
ME2



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	3201	3296	4786	6973	9596	4513	1.45206
2	1082	1067	1003	1044	1050	988	0.940019
3	594	617	617	620	622	616	1
4	269	268	268	269	270	268	1

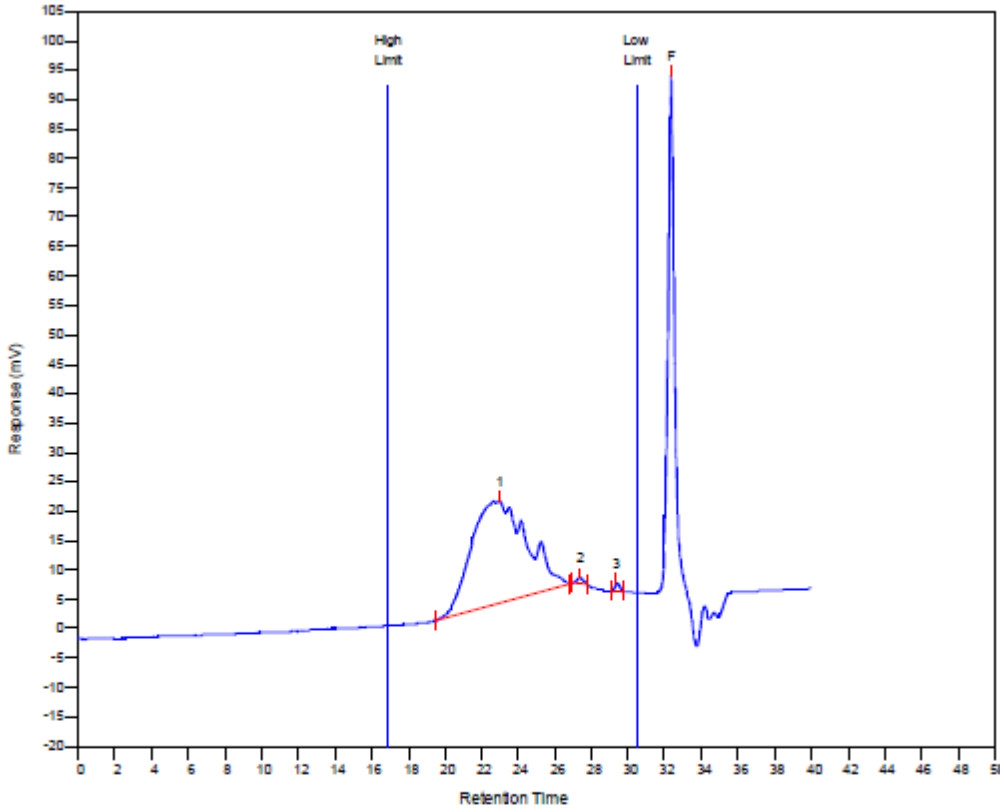
ME3



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	4993	3759	5845	8683	11827	5480	1.55493
2	645	652	654	658	661	653	1.00307
3	269	269	269	270	271	268	1

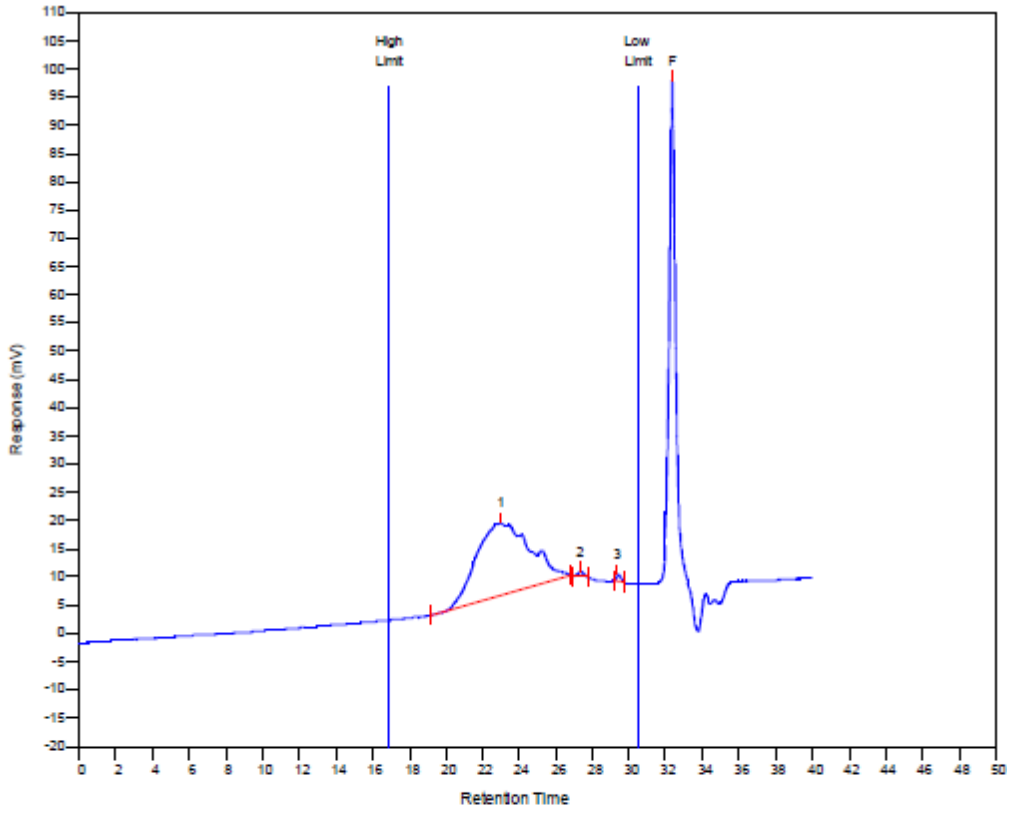
ME4



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	4993	3415	5183	7654	10539	4870	1.51772
2	649	660	661	665	668	660	1.00152
3	269	268	268	269	270	268	1

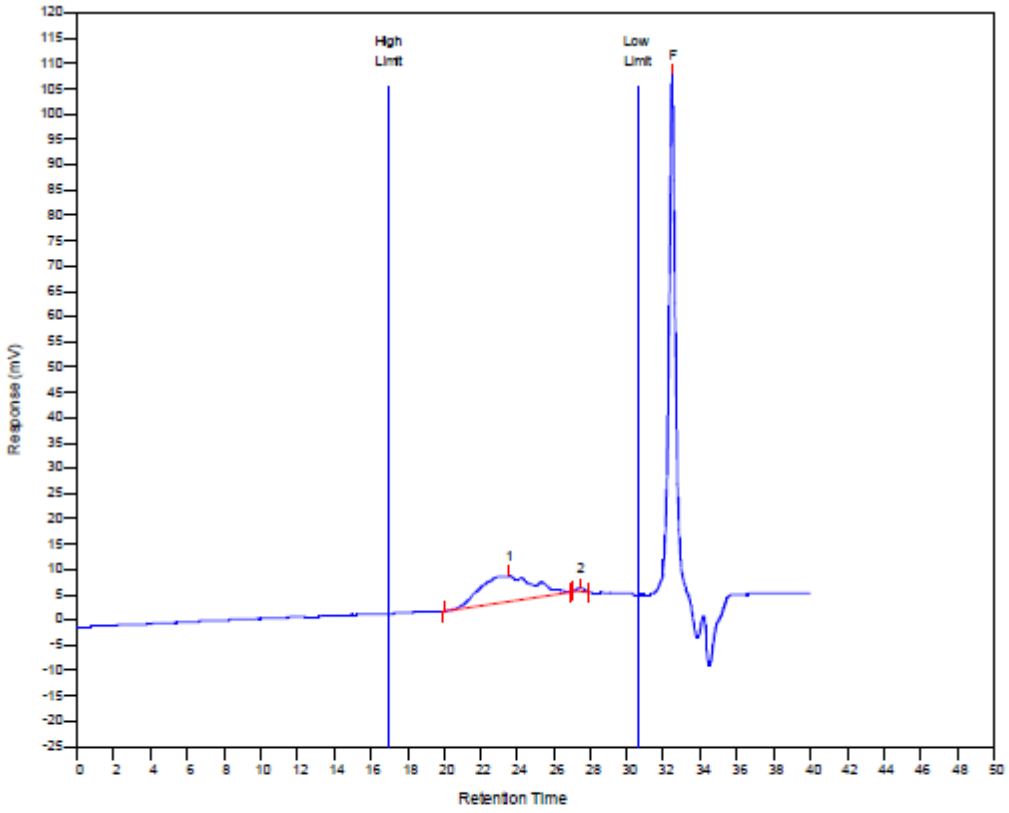
ME5



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	4155	3192	4692	6762	9155	4429	1.46992
2	662	657	658	662	664	657	1.00152
3	269	267	267	268	269	267	1

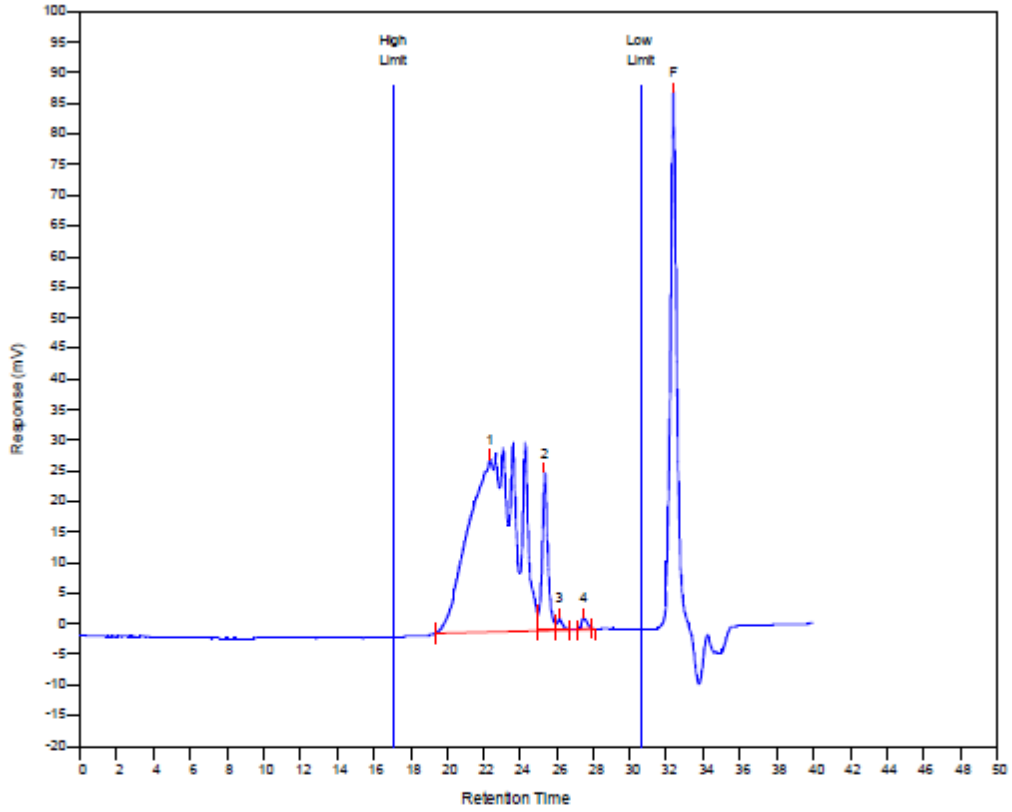
ME8



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	4064	2969	4220	5854	7647	4006	1.42135
2	663	655	657	661	664	657	1.00305

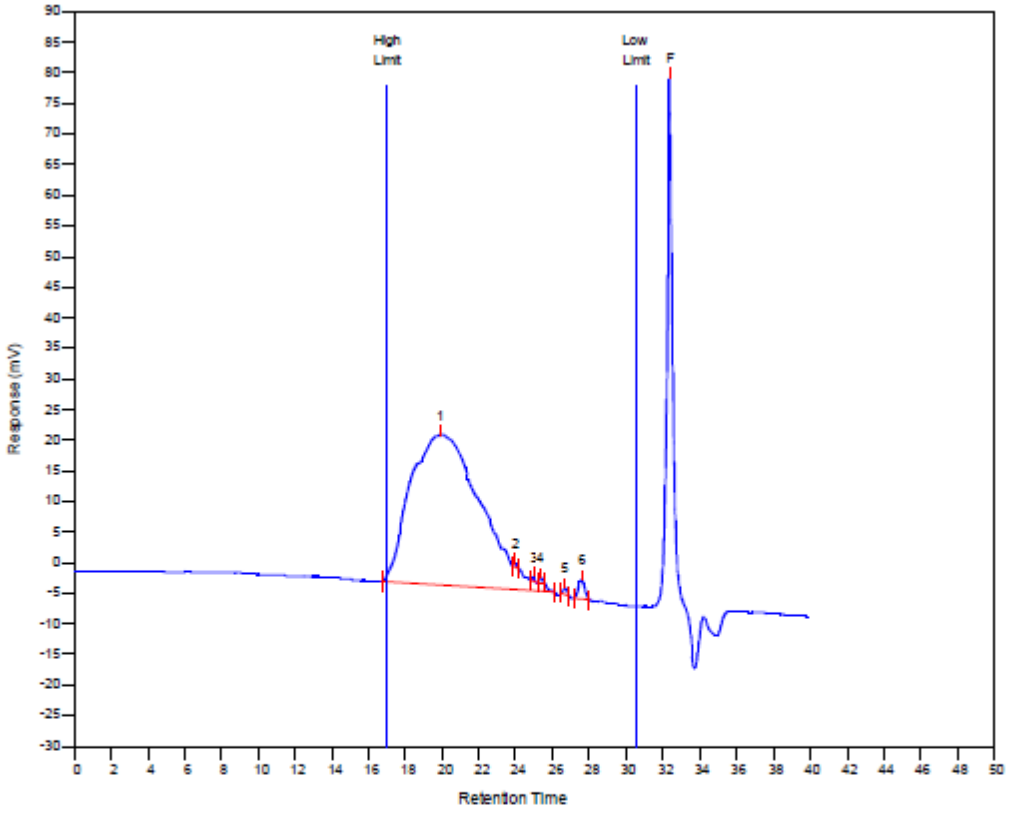
YP40



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2347	4538	6439	9413	13041	6077	1.41891
2	1507	1505	1483	1503	1509	1477	0.985382
3	1106	1128	1053	1095	1098	1037	0.933511
4	651	639	641	644	646	640	1.00313

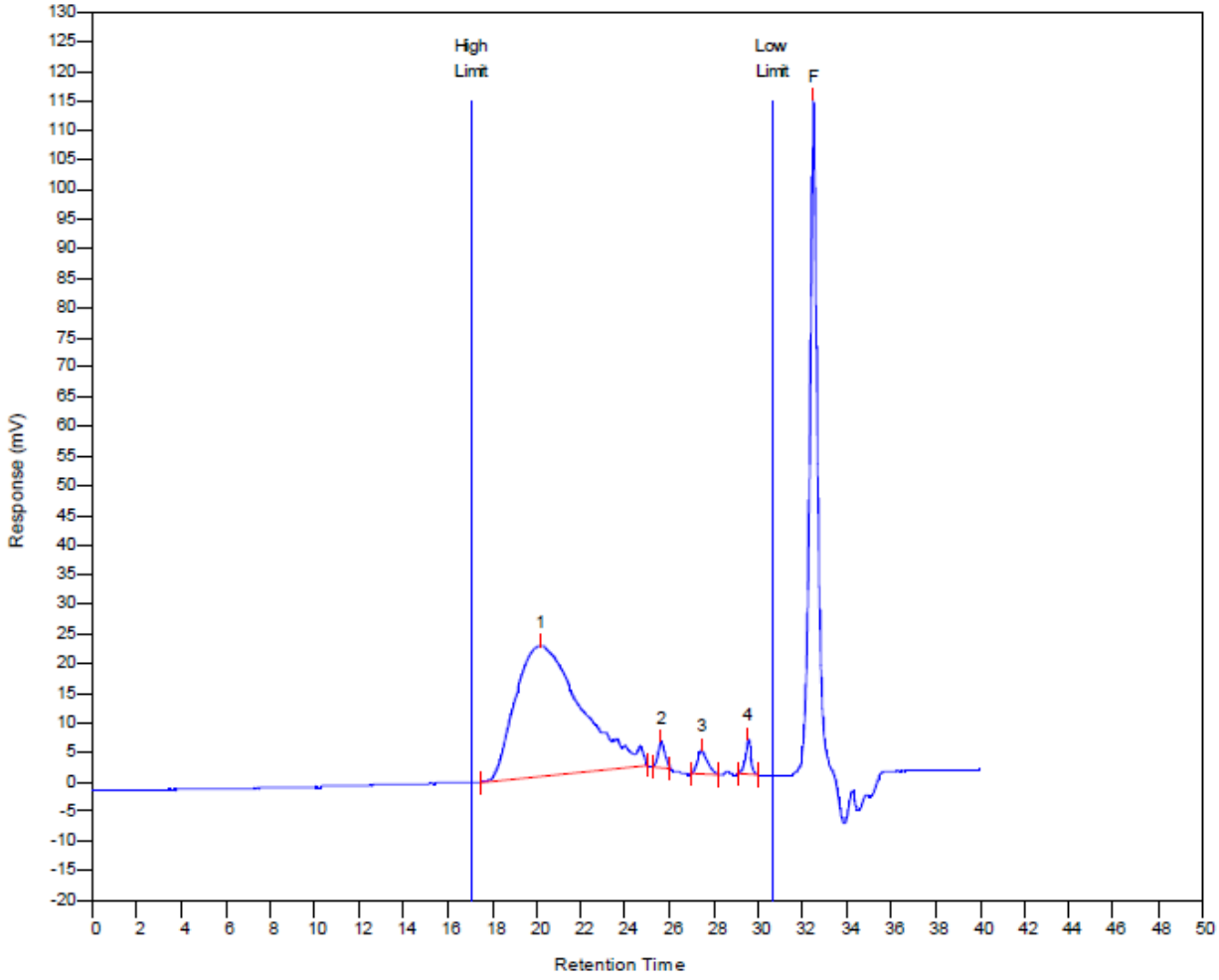
YP41



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	24785	10873	38211	100440	169109	31954	3.5143
2	2612	2651	2594	2624	2626	2581	0.978499
3	1758	1763	1749	1758	1759	1745	0.992059
4	1497	1498	1485	1494	1495	1482	0.991322
5	885	893	887	892	893	886	0.993281
6	612	624	626	629	631	625	1.00321

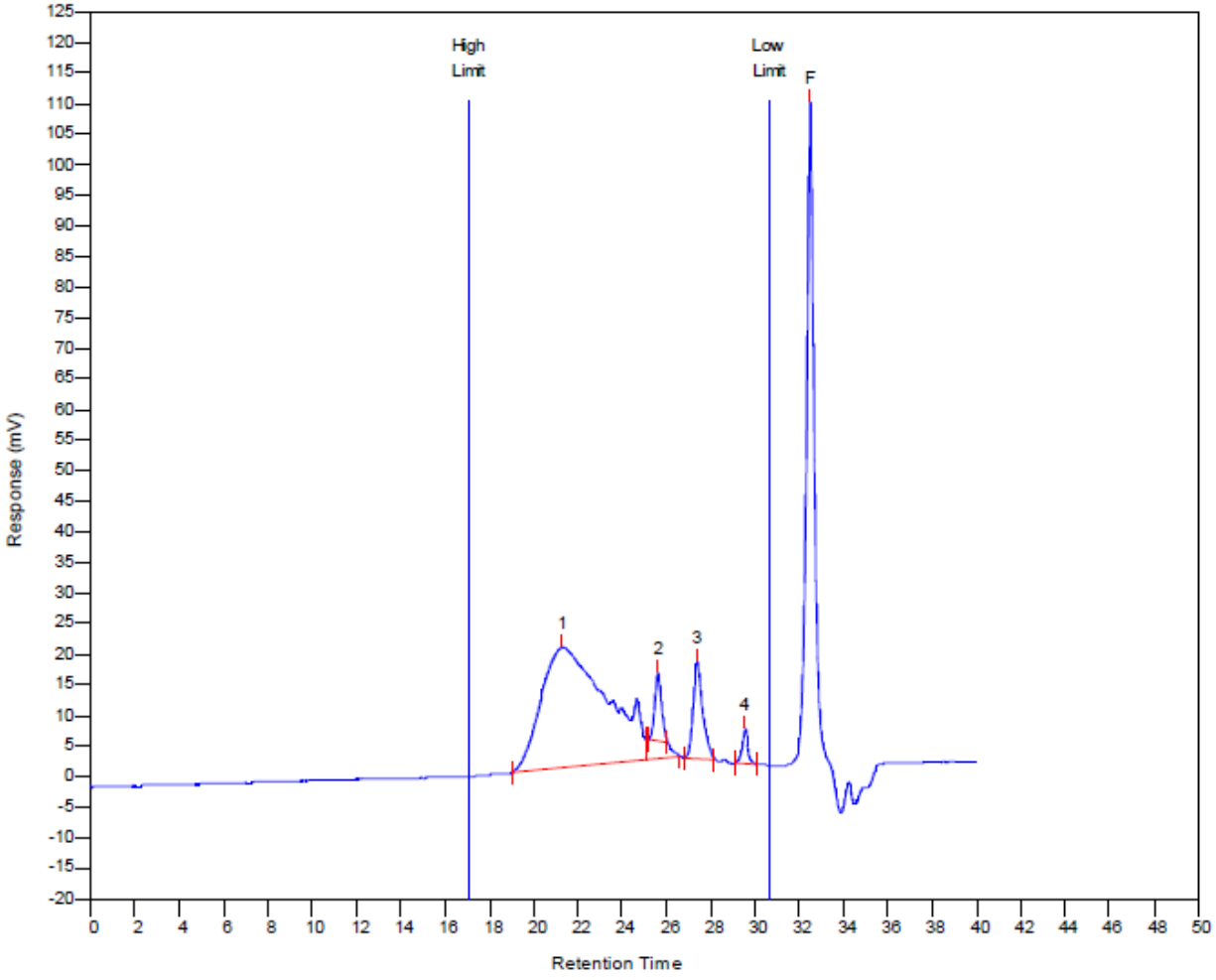
YP42



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	24722	10420	24572	46495	70012	21925	2.35816
2	1349	1345	1348	1353	1358	1347	1.00223
3	656	646	651	656	661	650	1.00774
4	268	268	269	270	271	268	1.00373

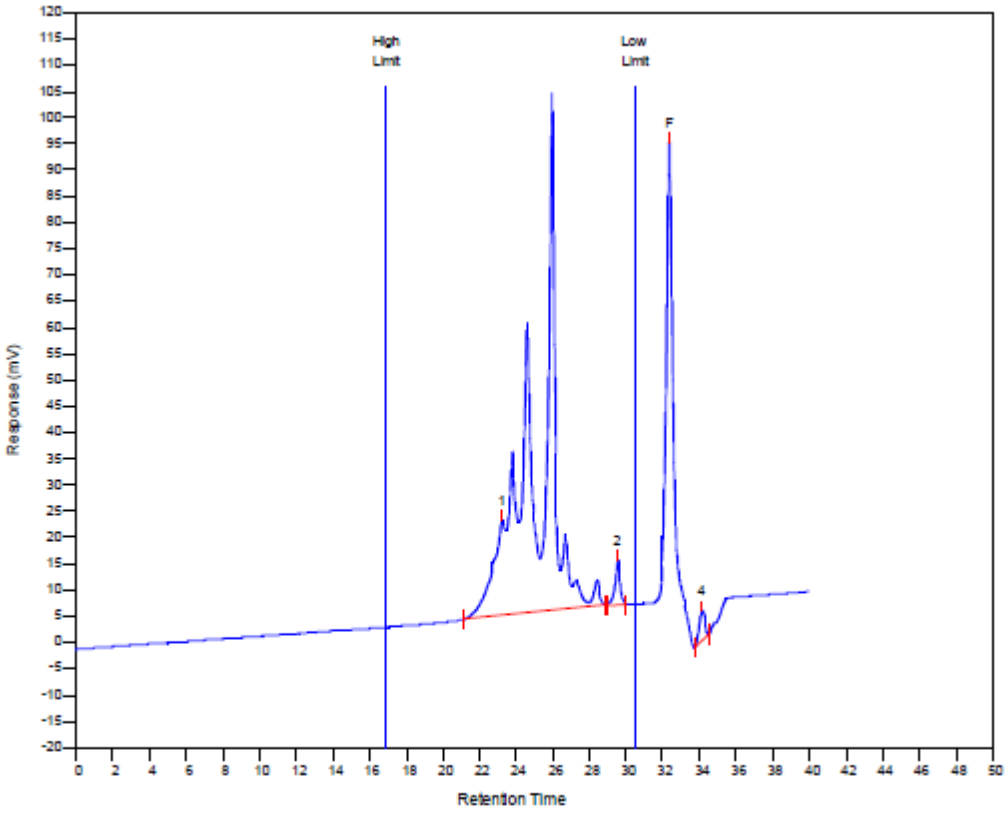
YP43



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	11014	5546	9613	15345	21263	8875	1.73332
2	1367	1354	1357	1362	1367	1356	1.00222
3	674	661	666	671	676	665	1.00756
4	268	267	268	269	271	268	1.00375

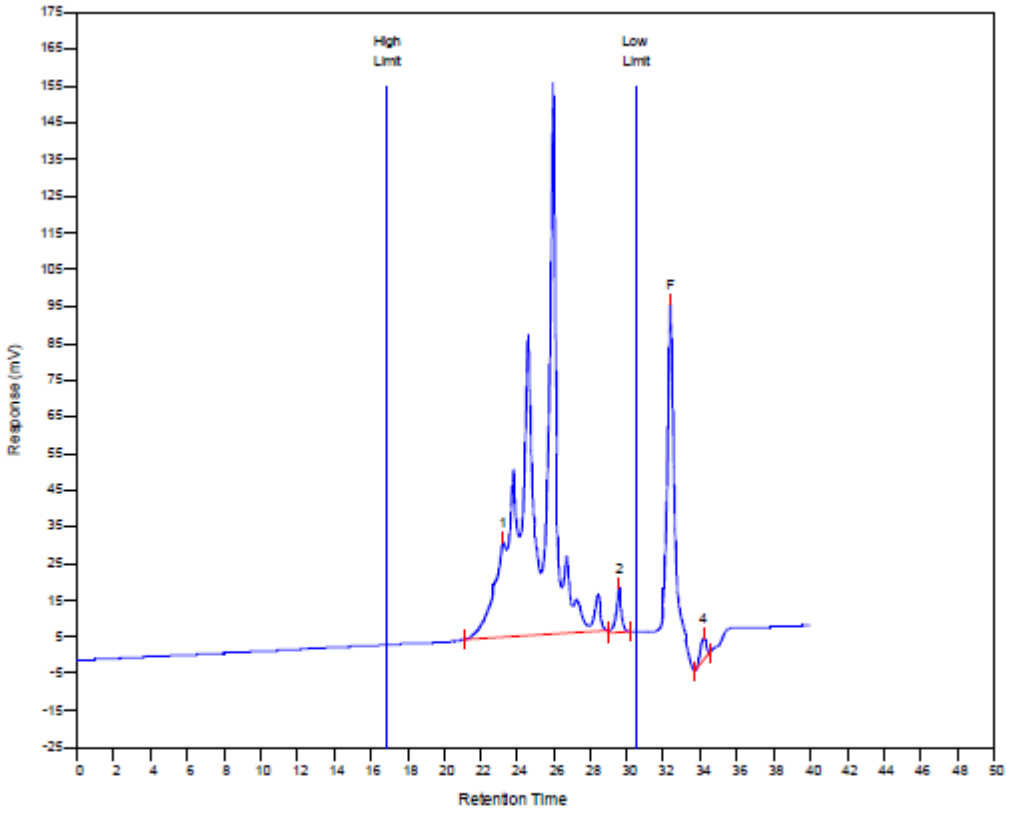
YP44



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1163	1508	2033	2781	3704	1940	1.34814

YP45

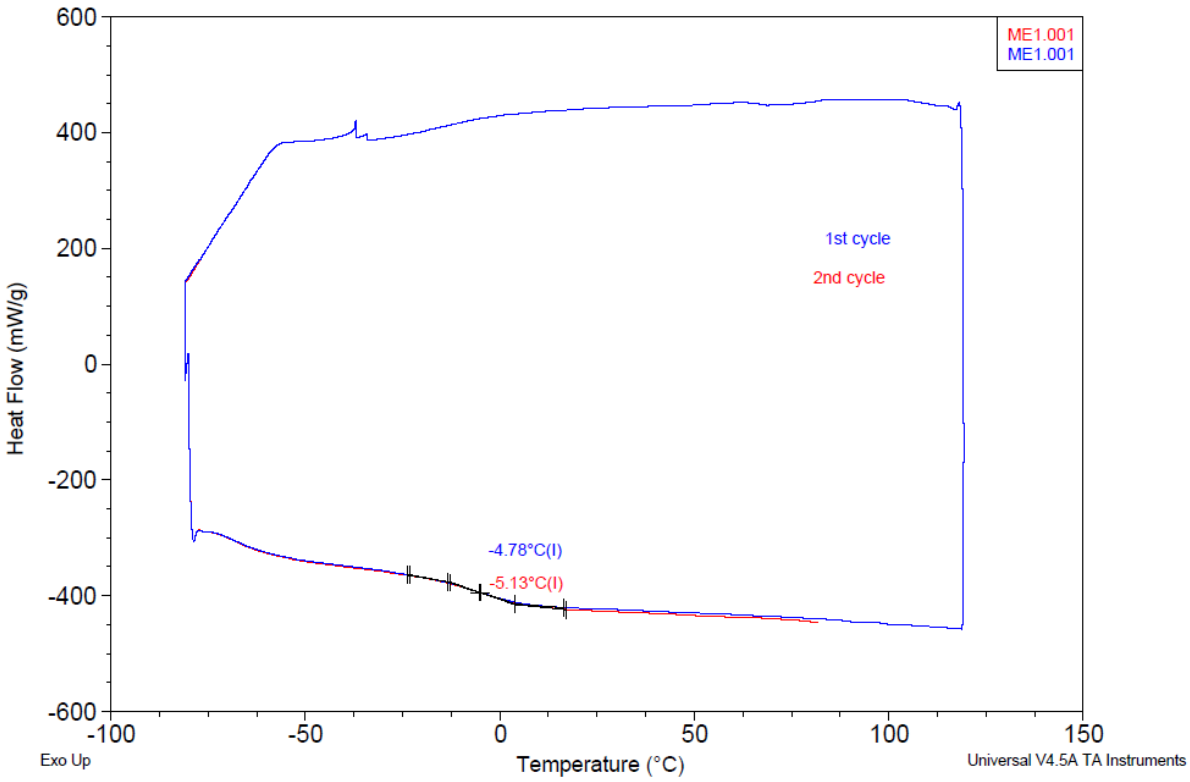


MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1170	1470	1992	2738	3685	1899	1.3551
2	252	254	255	257	259	254	1.00394

S9: DSC Thermograms

ME1



YP45