

APPENDIX A

EXPERIMENTAL PROCEDURE

COPOLYMERISATION OF EO/THF

Date:

Experiment number:

EO CAN N°: ____/

N°	Time	Action	Comments
1		Turn on the cooler bath equipment and EO can water bath.	
2		Record 1 st and 2 nd initial weight of EO Can Record weight of empty flask, magnetic stirrer and stoppers.	1 ST WEIGHT _____ 2 ND WEIGHT _____ FLASK WEIGHT _____
3		Add _____ g of THF in the flask	
4		Add _____ g of EG in the flask and stir the flask for 3 min (_____ molar % related THF).	
5		Add _____ g of catalyst, HBF ₄ ·Et ₂ O, to the THF and weigh flask.	WEIGHT _____
6		Stir for 3 min	
7		Maintain temperature around _____ °C for _____ min while passing N ₂ .	
8		Using a mechanical stirrer, stir the content of the flask by adjusting the air valve to 8.5 litres per min.	
9		The EO is transferred using a stainless steel needle (N° 18) through a rubber super seal inserted in the neck of the flask. Introduce EO _____ g by opening the can valve and adjusting the flow rate to _____ cm ³ /min for _____ h and _____ min.	STOP AT _____ hours
10		Stop the EO transfer by closing the can valve. Remove the needle from the flask.	
11		Weigh EO Can	1 ST WEIGHT _____ 2 ND WEIGHT _____ TOAL EO ADDED _____
12		If weight is less than expected go back to step 9. If weight is more than expected, add THF according to stoichiometry	
13		Maintain stirring at a temperature of _____ °C until all EO has reacted.	
14		Remove the flask from the bath and weigh ensuring the same configuration as in 2.	WEIGHT _____
15		Label the copolymer	21 (A, B,...) RC 201004
16		NEUTRALISE THE SAMPLE	SEE PROCEDURE

NEUTRALIZATION AND FILTRATION PROCESS

Date:

Experiment number:

Room: WH-97

Nº	Time	Action	Comments
1		Weigh the flask before neutralisation	1 st WEIGHT _____ 2 nd WEIGHT _____
2		Add a solution of ____ g NaHCO ₃ in ____ g of deionised water to the flask. Stir until no further sign of reaction (bubbles).	NaHCO ₃ _____ g
3		Add 600 ml (or three parts related to water) of chloroform to dissolve the organic phase. Stir until all foam disappears.	
4		Separate the organic from the inorganic phase using a separating funnel. Measure the pH of the inorganic phase.	
5		Add _____ g of deionised water to the flask, shake.	Water _____ g
6		Go to 4 and repeat cycle three times or until the inorganic phase is neutral.	
7		Add _____ g of MgSO ₄ to the organic phase and stir until it is transparent.	
8		Filter off MgSO ₄ and repeat step 7. Stir for 1 h	
9		Filter the sample under vacuum using 0.45 µm membrane filter.	
10		Pour the sample into a flask containing beads of molecular sieve 4Å for a period of 48 h	
11		Filter the sample under vacuum using 0.45 µm membrane filter.	
12		Weigh an empty rotary evaporator flask	1 st WEIGHT _____
13		Heat the sample in a water bath (67°C), and using a rotary evaporator remove the solvent under vacuum for 2 h. Re-weigh the flask.	2 nd WEIGHT _____
14		Place the sample under vacuum for 24 h. Note the final weight of the flask.	Vacuum mmHg _____ 3 rd WEIGHT _____

EXPERIMENTAL PARAMETERS

Experiment N:___ __/

Date_____/_____/_____

[illegible]

APPENDIX B

SEC RESULTS

Exp 1

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	22.99	1049.65	1393.34	1248.28	1.33
2	25.86			314.75	
3	26.19			266.63	

Inj 2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	23.02	958.92	1355.69	1226.56	1.41
2	26.85			186.85	
3	27.34			139.80	

Inj 3	Retention Time, min	Mn	Mw	MP	Polydispersity
1	23.02	960.05	1359.57	1227.22	1.42
2	26.82			186.32	
3	27.33			140.37	

Exp 2

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	22.43	1276.59	1931.71	1707.84	1.51
2	26.85			186.80	
3	27.30			142.58	

Inj 2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	22.43	1280.45	1964.11	1730.54	1.53
2	26.81			191.60	
3	27.28			144.85	

Inj 3	Retention Time, min	Mn	Mw	MP	Polydispersity
1	22.41	1297.47	1984.16	1745.54	1.53
2	26.81			191.04	
3	27.26			146.47	

Exp 3

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	22.21	1453.92	2317.77	1982.58	1.59
2	26.41			238.33	
3	26.77			195.26	

Inj 2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	22.19	1454.32	2322.72	2010.01	1.60
2	26.39			240.43	
3	26.77			195.47	

Inj 3	Retention Time, min	Mn	Mw	MP	Polydispersity
1	22.16	1502.65	2348.40	2052.33	1.56
2	26.07			283.99	
3	26.41			238.33	

Exp 4A

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	22.30	1090.94	1533.93	1444.18	1.41
2	25.86			241.73	
3	26.53			165.91	

Inj 2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	22.24	1126.01	1585.39	1493.23	1.41
2	25.78			252.43	
3	26.44			174.04	

Inj 3	Retention Time, min	Mn	Mw	MP	Polydispersity
1	22.24	1103.05	1588.38	1497.62	1.44
2	26.42			176.84	
3	26.91			130.81	

Exp 4B

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	22.07	1234.66	1737.81	1646.19	1.14
2	26.47			171.69	
3	26.89			132.47	

Inj 2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	22.03	1257.39	1783.19	1692.66	1.42
2	26.42			176.85	
3	26.84			136.72	

Inj 3	Retention Time, min	Mn	Mw	MP	Polydispersity
1	22.03	1253.73	1774.98	1692.44	1.42
2	26.41			177.09	
3	26.84			137.05	

Exp 4C

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	22.01	1265.83	1838.14	1710.74	1.45
2	26.01			222.67	
3	26.36			182.93	

Inj 2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	22.00	1274.71	1851.57	1724.51	1.45
2	26.33			185.71	
3	26.78			141.67	

Inj 3	Retention Time, min	Mn	Mw	MP	Polydispersity
1	22.01	1264.81	1837.44	1711.65	1.45
2	26.00			223.69	
3	26.33			185.79	

Exp 4D

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.94	1313.99	1924.31	1779.52	1.46
2	26.31			187.87	
3	26.78			141.76	

Inj 2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.95	1312.41	191.87	1772.06	1.46
2	26.35			183.82	
3	26.83			137.39	

Inj 3	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.94	1312.35	1918.51	1779.17	1.46
2	26.33			189.59	
3	26.83			138.11	

Exp 5

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	22.18	1214.47	1559.12	1429.17	1.28
2	22.21	1198.43	1535.19	1409.28	1.28

Exp 6

Inj	Retention Time, min	Mn	Mw	MP	Polydispersity
1	24.35	501.48	680.88	613.08	1.36
2	24.30	516.85	700.51	625.91	1.36
3	24.32	512.51	695.06	621.27	1.36

Exp 7

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
2	21.80	1940.52	3004.57	2986.71	
3	26.82	213.35	214.35	214.81	
4	27.43	149.60	149.88	149.03	
5	27.87	111.64	111.91	111.01	

Inj 2	Retention Time, min	Mn	Mw	MP	Polydispersity
2	21.80	1986.41	3030.02	2997.09	1.53
3	26.82	213.43	214.44	214.90	1.00
4	27.43	148.22	148.56	149.11	1.00
5	27.87	111.70	111.96	111.05	1.00

Inj 3	Retention Time, min	Mn	Mw	MP	Polydispersity
2	21.79	2028.19	3059.42	3015.05	1.51
3	26.81	213.76	214.77	215.22	1.00
4	27.43	149.20	149.55	148.73	1.00
5	27.86	112.50	112.67	111.52	1.00

Exp 8B1A

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.47	2586.83	3779.94	3521.58	1.46
2	26.30	255.90	256.03	253.82	1.00
3	27.34	141.90	142.25	141.32	1.00
4	27.77	107.22	107.47	106.95	1.00

Inj 2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.47	2494.16	3697.11	3513.54	1.48
2	26.31	253.77	253.86	252.12	1.00
3	27.36	140.02	140.37	139.77	1.00
4	27.79	106.27	106.49	105.72	1.00

Inj 3	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.45	2580.90	3770.48	3570.06	1.46
2	26.28	258.10	258.19	255.66	1.00
3	27.36	140.72	141.05	139.48	1.00
4	27.77	107.45	107.65	106.78	1.00

Exp 8B2A

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.31	2905.31	4904.67	4002.22	1.69
2	26.32	248.72	248.99	251.08	1.00
3	27.33	141.62	142.03	142.27	1.00
4	27.77	107.84	108.00	106.73	1.00

Inj 2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.27	3043.18	5003.89	4144.21	1.64
2	26.34	250.25	250.59	248.74	1.00
3	27.33	143.20	143.65	141.87	1.00
4	27.74	109.74	109.89	108.92	1.00

Inj 3	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.31	3033.74	4969.23	4012.01	1.64
2	26.31	248.78	249.02	251.84	1.00
3	27.37	140.59	141.11	139.04	1.00
4	27.76	108.28	108.38	107.65	1.00

Exp 9

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	22.07	1957.36	3046.96	2893.61	1.56
2	26.91	235.42	236.09	238.76	1.00
3	27.94	132.05	132.38	130.09	1.00
4	28.39	95.21	95.48	94.63	1.00

Inj 2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	22.04	2006.46	3133.69	2960.93	1.56
2	26.87	241.35	242.09	244.88	1.00
3	27.90	134.83	135.18	133.51	1.00
4	28.35	98.02	98.34	97.72	1.00

Inj 3	Retention Time, min	Mn	Mw	MP	Polydispersity
1	22.05	2001.68	3119.12	2944.64	1.56
2	26.87	242.59	242.94	244.06	1.00
3	27.91	133.58	133.98	133.00	1.00
4	28.36	97.15	97.44	97.44	1.00

Exp 10

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	24.02	812.68	1010.28	913.30	1.24
2	27.15	209.11	209.42	210.46	1.00
3	27.89	134.57	135.03	134.63	1.00

Inj 2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	24.01	821.76	1022.49	916.88	1.24
2	27.14	211.32	211.69	211.46	1.00
3	27.87	136.62	137.06	136.30	1.00

Exp 11

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.49	2215.73	3428.10	3173.96	1.55
2	26.40	205.75	208.66	230.17	1.01
3	27.36	128.91	129.35	127.97	1.00
4	27.82	91.97	92.24	92.17	1.00

Inj 2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.50	2185.10	3384.40	3137.30	1.55
2	26.41	203.57	206.58	229.50	1.01
3	27.35	128.63	128.99	129.12	1.00
4	27.82	91.44	91.83	92.31	1.00

Inj 3	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.47	2219.32	3473.07	3219.49	1.56
2	26.38	208.35	211.33	233.18	1.01
3	27.33	131.04	131.39	131.33	1.00
4	27.80	93.53	93.92	93.43	1.00

Exp 12

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.17	2850.37	4664.69	4111.00	1.64
2	26.71	191.28	192.08	193.14	1.00
3	27.27	138.07	138.39	136.17	1.00
4	27.74	96.52	97.01	97.61	1.01

Inj 2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.17	2822.72	4630.94	4096.34	1.64
2	26.72	192.80	193.54	191.88	1.00
3	27.28	136.29	136.72	135.43	1.00
4	27.73	97.03	97.50	98.25	1.00

Inj 3	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.14	2888.05	4750.86	4216.93	1.65
2	26.68	196.03	196.86	196.13	1.00
3	27.26	140.33	140.64	137.19	1.00
4	27.71	99.01	99.48	100.24	1.00

exp 13

inj 3	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.26	2696.11	4157.10	3848.45	1.54
2	26.25	256.79	257.38	252.93	1.00
3	26.64	201.72	202.33	204.45	1.00
4	27.24	144.12	144.52	142.72	1.00
5	27.69			104.85	

inj 2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.27	2665.60	4091.00	3822.82	1.53
2	26.24	253.43	253.76	254.04	1.00
3	26.68	199.94	200.58	200.54	1.00
4	27.24	142.62	143.02	142.27	1.00
5	27.70			104.23	

inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.26	2679.80	4121.13	3845.19	1.54
2	26.25	253.72	254.10	252.93	1.00
3	26.65	200.42	201.01	203.61	1.00
4	27.22	143.76	144.15	143.95	1.00
5	27.68			105.91	

Exp 14

inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.40	2449.12	3748.67	3450.57	1.53
2	25.08			447.49	
3	26.79	184.55	185.21	188.10	1.00
4	27.34	133.70	134.05	133.84	1.00
5	27.81	94.78	95.25	96.07	1.00
6	28.96				

inj2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.38	2509.24	3761.90	3487.93	1.50
2	25.09			444.08	
3	26.81	186.02	186.84	185.43	1.00
4	27.36	132.60	132.94	131.74	1.00
5	27.83	94.00	94.49	94.74	1.01
6	28.98				

inj 3	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.39	2536.14	3798.15	3462.86	1.50
2	25.06			451.14	
3	26.78	187.19	187.96	188.88	1.00
4	27.34	133.74	134.11	133.84	1.00
5	27.81	94.89	95.40	96.01	1.01
6	28.96				

Exp 15

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	22.10	1481.13	2181.92	1981.10	1.47
2	26.48	132.23	136.24	131.32	1.03
3	27.07	70.22	70.63	70.32	1.01
4	27.52	39.56	40.15	40.18	1.02

Exp 16

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.90	1687.42	2317.87	2239.83	1.37
2	26.58	117.64	119.19	119.68	1.01
3	27.62	33.52	34.27	34.79	1.02

Inj 2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.94	1680.76	2303.17	2187.75	1.37
2	26.58	117.33	118.85	119.11	1.01
3	27.17	63.21	63.68	62.27	1.01
4	27.62	33.20	33.92	34.73	1.02

Exp 17

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.77	1493.15	2211.08	2327.21	1.48
2	26.55	133.10	135.81	131.11	1.02
3	27.15	73.62	73.96	72.65	1.00
4	27.58	43.04	43.57	43.79	1.01

inj2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.76	1470.39	2207.57	2346.72	1.50
2	26.54	131.02	132.84	132.06	1.01
3	27.14	73.83	74.19	73.12	1.00
4	27.58	42.45	43.12	44.28	1.02

inj3	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.76	1469.13	2198.32	2341.14	1.50
2	26.54	133.24	135.90	131.60	1.02
3	27.14	73.78	74.09	73.04	1.00
4	27.58	42.58	43.16	44.08	1.01

Exp 18

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.59	1637.48	2489.46	2626.05	1.52
2	26.53	130.31	131.79	132.45	1.01
3	27.13	73.79	74.18	74.00	1.01
4	27.58	42.83	43.53	44.28	1.02

Inj 2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.60	1615.70	2470.93	2621.03	1.53
2	26.54	129.78	131.27	131.90	1.01
3	27.14	73.24	73.64	72.91	1.01
4	27.58	42.58	43.26	44.06	1.02

Inj3	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.59	1592.87	2480.64	2637.53	1.56
2	26.52	131.93	133.42	134.11	1.01
3	27.13	74.68	75.08	74.23	1.01
4	27.56	43.69	44.36	45.18	1.02

Exp 19

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.04	3978.58	5961.96	4598.30	1.50
2	25.03			457.22	
3	26.77	188.17	189.01	190.18	1.00
4	27.82	93.21	93.67	95.45	1.00

inj 2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.03	4028.31	6061.46	4663.15	1.50
2	25.01			460.20	
3	26.75	190.61	191.33	192.19	1.00
4	27.80	94.81	95.16	96.68	1.00

inj 3	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.04	4145.32	6061.18	4607.10	1.46
2	25.03			456.02	
3	26.77	188.05	188.85	190.03	1.00
4	27.83	92.94	93.35	95.04	1.00

Exp 20

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.57	2044.14	3008.59	3020.18	1.47
2	25.07			449.21	
3	26.78	184.90	185.70	188.43	1.00
4	27.37	131.95	132.31	130.66	1.00
5	27.82	94.38	94.90	95.83	1.01
6	28.33			63.77	
7	28.96				

inj 2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.58	1969.80	2940.39	2998.31	1.49
2	25.09			444.08	
3	26.79	185.01	185.85	187.79	1.00
4	27.39	130.36	130.67	128.81	1.00
5	27.83	93.14	93.65	94.78	1.01
6	28.35			62.78	
7	28.98				

inj 3	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.57	2277.99	3125.56	3028.45	1.37
2	26.28			248.65	
3	26.82	185.94	186.82	184.80	1.00
4	27.36	132.02	132.34	131.92	1.00
5	27.82	94.14	94.65	95.65	1.01
6	28.34			63.34	
7	28.96				

Exp 21

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	20.92	2481.54	4260.83	3866.66	1.72
2	26.01	249.99	255.09	231.40	1.02
3	26.87	133.02	134.24	133.48	1.01
4	27.81	59.53	60.73	60.69	1.02

Inj 2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	20.93	2838.88	4480.50	3822.87	1.58
2	26.02	237.32	240.25	230.65	1.01
3	26.89	132.94	134.16	131.61	1.01
4	27.82	58.22	59.66	60.21	1.02

Inj 3	Retention Time, min	Mn	Mw	MP	Polydispersity
1	20.91	2876.75	4561.51	3894.94	1.59
2	25.99	241.28	244.20	234.08	1.01
3	26.88	133.35	134.65	132.33	1.01
4	27.79	59.98	61.42	61.95	1.02

Exp 22

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	20.81	3226.18	5486.95	4276.85	1.70
2	24.63	456.88	458.47	462.40	1.00
3	26.01	240.30	242.77	232.08	1.01
4	26.90	133.47	134.46	130.09	1.01
5	27.79	61.33	62.28	61.63	1.02
6	28.40			32.46	

Inj 2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	20.80	3260.37	5507.48	4306.51	1.69
2	24.62	456.76	458.42	462.92	1.00
3	26.01	239.13	241.42	232.08	1.01
4	26.86	133.01	134.15	134.29	1.01
5	27.79	61.20	62.17	61.61	1.02
6	28.40			32.56	

Inj 3	Retention Time, min	Mn	Mw	MP	Polydispersity
1	20.83	3230.93	5420.69	4209.02	1.68
2	24.65	456.79	458.55	457.26	1.00
3	26.03	234.06	235.79	228.77	1.01
4	26.89	132.21	133.59	131.07	1.01
5	27.81	59.94	60.92	60.26	1.02
6	28.42			31.75	

Exp 23

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	20.63	4255.66	8569.32	9676.40	2.01
2	25.27	460.48	461.89	466.00	1.00
3	27.07	199.77	200.87	191.98	1.01
4	28.07	106.32	110.04	95.68	1.03

Inj 2	Retention Time	Mn	Mw	MP	Polydispersity
1	20.63	4322.52	8638.16	9735.43	2.00
2	25.26	468.42	470.34	468.90	1.00
3	27.02	201.50	202.52	197.83	1.01
4	28.06	107.25	110.97	96.73	1.03

Inj 3	Retention Time	Mn	Mw	MP	Polydispersity
1	20.63	4376.25	8723.76	9778.32	1.99
2	25.25	472.92	475.27	469.72	1.00
3	26.99	200.64	201.65	201.55	1.01
4	28.05	107.96	111.69	96.94	1.03

Exp 24

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	20.58	4659.69	9687.56	10354.21	2.08
2	25.25	465.41	466.77	469.78	1.00
3	27.05	200.28	201.31	194.41	1.01
4	28.05	104.04	107.12	97.34	1.03

Inj 2	Retention Time	Mn	Mw	MP	Polydispersity
1	20.58	4861.19	9753.36	10346.72	2.01
2	25.22	507.82	515.34	475.86	1.01
3	27.02	199.28	200.29	198.61	1.01
4	28.04	102.92	105.79	97.77	1.03

Inj 3	Retention Time	Mn	Mw	MP	Polydispersity
1	20.57	4847.05	9821.42	10441.45	2.03
2	25.23	503.09	511.76	473.89	1.02
3	27.03	200.08	201.07	196.86	1.00
4	28.03	104.41	107.45	98.42	1.03

Exp 25

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	20.66	4192.68	8223.71	9435.15	1.96
2	25.24	494.27	499.46	471.97	1.01
3	26.98	204.87	205.84	202.34	1.00
4	28.03	112.06	115.74	98.59	1.03

Inj 2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	20.66	4271.52	8279.88	9405.63	1.94
2	25.21	493.58	503.12	478.36	1.02
3	26.99	203.60	204.66	201.61	1.01
4	28.00	112.27	115.89	101.07	1.03

Inj 3	Retention Time, min	Mn	Mw	MP	Polydispersity
1	20.65	4283.70	8312.48	9529.14	1.94
2	25.21	494.91	504.98	478.38	1.02
3	26.97	205.06	206.07	204.06	1.00
4	27.58	113.79	117.49	137.73	1.03

Exp 26

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.22	3995.36	7716.37	5137.47	1.93
2	25.21	499.92	506.29	477.77	1.01
3	26.96	208.35	209.41	205.76	1.01
4	27.56	117.84	121.52	139.69	1.03

Inj 2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.21	4116.64	7889.14	5235.53	1.92
2	25.16	504.02	515.02	488.04	1.02
3	26.93	209.80	210.82	208.60	1.00
4	27.55	118.37	122.11	141.02	1.03

Inj 3	Retention Time, min	Mn	Mw	MP	Polydispersity
1	21.21	4114.76	7871.05	5194.33	1.91
2	25.16	505.72	516.07	488.34	1.02
3	26.94	209.81	210.85	208.07	1.00
4	27.56	118.73	122.58	140.48	1.03

Exp 27

Inj 1	Retention Time, min	Mn	Mw	MP	Polydispersity
1	20.63	4313.45	8447.96	9704.89	1.96
2	25.18	498.43	507.08	485.23	1.02
3	26.89	210.64	211.61	213.67	1.00
4	27.56	121.37	124.92	140.39	1.03

Inj 2	Retention Time, min	Mn	Mw	MP	Polydispersity
1	20.63	4362.97	8481.49	9778.73	1.94
2	25.17	504.88	515.64	486.95	1.02
3	26.92	210.79	211.76	209.45	1.00
4	27.55	121.40	125.09	141.10	1.03

Inj 3	Retention Time, min	Mn	Mw	MP	Polydispersity
1	20.64	4343.08	8450.58	9649.88	1.95
2	25.15	502.80	512.99	489.56	1.02
3	26.90				
4	27.55	121.20	124.92	140.95	1.03

Percentage of each component**Exp 11**

Retention Time, min	% Area
21.47	98.88
26.38	0.48
27.35	0.23
27.78	0.40

Exp 12

Retention Time, min	% Area
21.17	98.78
26.72	0.24
27.28	0.18
27.73	0.62
28.28	0.18

Exp 13

Retention Time, min	% Area
21.26	98.17
26.64	1.05
27.24	0.18
27.69	0.60

Exp 15

Retention Time, min	% Area
22.10	97.16
26.48	1.81
27.07	0.14
27.52	0.89

Exp 16

Retention Time, min	% Area
21.94	97.31
26.58	1.58
27.17	0.14
27.62	0.97

Exp 17

Retention Time, min	% Area
21.74	92.17
26.53	1.22
27.13	0.17
27.58	0.80
29.03	5.65

APPENDIX C

NMR SPECTRA

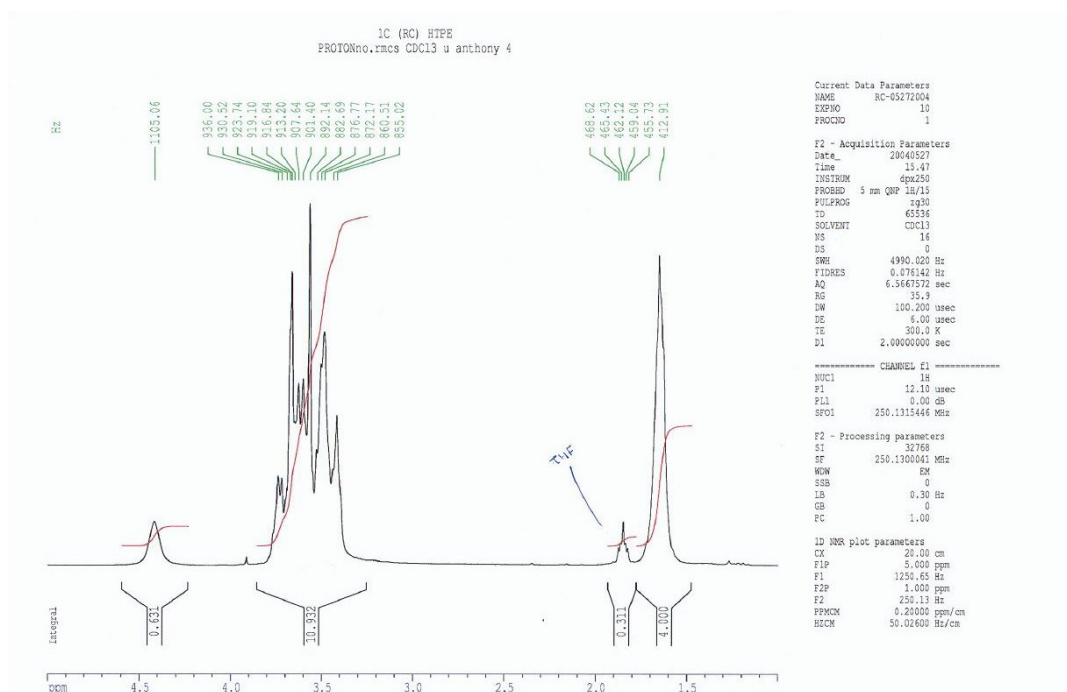


Figure 1. Proton NMR spectrum from experiment 1

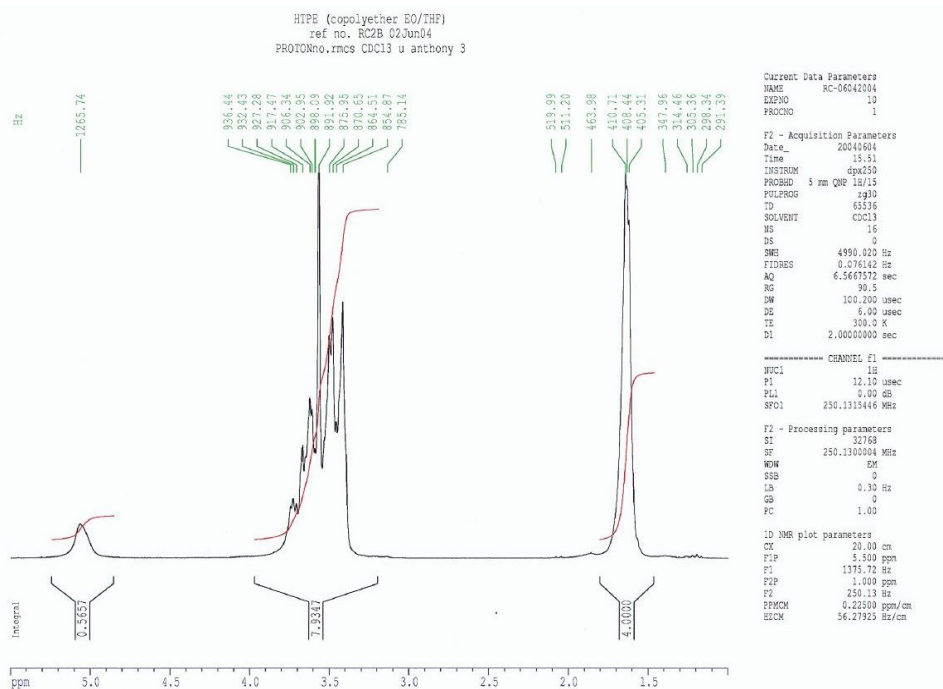


Figure 2. Proton NMR spectrum from experiment 2

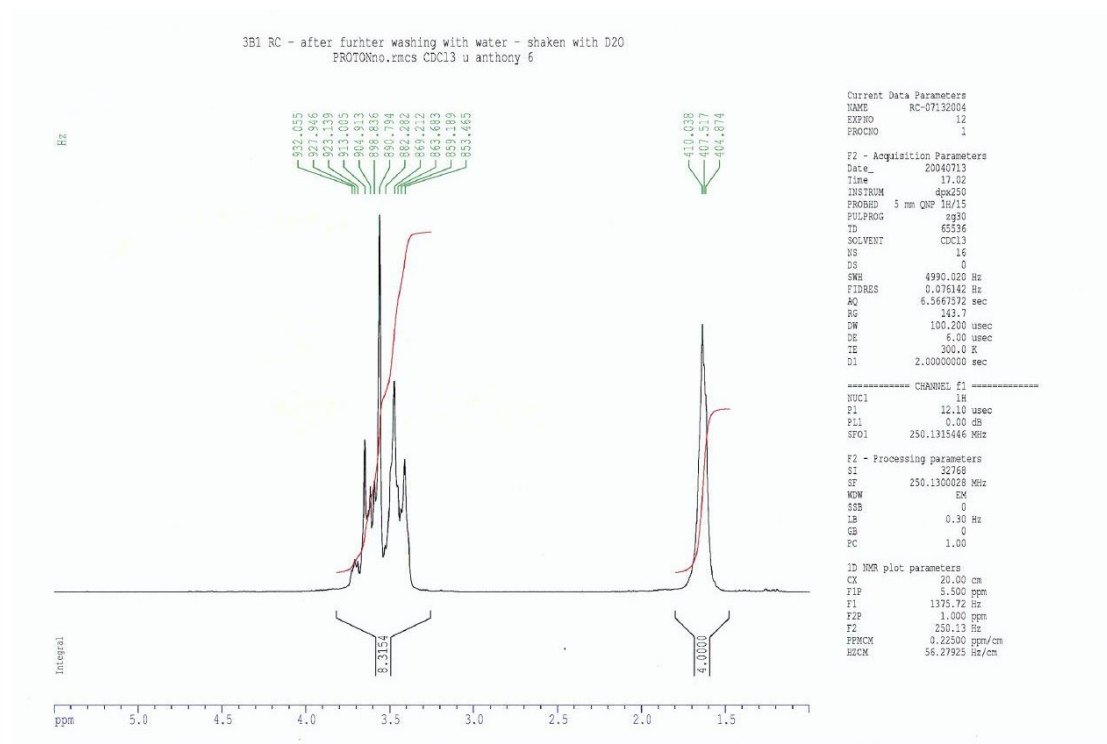


Figure 3. Proton NMR spectrum from experiment 3

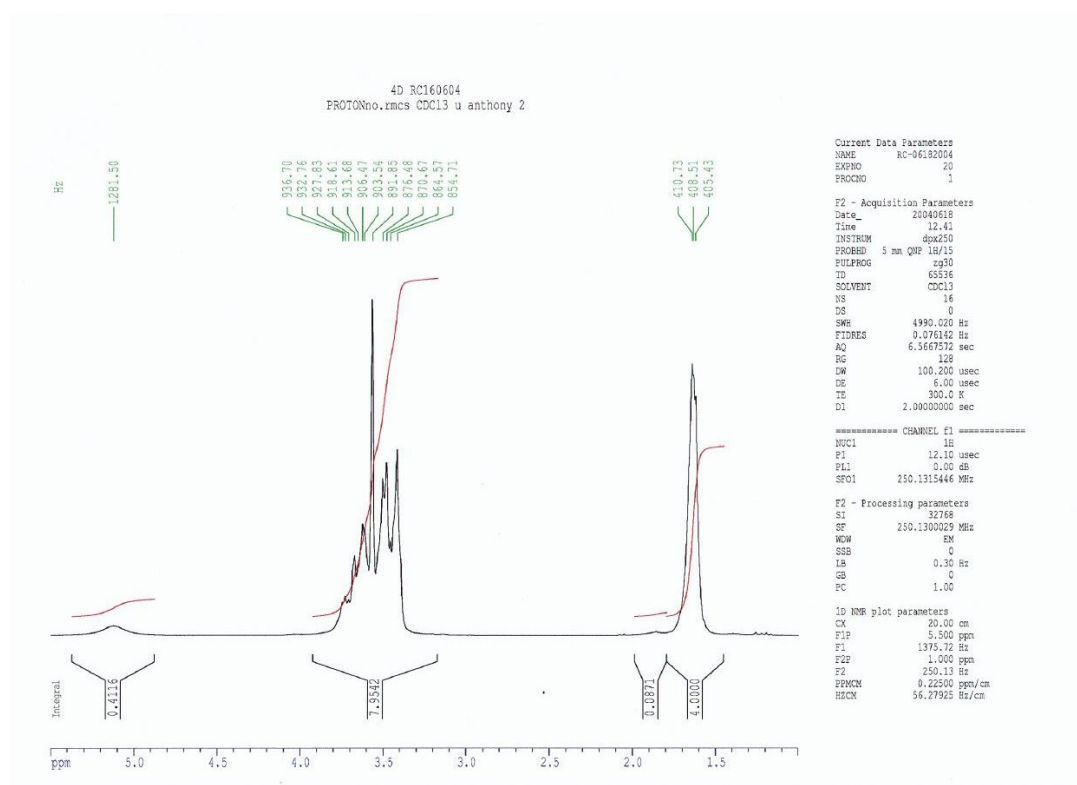


Figure 4. Proton NMR spectrum from experiment 4D

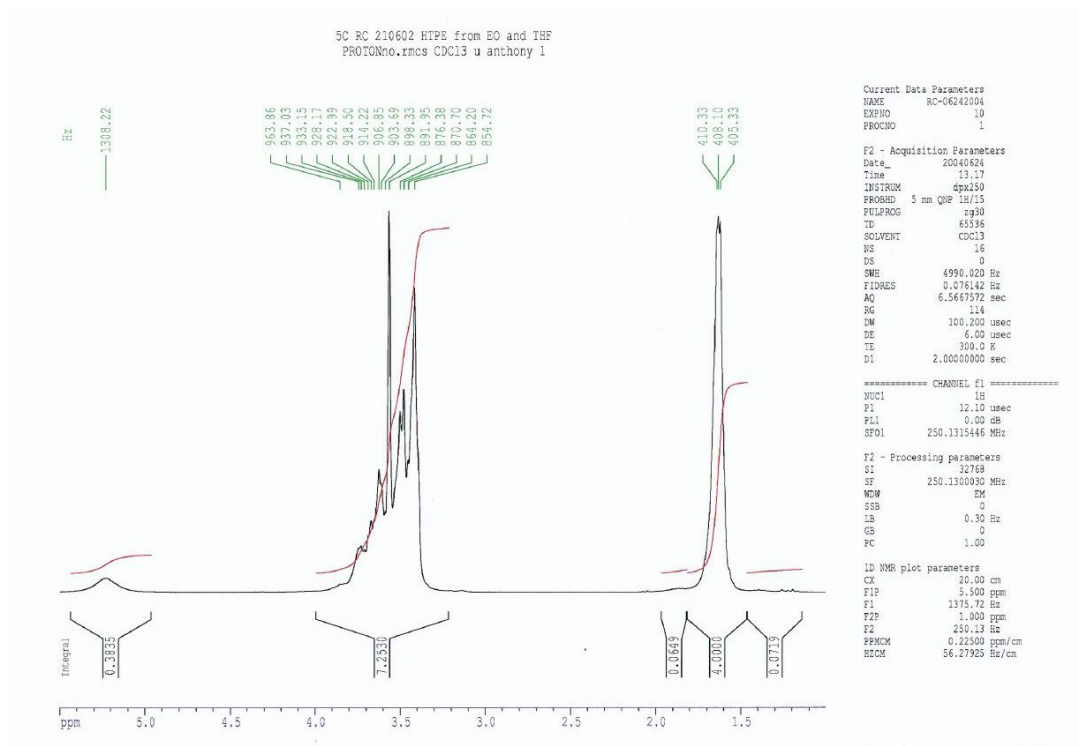


Figure 5. Proton NMR spectrum from experiment 5

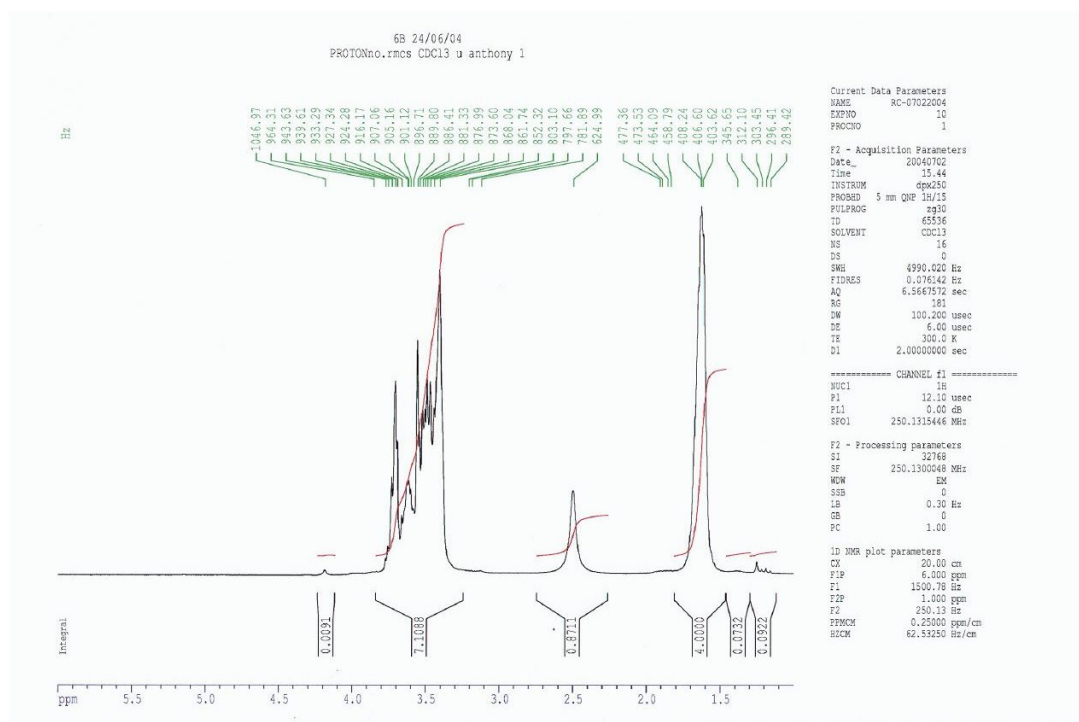


Figure 6. Proton NMR spectrum from experiment 6

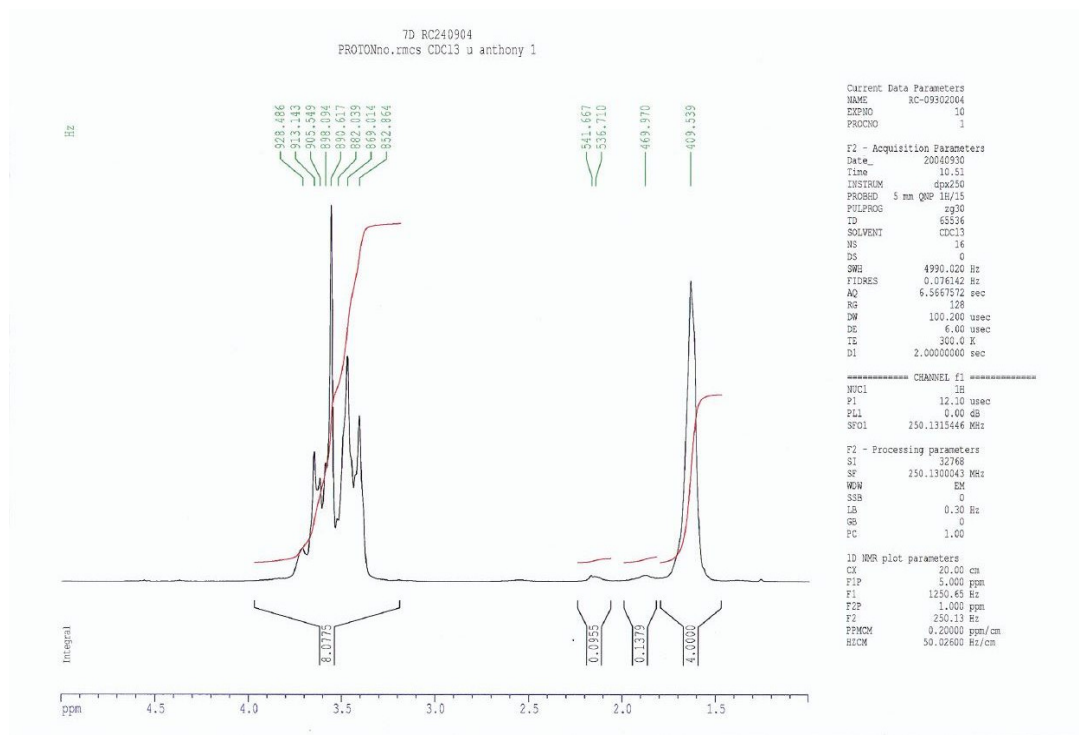


Figure 7. Proton NMR spectrum from experiment 7

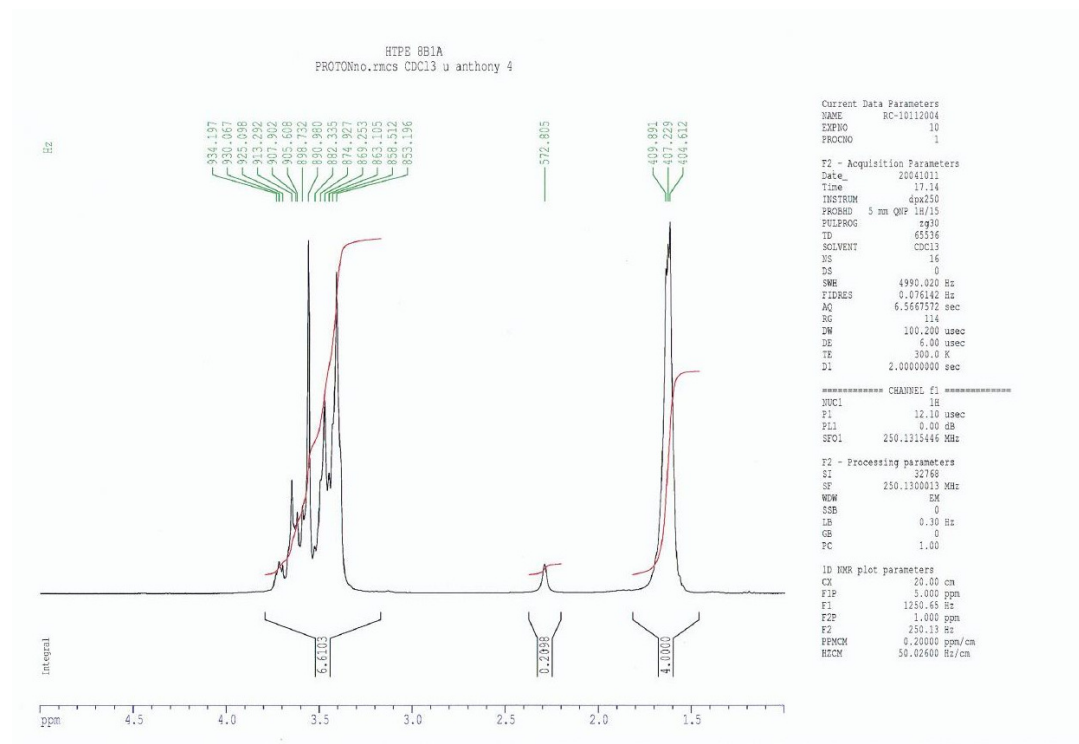


Figure 8. Proton NMR spectrum from experiment 8B1A

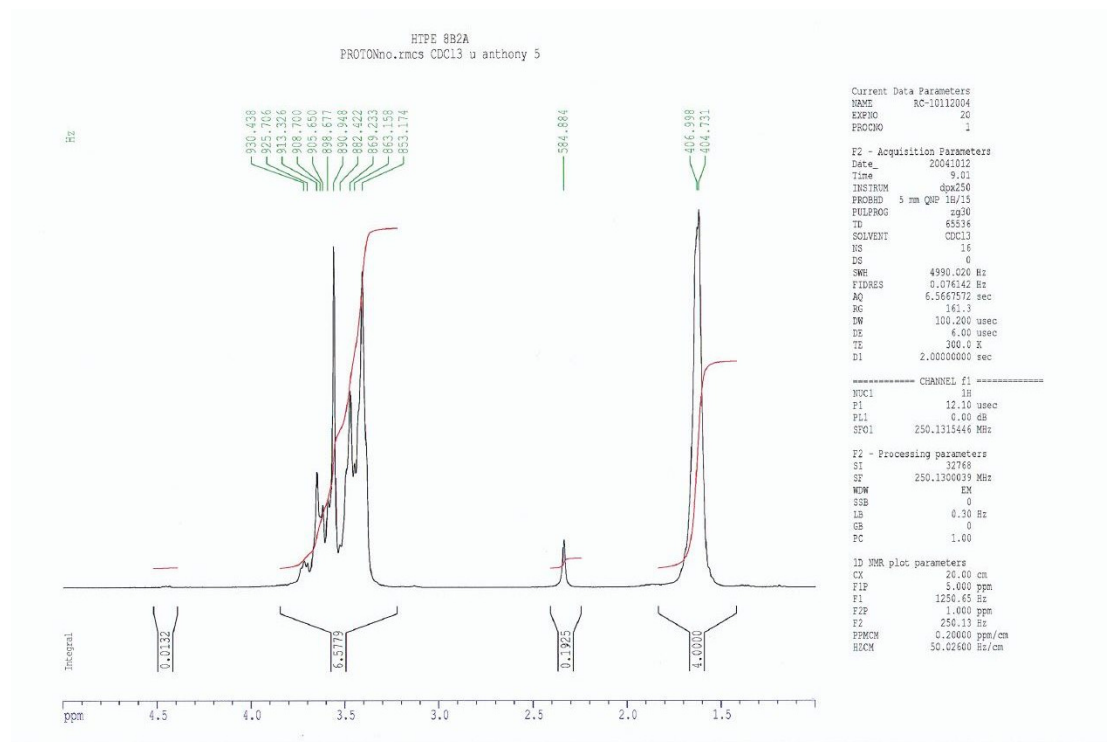


Figure 9. Proton NMR spectrum from experiment 8B2A

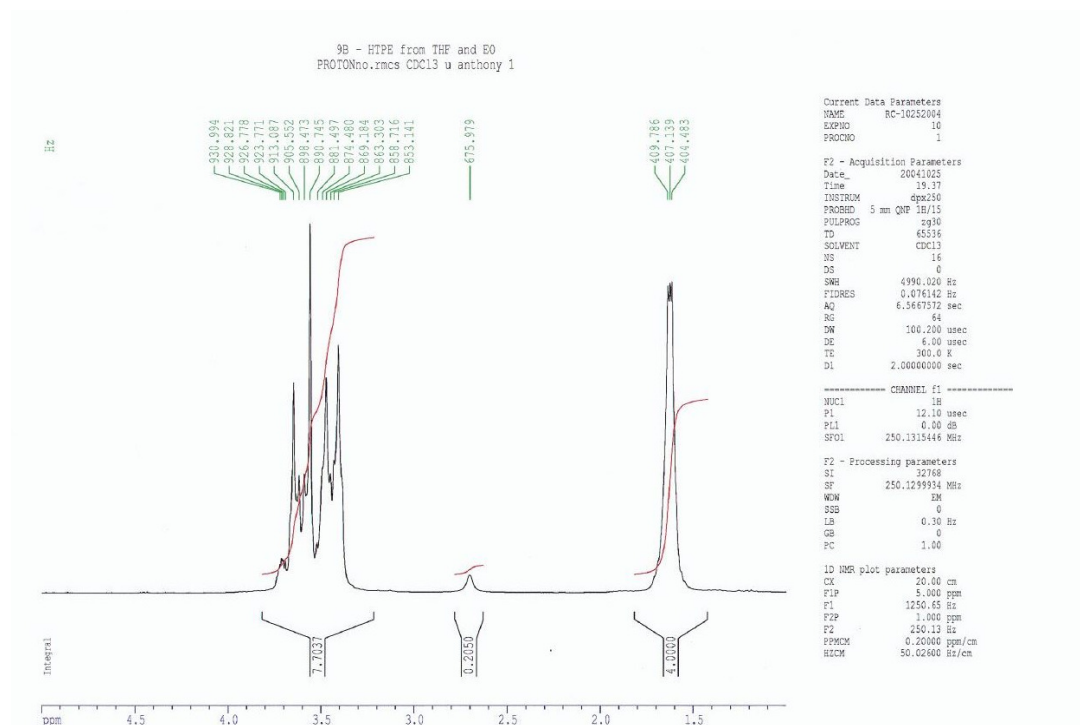


Figure 10. Proton NMR spectrum from experiment 9

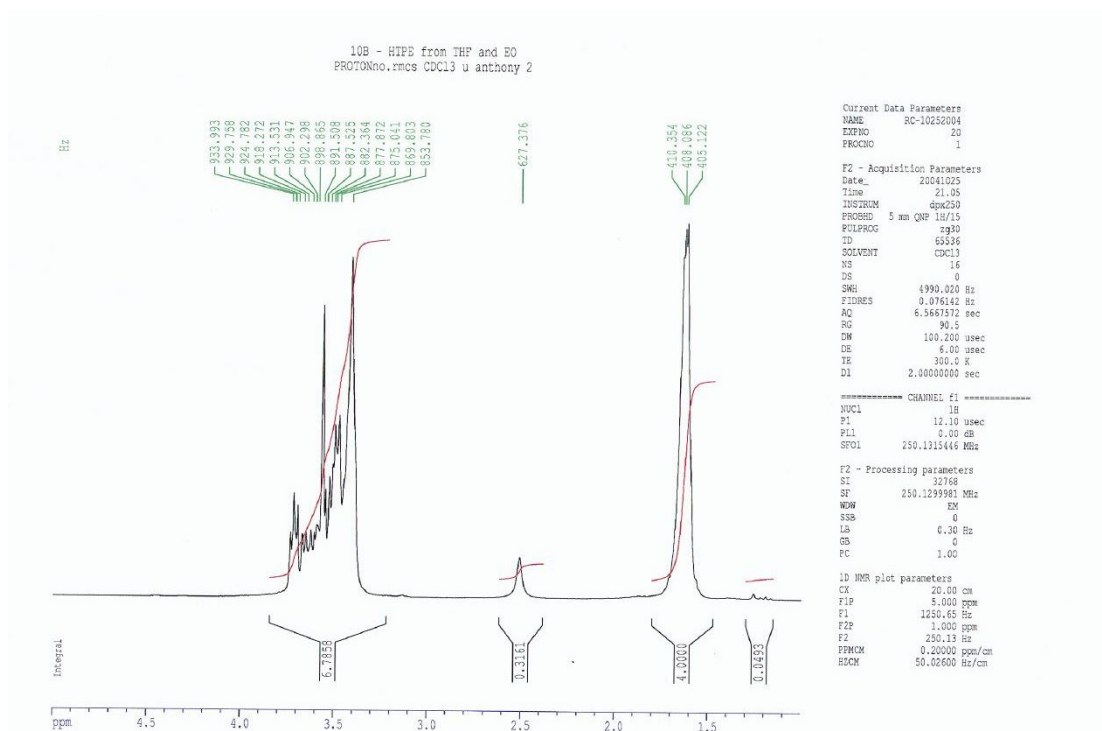


Figure 11. Proton NMR spectrum from experiment 10

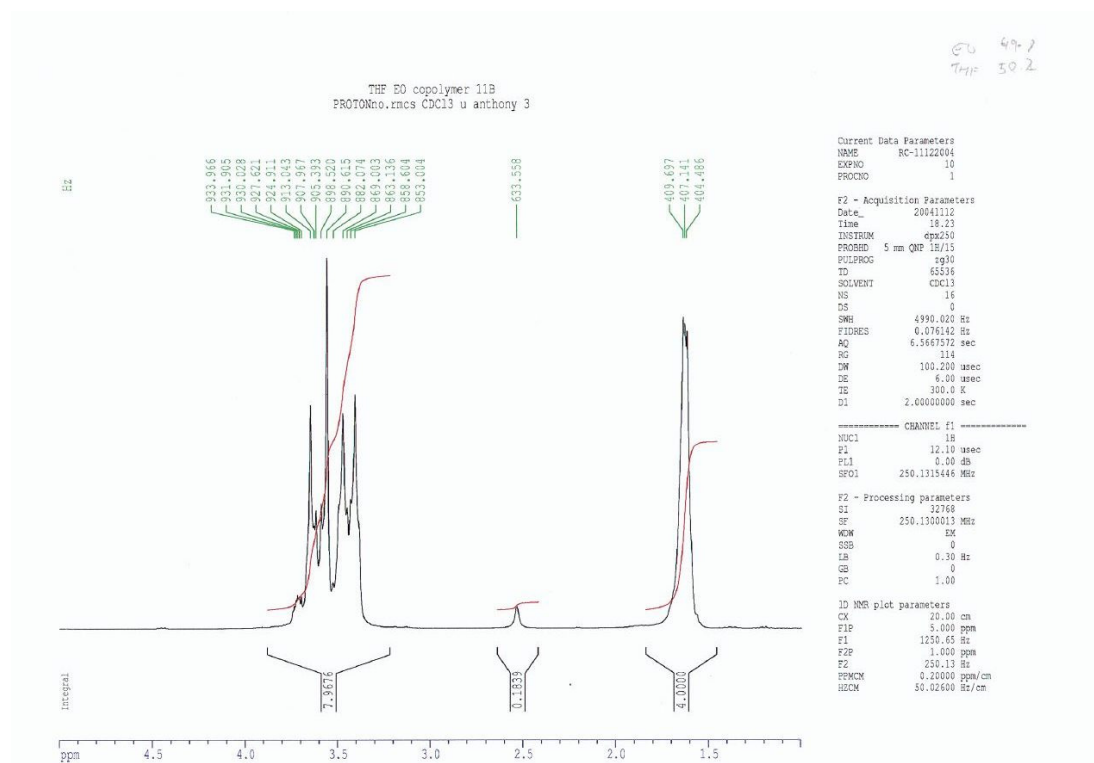


Figure 12. Proton NMR spectrum from experiment 11

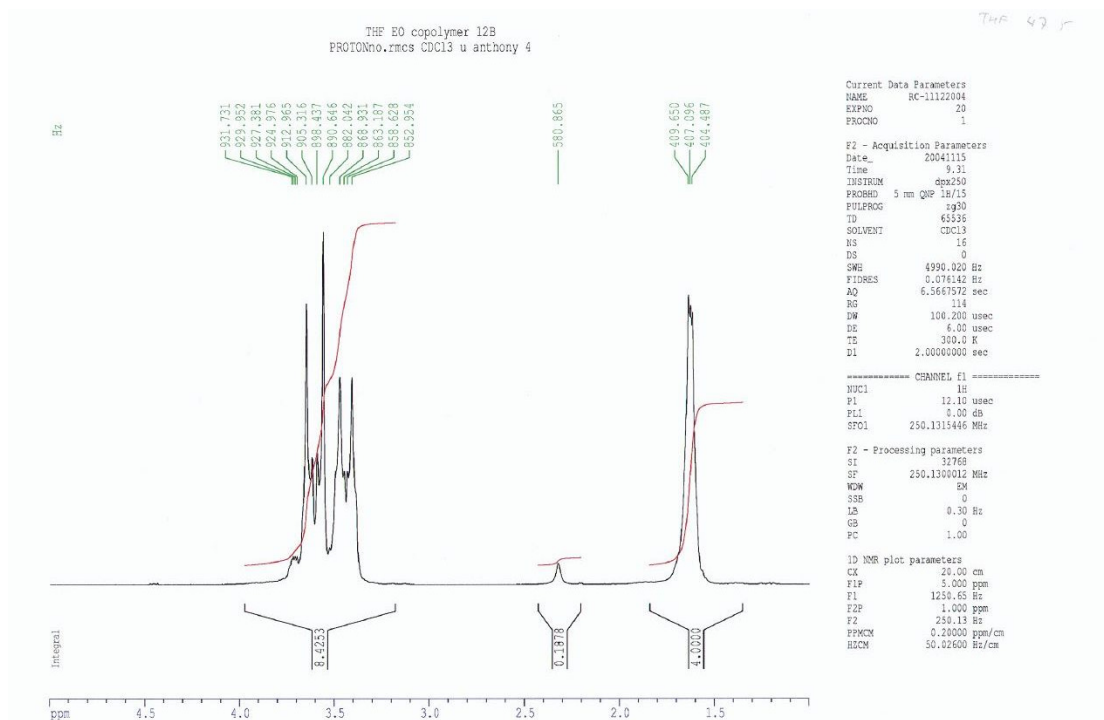


Figure 13. Proton NMR spectrum from experiment 12

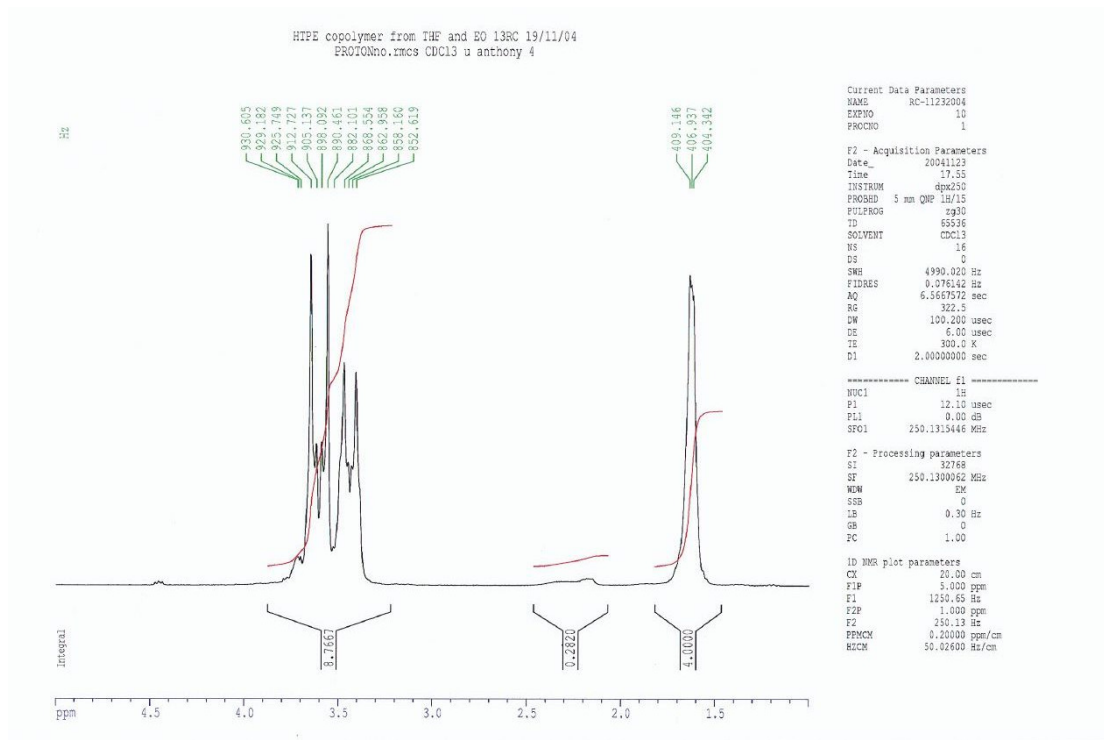


Figure 14. Proton NMR spectrum from experiment 13

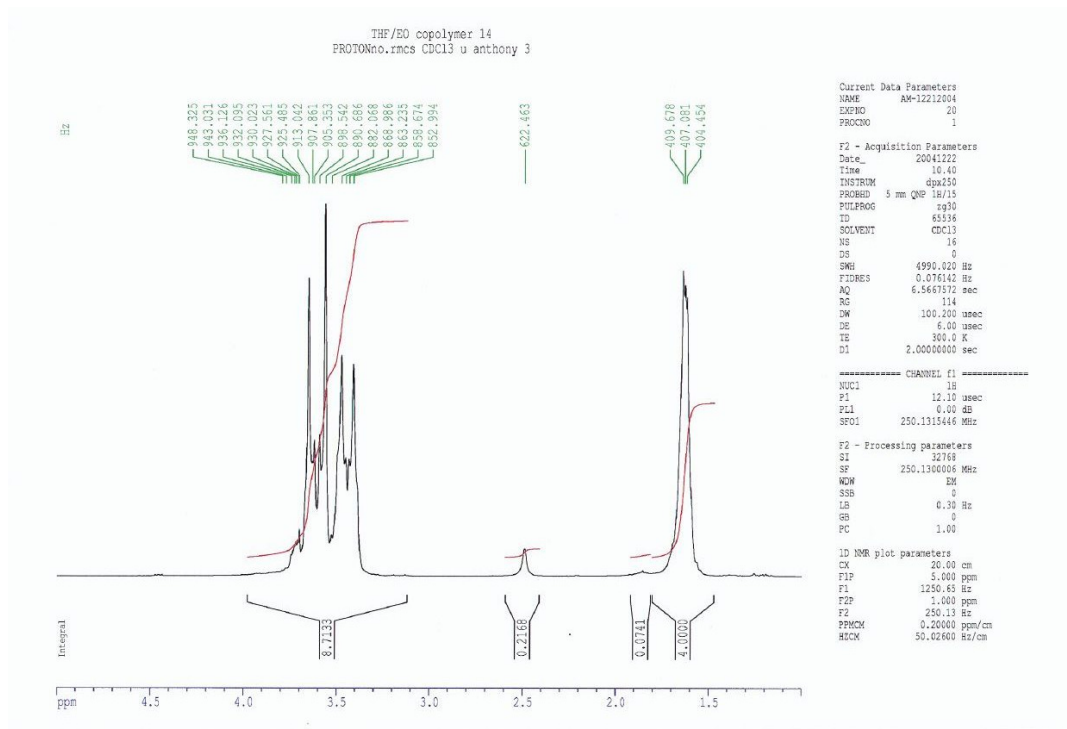


Figure 15. Proton NMR spectrum from experiment 14

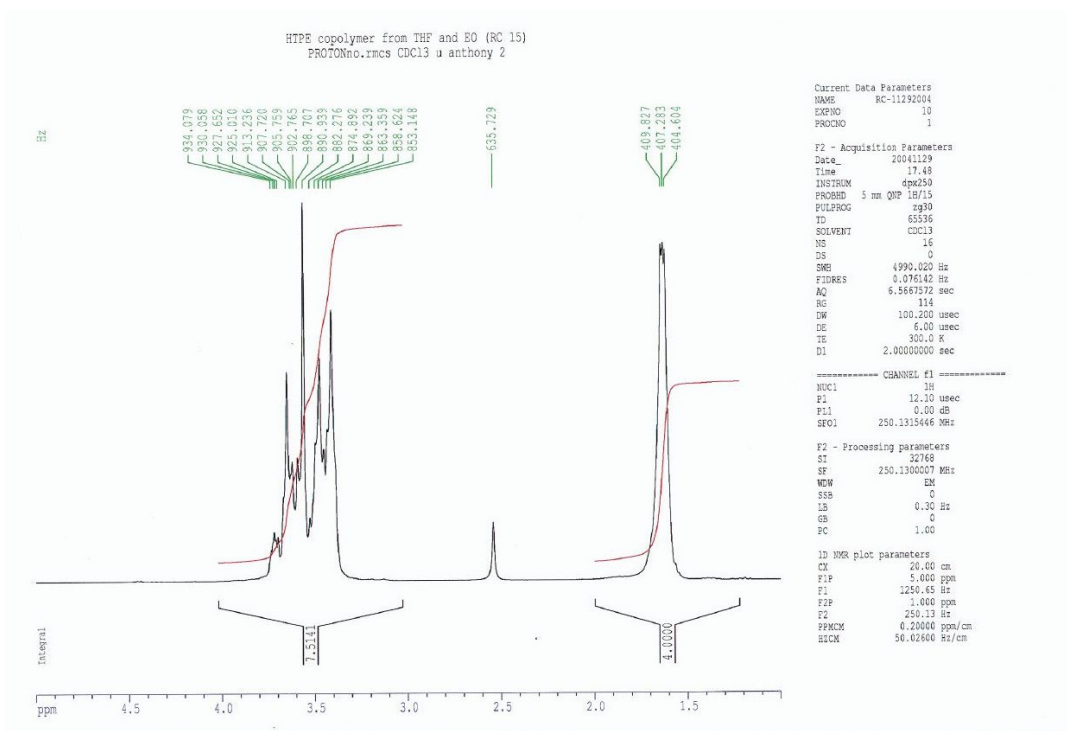


Figure 16. Proton NMR spectrum from experiment 15

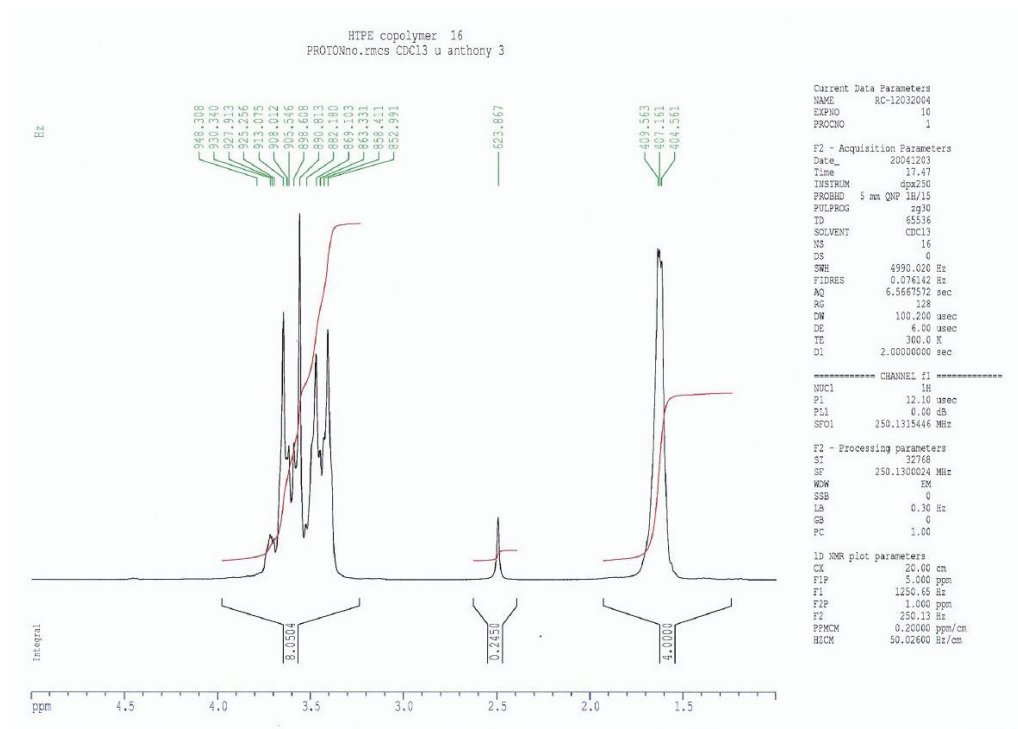


Figure 17. Proton NMR spectrum from experiment 16

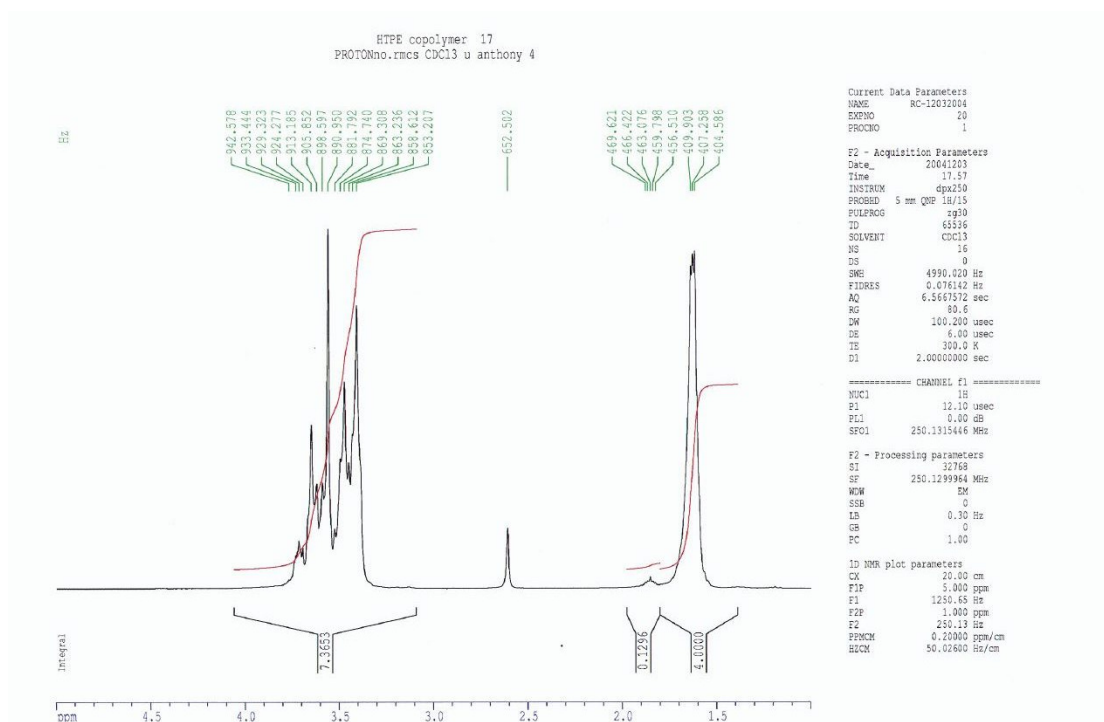


Figure 18. Proton NMR spectrum from experiment 17

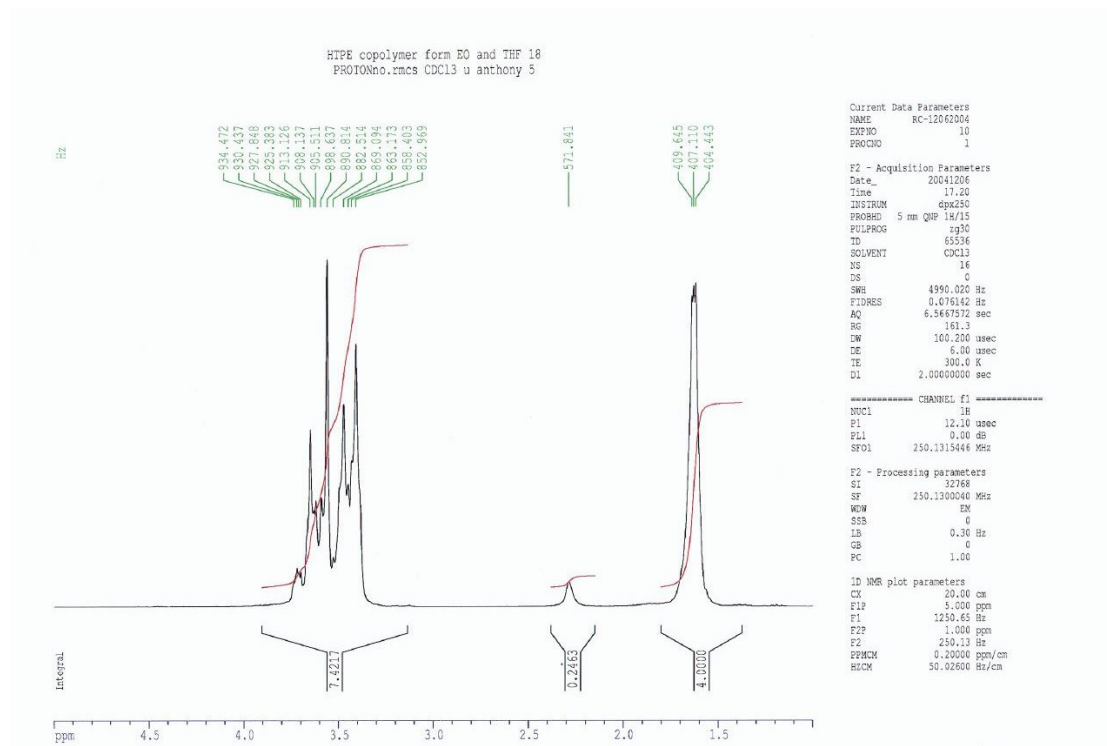


Figure 19. Proton NMR spectrum from experiment 18

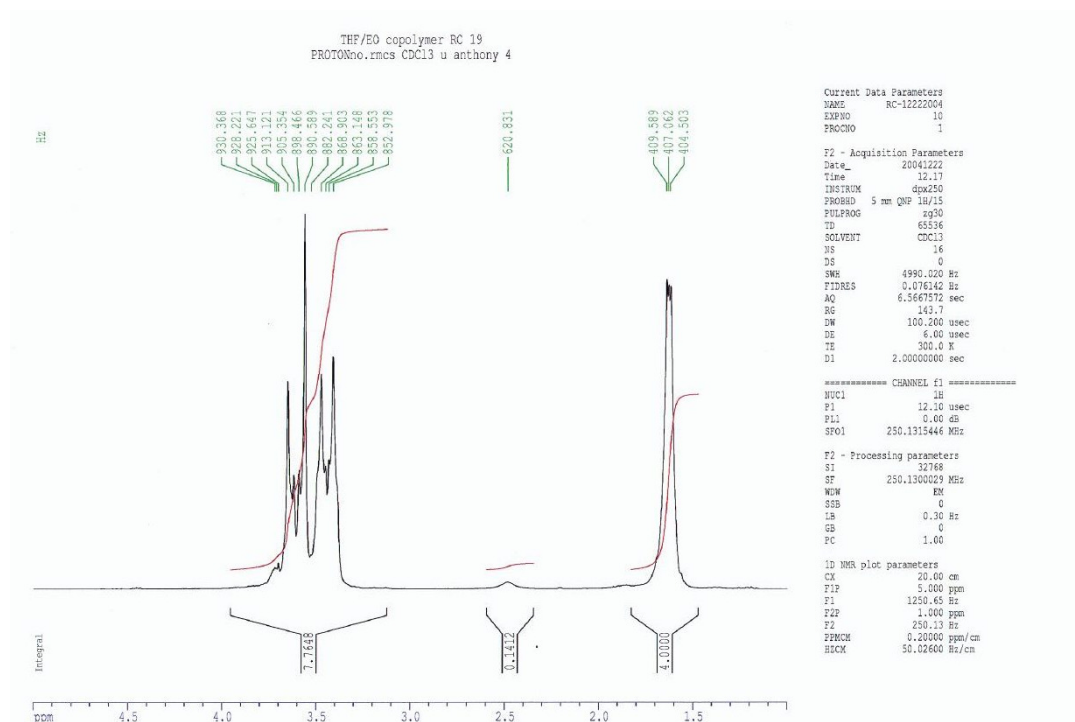


Figure 20. Proton NMR spectrum from experiment 19

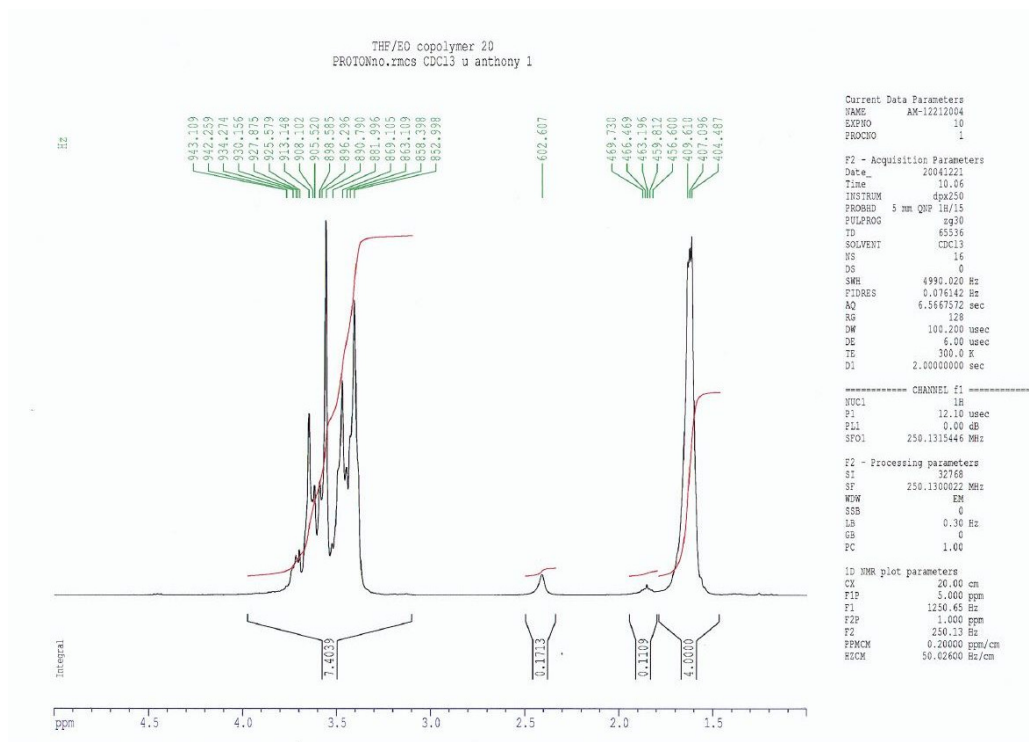


Figure 21. Proton NMR spectrum from experiment 20

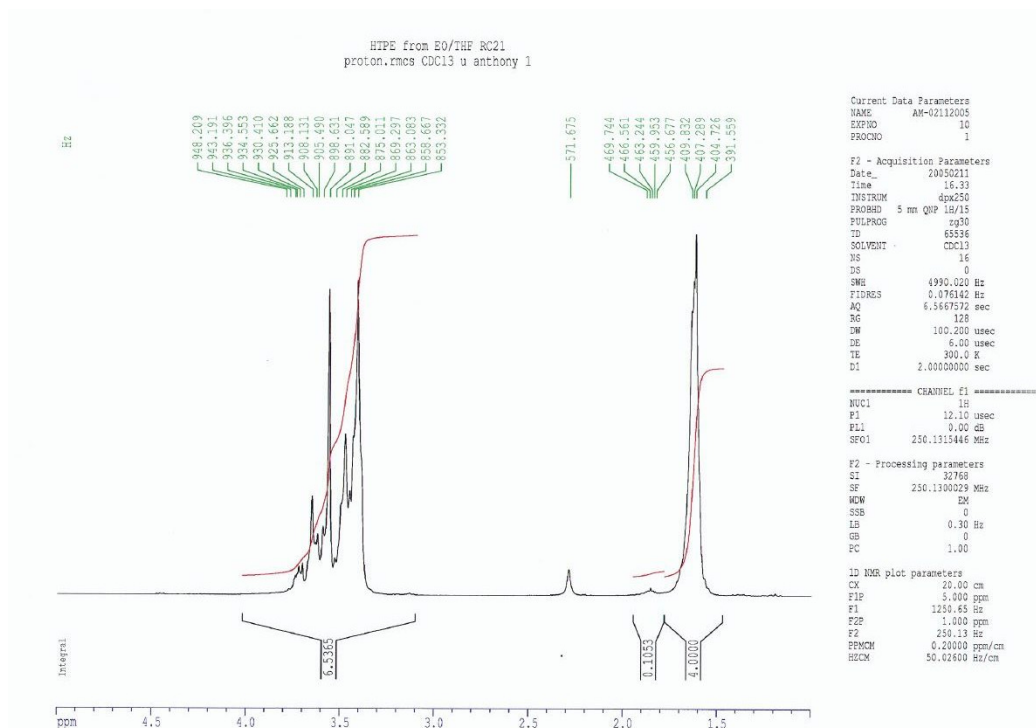


Figure 22. Proton NMR spectrum from experiment 21

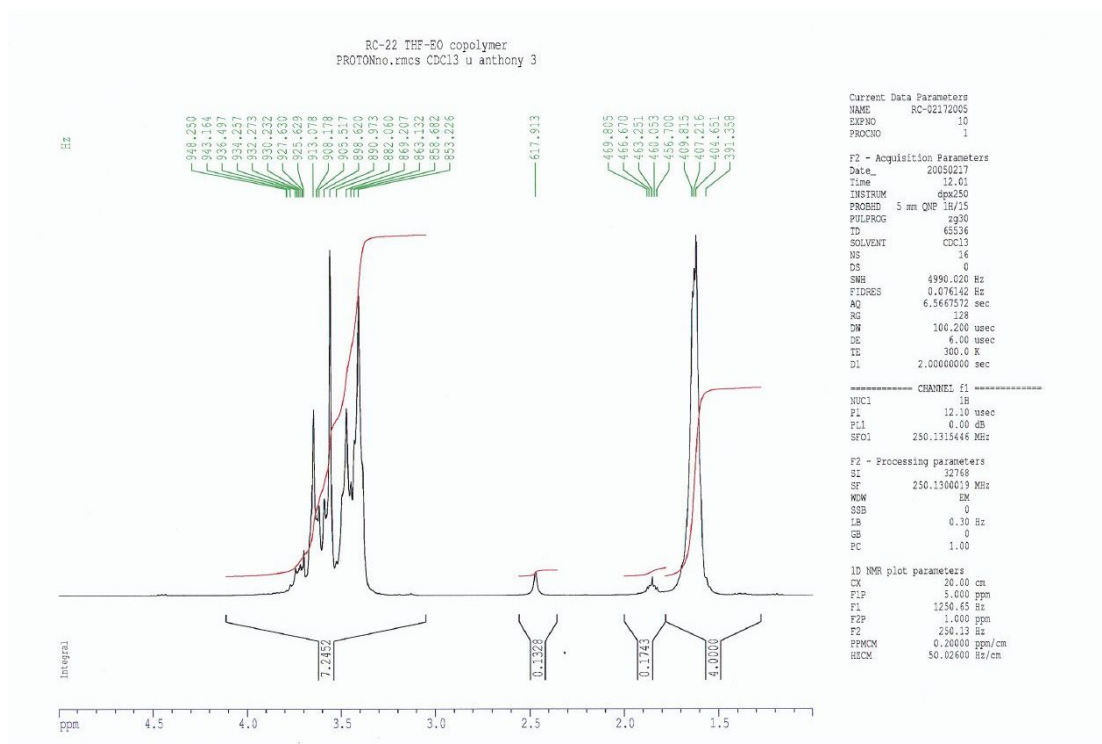


Figure 23. Proton NMR spectrum from experiment 22

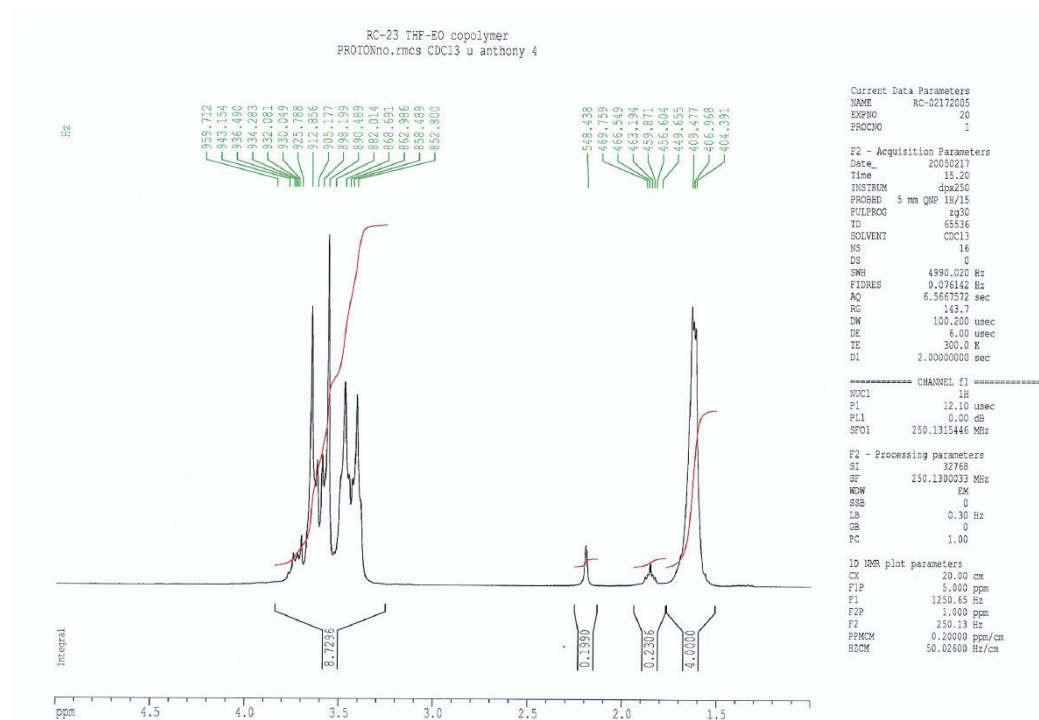


Figure 24. Proton NMR spectrum from experiment 23

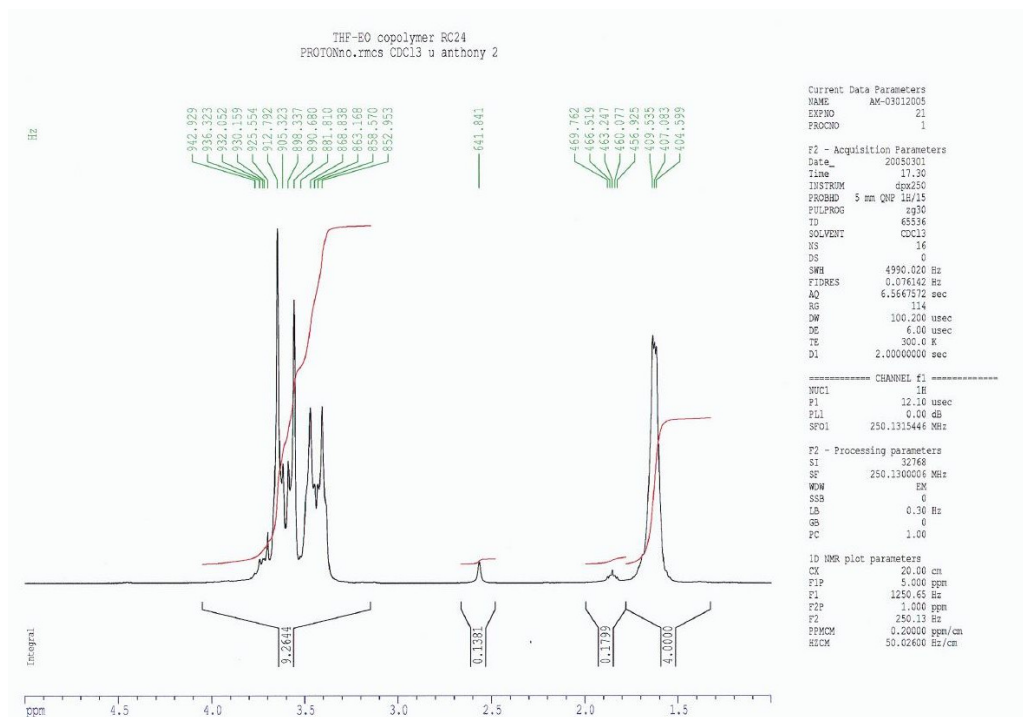


Figure 25. Proton NMR spectrum from experiment 24

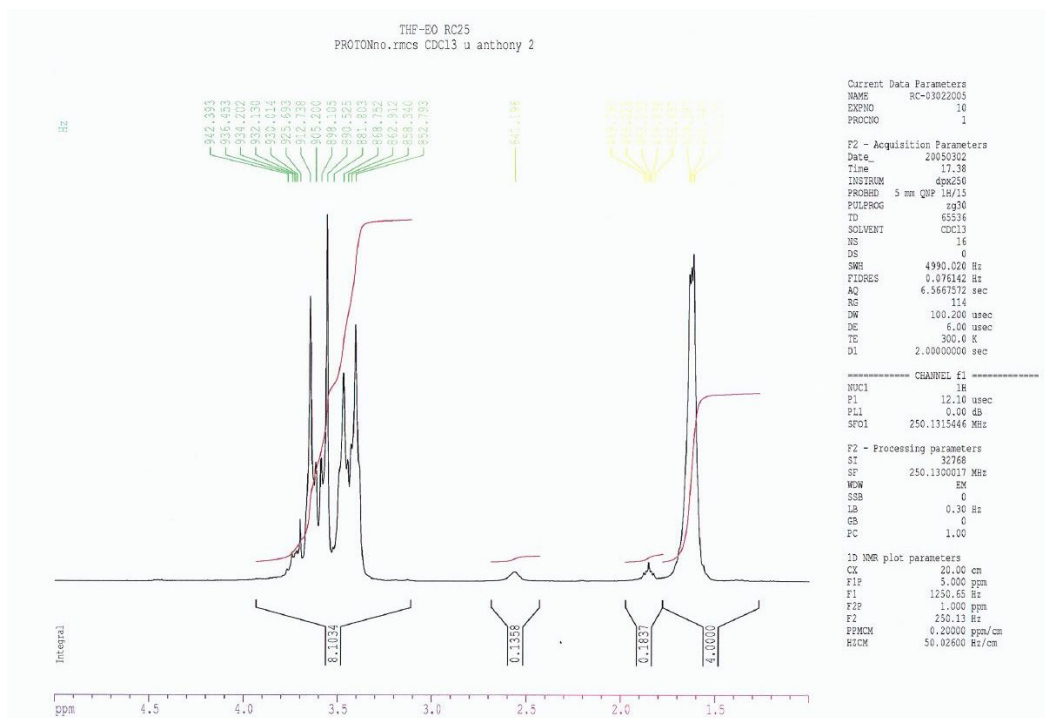


Figure 26. Proton NMR spectrum from experiment 25

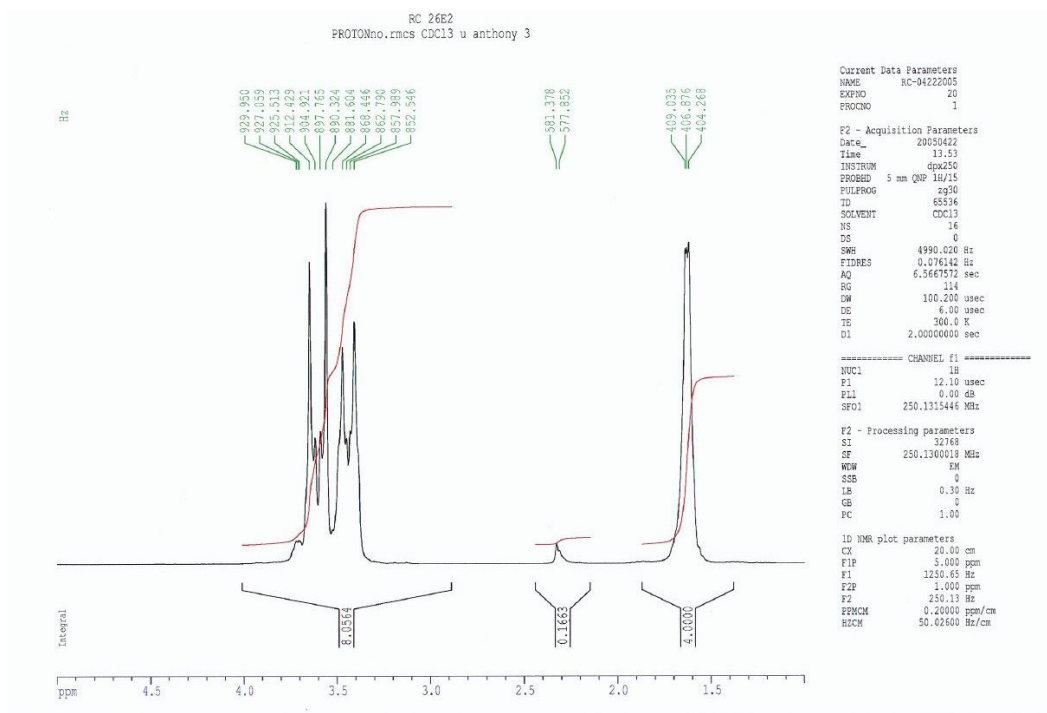


Figure 27. Proton NMR spectrum from experiment 26

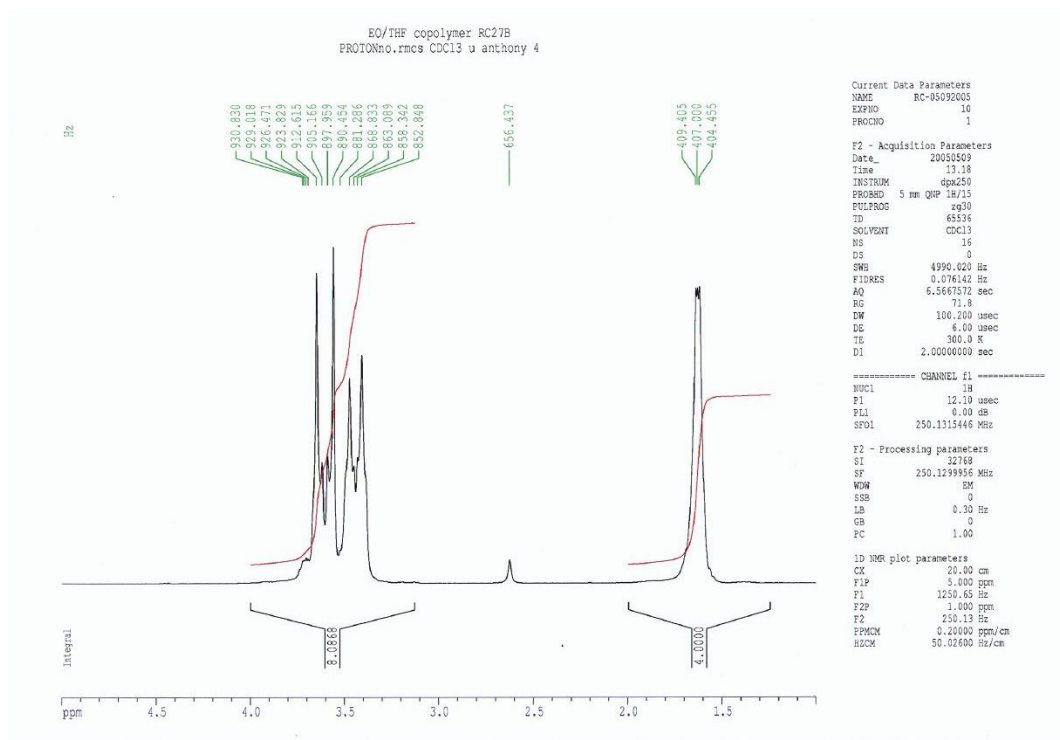


Figure 28. Proton NMR spectrum from experiment 27

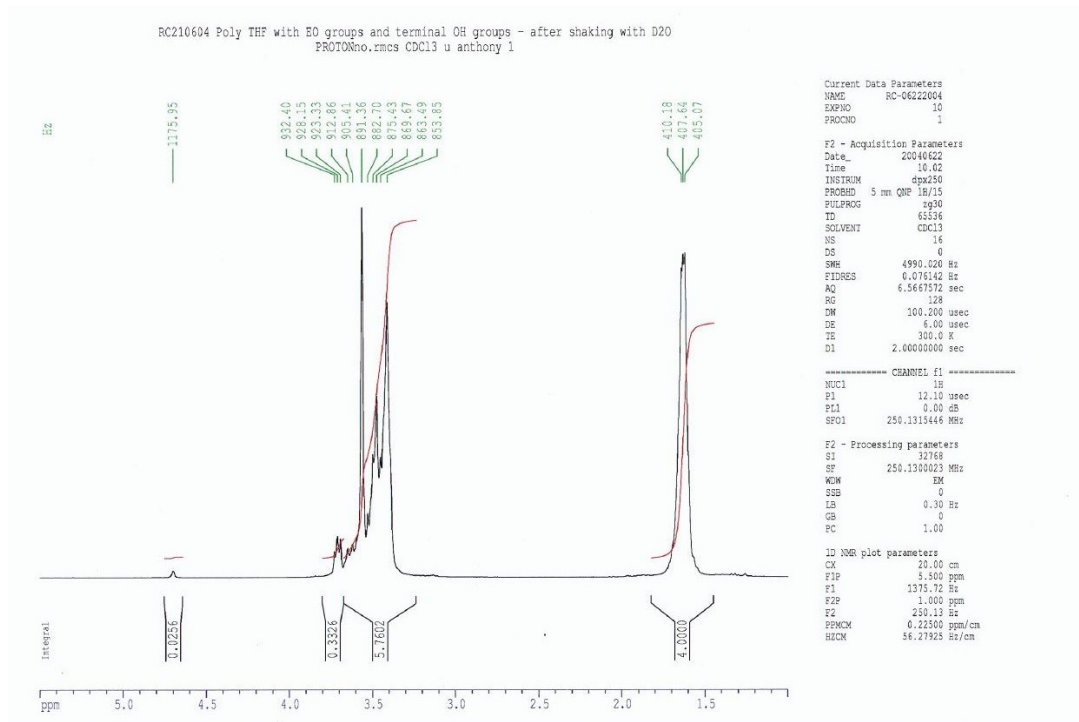


Figure 29. Proton NMR spectrum of Aldrich THF-EO copolymer

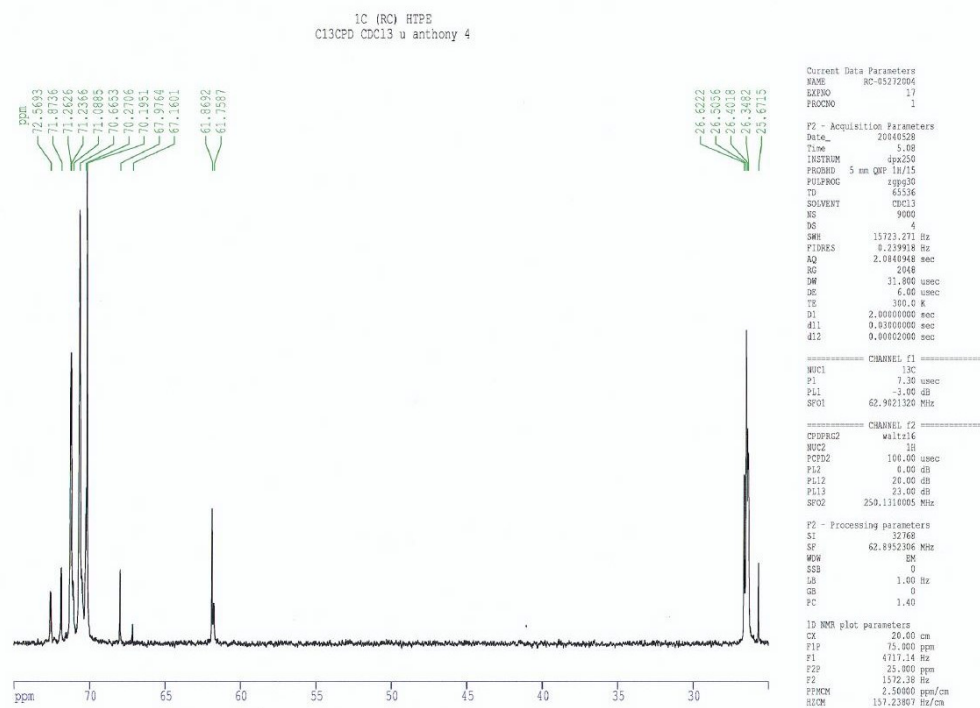


Figure 30. Carbon NMR spectrum from experiment 1

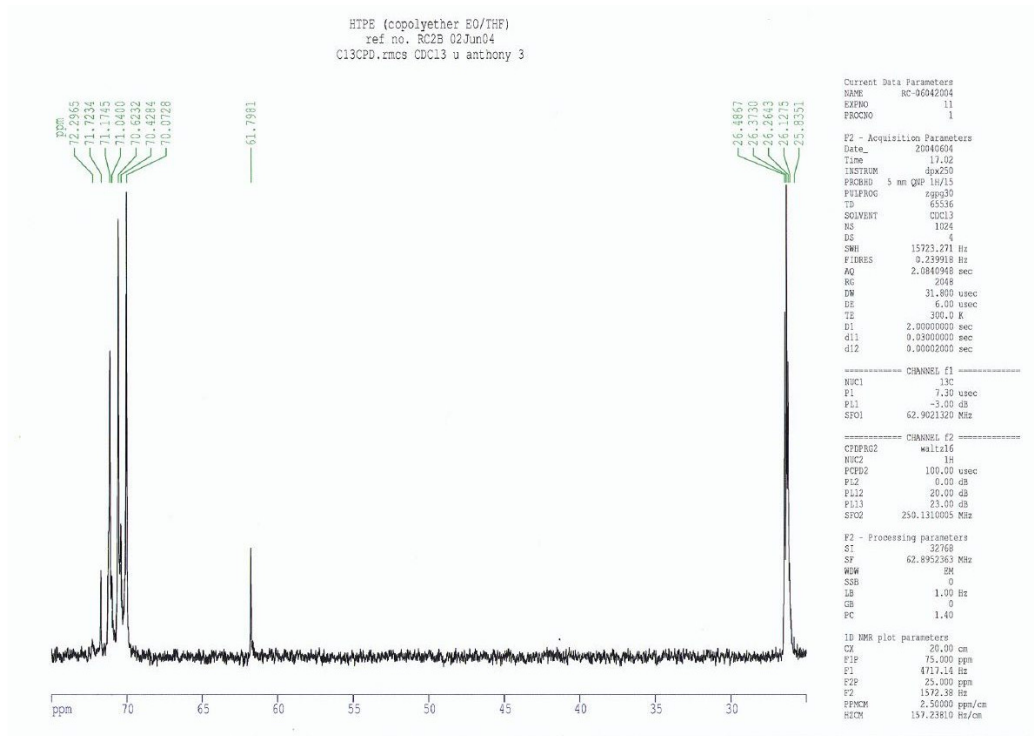


Figure 31. Carbon NMR spectrum from experiment 2

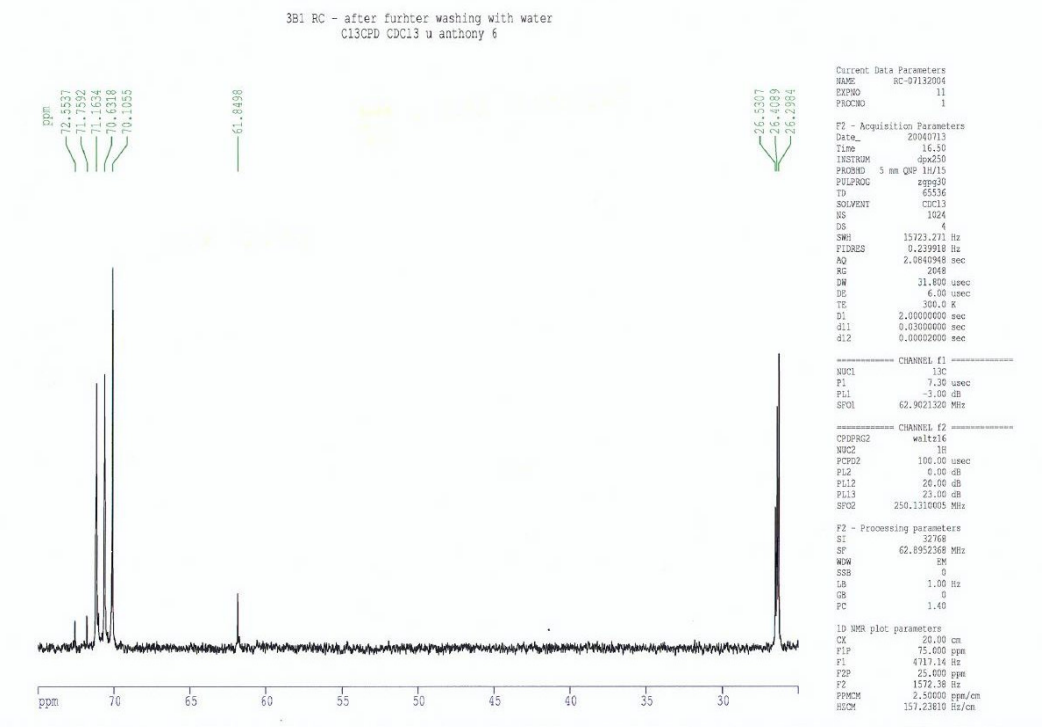


Figure 32. Carbon NMR spectrum from experiment 3

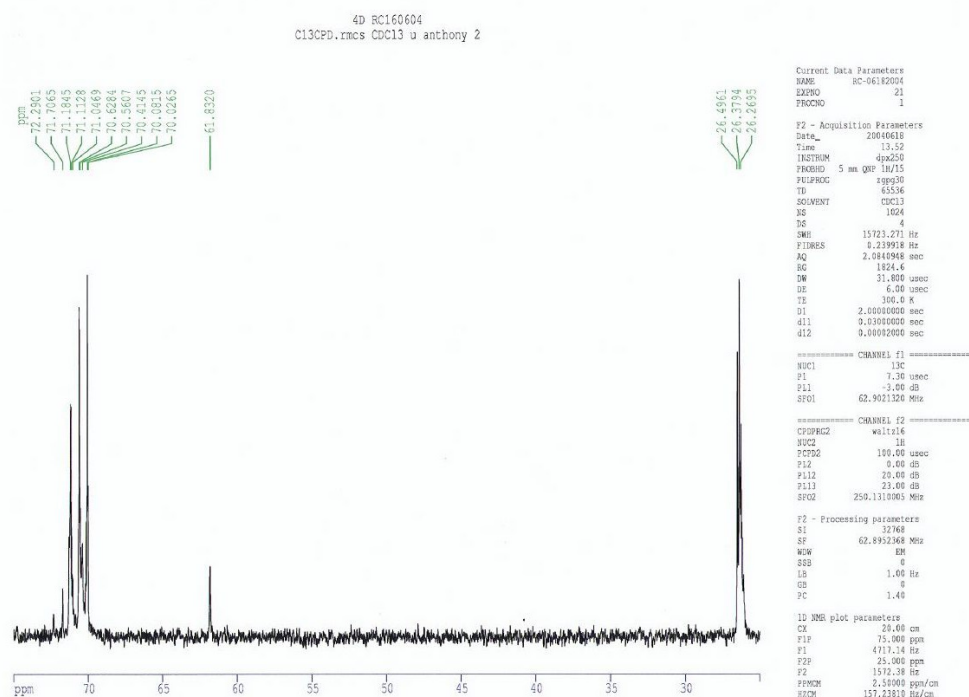


Figure 33. Carbon NMR spectrum from experiment 4D

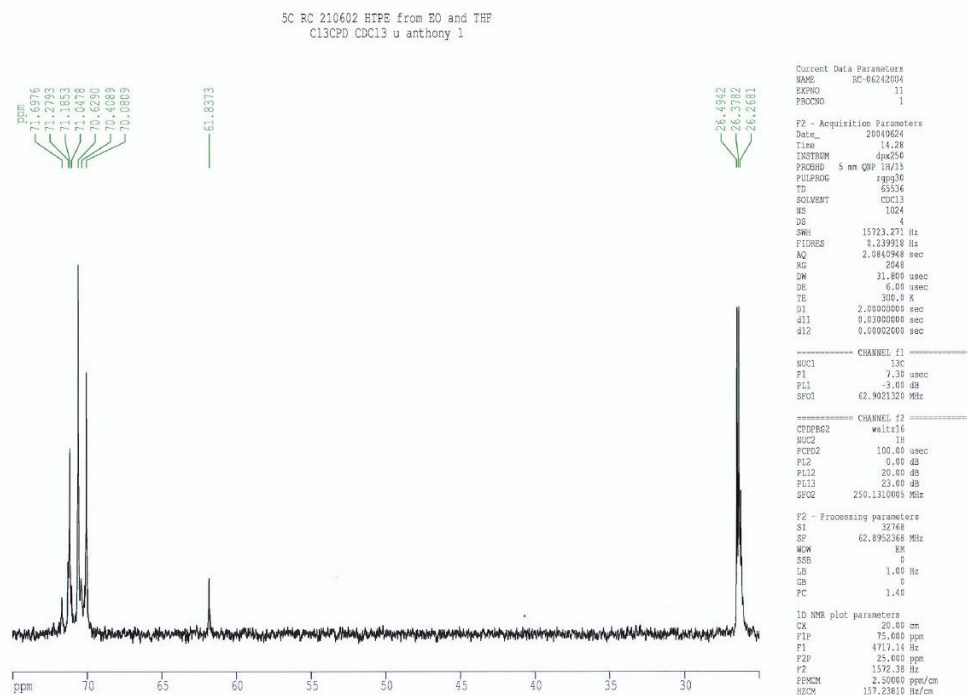


Figure 34. Carbon NMR spectrum from experiment 5

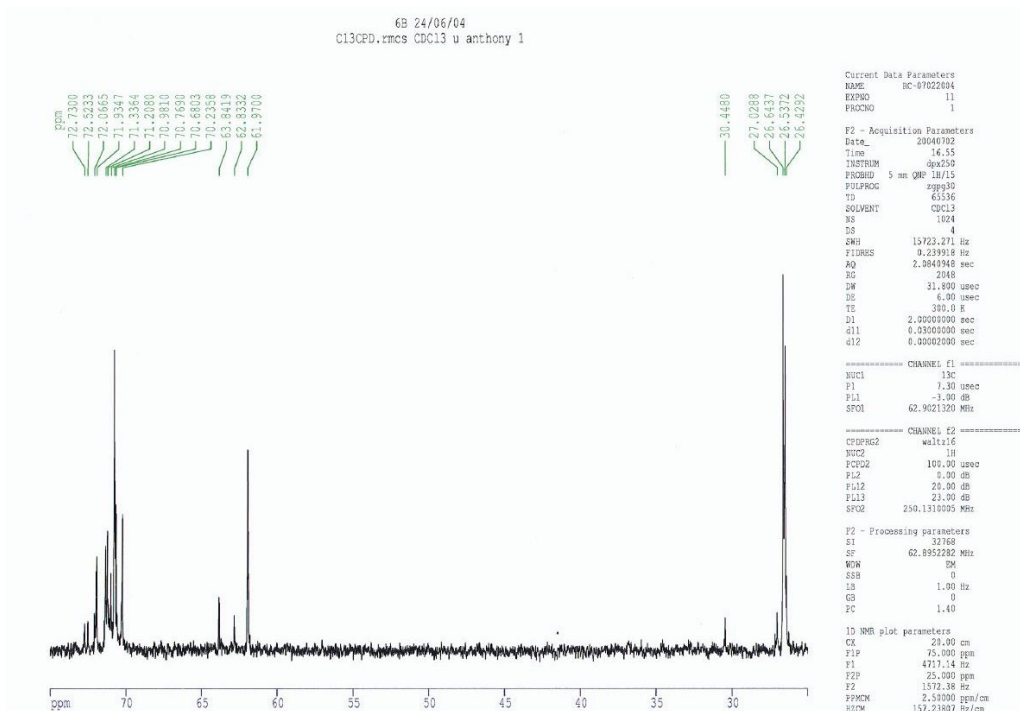


Figure 35. Carbon NMR spectrum from experiment 6

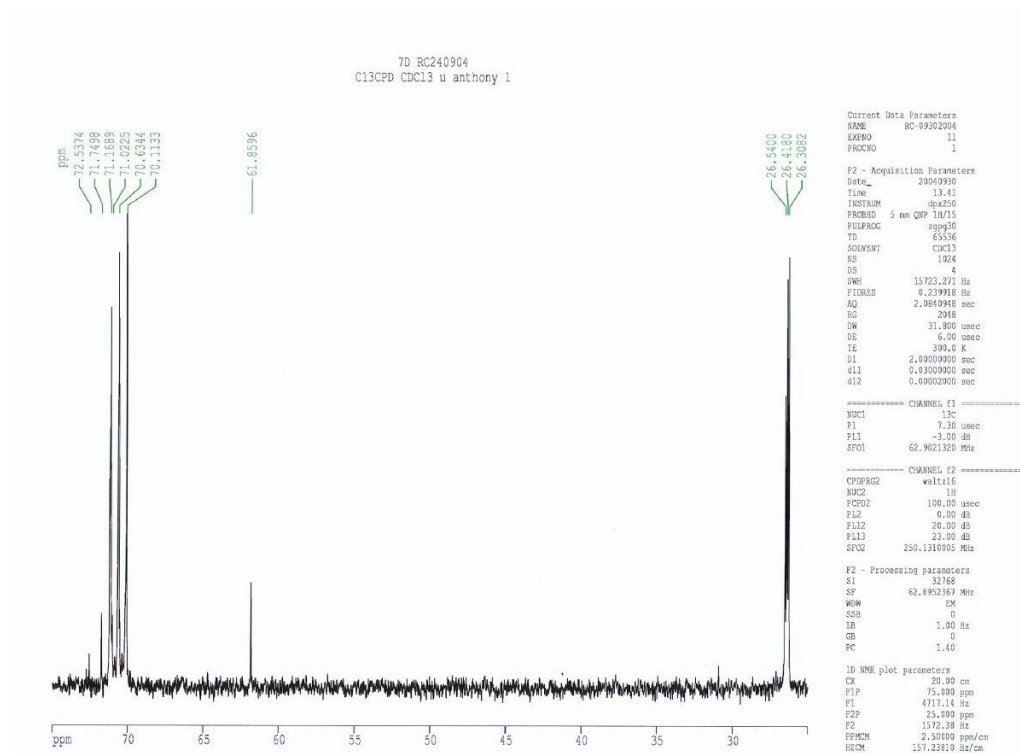


Figure 36. Carbon NMR spectrum from experiment 7

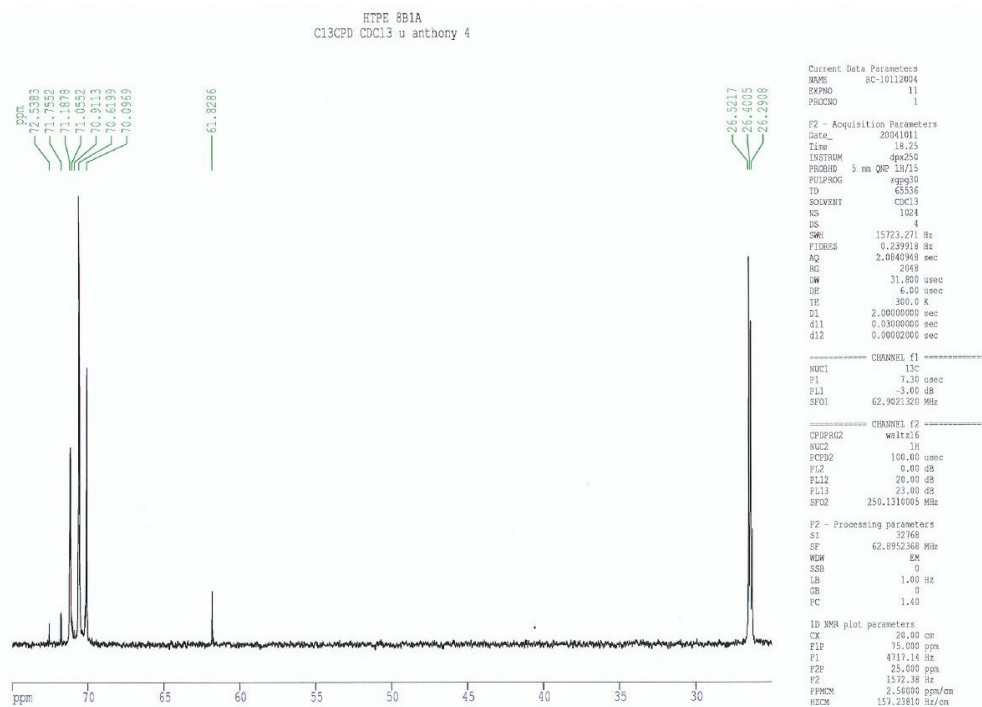


Figure 37. Carbon NMR spectrum from experiment 8B1A

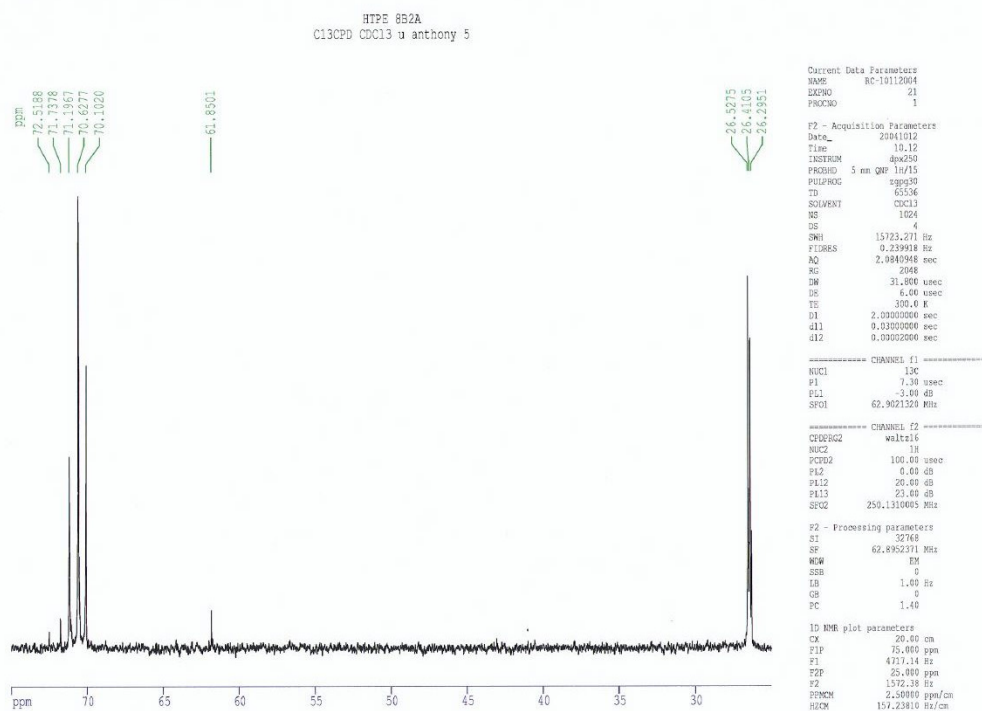


Figure 38. Carbon NMR spectrum from experiment 8B2A

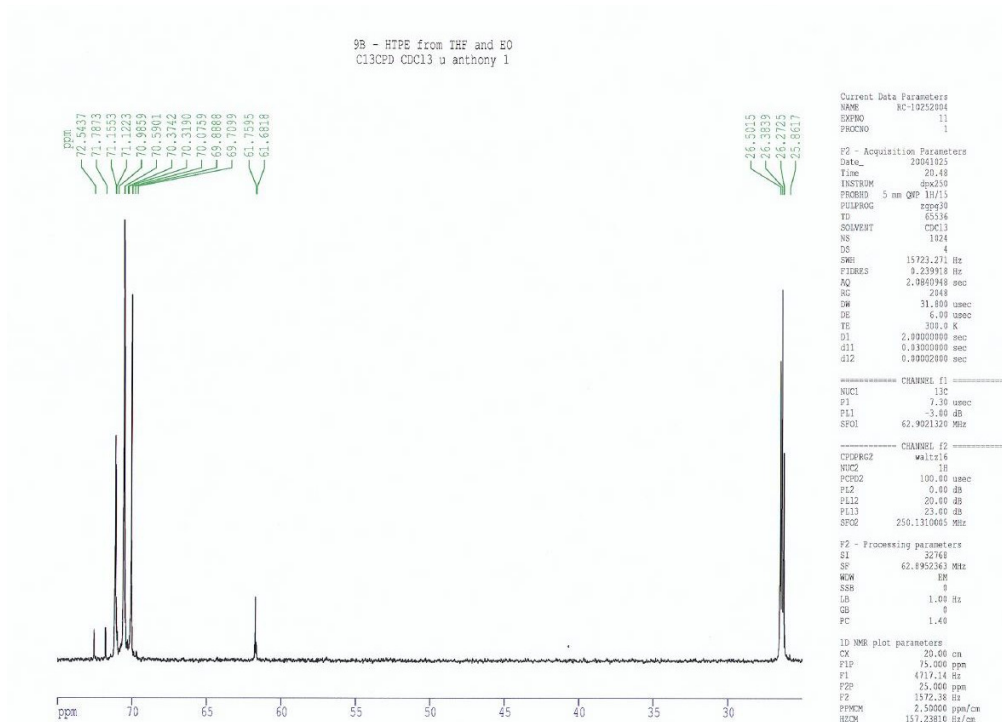


Figure 39. Carbon NMR spectrum from experiment 9

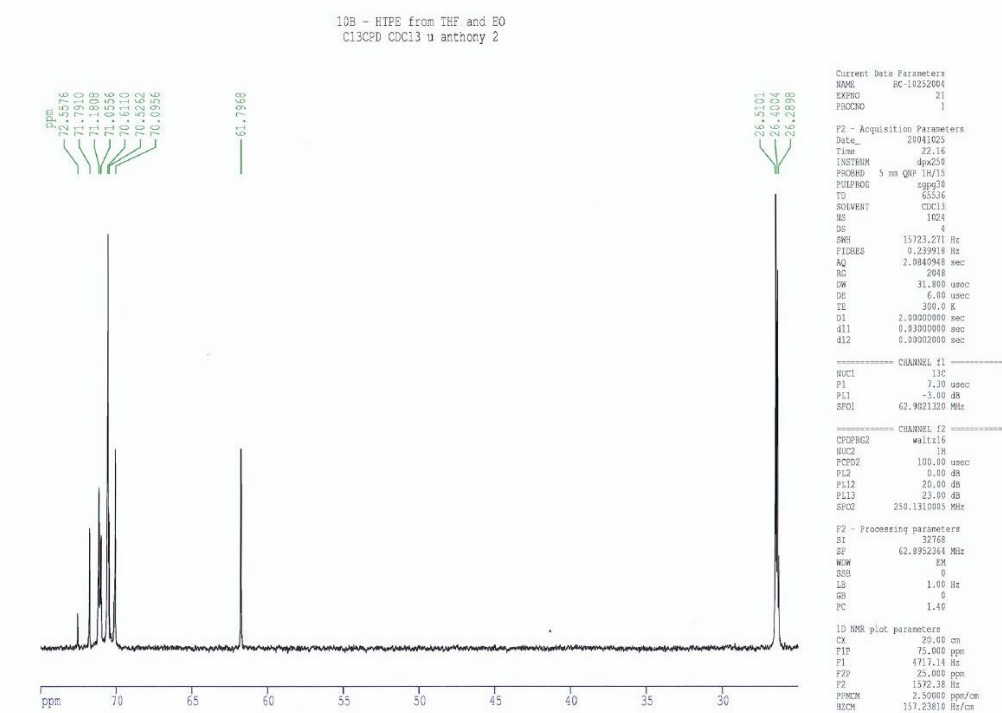


Figure 40. Carbon NMR spectrum from experiment 10

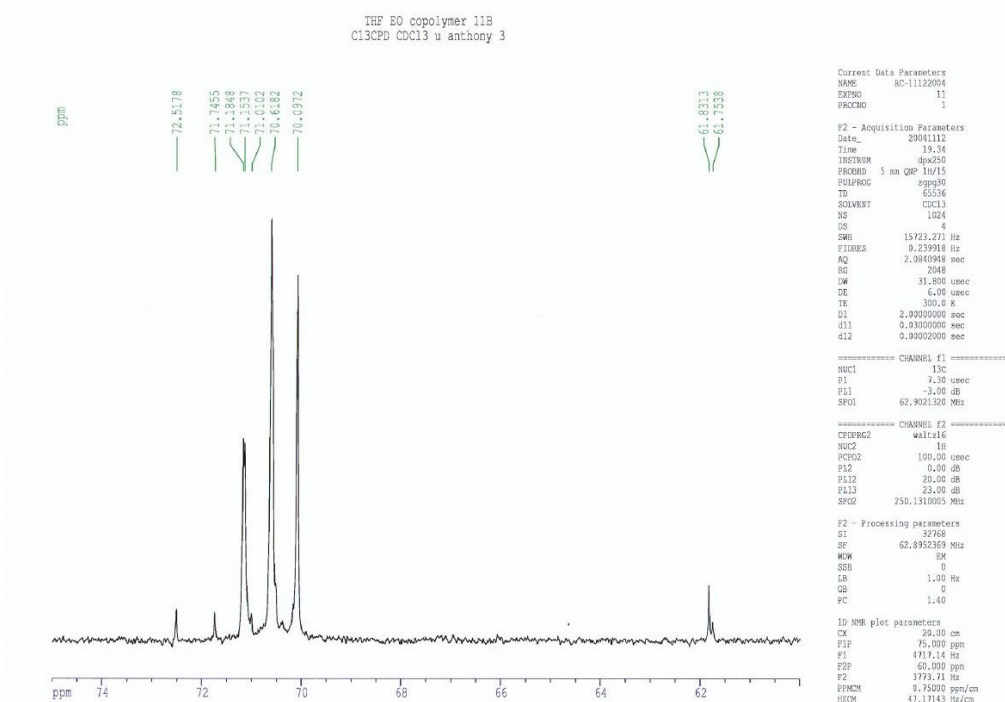


Figure 41. Carbon NMR spectrum from experiment 11

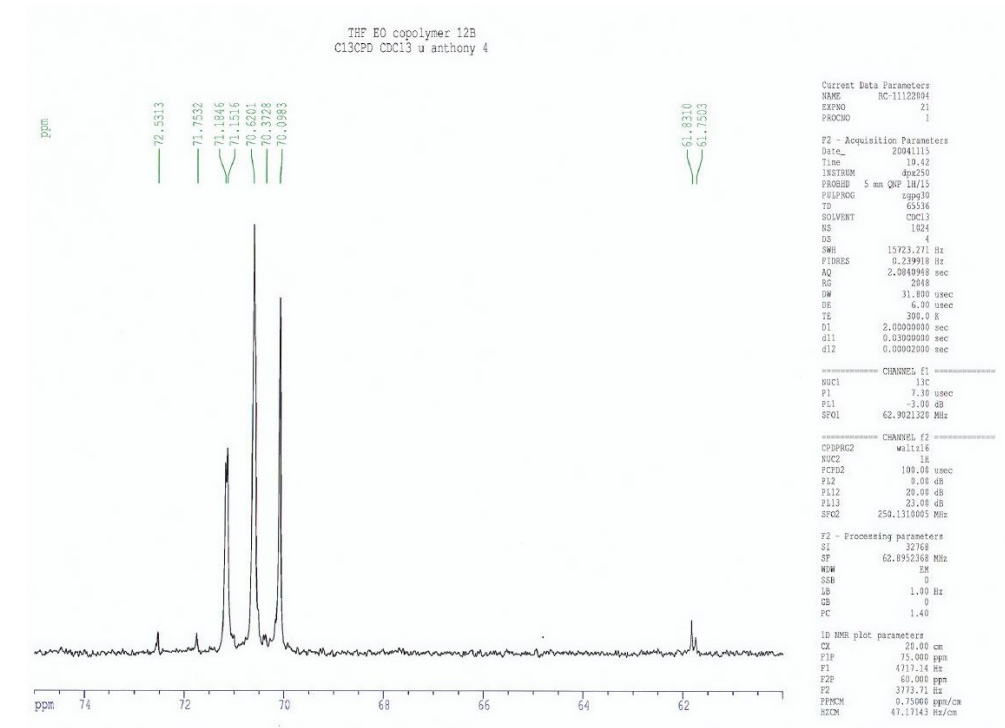


Figure 42. Carbon NMR spectrum from experiment 12

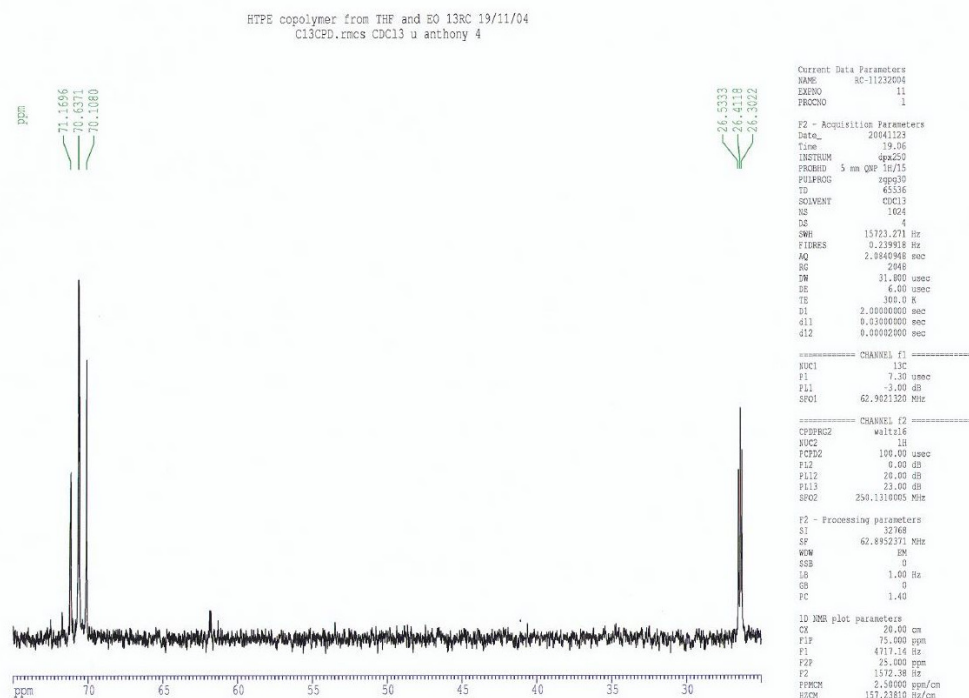


Figure 43. Carbon NMR spectrum from experiment 13

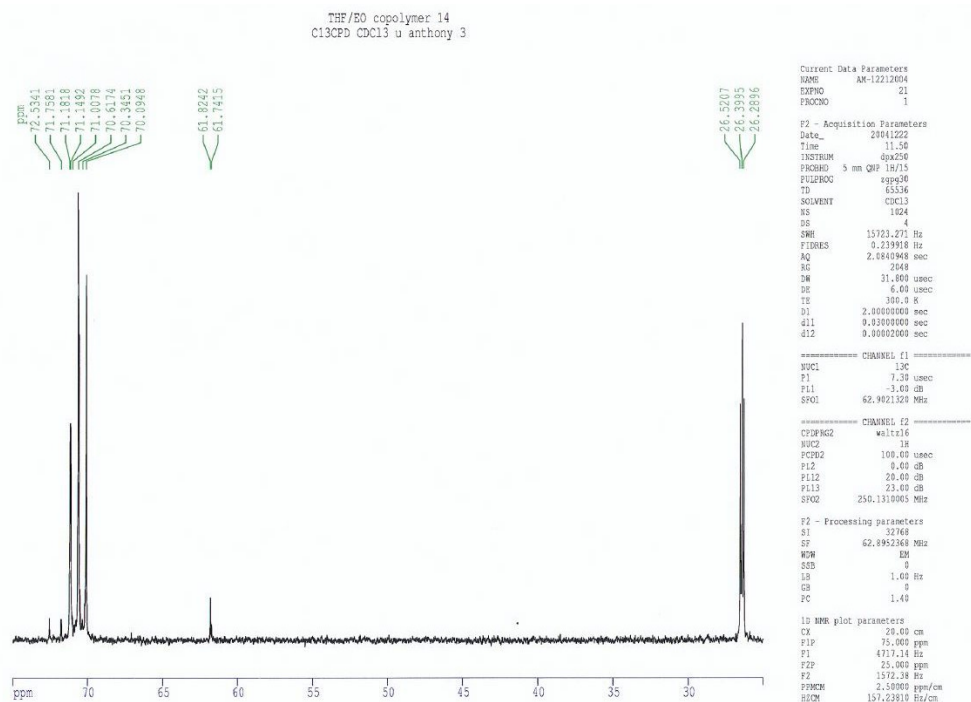


Figure 44. Carbon NMR spectrum from experiment 14

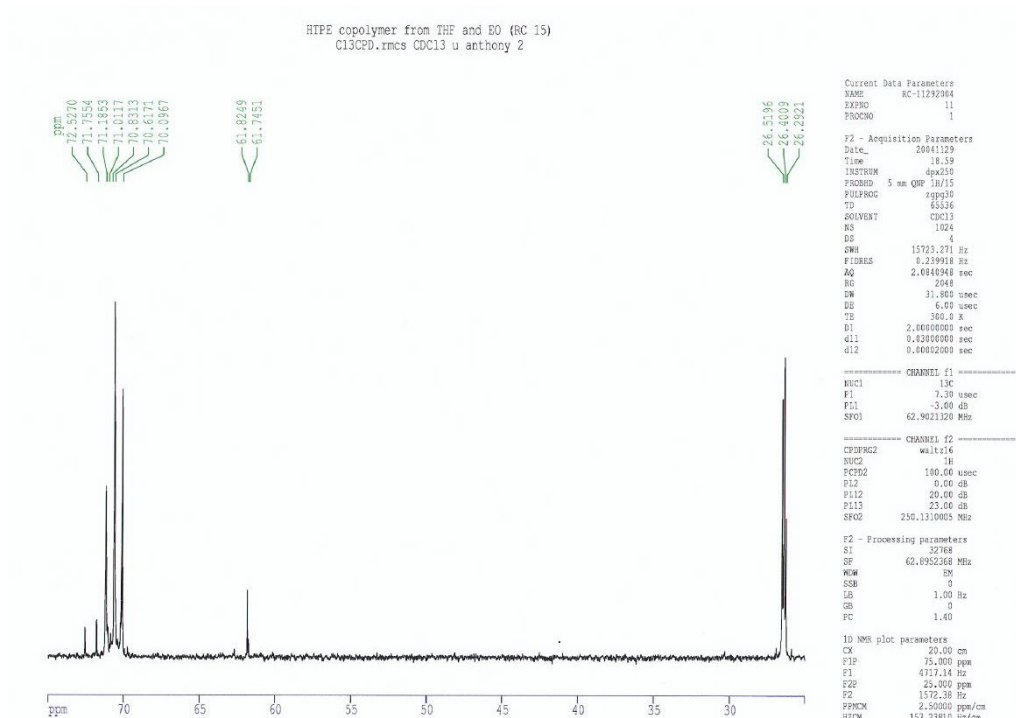


Figure 45. Carbon NMR spectrum from experiment 15

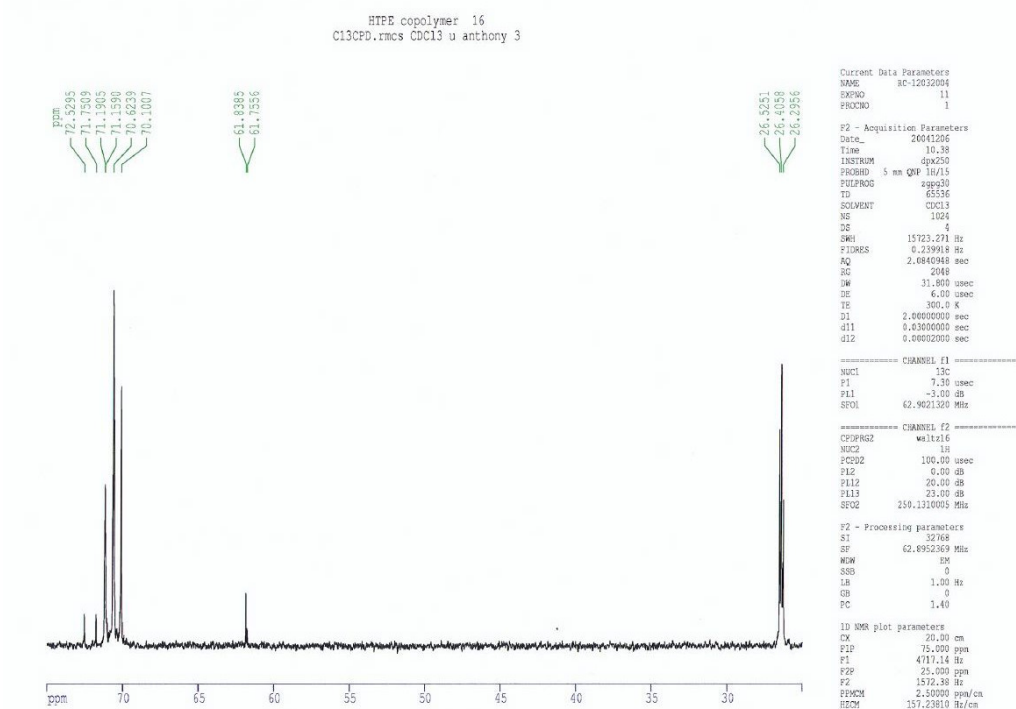


Figure 46. Carbon NMR spectrum from experiment 16

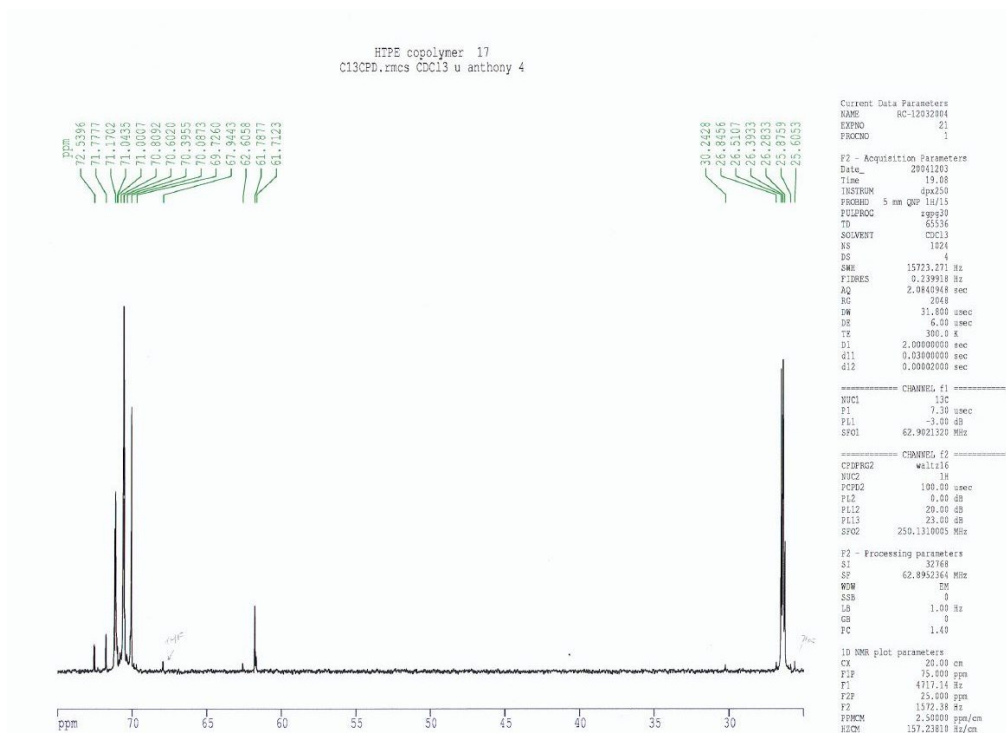


Figure 47. Carbon NMR spectrum from experiment 17

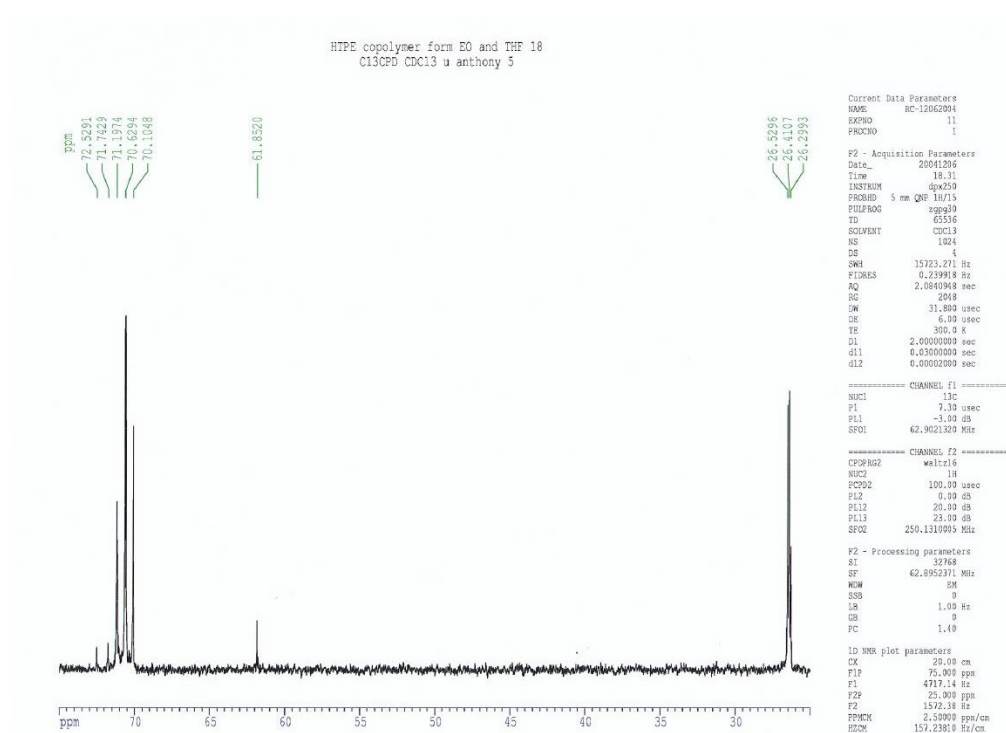


Figure 48. Carbon NMR spectrum from experiment 18

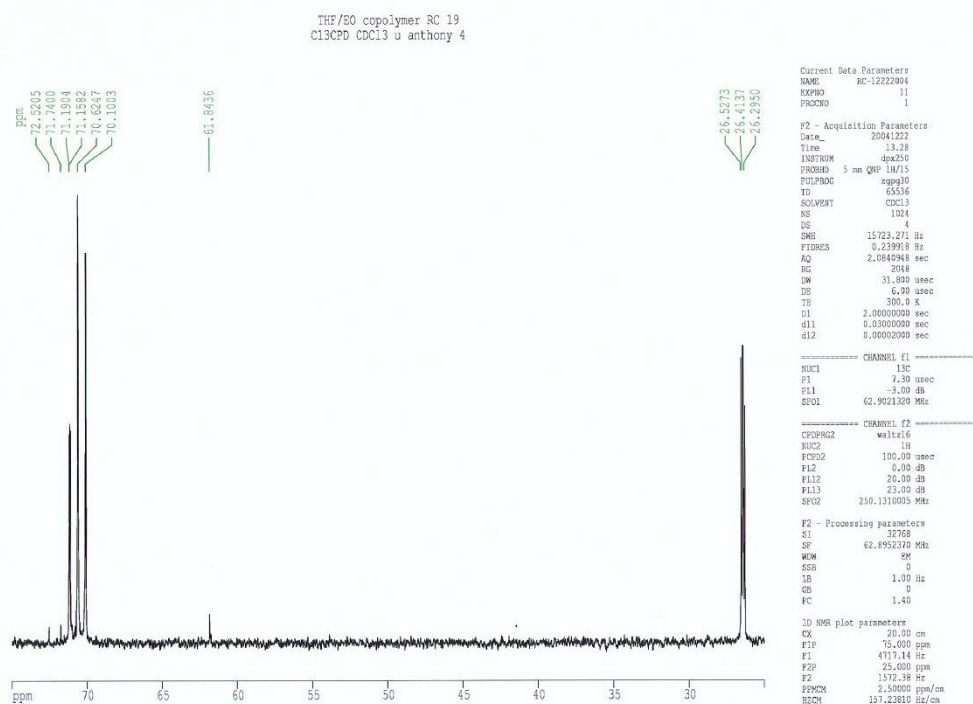


Figure 49. Carbon NMR spectrum from experiment 19

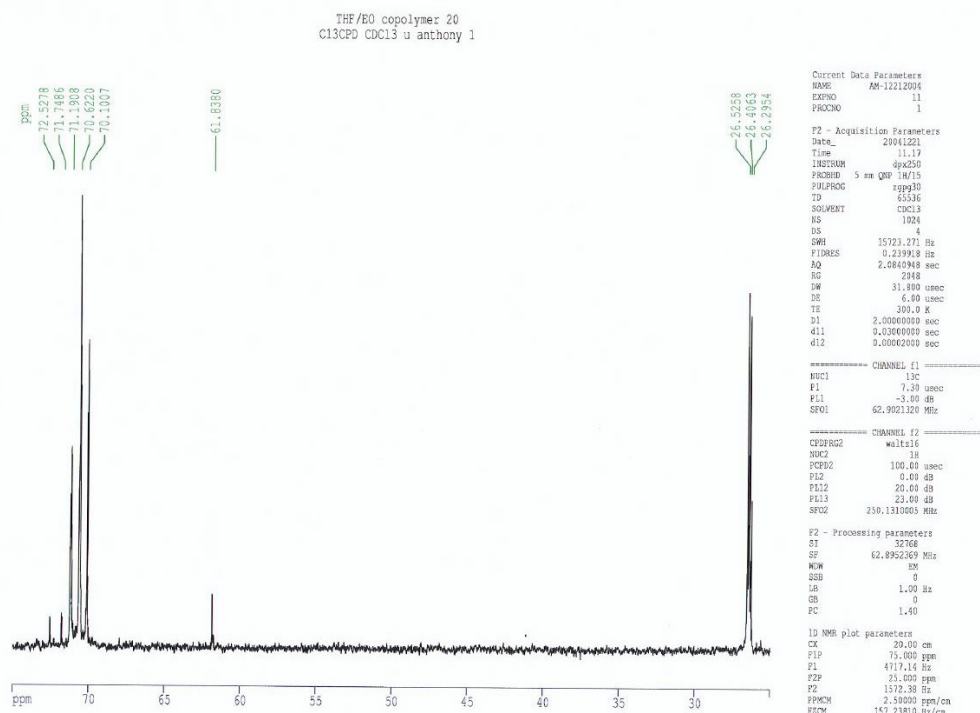


Figure 50. Carbon NMR spectrum from experiment 20

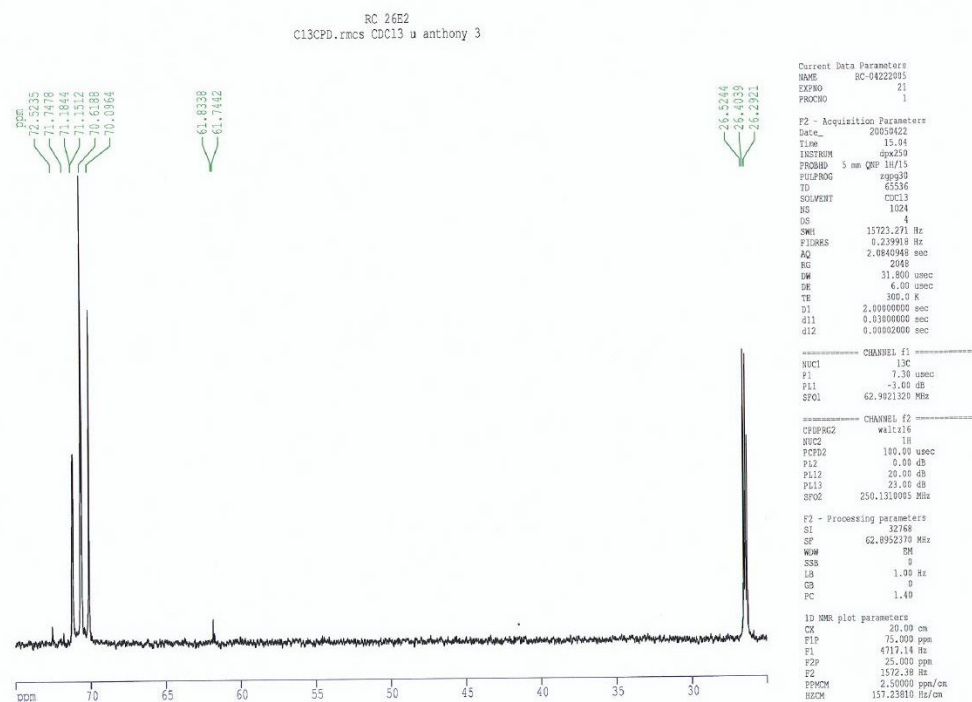


Figure 51. Carbon NMR spectrum from experiment 26

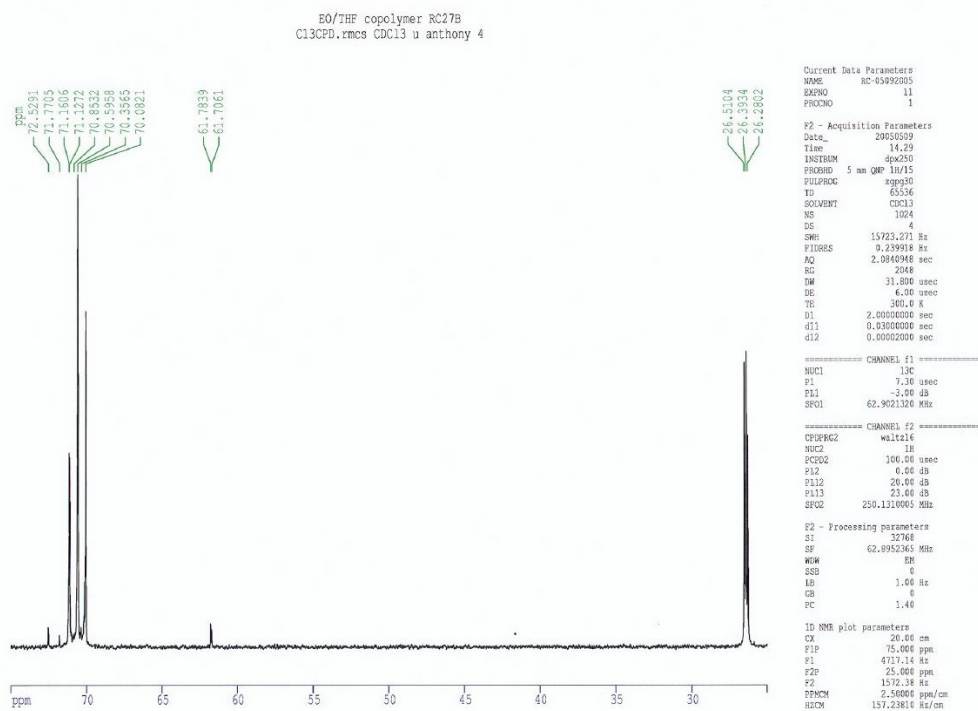


Figure 52. Carbon NMR spectrum from experiment 27

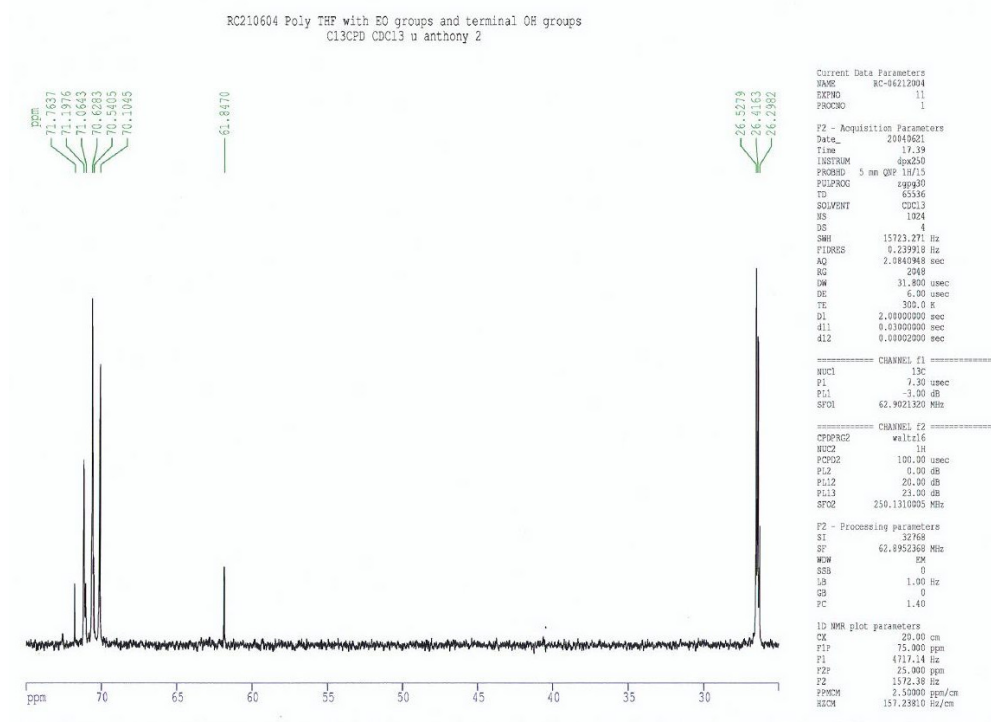


Figure 53. Carbon NMR spectrum of Aldrich THF-EO copolymer

APPENDIX D

DIFFERENTIAL SCANNING CALORIMETRY THERMOGRAMS

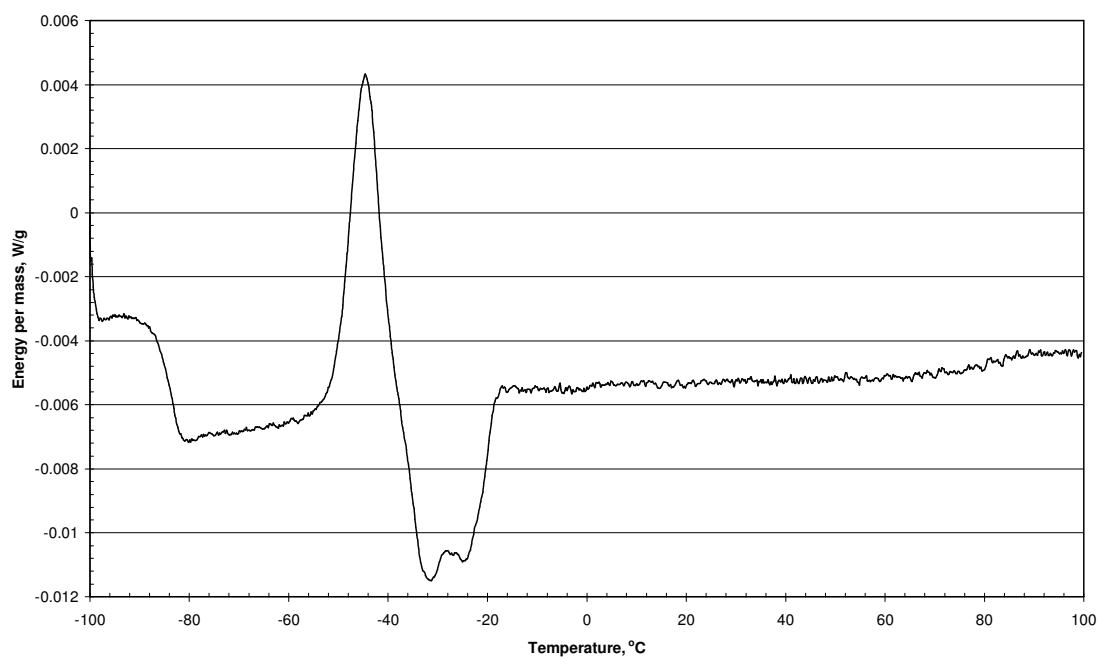


Figure 1. Experiment 1, DSC curve

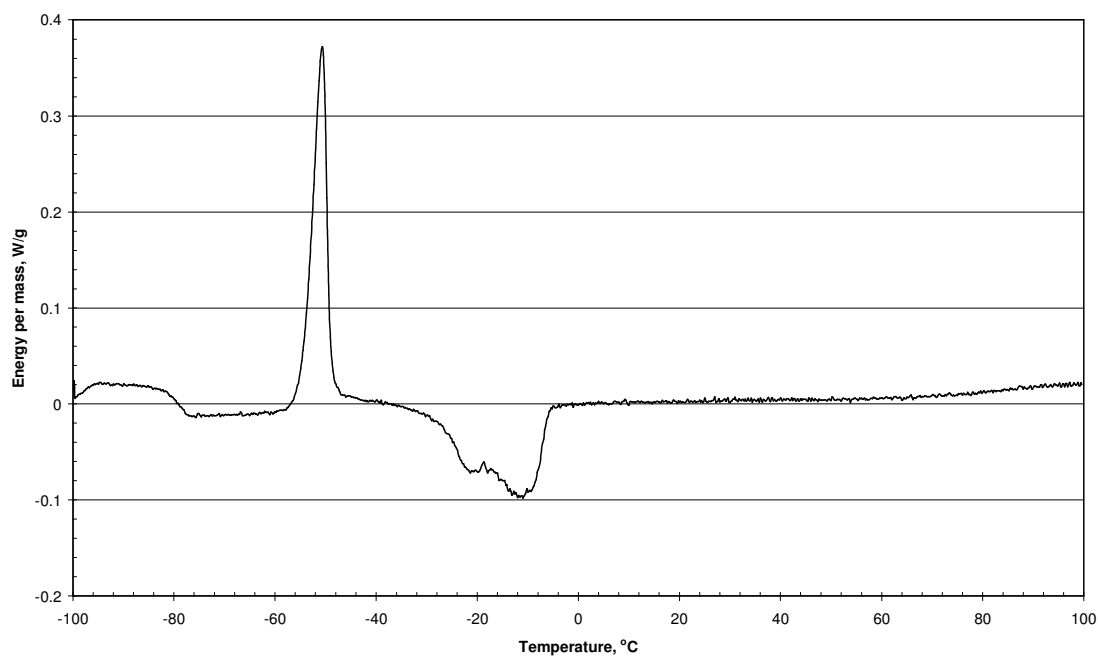
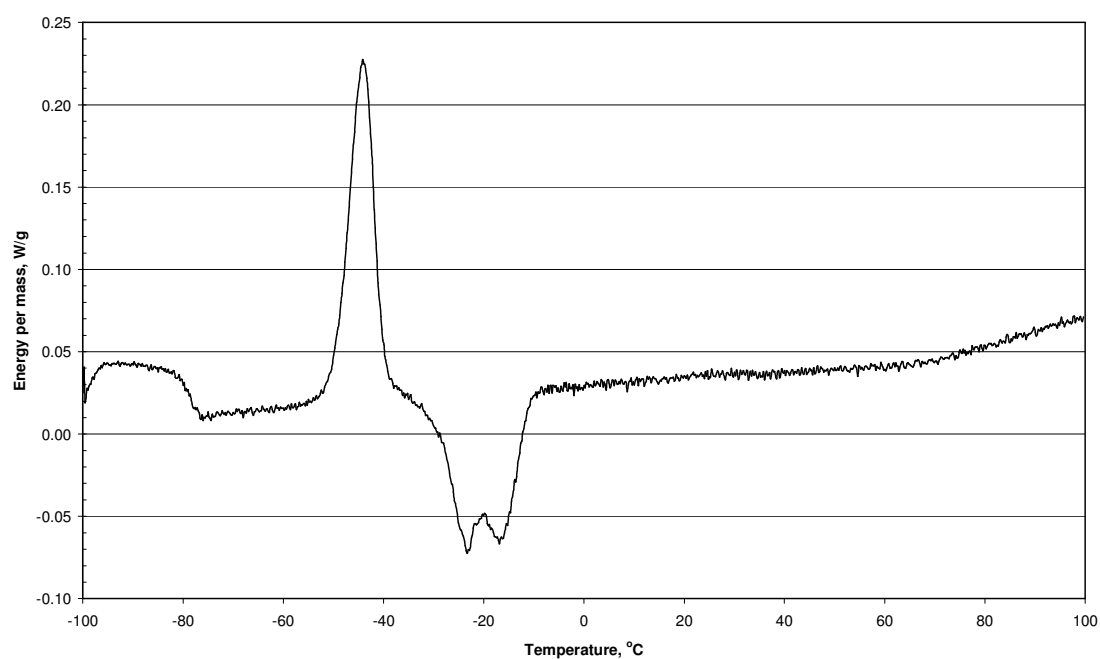
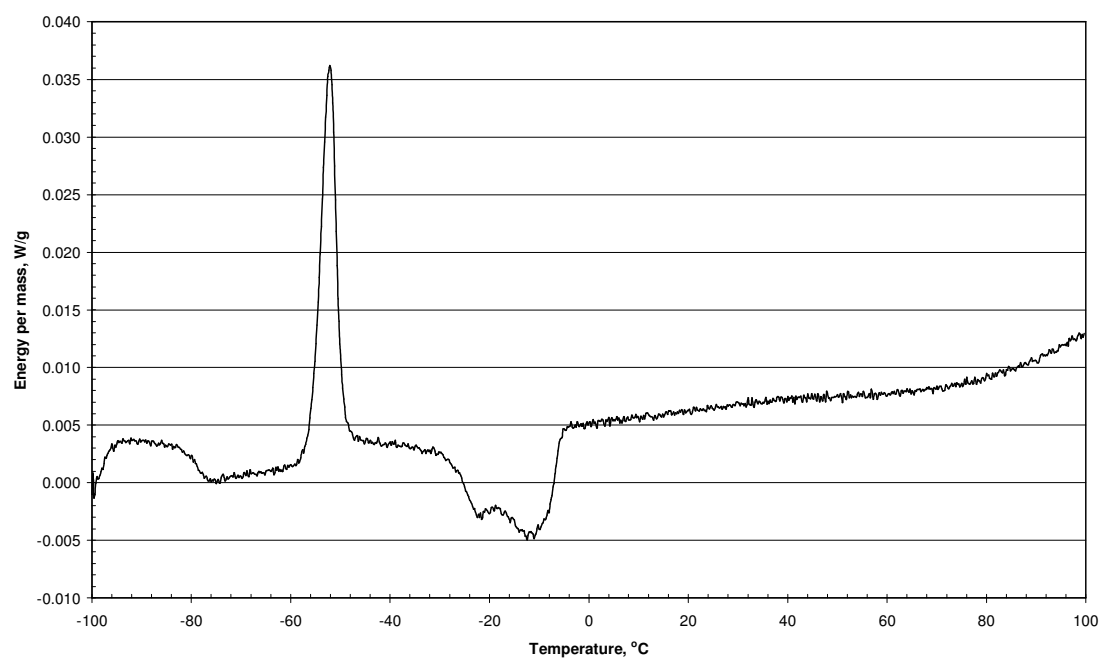
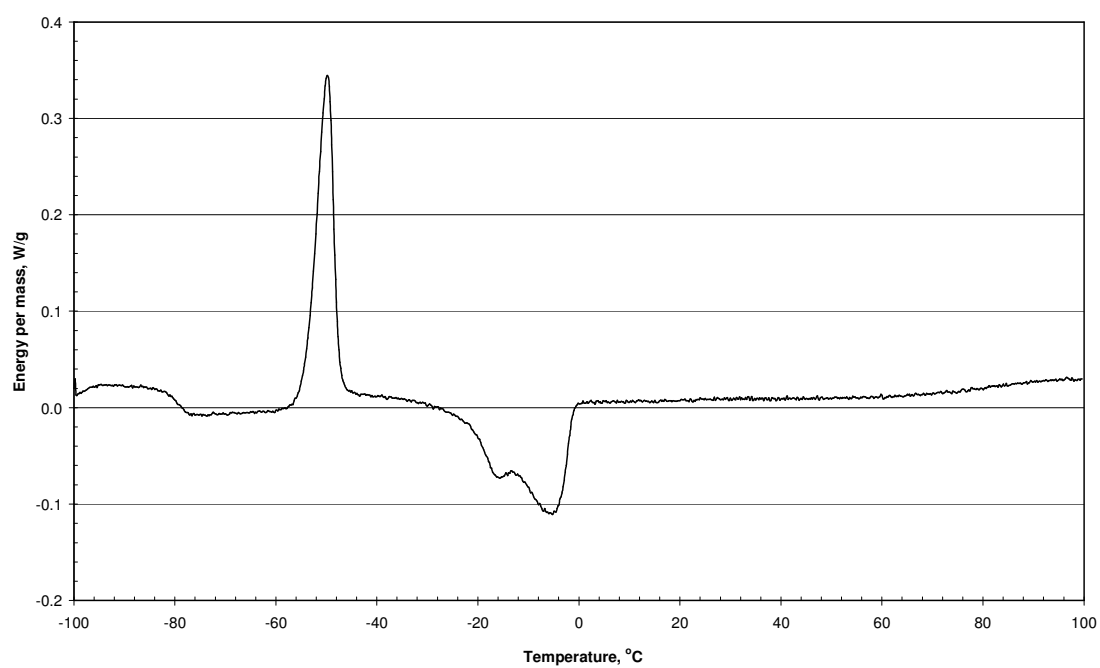
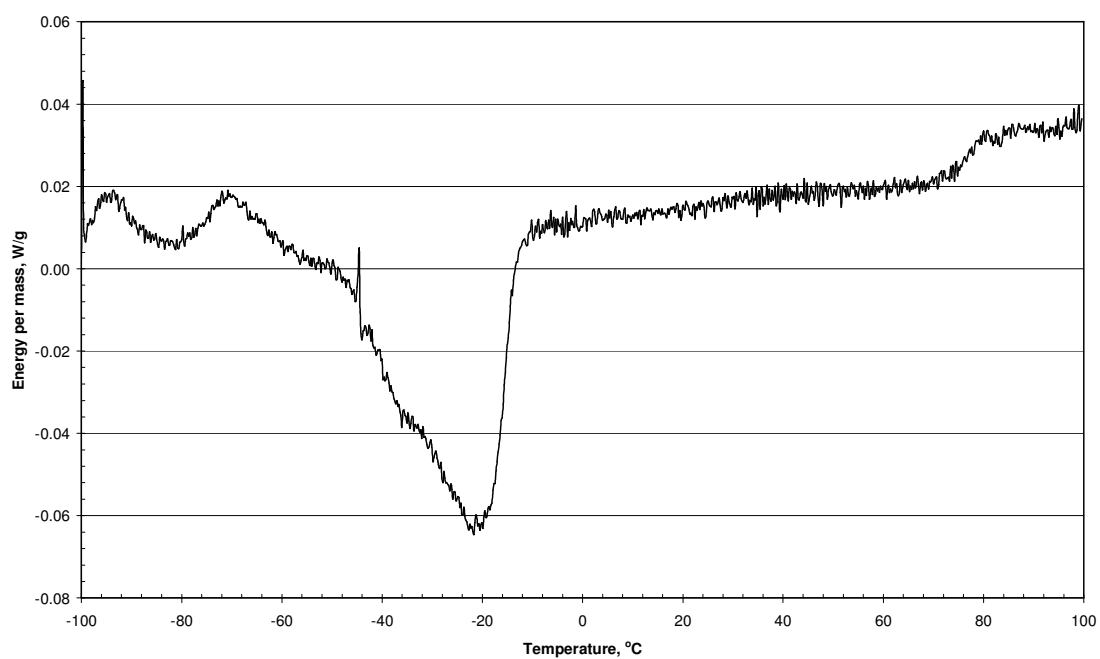
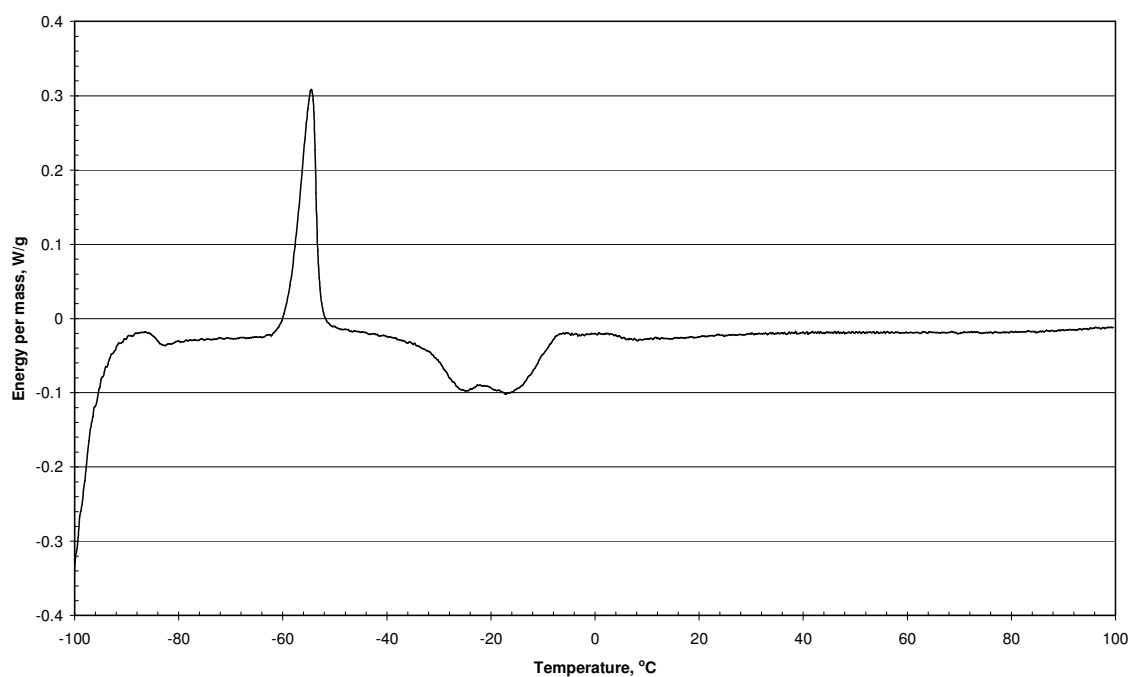
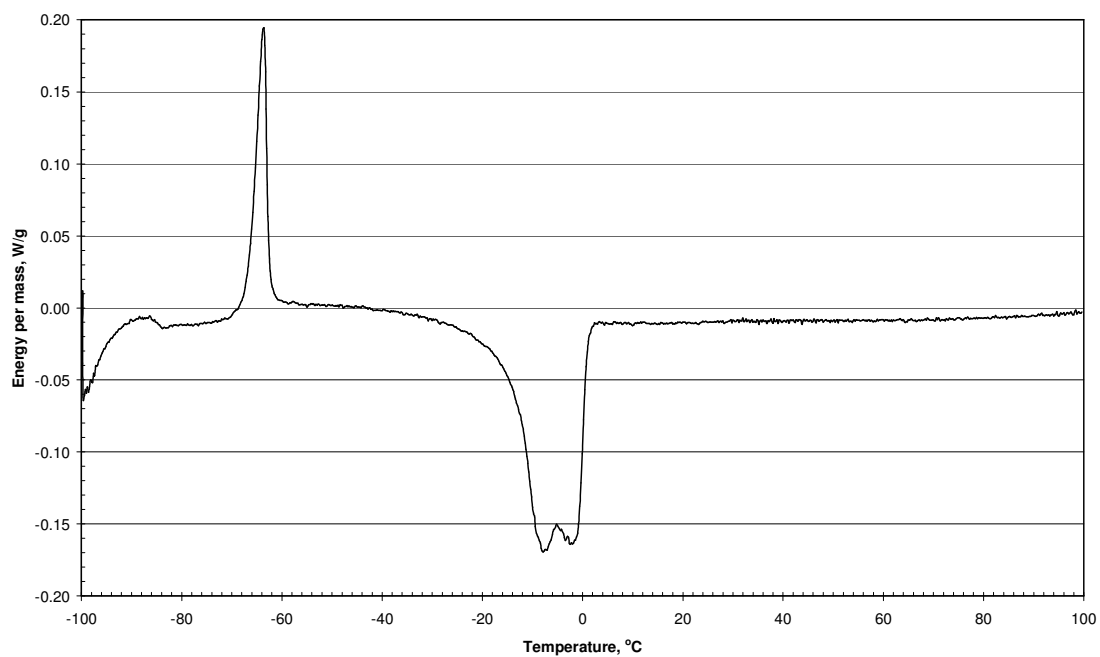
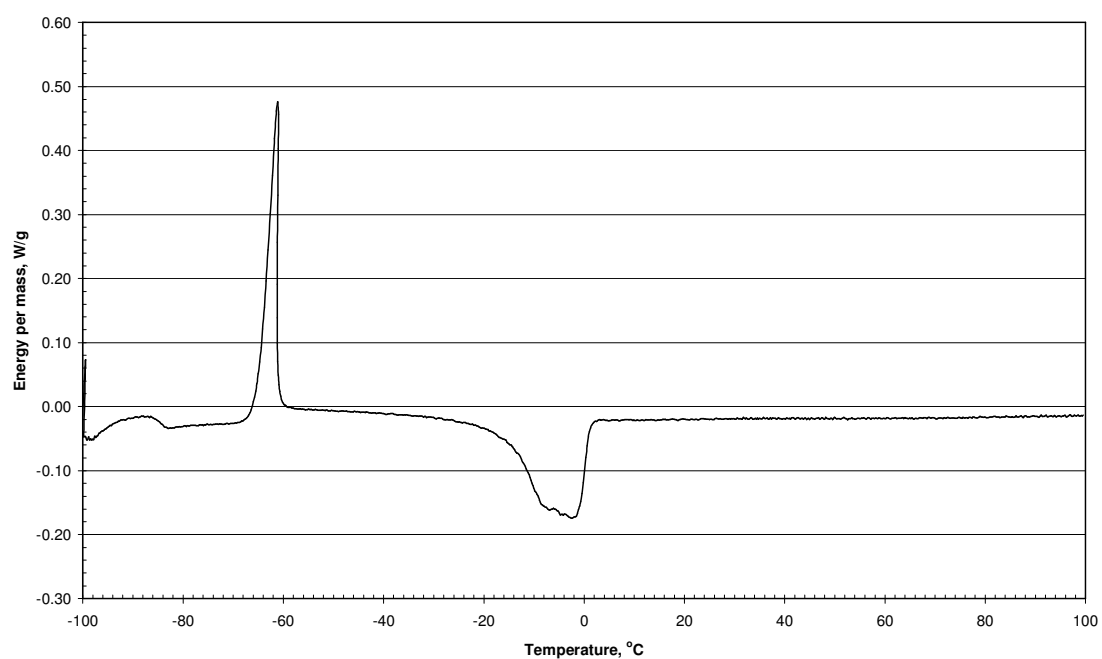
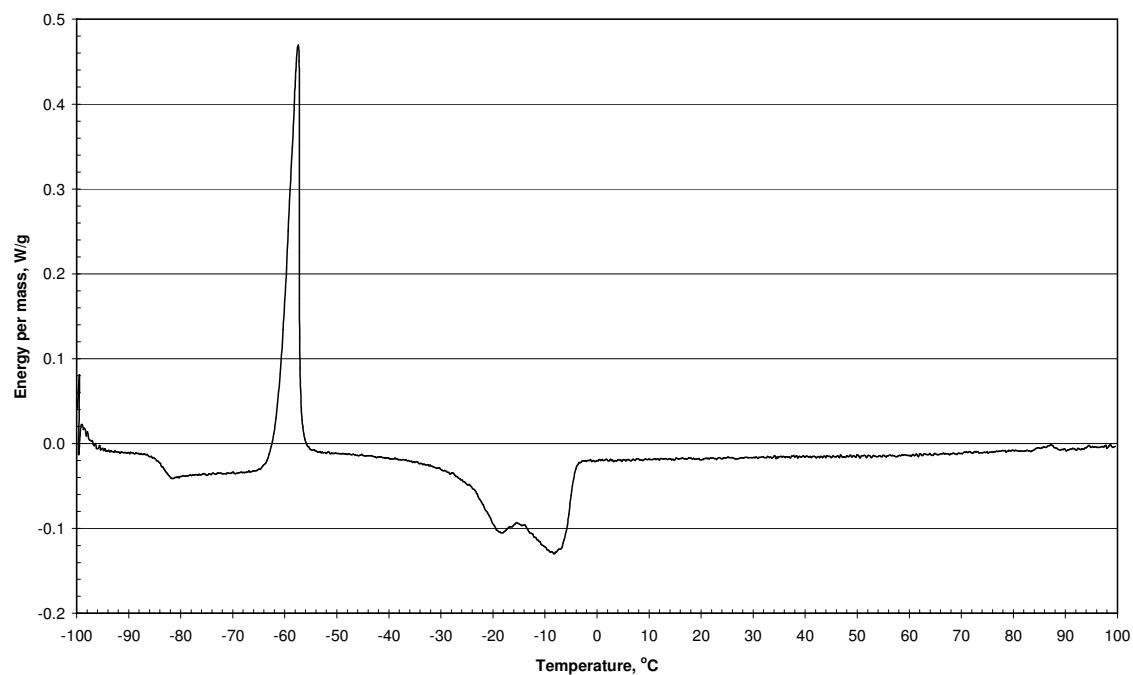


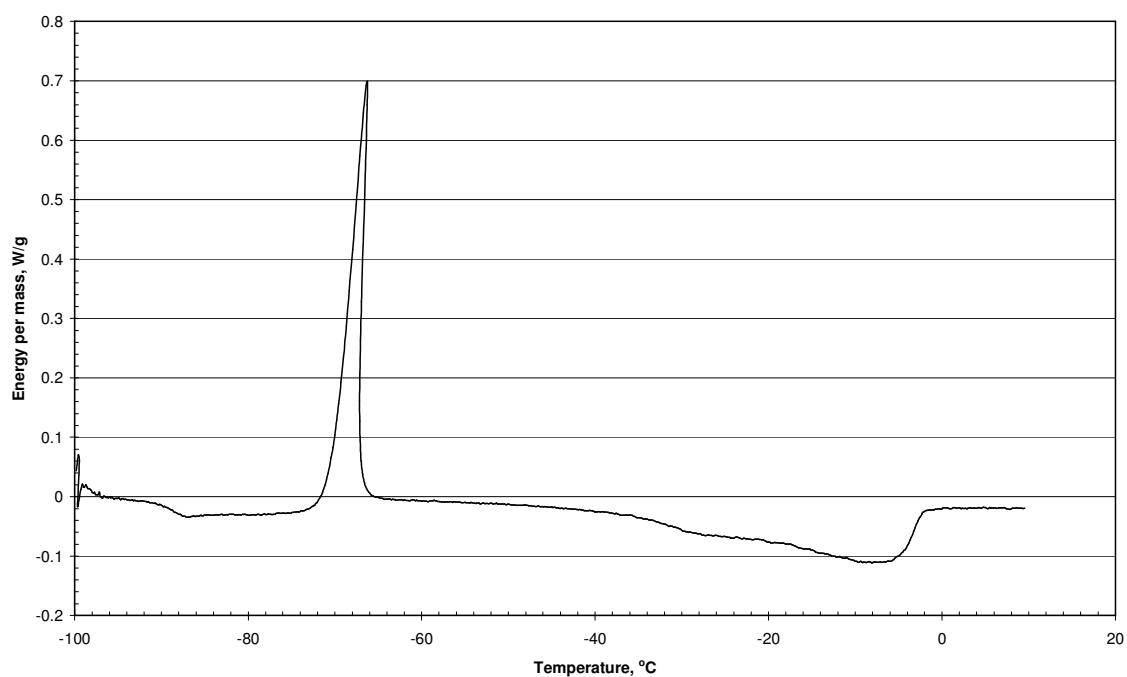
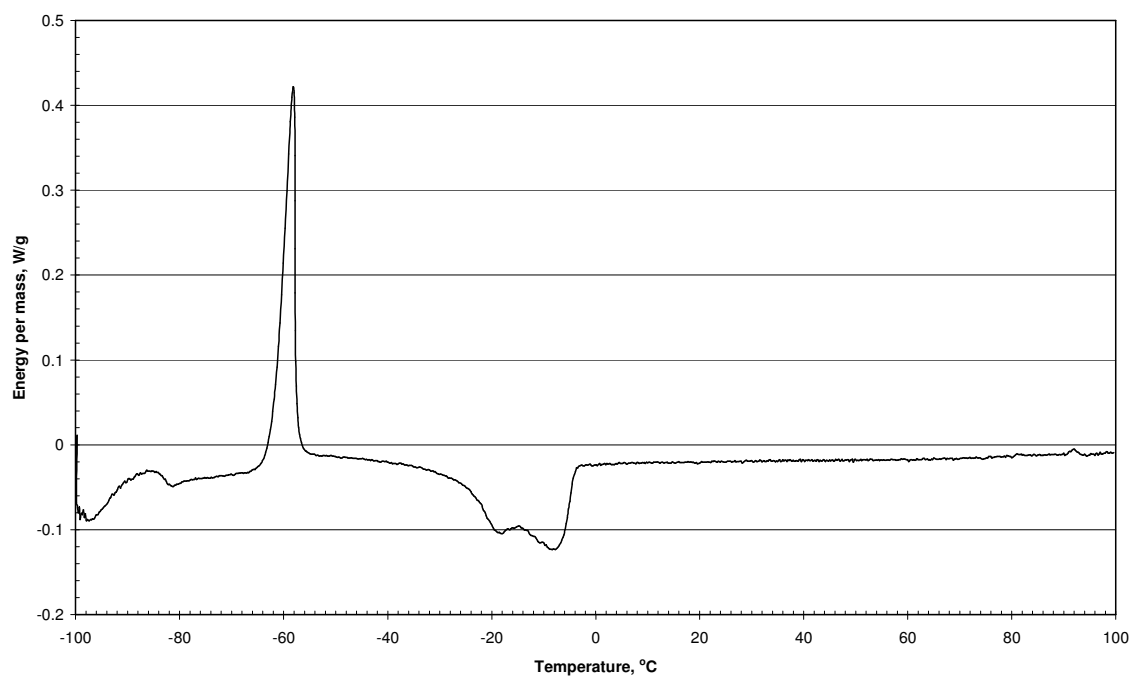
Figure 2. Experiment 2, DSC curve

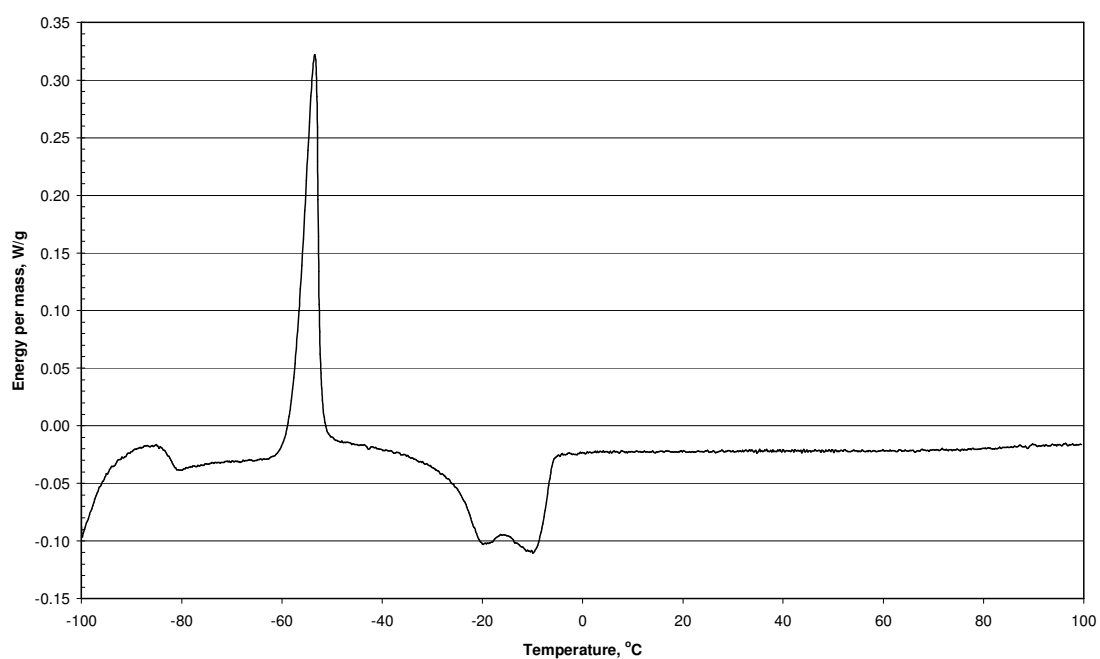
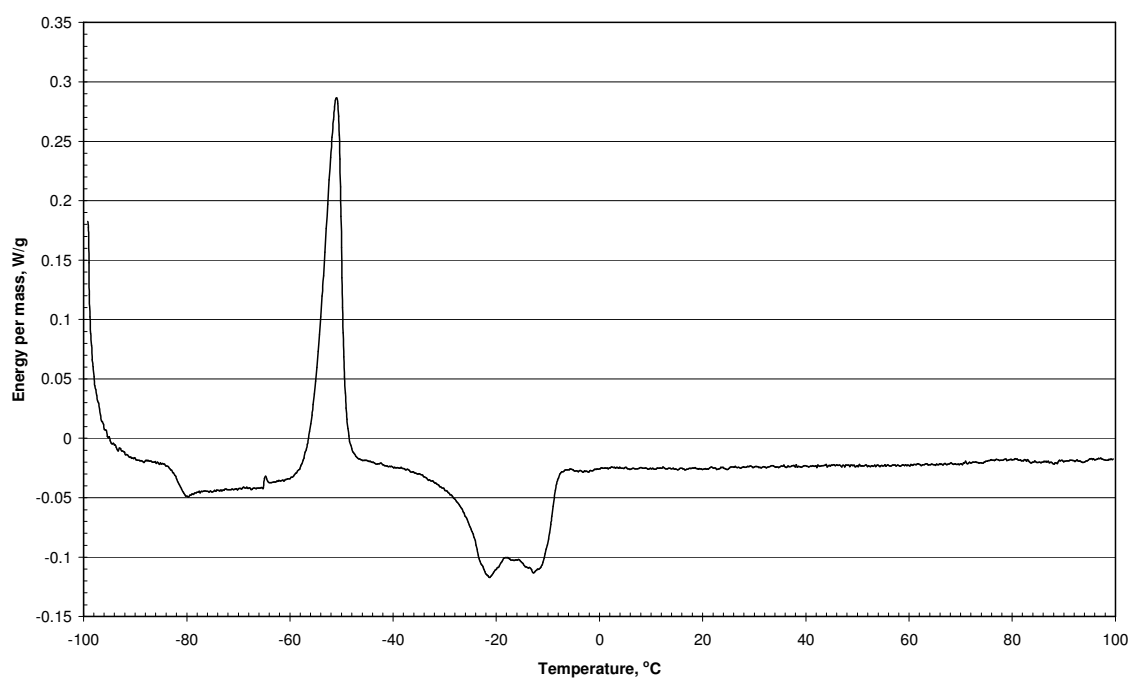
**Figure 3. Experiment 3, DSC curve****Figure 4. Experiment 4D, DSC curve**

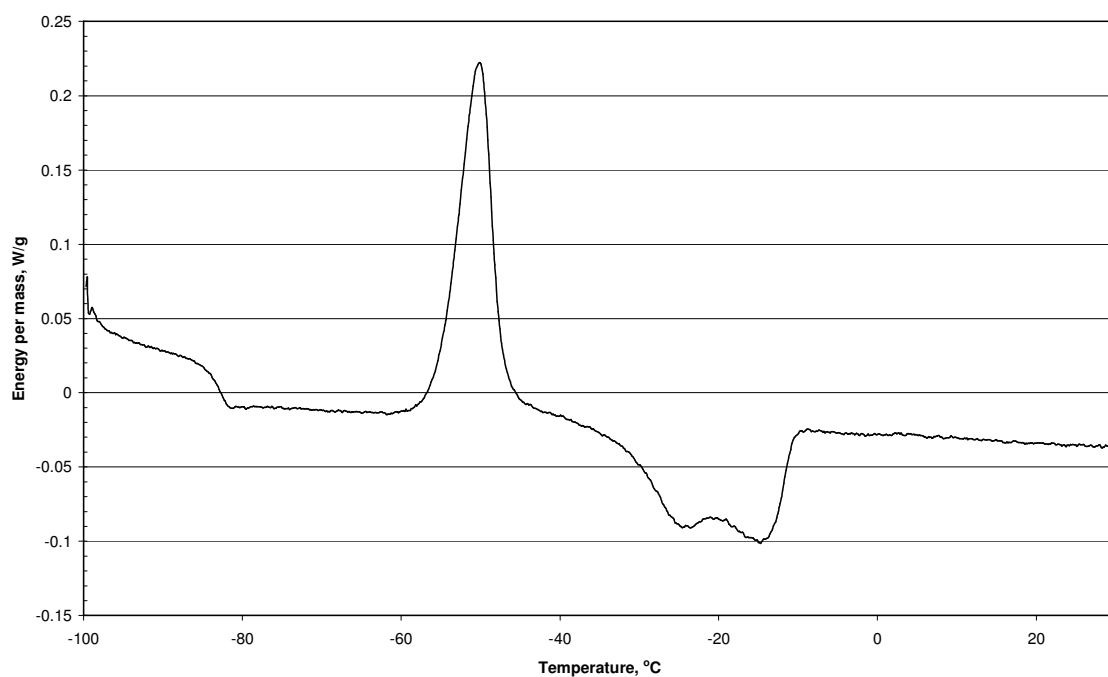
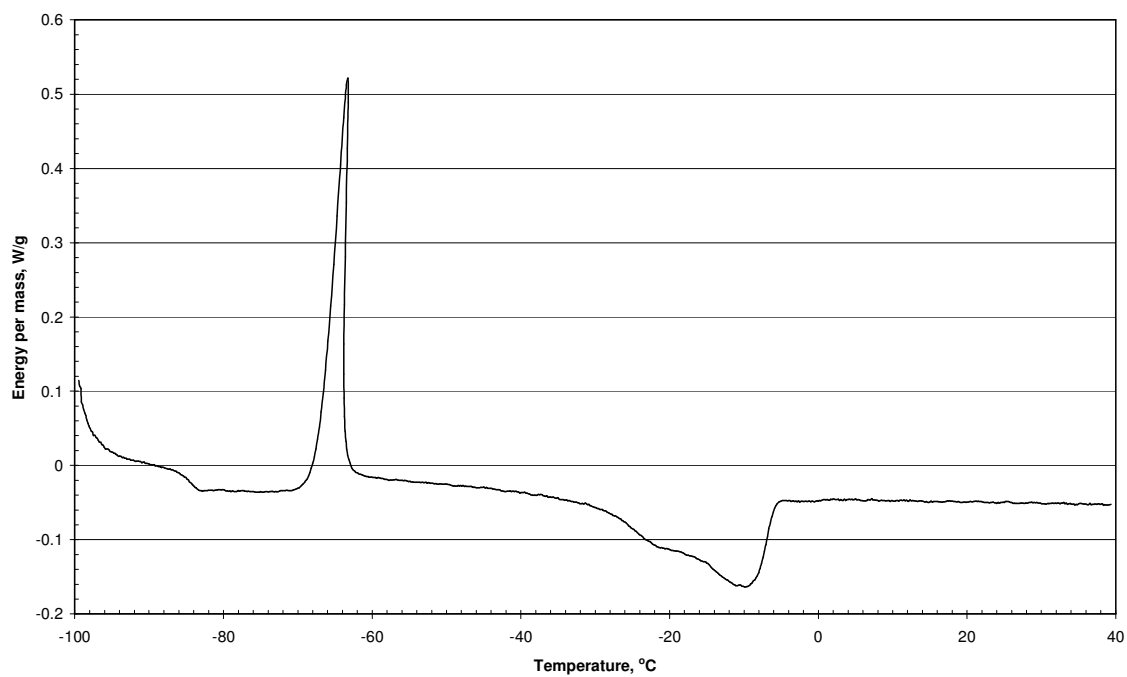
**Figure 5. Experiment 5C, DSC curve****Figure 6. Experiment 6C, DSC curve**

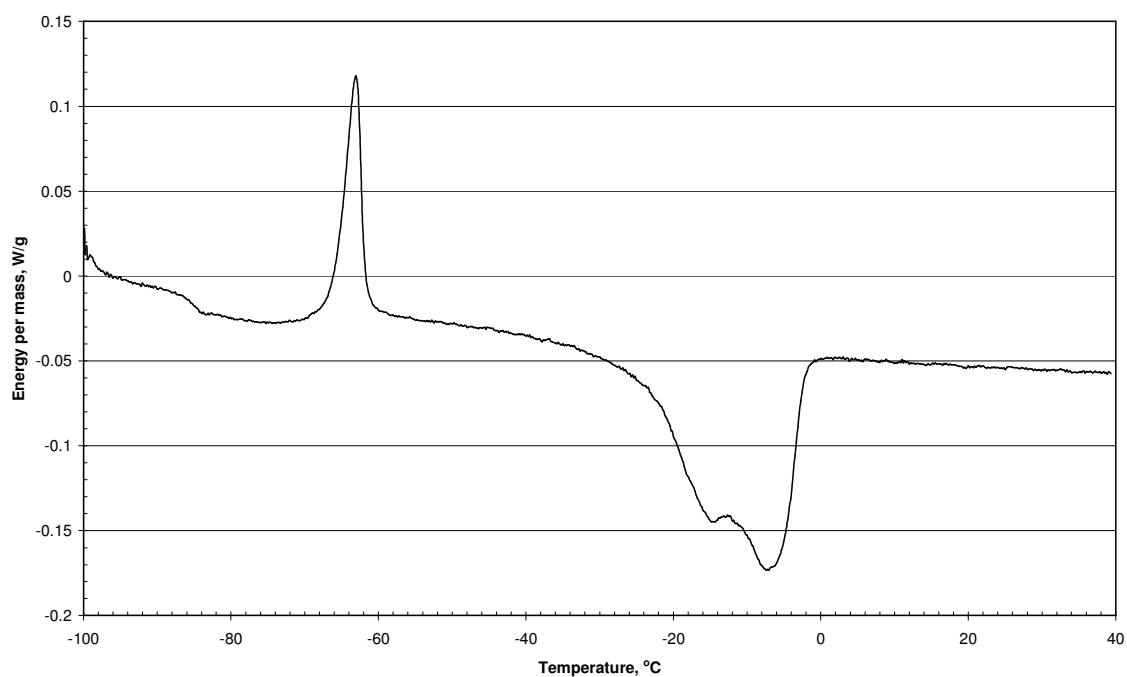
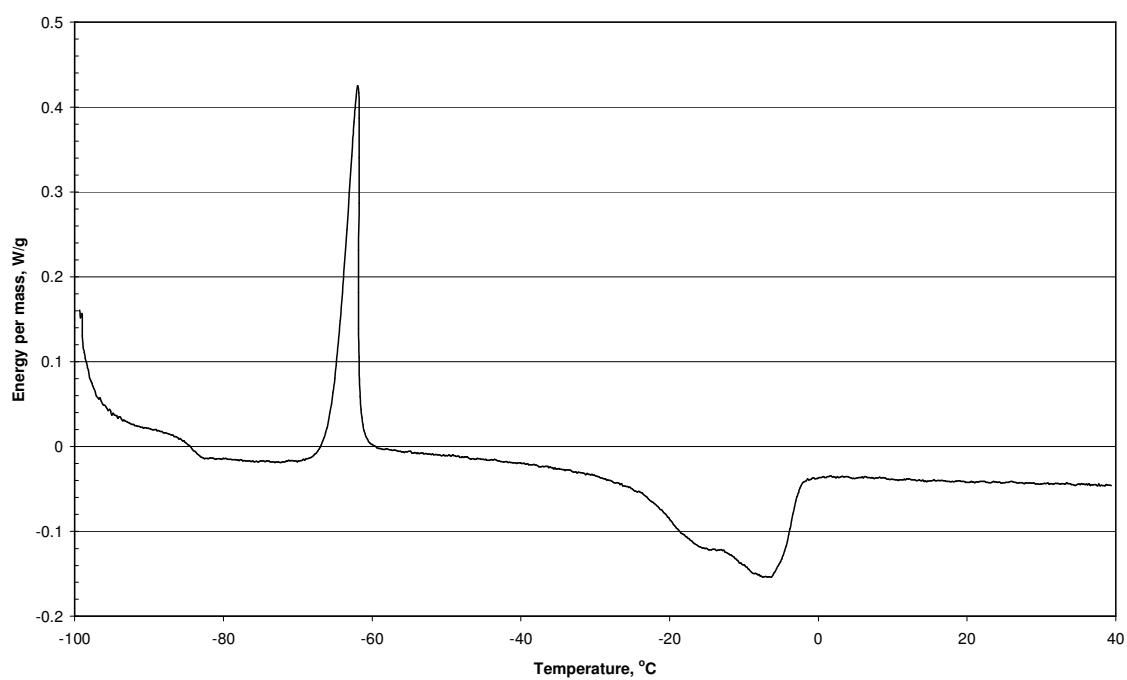
**Figure 7. Experiment 7D, DSC curve****Figure 8. Experiment 8B1A, DSC curve**

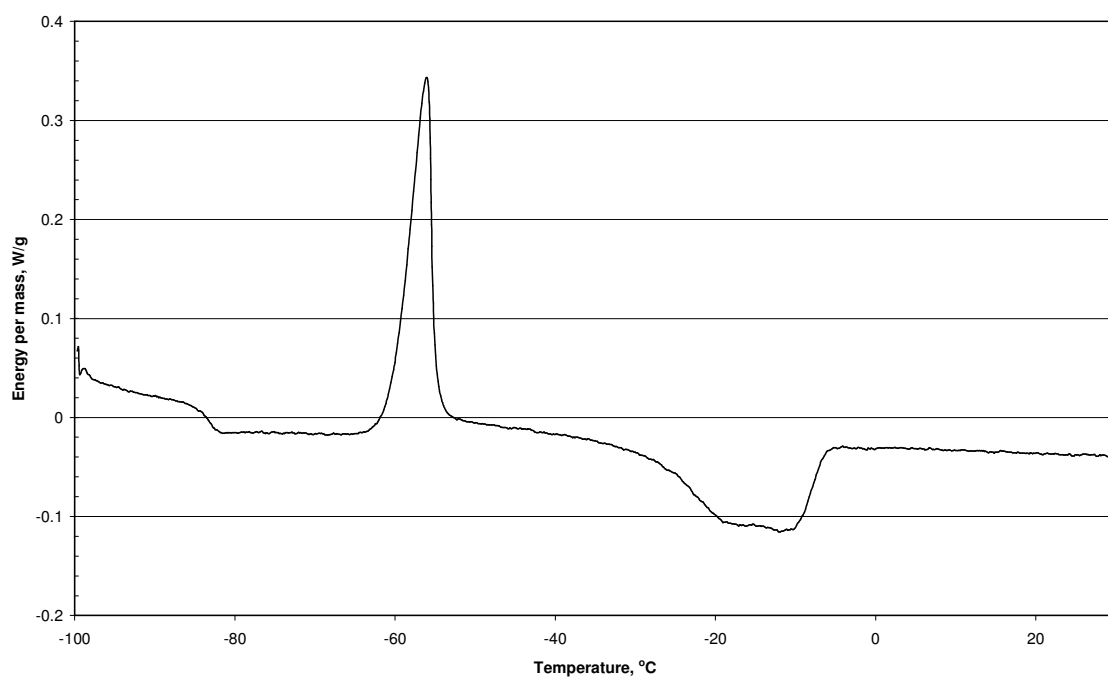
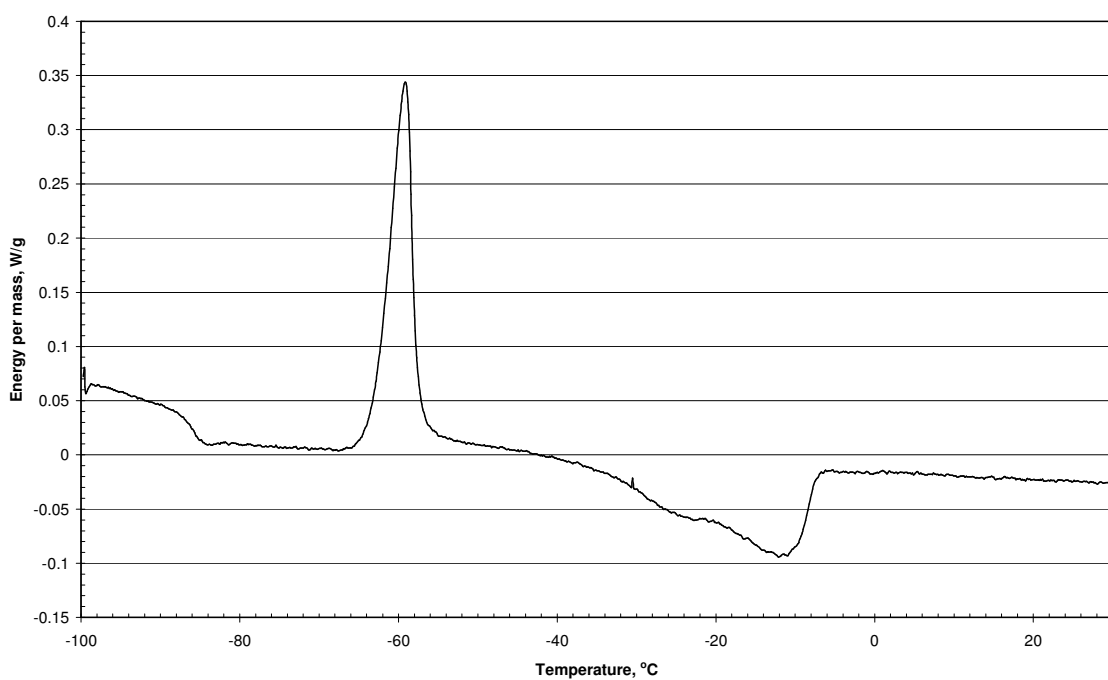
**Figure 9. Experiment 8B2A, DSC curve****Figure 10. Experiment 9B, DSC curve**

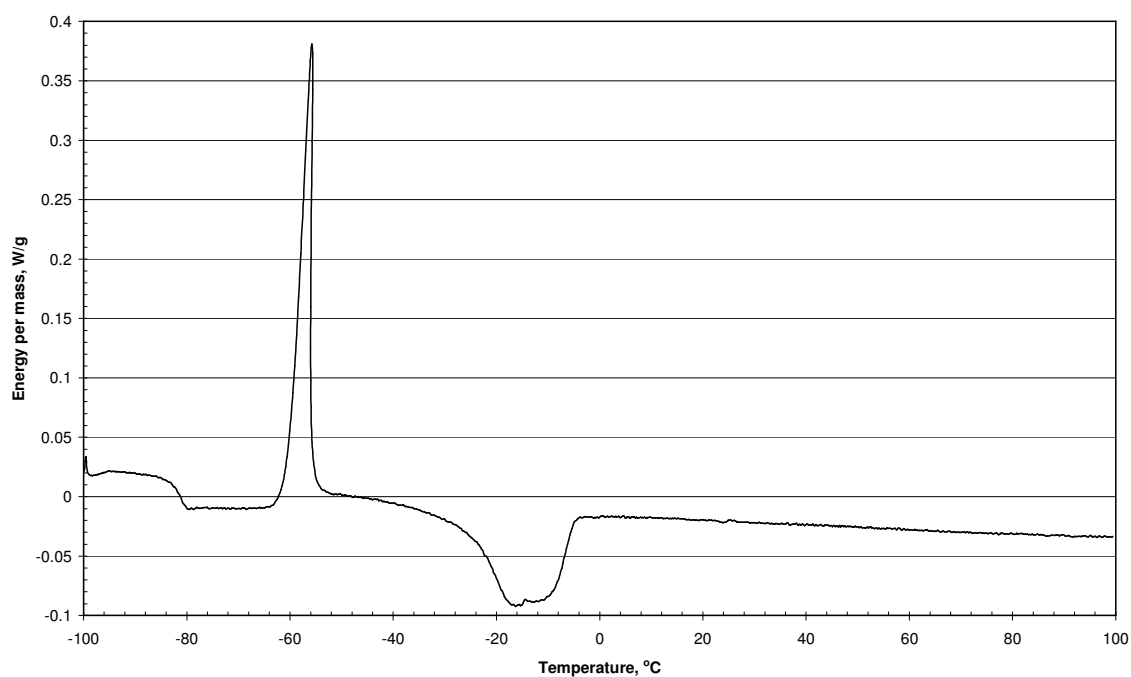
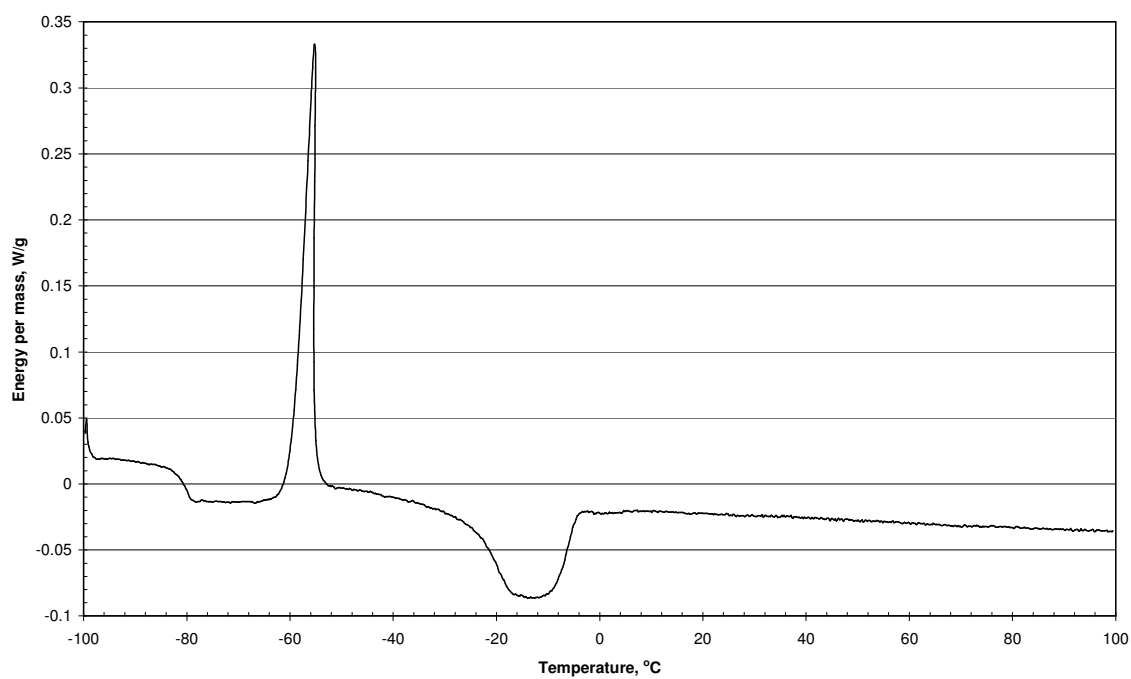
**Figure 11. Experiment 10B, DSC curve****Figure 12. Experiment 11B, DSC curve**

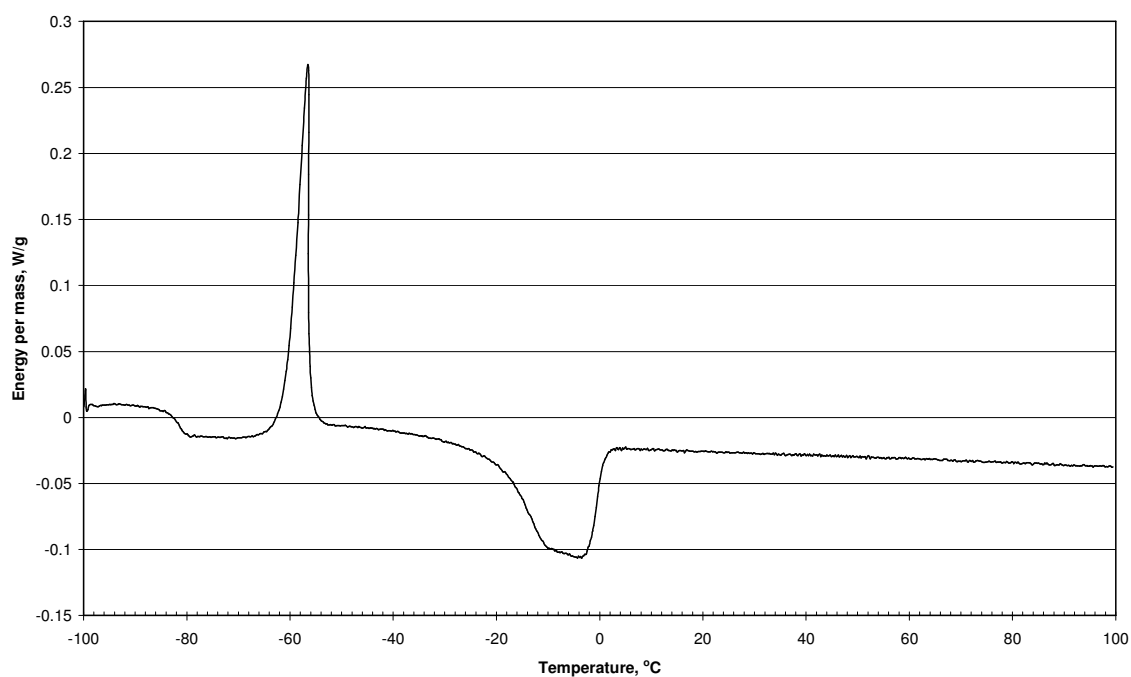
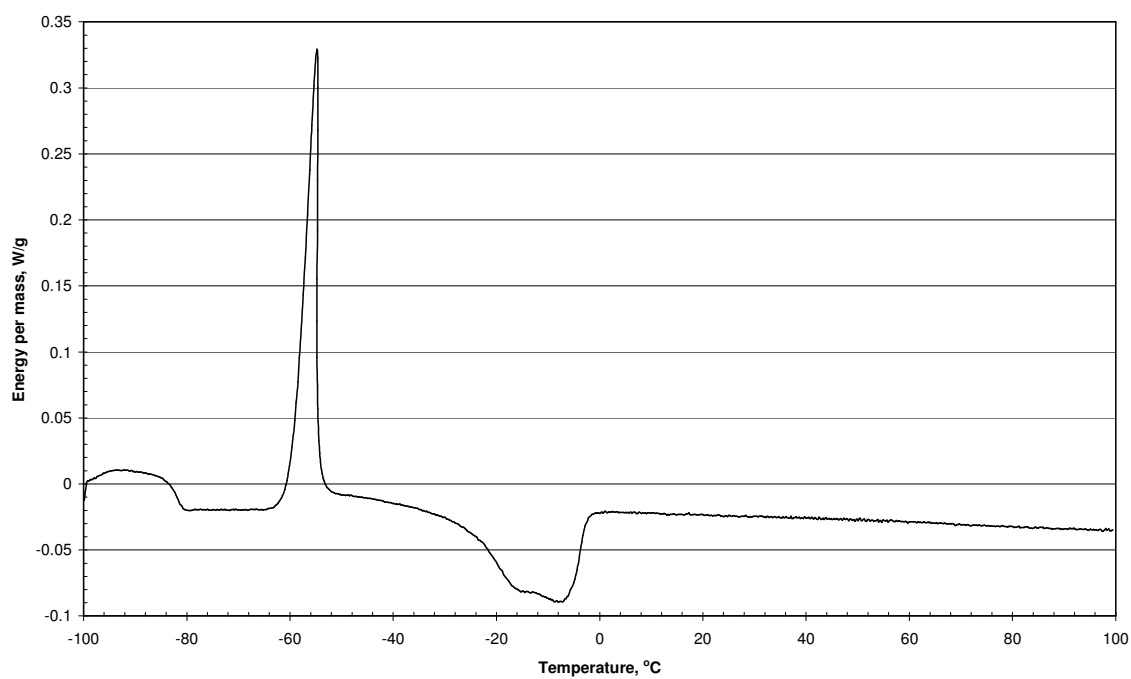
**Figure 13. Experiment 12B, DSC curve****Figure 14. Experiment 13, DSC curve**

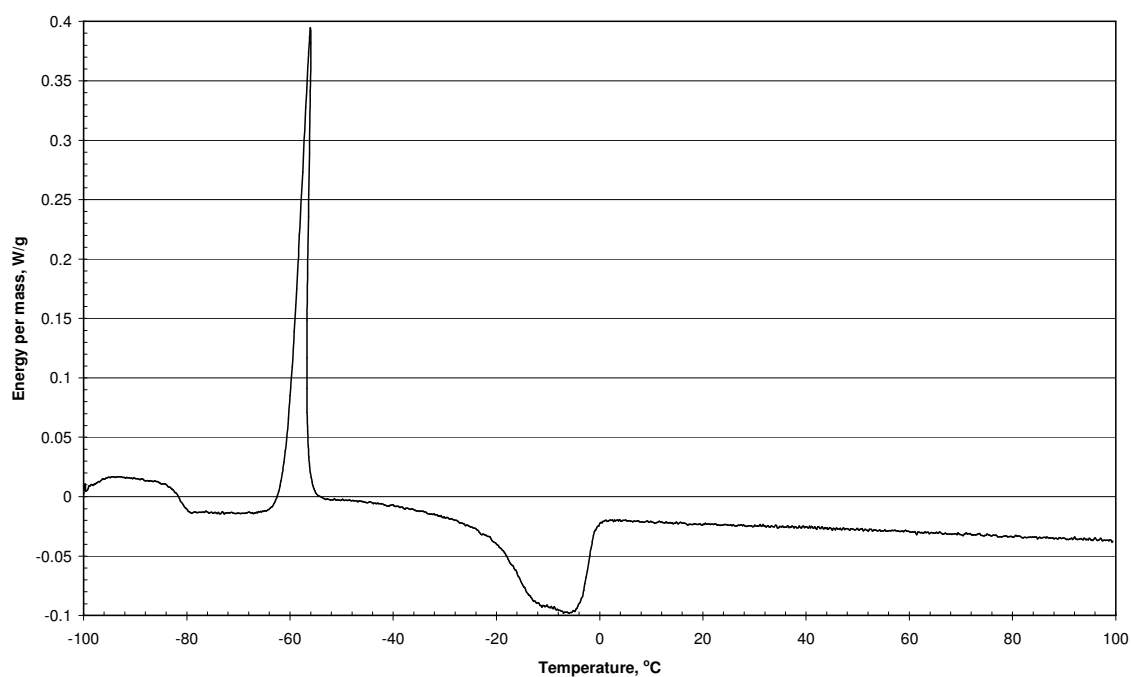
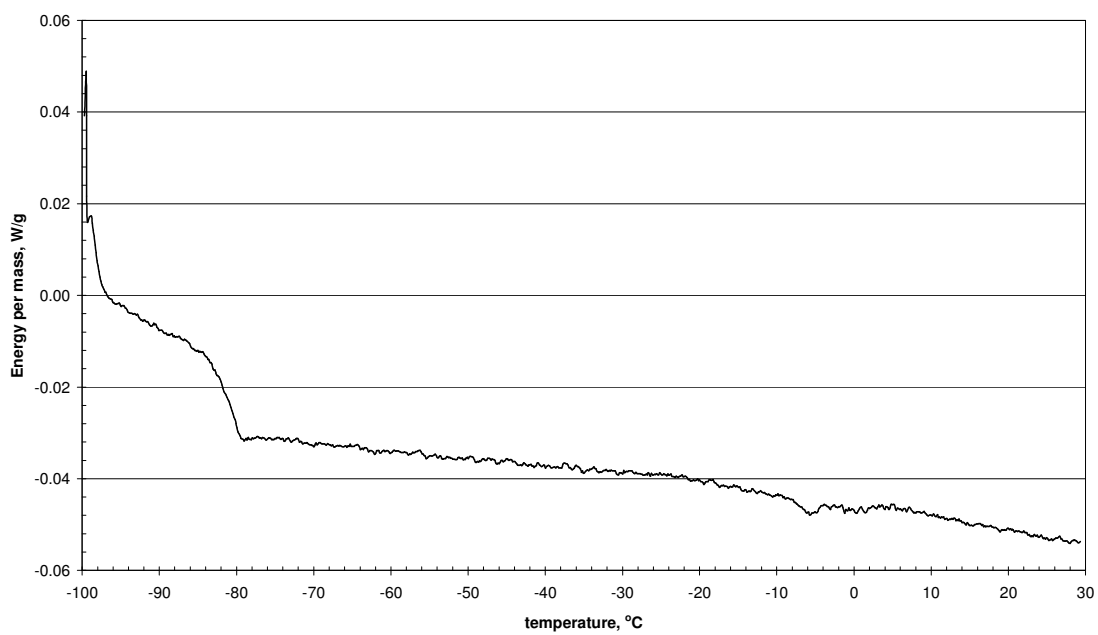
**Figure 15. Experiment 14, DSC curve****Figure 16. Experiment 15, DSC curve**

**Figure 17. Experiment 17, DSC curve****Figure 18. Experiment 18, DSC curve**

**Figure 19. Experiment 19, DSC curve****Figure 20. Experiment 20, DSC curve**

**Figure 21. Experiment 23, DSC curve****Figure 22. Experiment 24, DSC curve**

**Figure 23. Experiment 25, DSC curve****Figure 24. Experiment 26, DSC curve**

**Figure 25. Experiment 27, DSC curve****Figure 26. HTPB R45M, DSC curve**

APPENDIX E

THERMAL DECOMPOSITION AND THERMOGRAVIMETRIC ANALYSIS

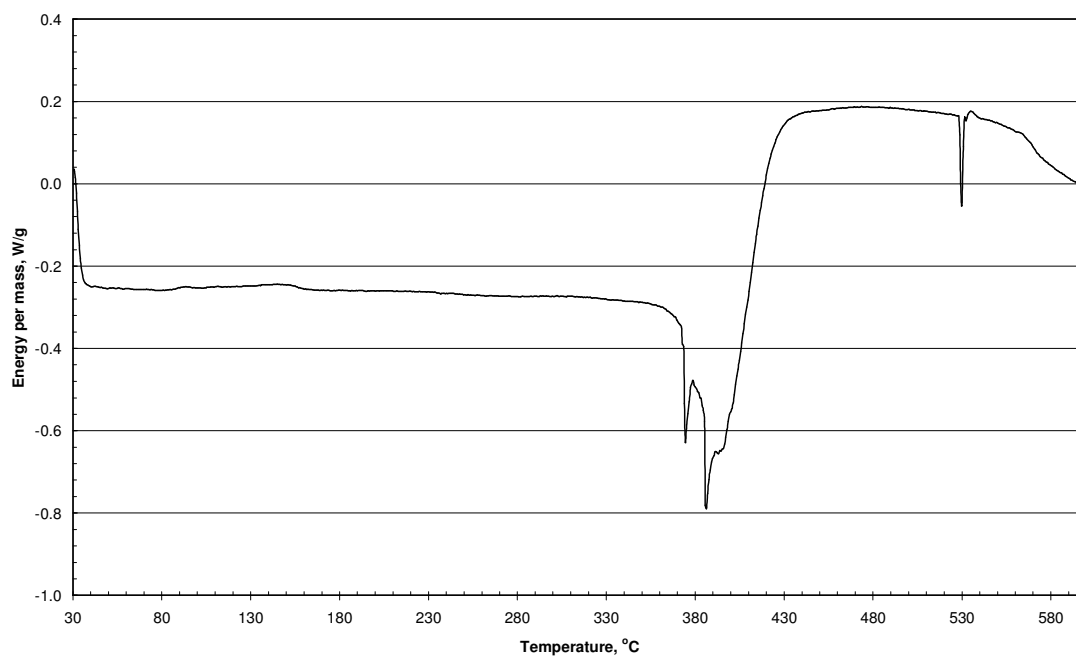


Figure 1. Experiment 9, DSC thermal decomposition curve

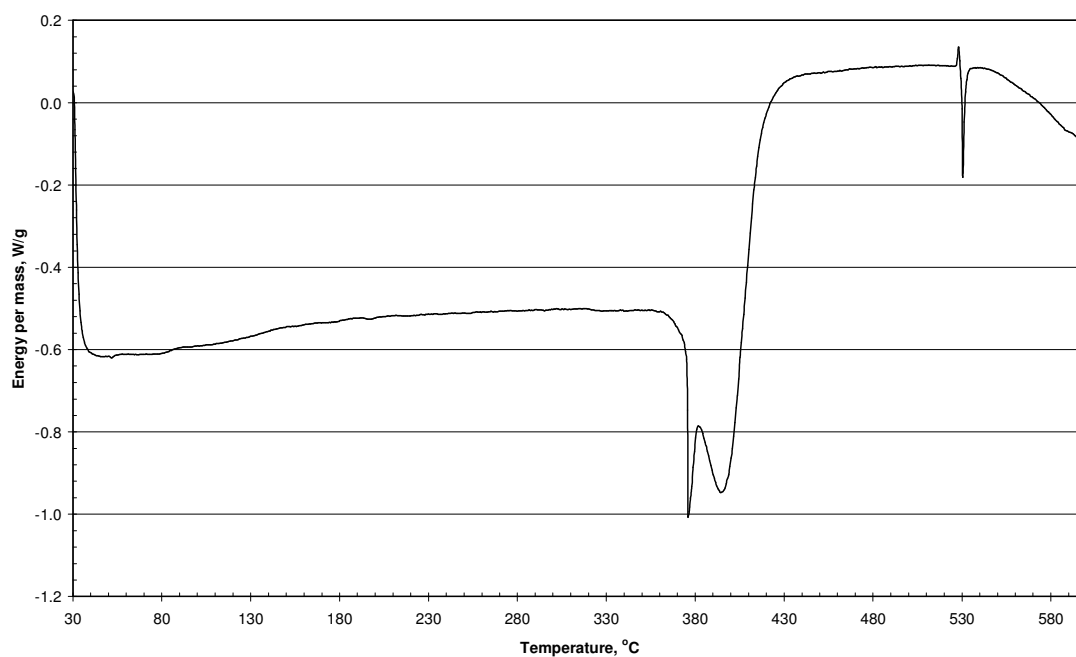


Figure 2. Experiment 13, DSC thermal decomposition curve

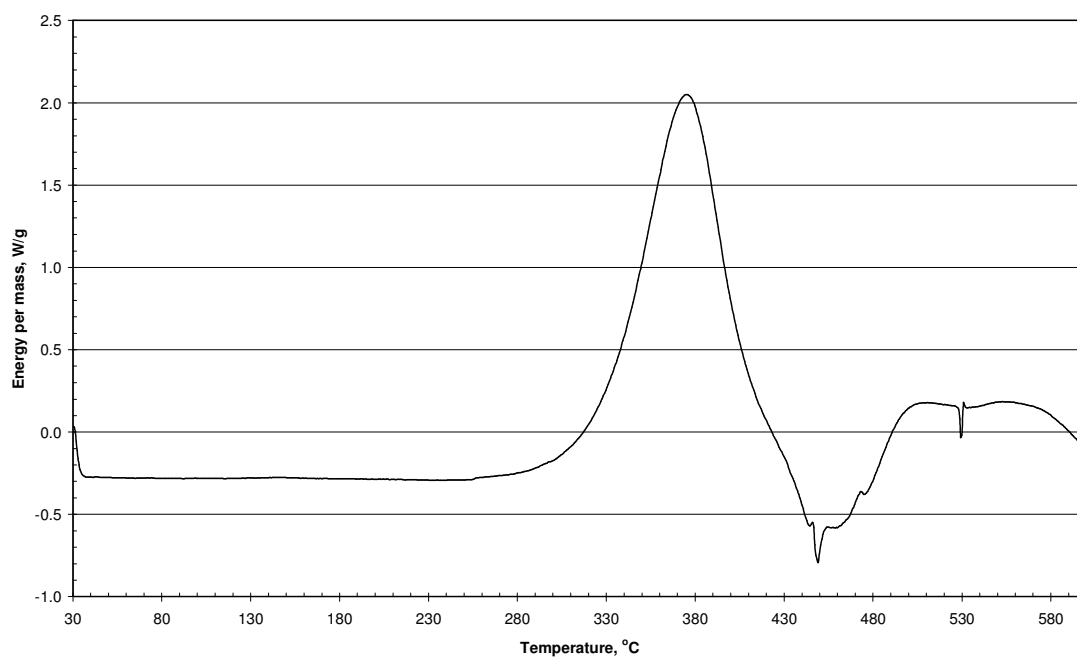


Figure 3. HTPB R45M, DSC thermal decomposition curve

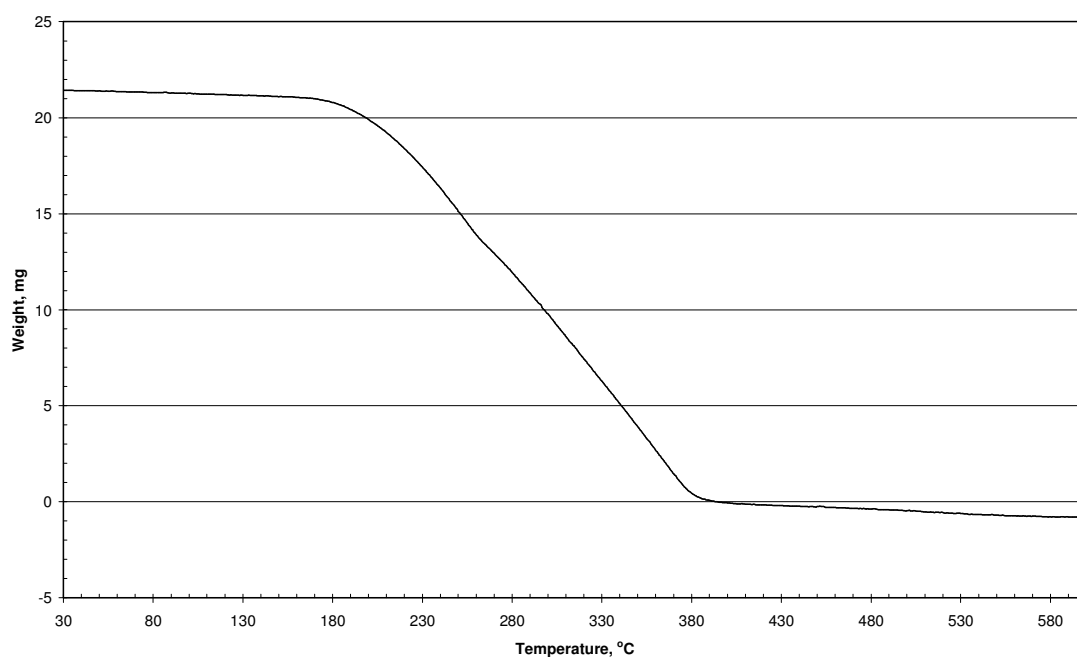


Figure 4. Experiment 9 DSC thermogravimetric analysis

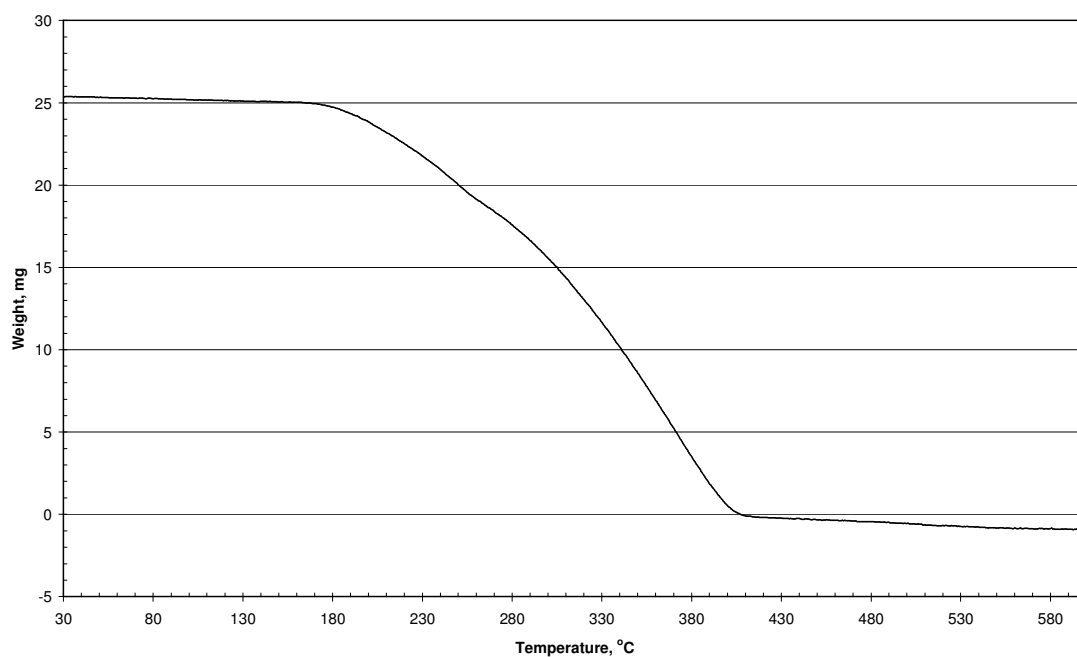


Figure 5. Experiment 13, thermogravimetric analysis

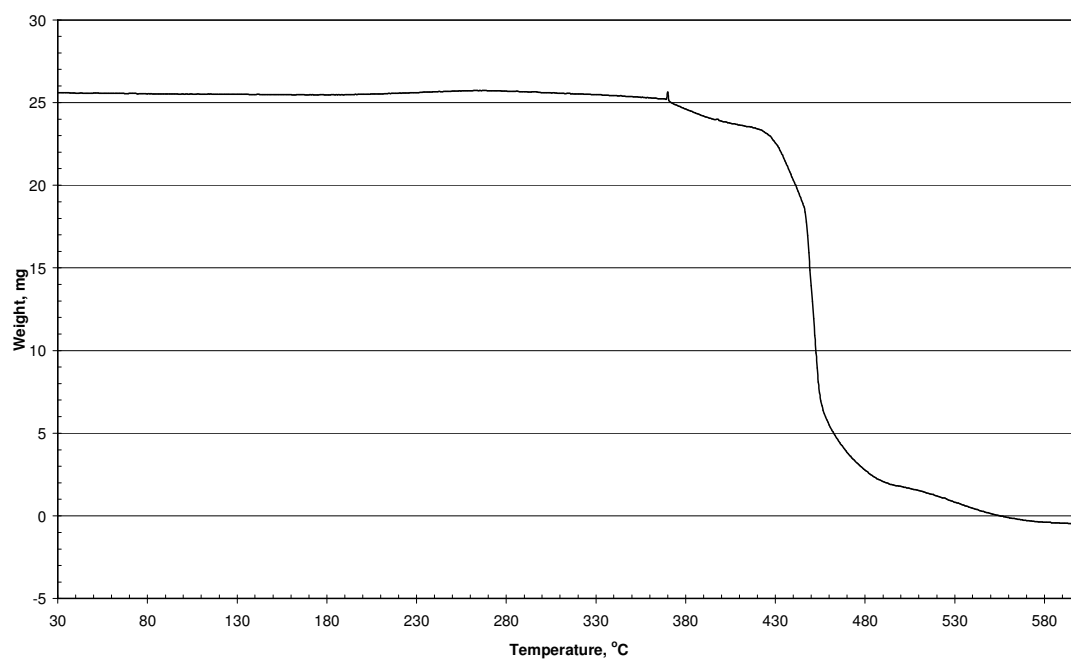


Figure 6. HTPB R45M, thermogravimetric analysis

APPENDIX F

INFRA RED SPECTRA

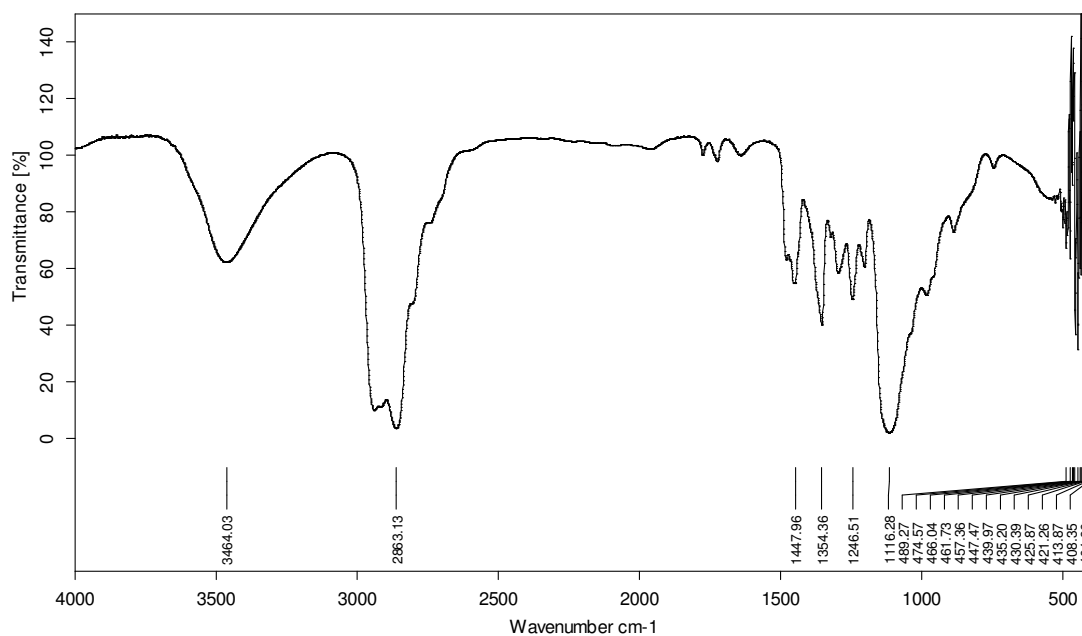


Figure 1. Experiment 1, HTPE FTIR spectrum

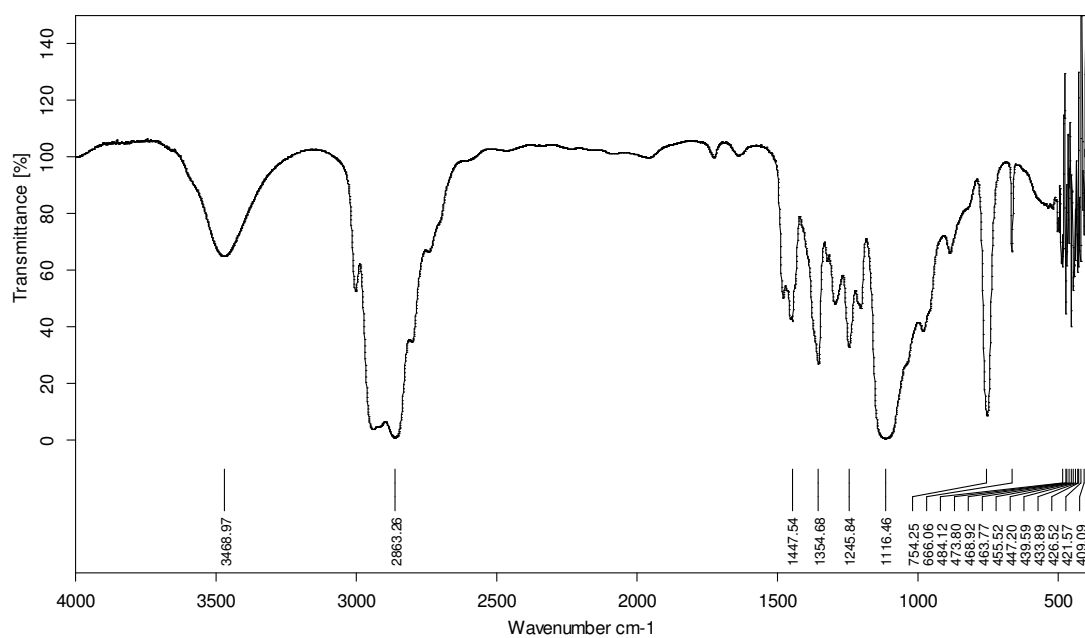
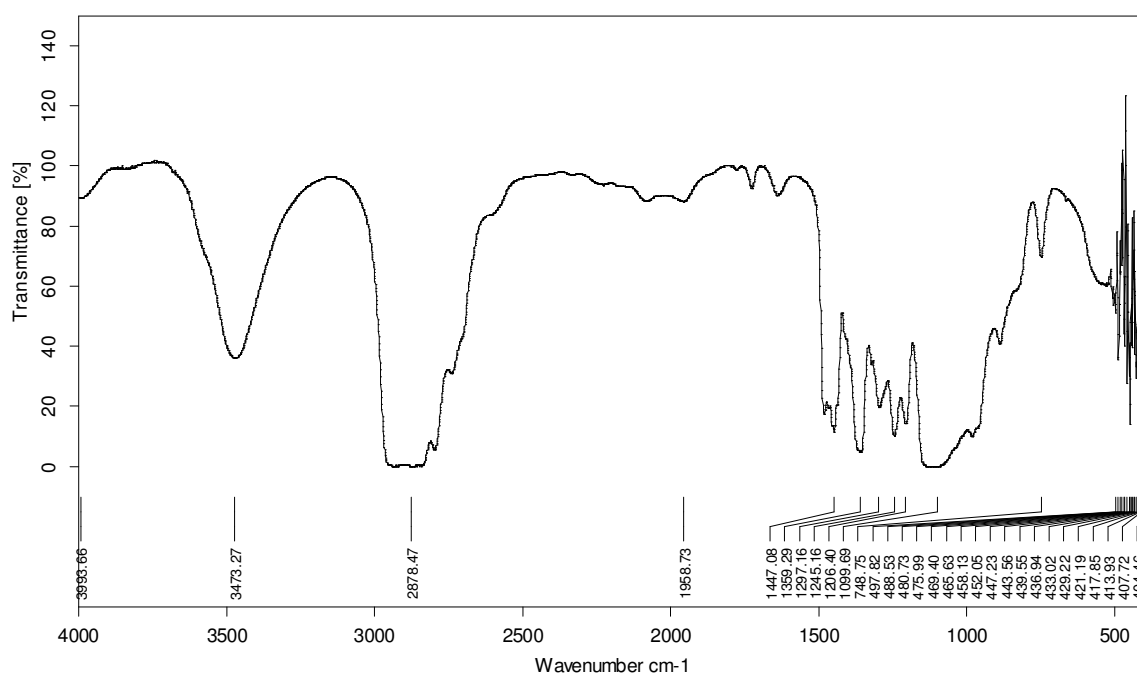
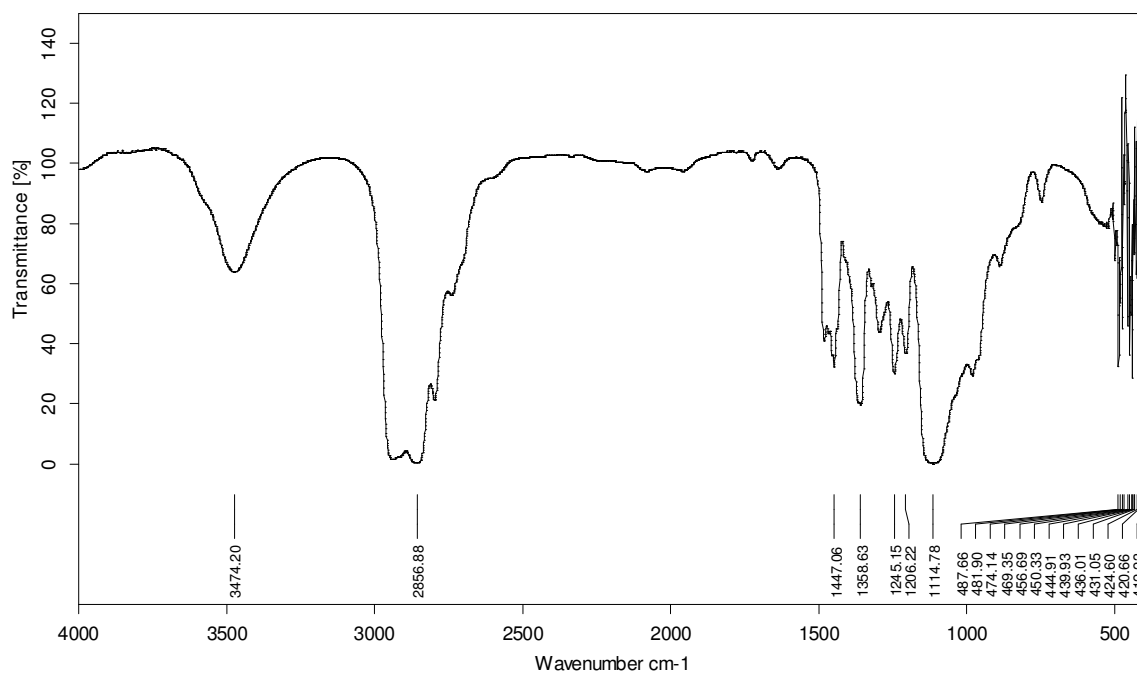


Figure 2. Experiment 3, HTPE FTIR spectrum

**Figure 3. Experiment 8B1A, HTPE FTIR spectrum****Figure 4. Experiment 8B2A, HTPE FTIR spectrum**

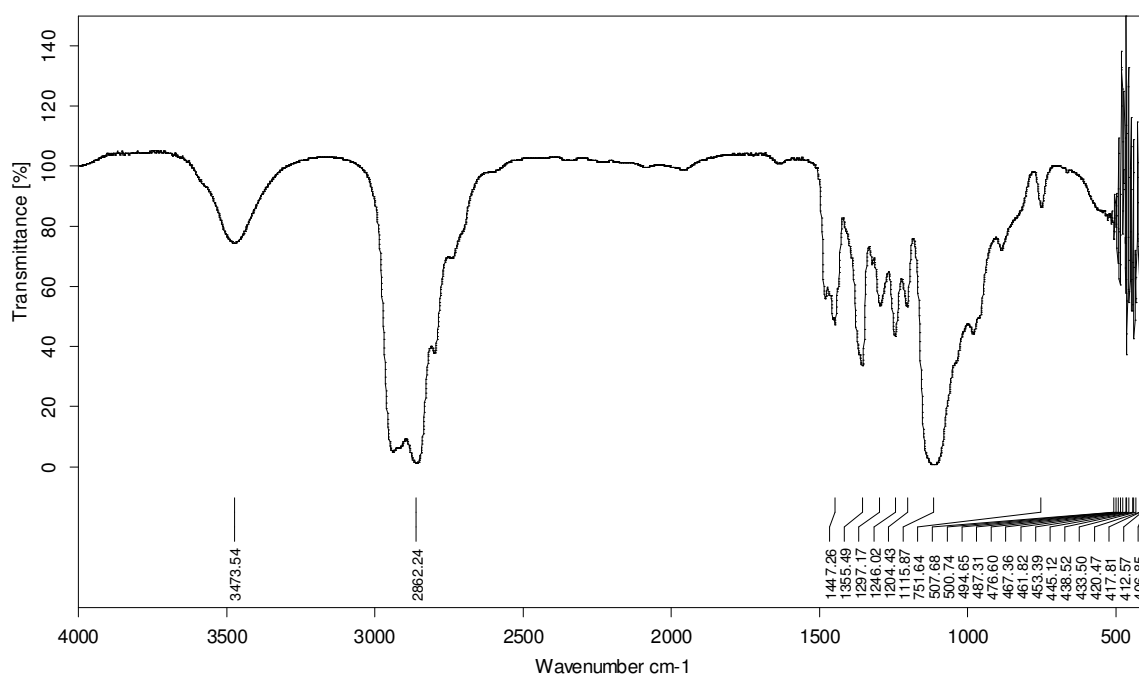


Figure 5. Experiment 11, HTPE FTIR spectrum

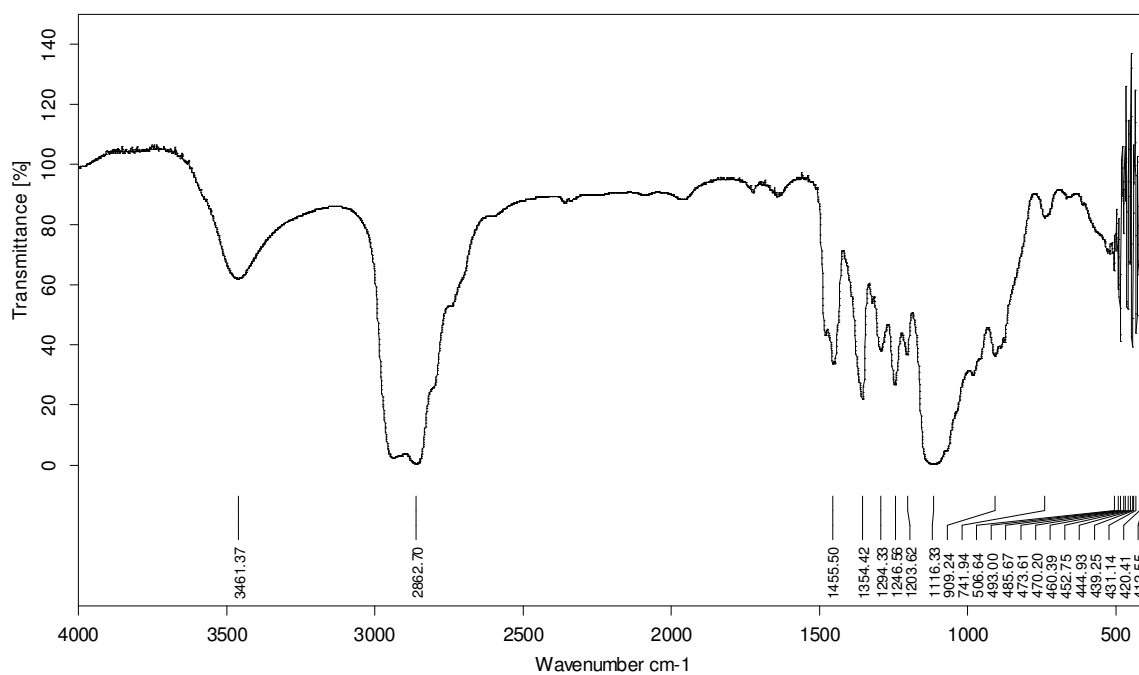


Figure 6. Experiment 12A, HTPE FTIR spectrum

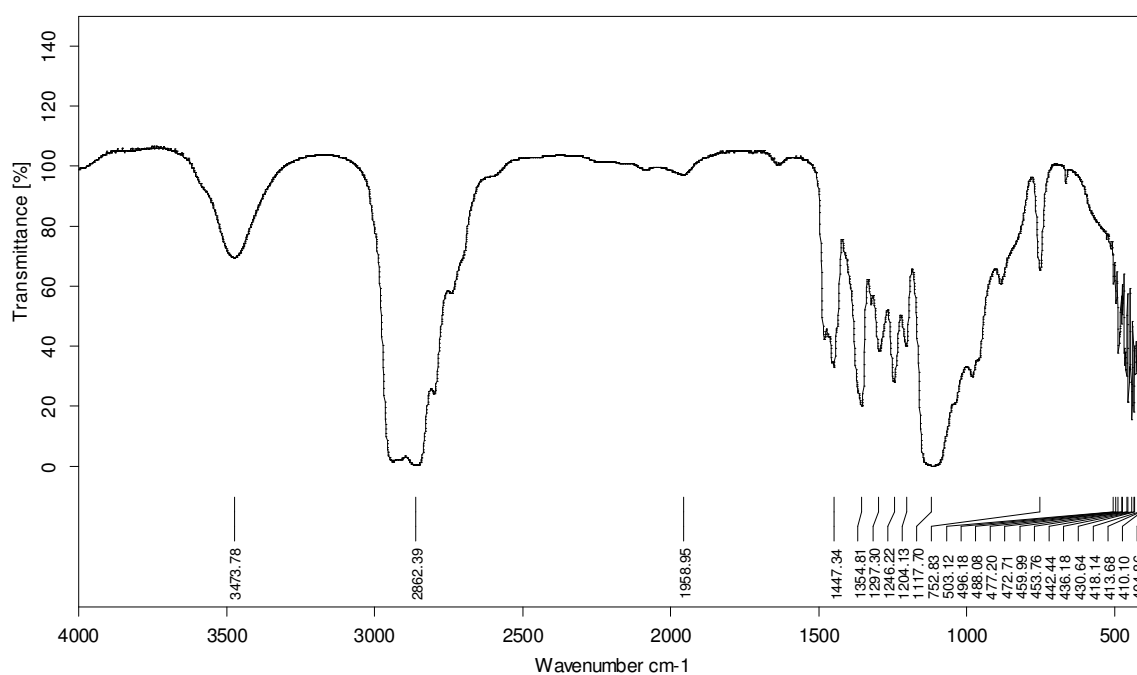


Figure 7. Experiment 12, HTPE FTIR spectrum

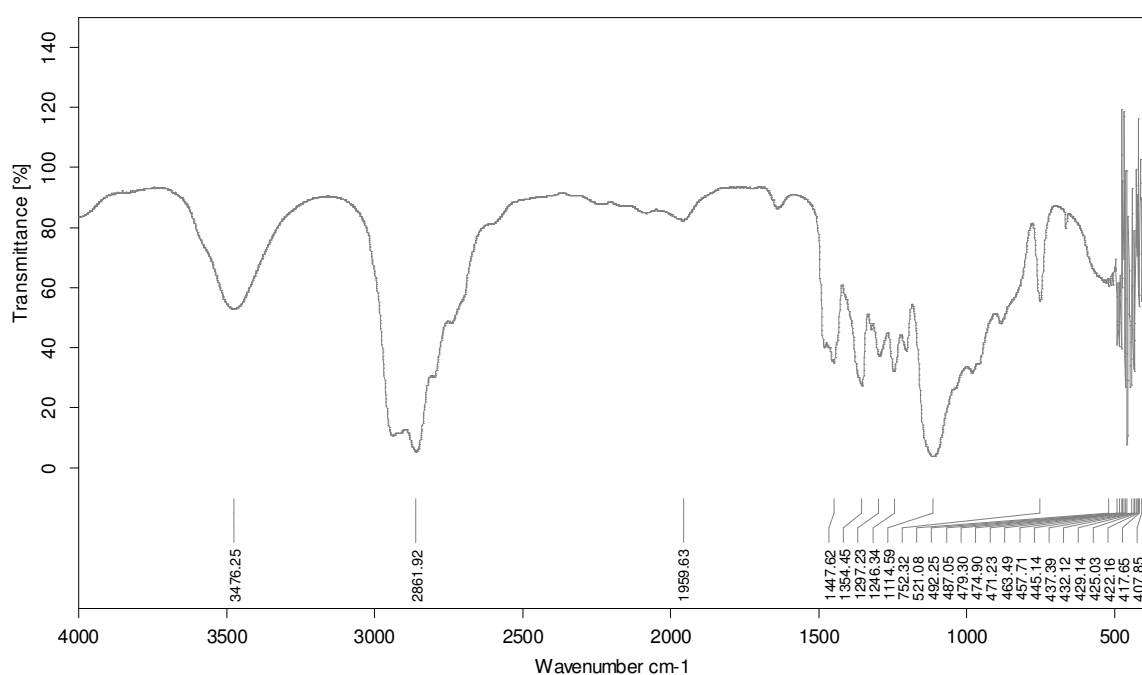


Figure 8. Experiment 13, HTPE FTIR spectrum

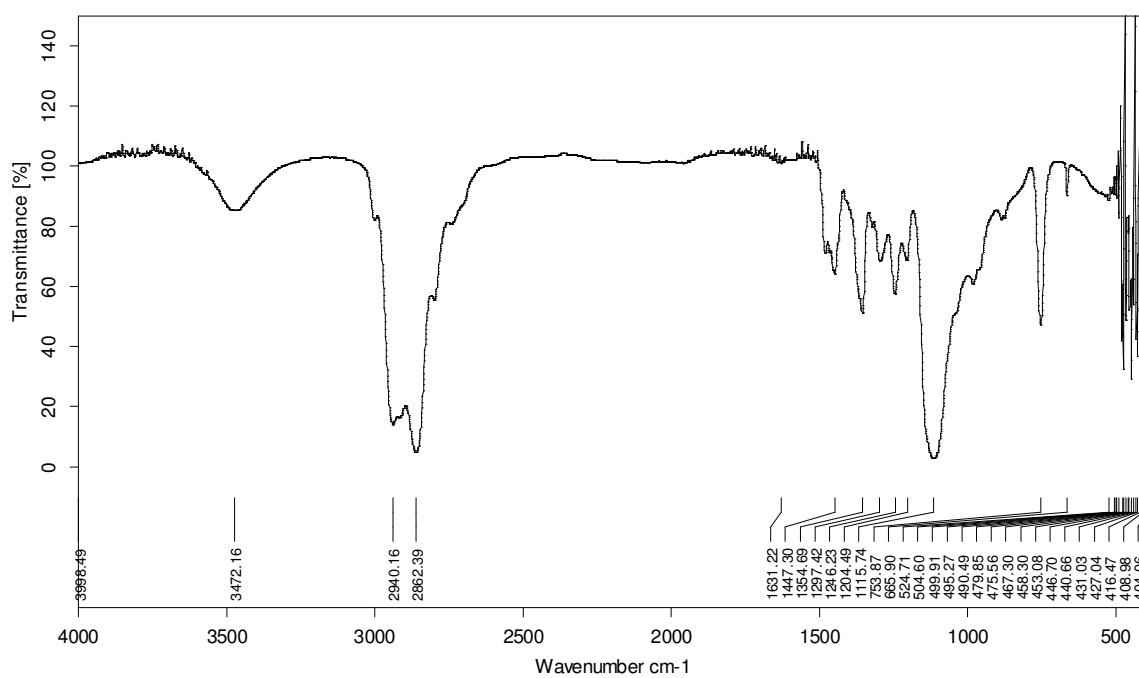


Figure 9. Experiment 14, HTPE FTIR spectrum

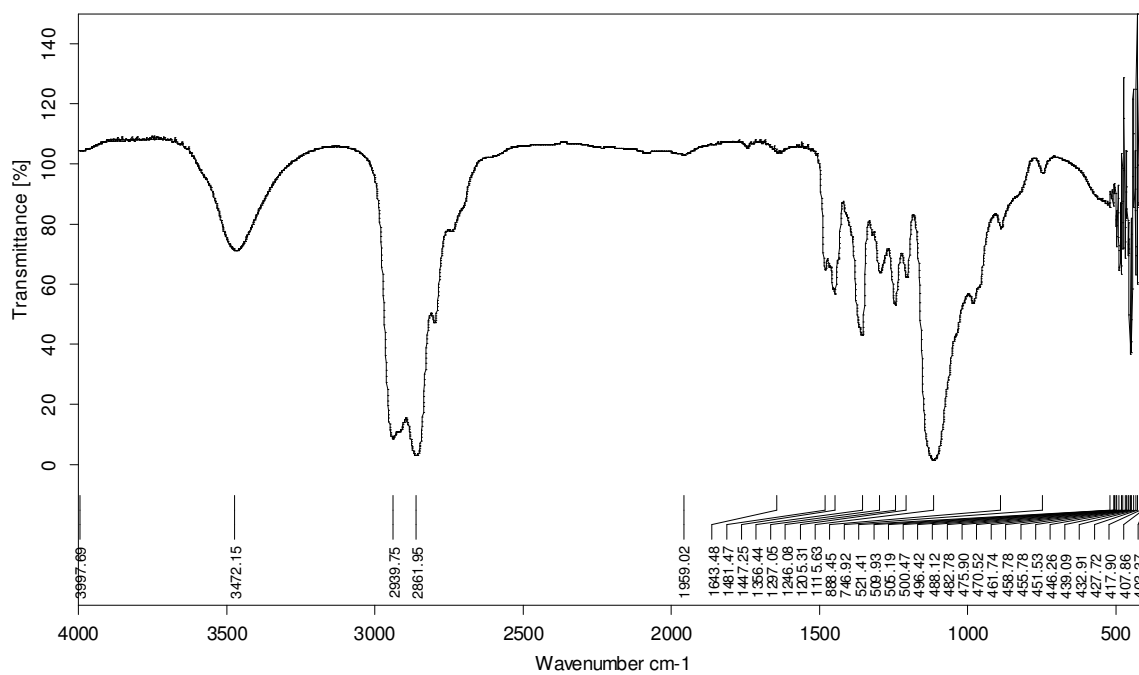
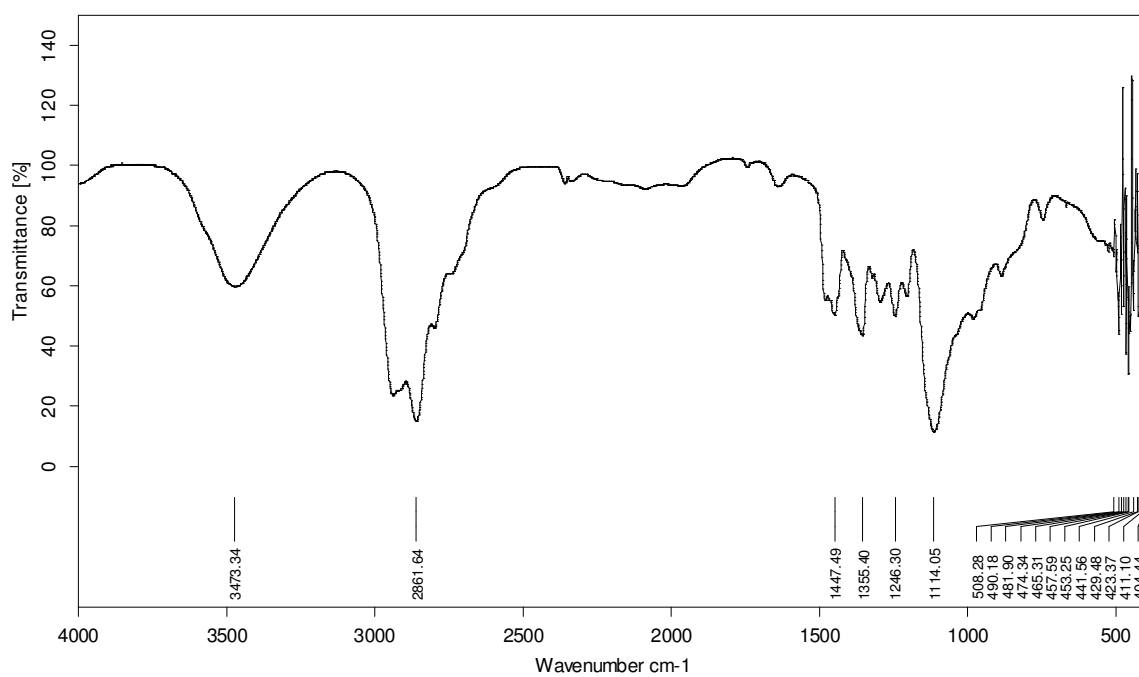
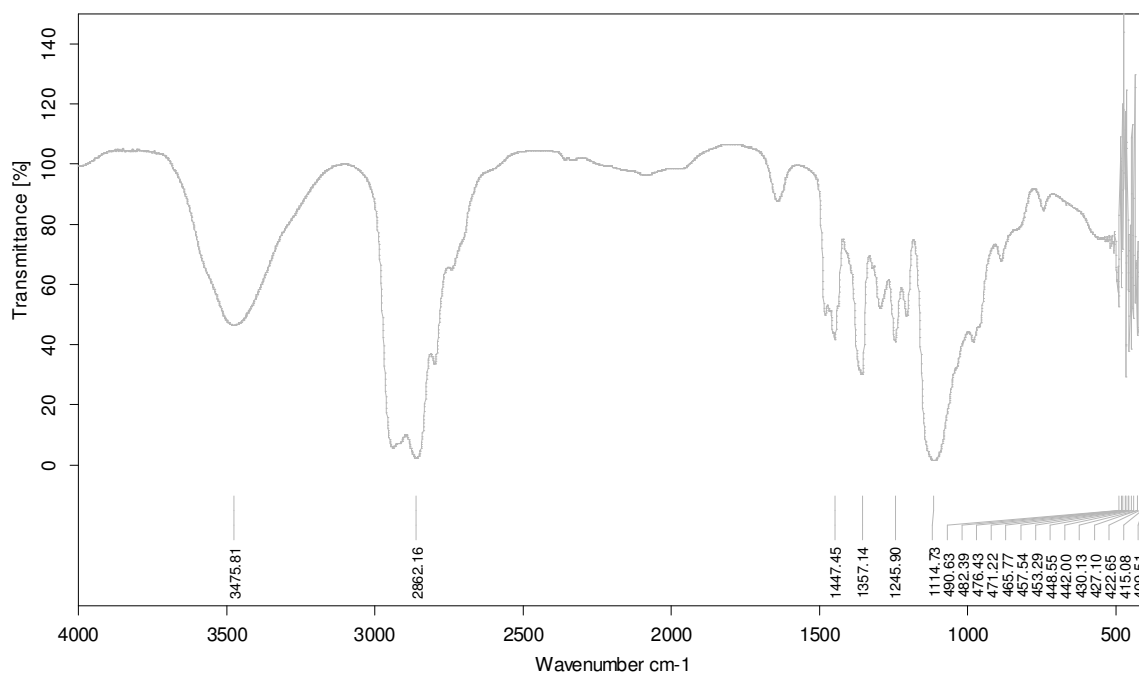


Figure 10. Experiment 15, HTPE FTIR spectrum

**Figure 11. Experiment 16, HTPE FTIR spectrum****Figure 12. Experiment 17, HTPE FTIR spectrum**

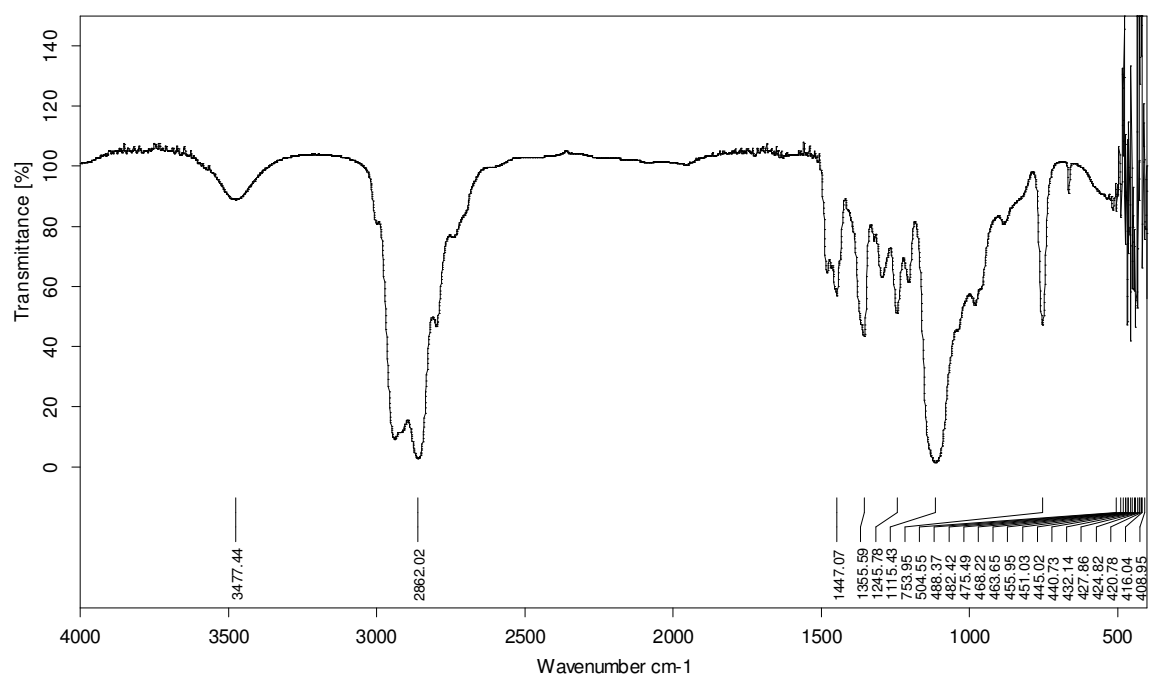


Figure 13. Experiment 19, HTPE FTIR spectrum

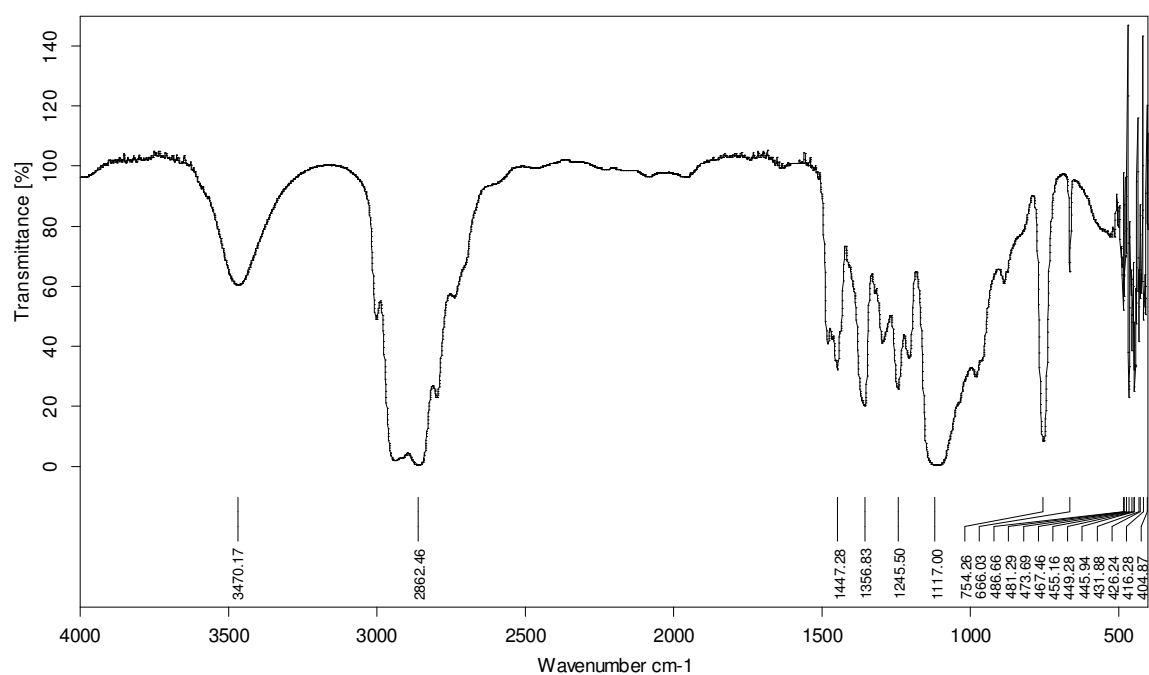
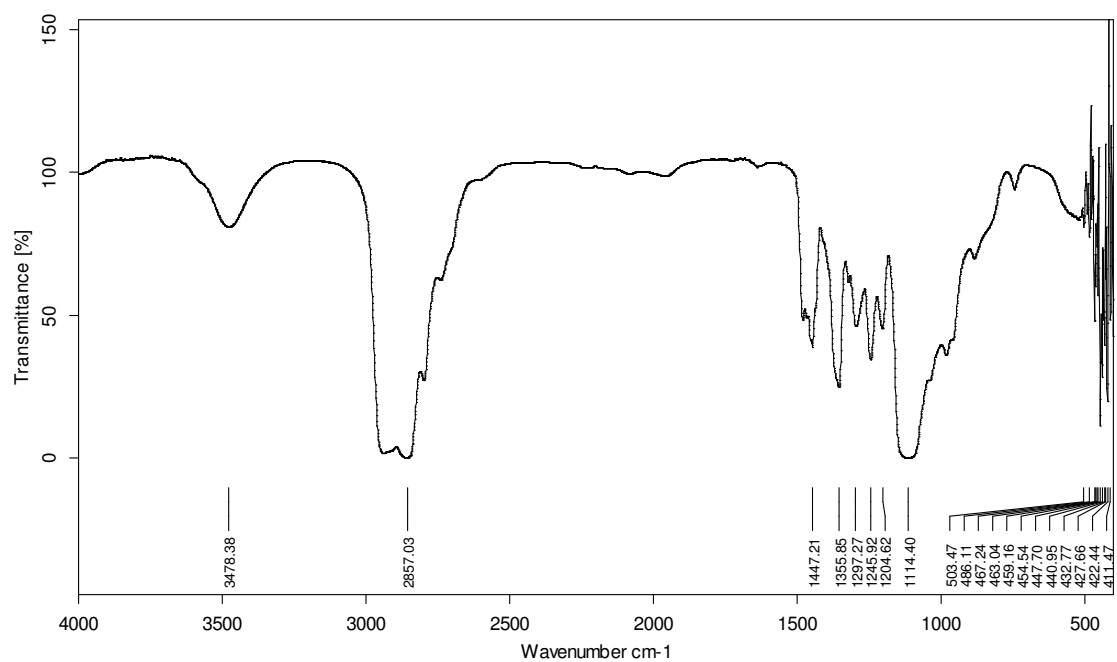
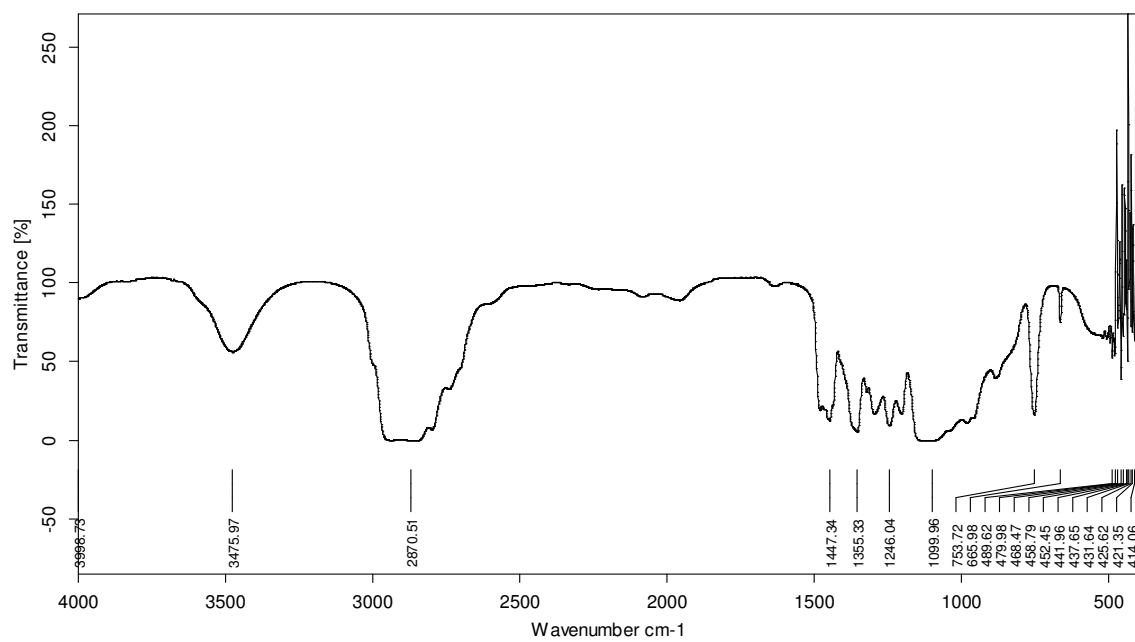


Figure 14. Experiment 20, HTPE FTIR spectrum

**Figure 15. Experiment 25, HTPE FTIR spectrum****Figure 16. Experiment 26, HTPE FTIR spectrum**

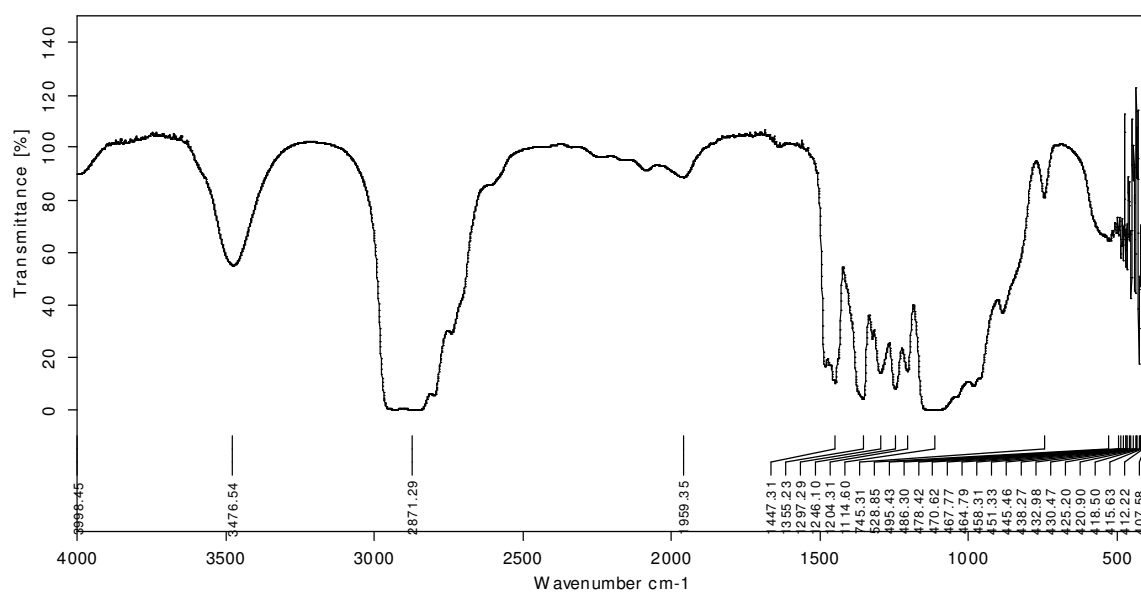


Figure 17. Experiment 27, HTPB FTIR spectrum

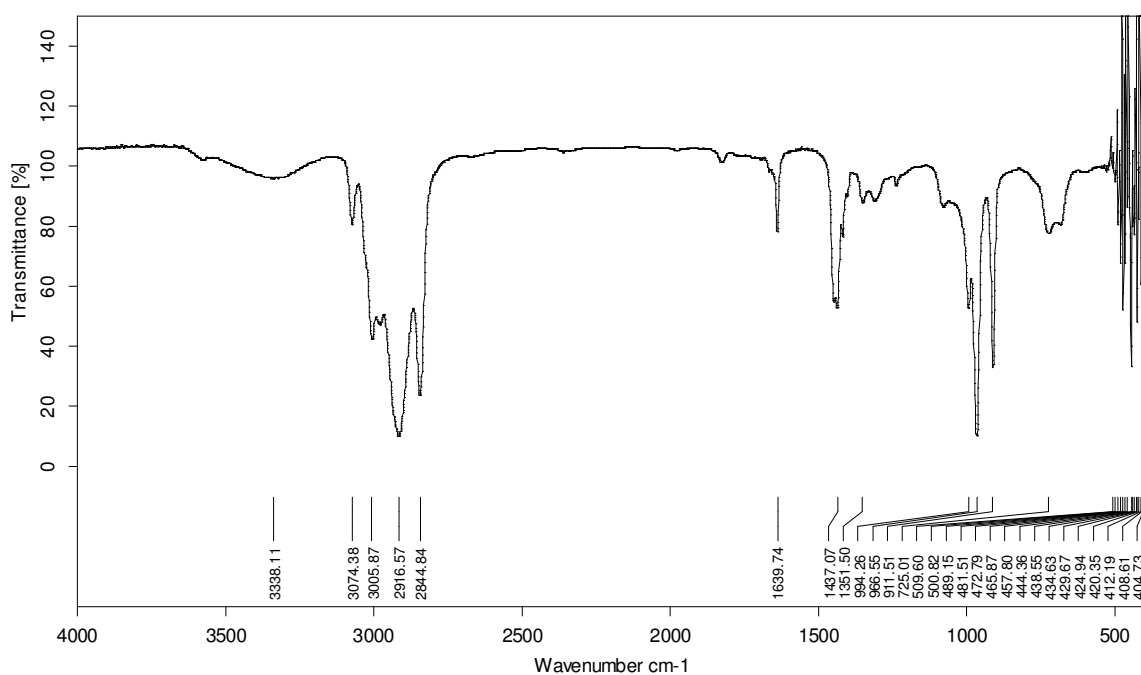


Figure 18. HTPB, FTIR spectrum

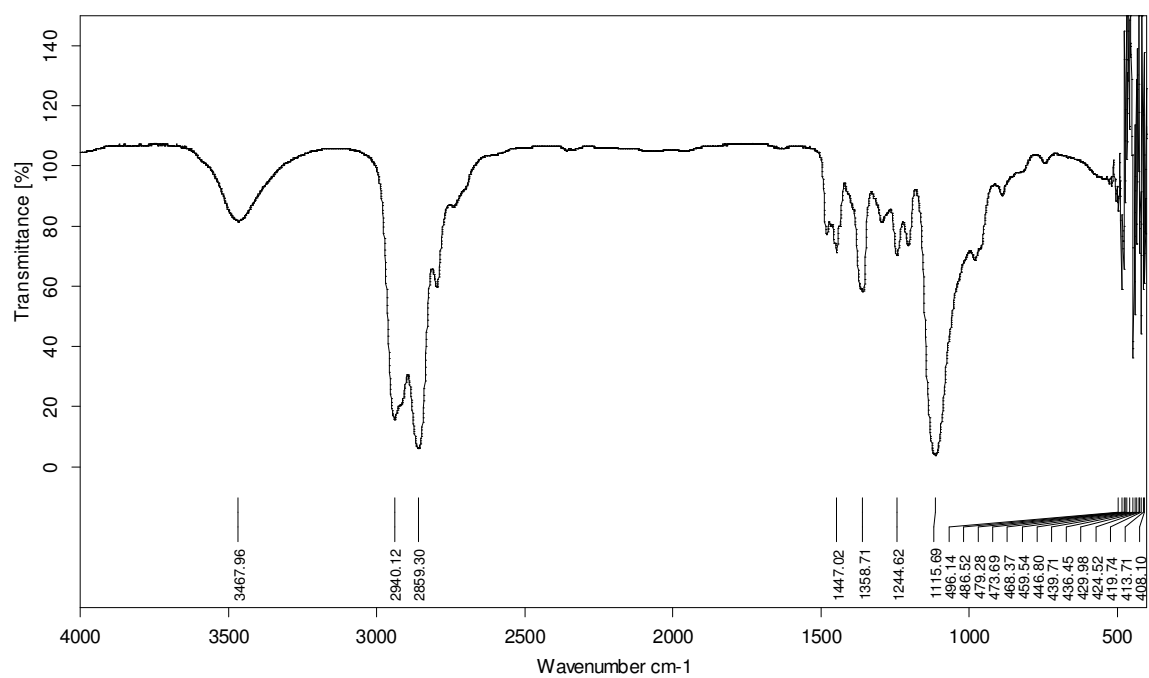


Figure 19. Aldrich THF-EO copolymer, FTIR spectrum

APPENDIX G

GC-MS CHROMATOGRAMS

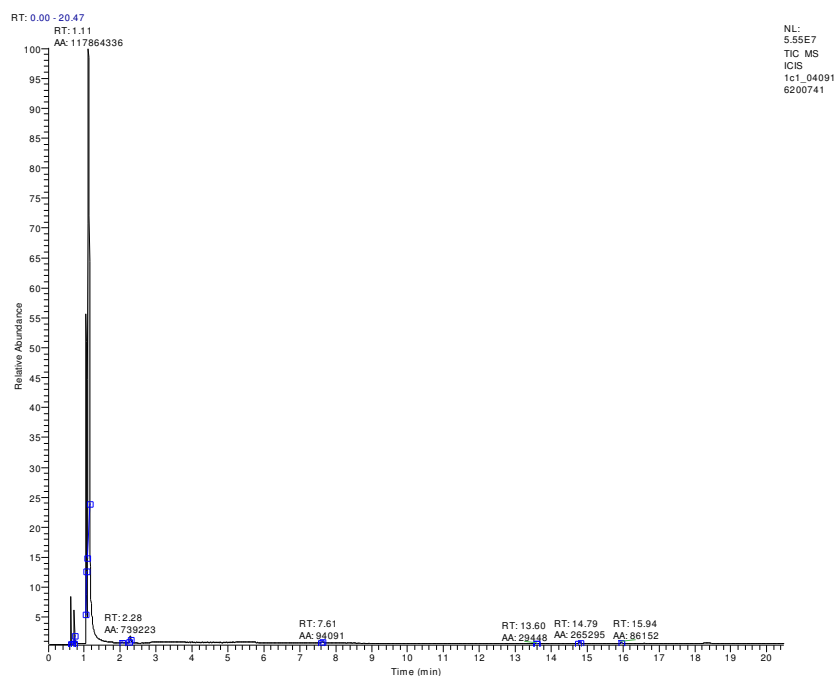


Figure 1. Total ion chromatogram (TIC) of volatile components in HTPE copolymer, experiment 1

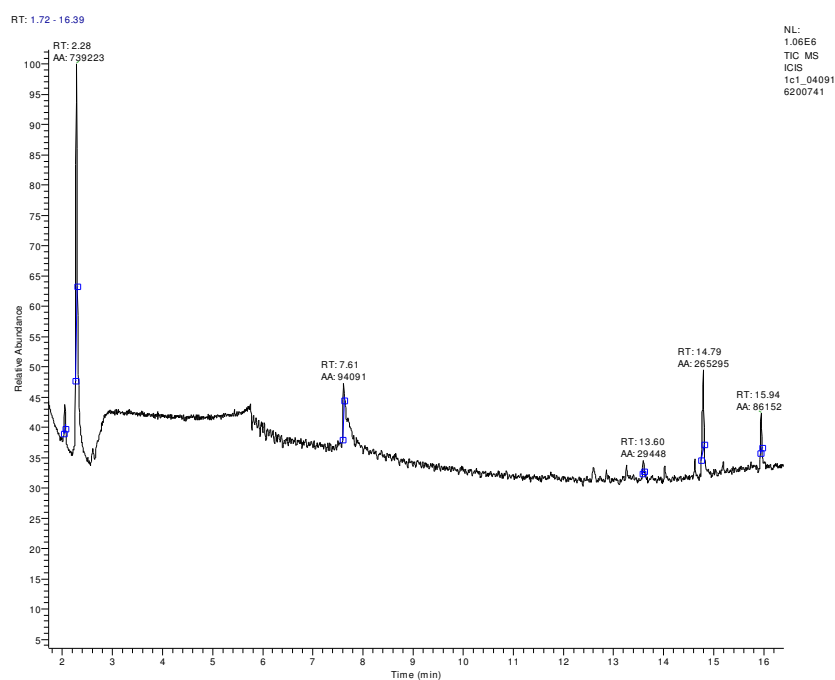


Figure 2. Total ion chromatogram (retention time > 1 min) of volatile components in HTPE copolymer, experiment 1.

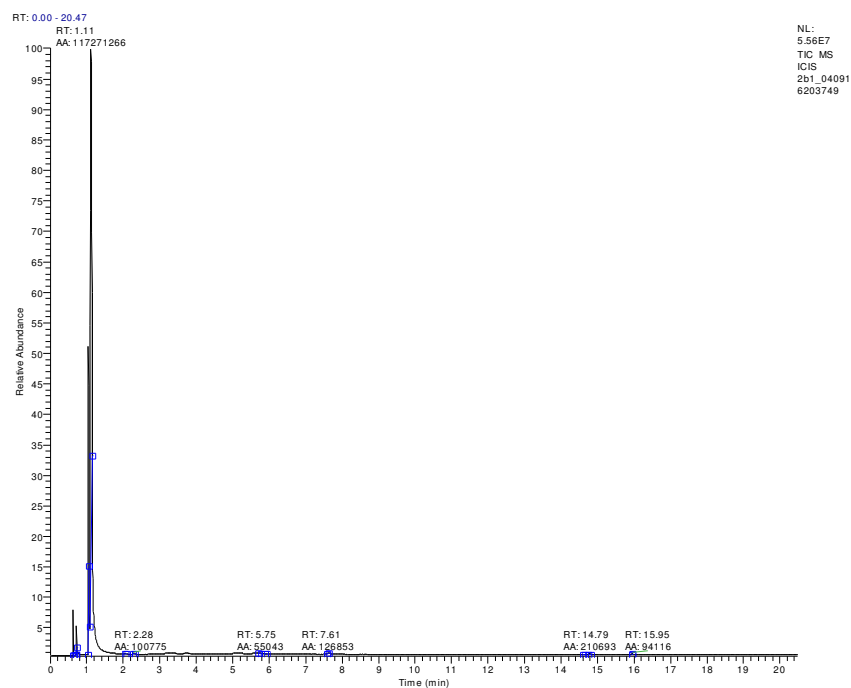


Figure 3. Total ion chromatogram (TIC) of volatile components in HTPC copolymer, experiment 2.

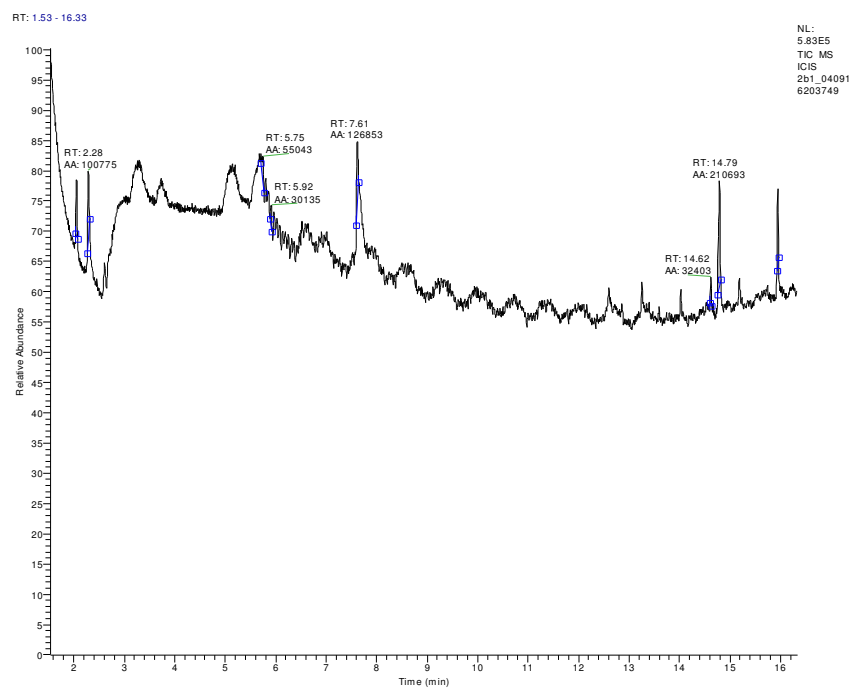


Figure 4. Total ion chromatogram (retention time > 1 min) of volatile components in HTPC copolymer, experiment 2.

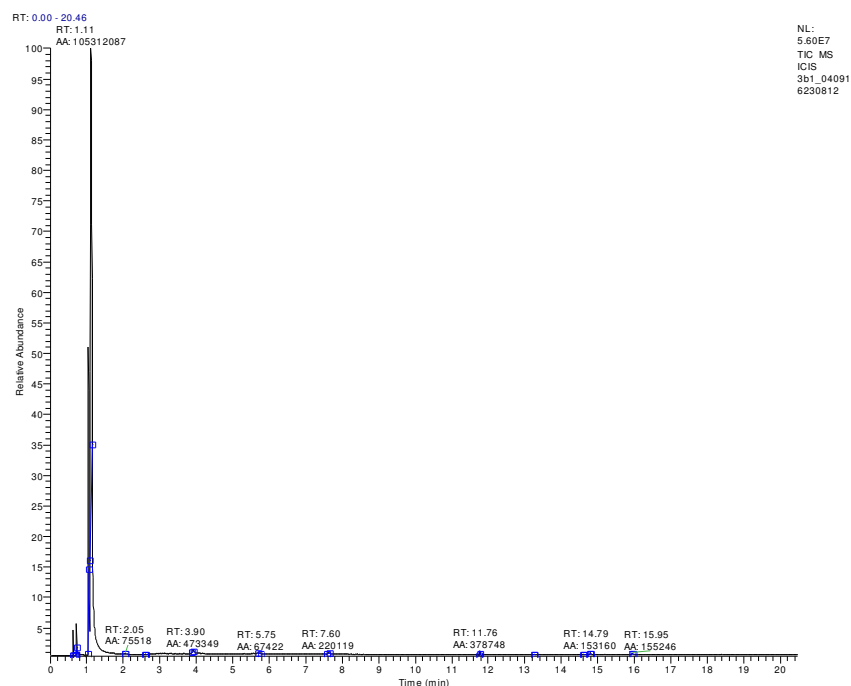


Figure 5. Total ion chromatogram (TIC) of volatile components in HTPC copolymer, experiment 3B1.

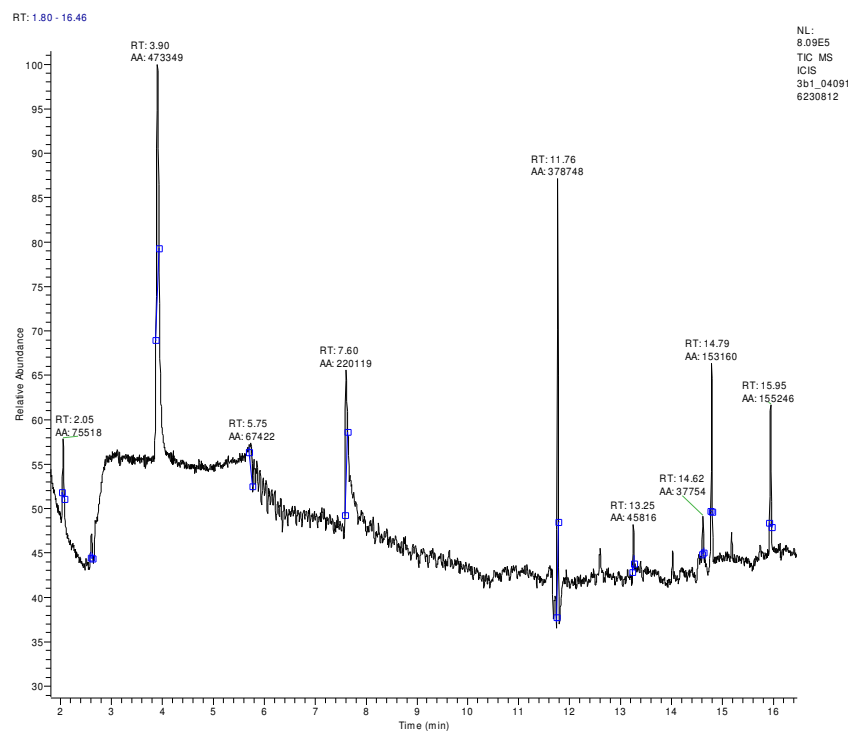


Figure 6. Total ion chromatogram (retention time > 1 min) of volatile components in HTPC copolymer, experiment 3B1.

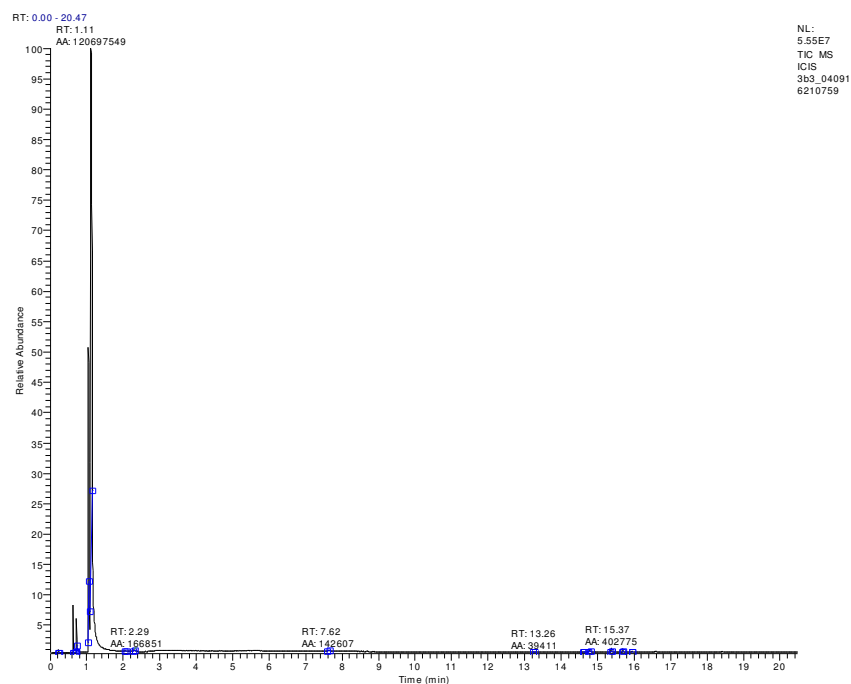


Figure 7. Total ion chromatogram (TIC) of volatile components in HTPC copolymer, experiment 3

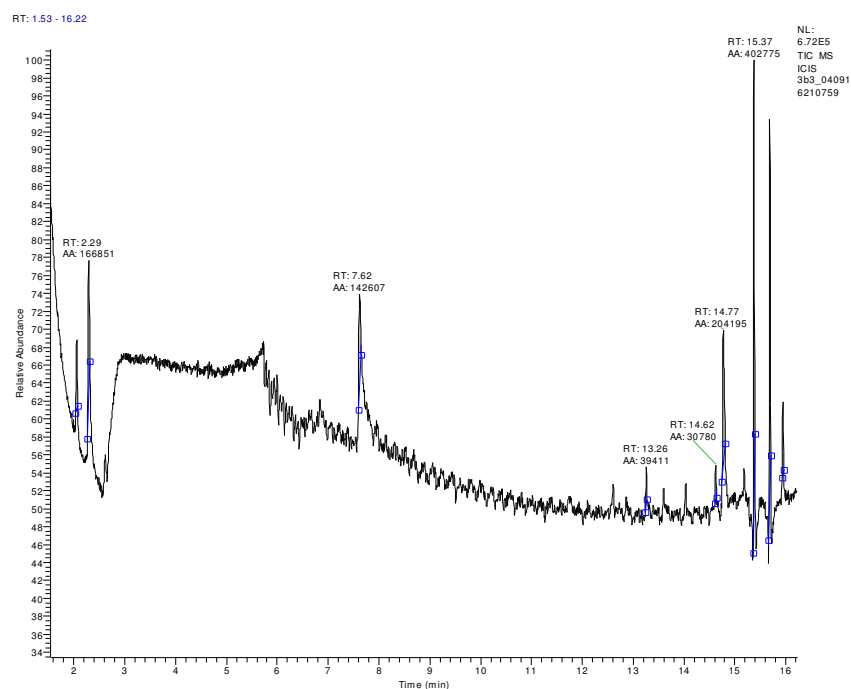


Figure 8. Total ion chromatogram (retention time > 1 min) of volatile components in HTPC copolymer, experiment 3.

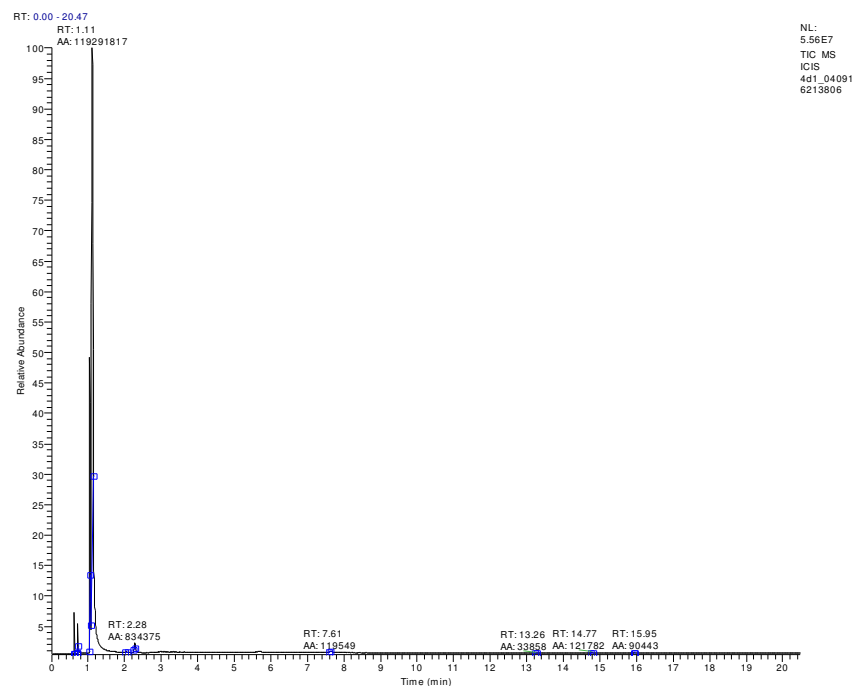


Figure 9. Total ion chromatogram (TIC) of volatile components in HTPE copolymer, experiment 4

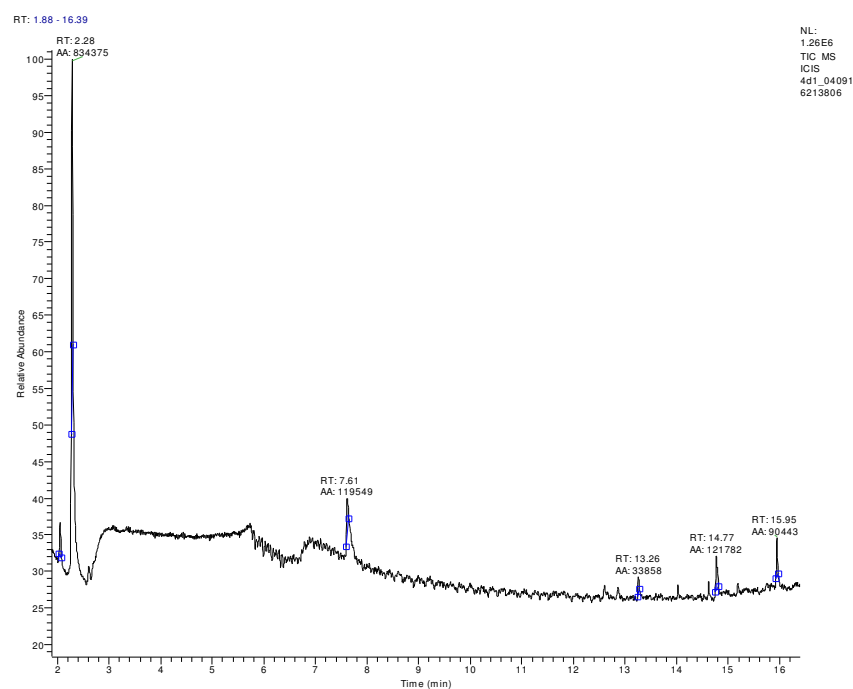


Figure 10. Total ion chromatogram (retention time > 1 min) of volatile components in HTPE copolymer, experiment 4.

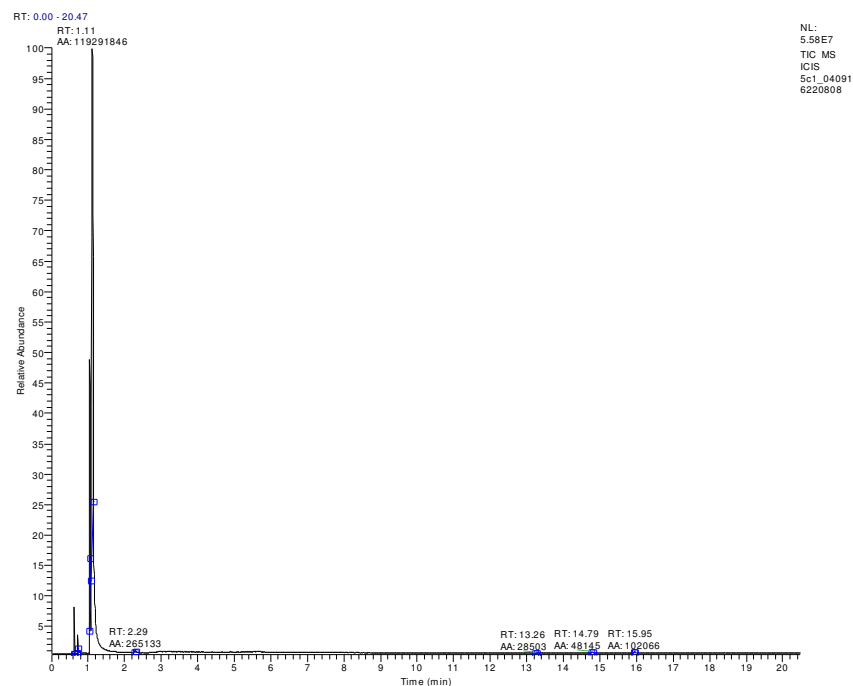


Figure 11. Total ion chromatogram (TIC) of volatile components in HTPE copolymer, experiment 5.

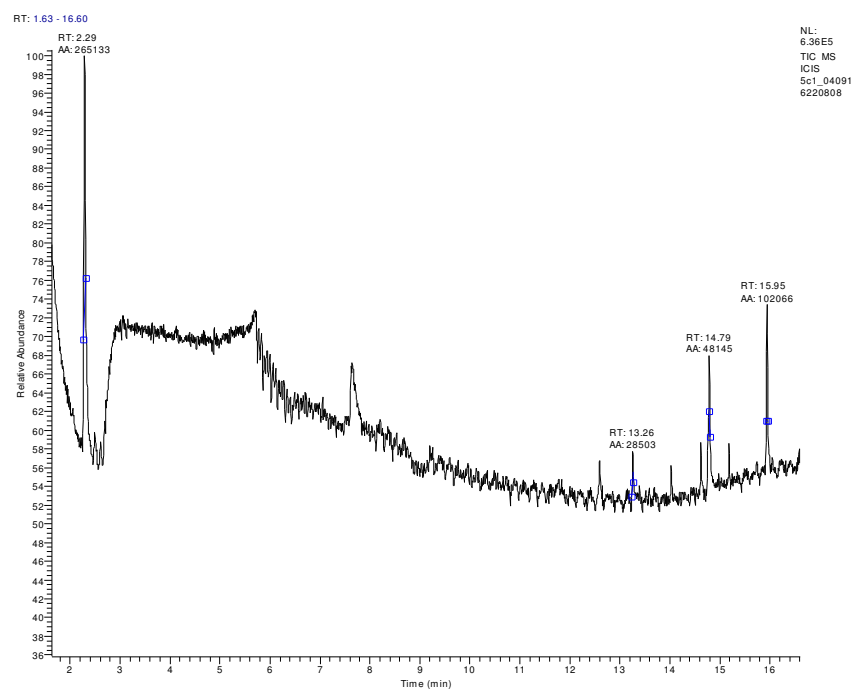


Figure 12. Total ion chromatogram (retention time > 1 min) of volatile components in HTPE copolymer, experiment 5.

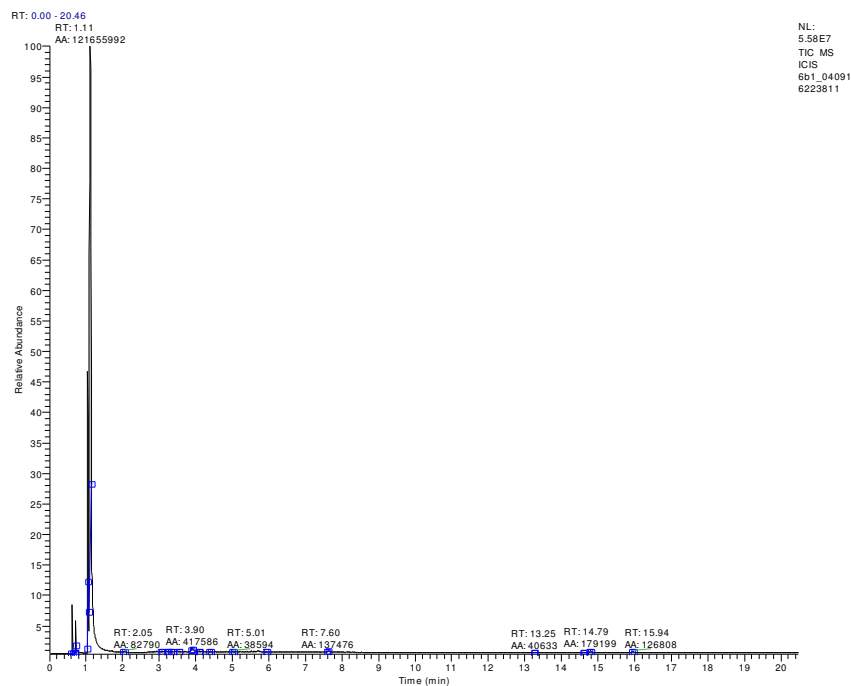


Figure 13. Total ion chromatogram (TIC) of volatile components in HTPE copolymer, experiment 6.

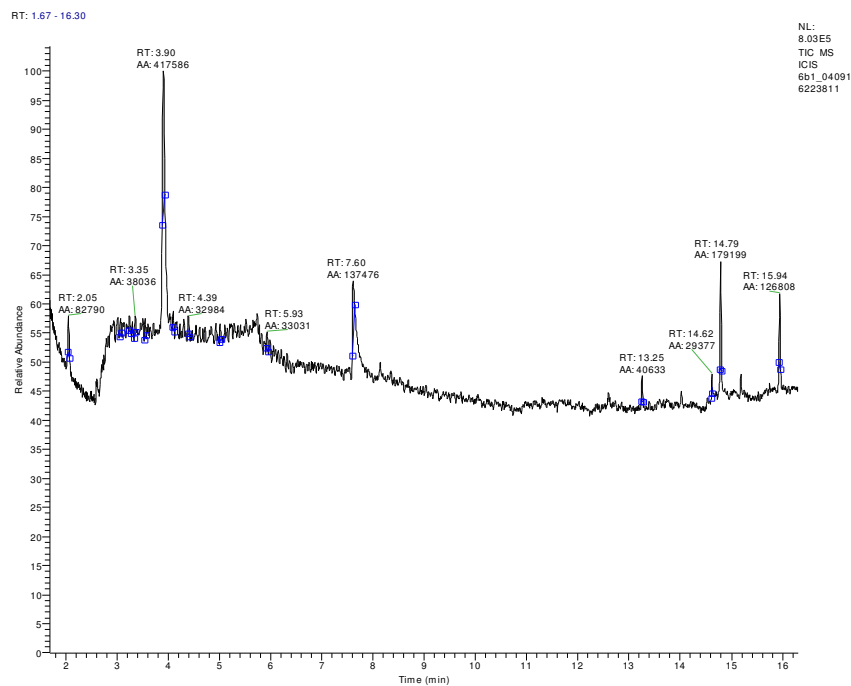


Figure 14. Total ion chromatogram (retention time > 1 min) of volatile components in HTPE copolymer, experiment 6.

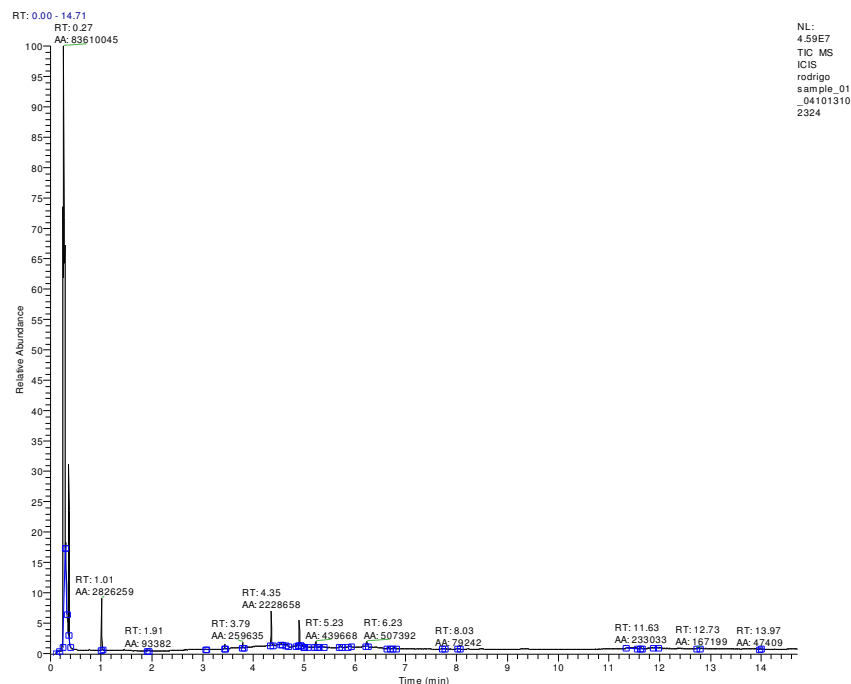


Figure 15. Total ion chromatogram (TIC) of volatile components in HTPC copolymer, experiment 7.

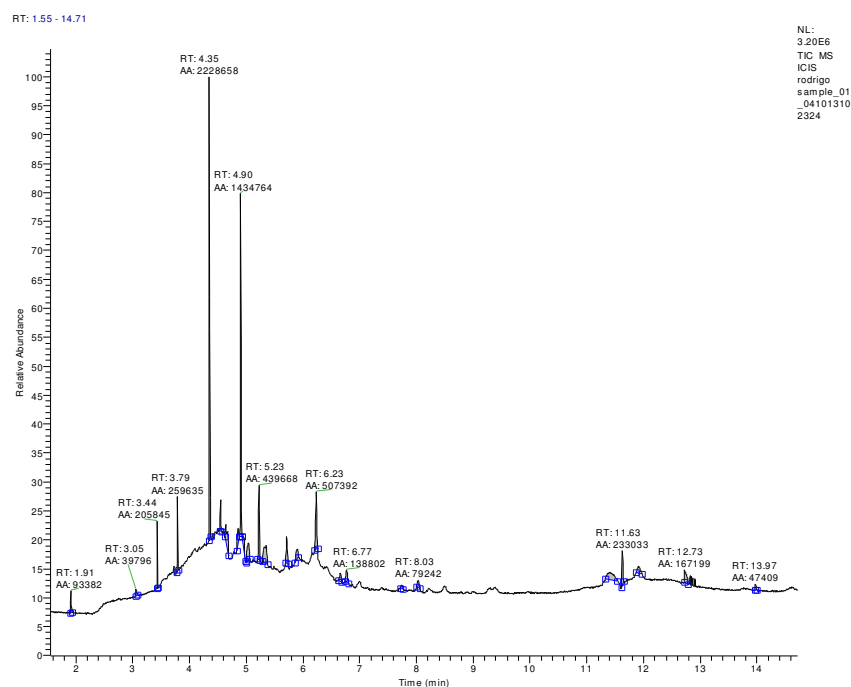


Figure 16. Total ion chromatogram (retention time > 1 min) of volatile components in HTPC copolymer, experiment 7.

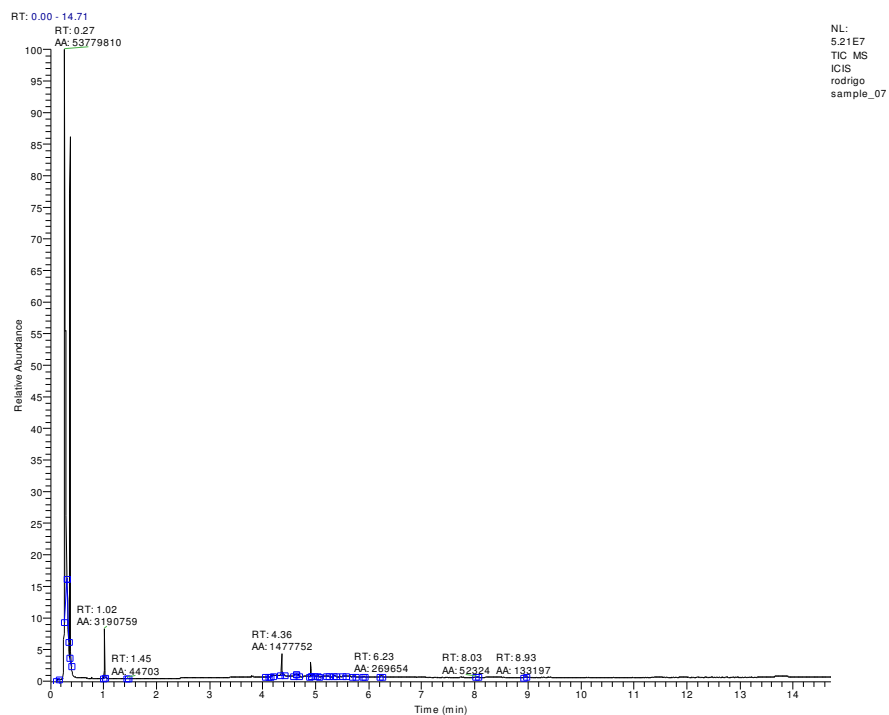


Figure 17. Total ion chromatogram (TIC) of volatile components in HTPC copolymer, experiment 8B1A.

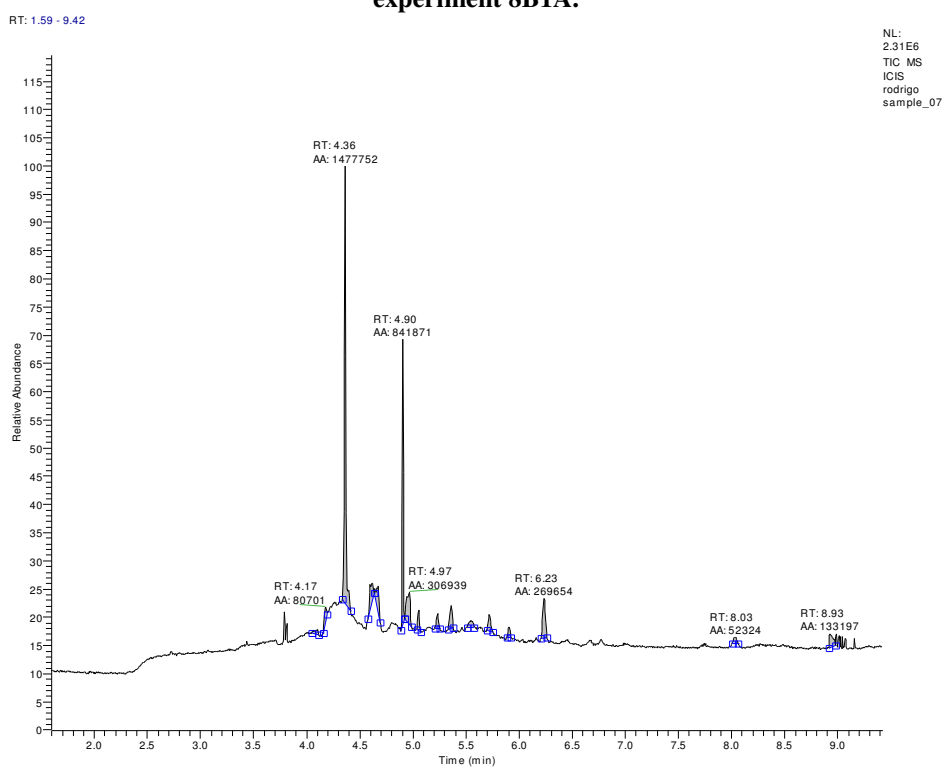


Figure 18. Total ion chromatogram (retention time > 1 min) of volatile components in HTPC copolymer, experiment 8B1A.

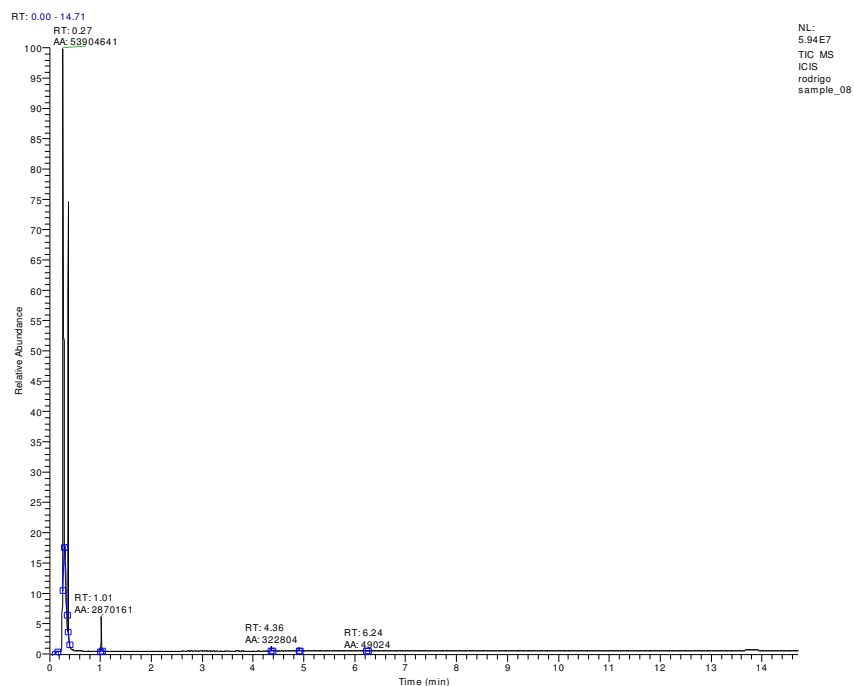


Figure 19. Total ion chromatogram (TIC) of volatile components in HTPE copolymer, experiment 8B2A.

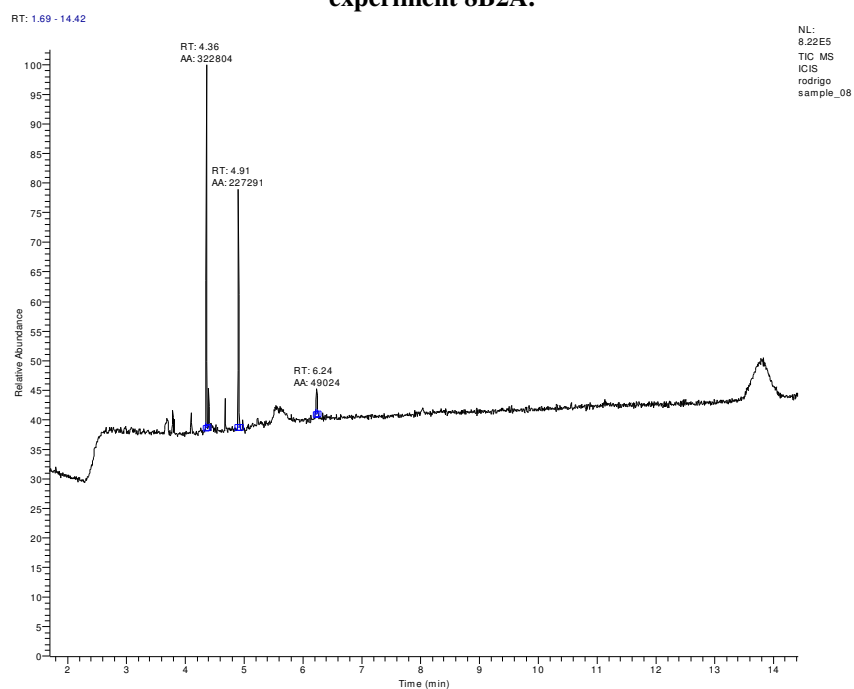


Figure 20. Total ion chromatogram (retention time > 1 min) of volatile components in HTPE copolymer, experiment 8B2A.

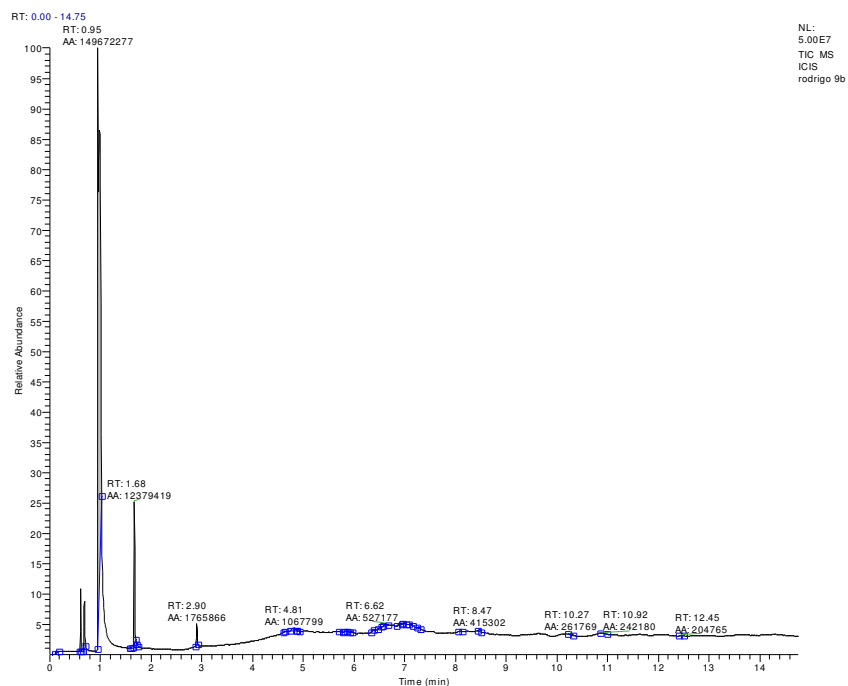


Figure 21. Total ion chromatogram (TIC) of volatile components in HTPC copolymer, experiment 9.

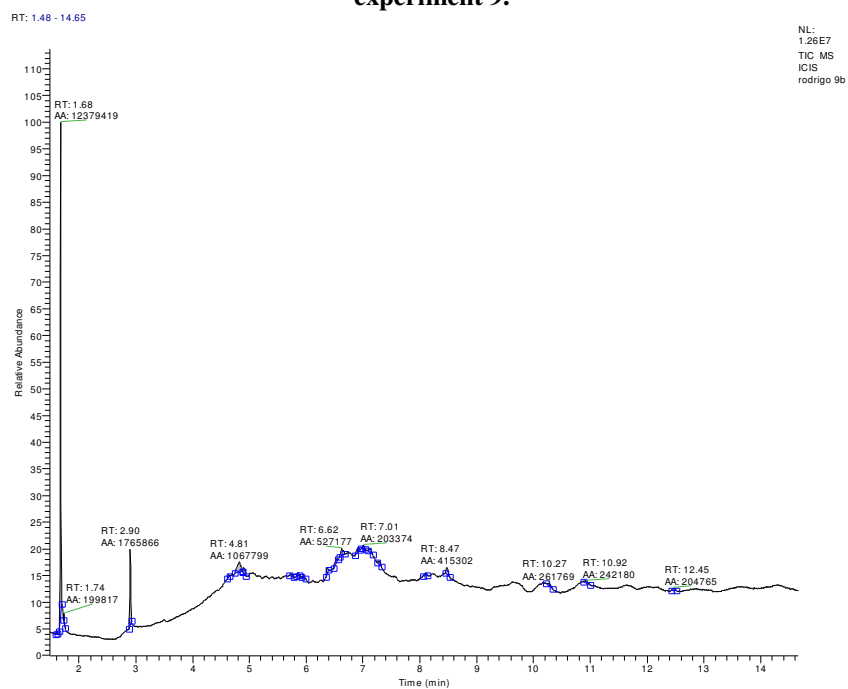


Figure 22. Total ion chromatogram (retention time > 1 min) of volatile components in HTPC copolymer, experiment 9.

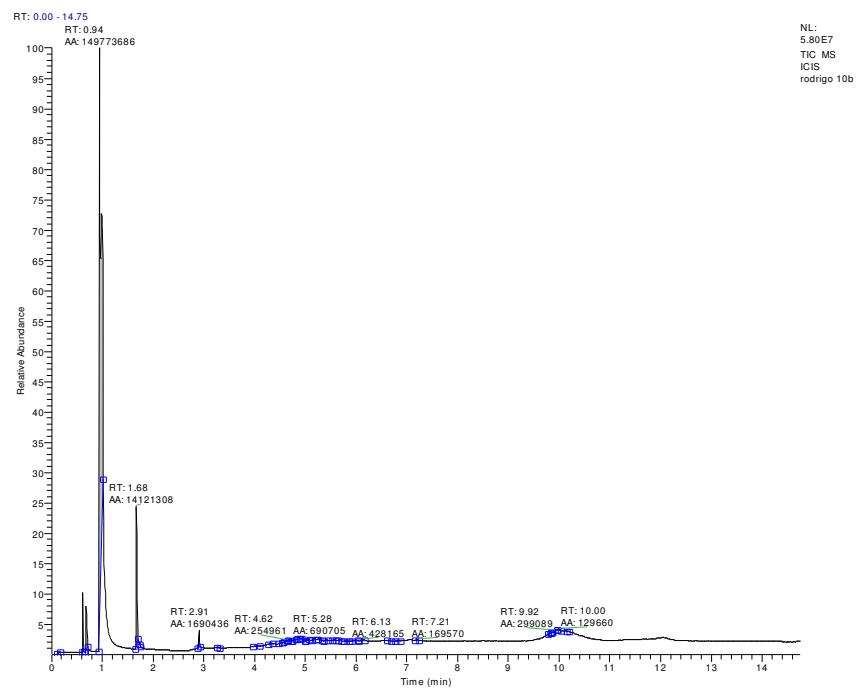


Figure 23. Total ion chromatogram (TIC) of volatile components in HTPE copolymer, experiment 10.

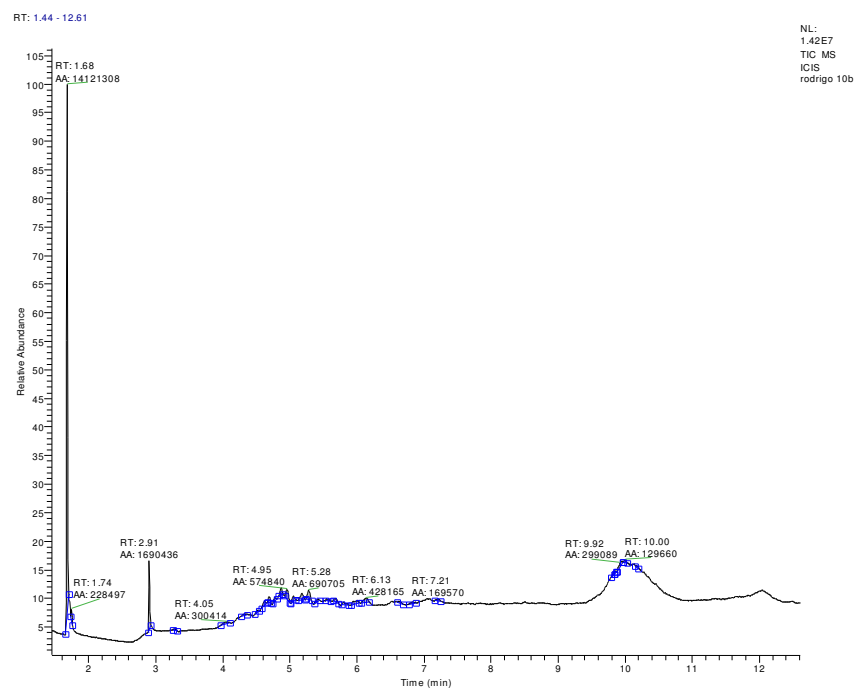


Figure 24. Total ion chromatogram (retention time > 1 min) of volatile components in HTPE copolymer, experiment 10.

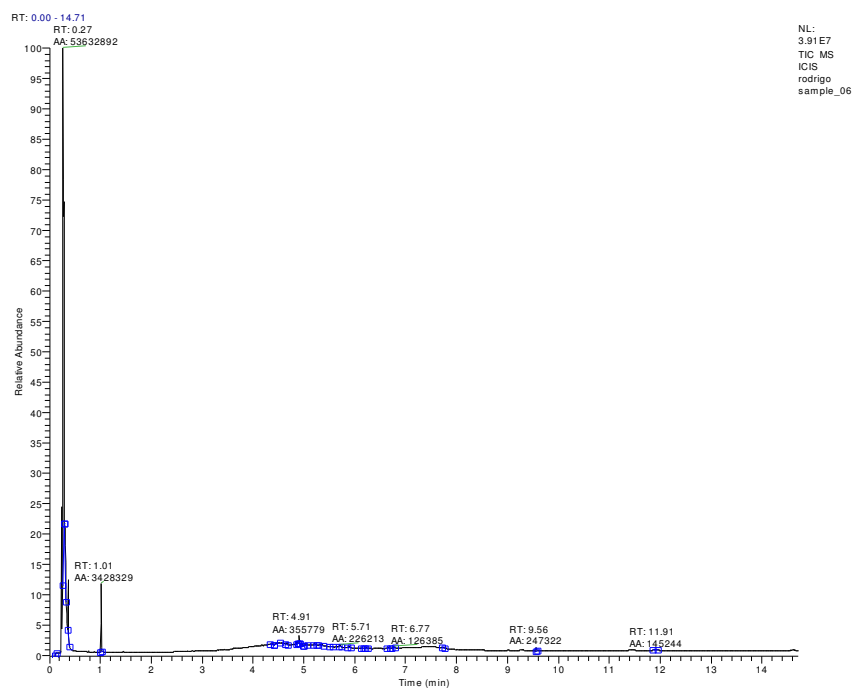


Figure 25. Total ion chromatogram (TIC) of volatile components in Aldrich THF-EO copolymer

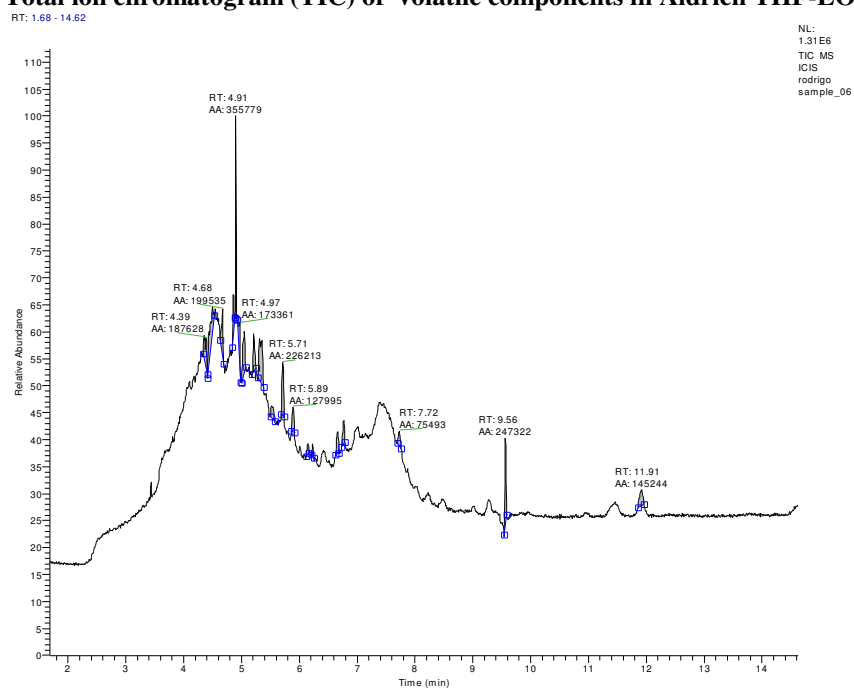


Figure 26. Total ion chromatogram (retention time > 1 min) of volatile components in Aldrich THF-EO copolymer.

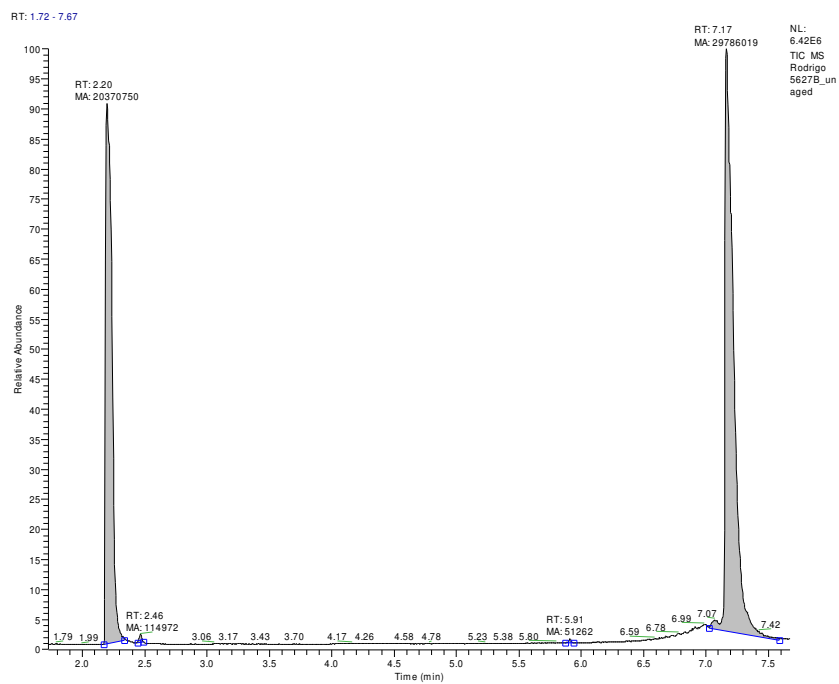


Figure 27. TIC of volatile components in gumstock 5G27B not aged

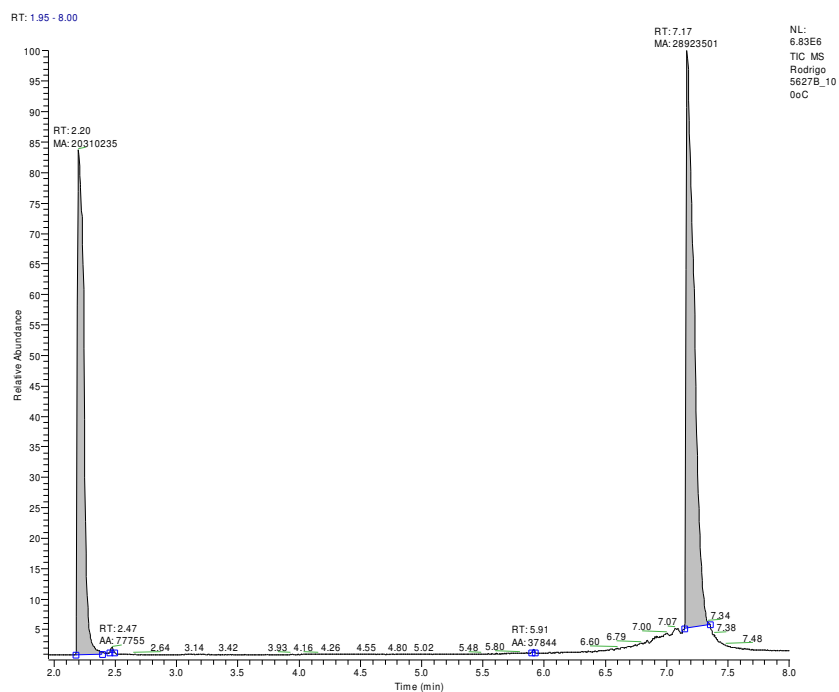


Figure 28. TIC of volatile components in gumstock 5G27B aged at 100°C for 60 min

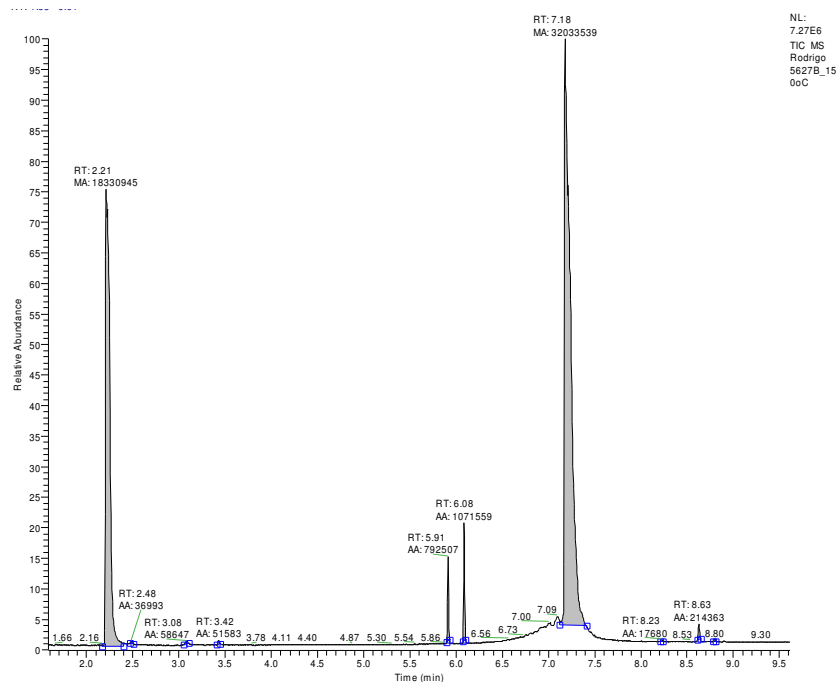


Figure 29. TIC of volatile components in gumstock 5G27B aged at 150°C for 60 min

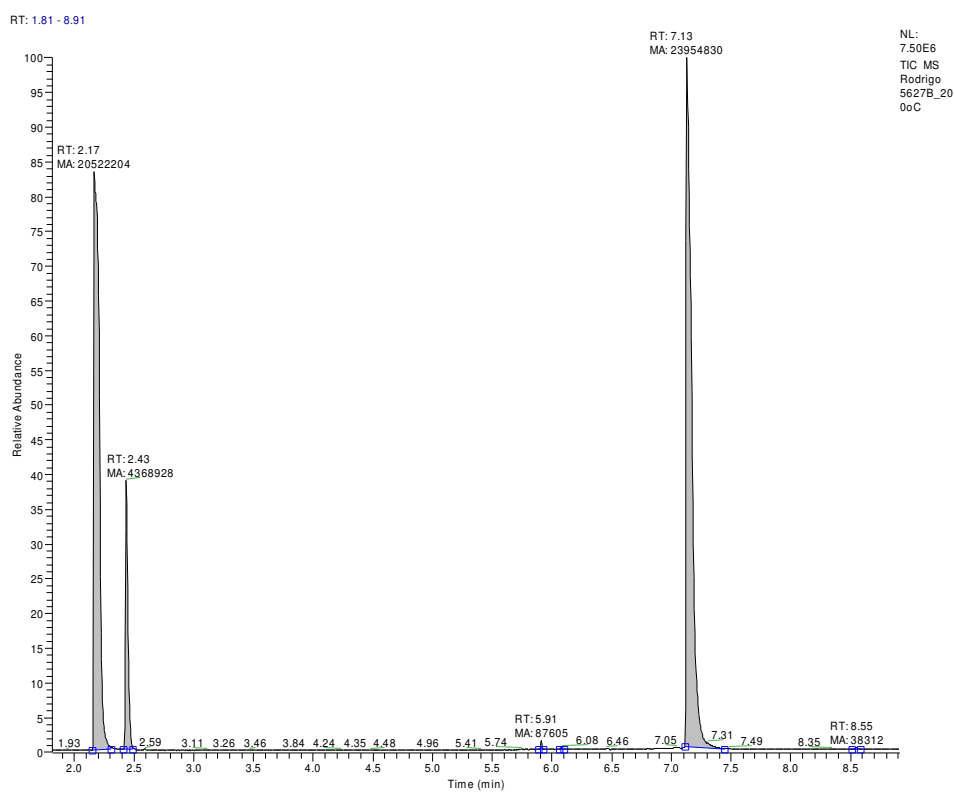


Figure 30. TIC of volatile components in gumstock 5G27B aged at 200°C for 60 min

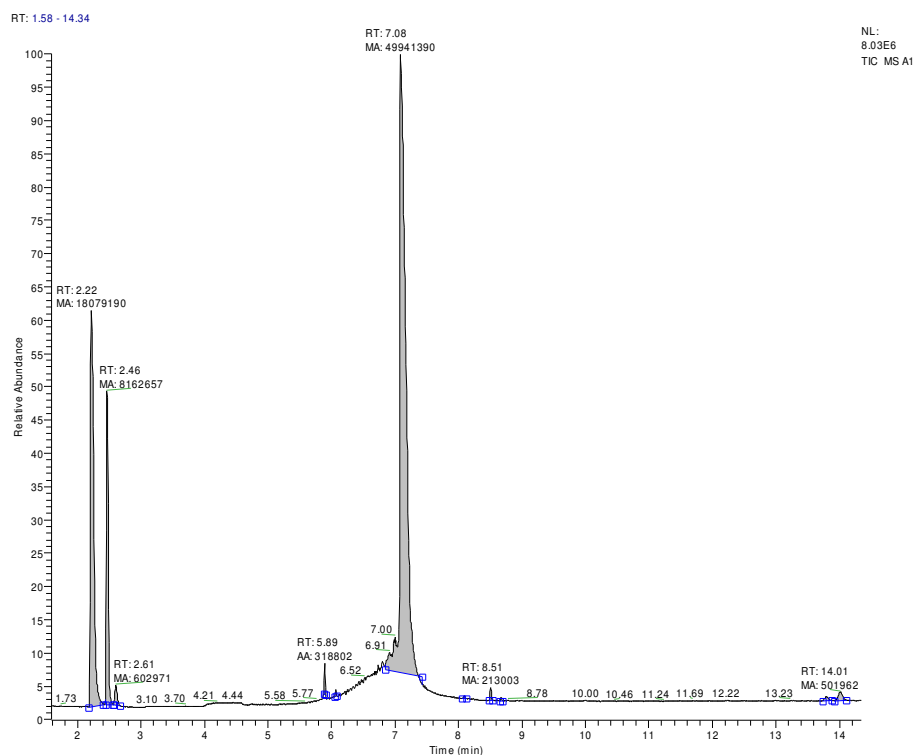


Figure 31. TIC of volatile components in n-BuNENA aged at 100°C for 30 min

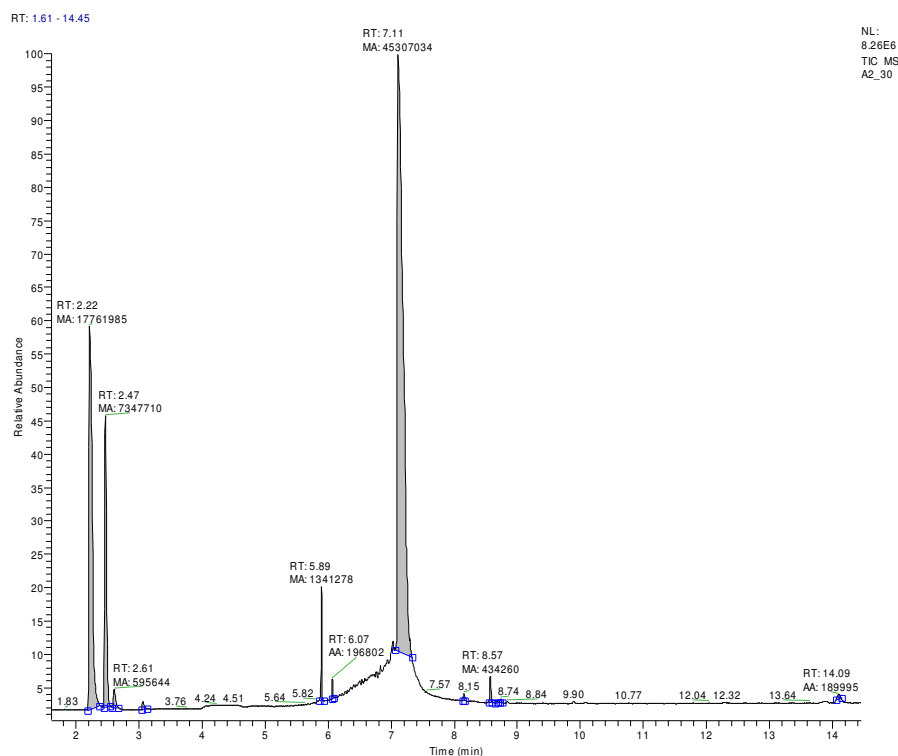


Figure 32. TIC of volatile components in n-BuNENA aged at 150°C for 30 min

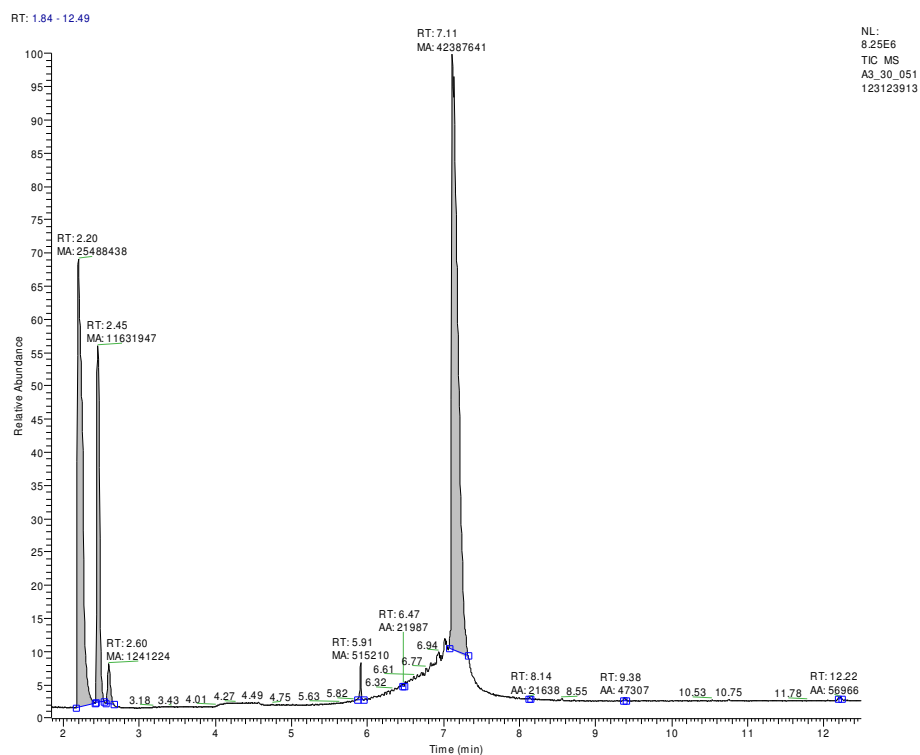


Figure 33. TIC of volatile components in n-BuNENA aged at 200°C for 30 min

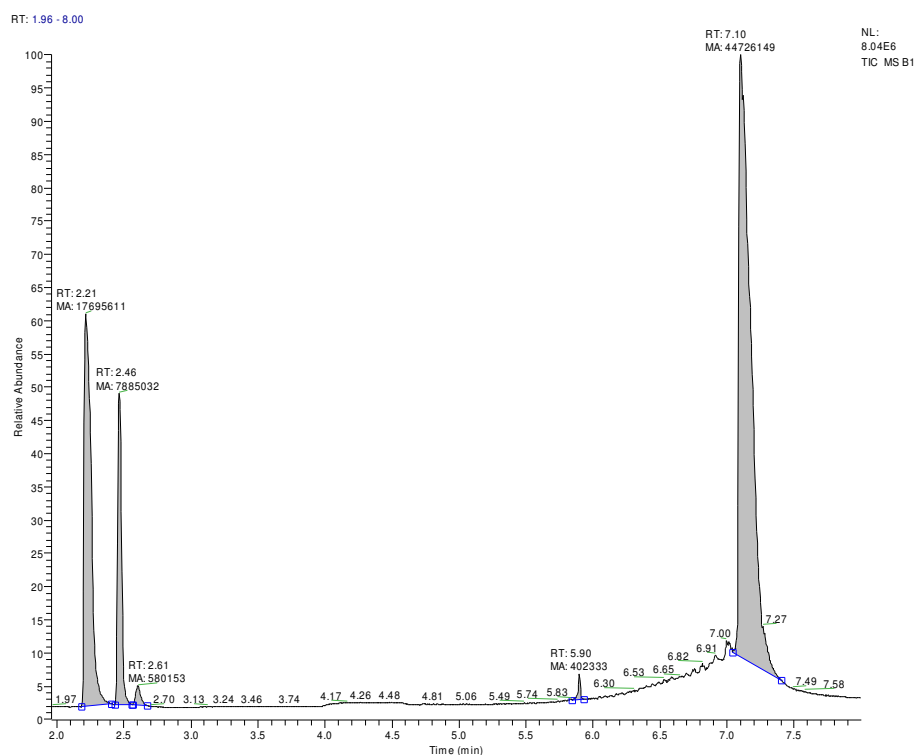


Figure 34. TIC of volatile components in pre-polymer HTPE 27B aged at 100°C for 30 min

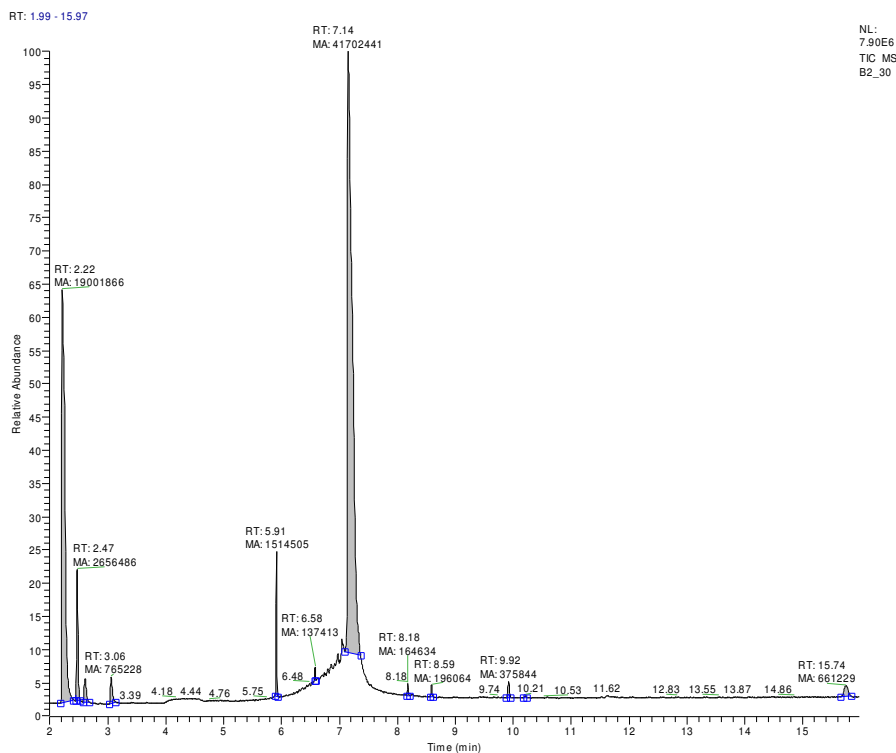


Figure 35. TIC of volatile components in pre-polymer HTPE 27B aged at 150°C for 30 min

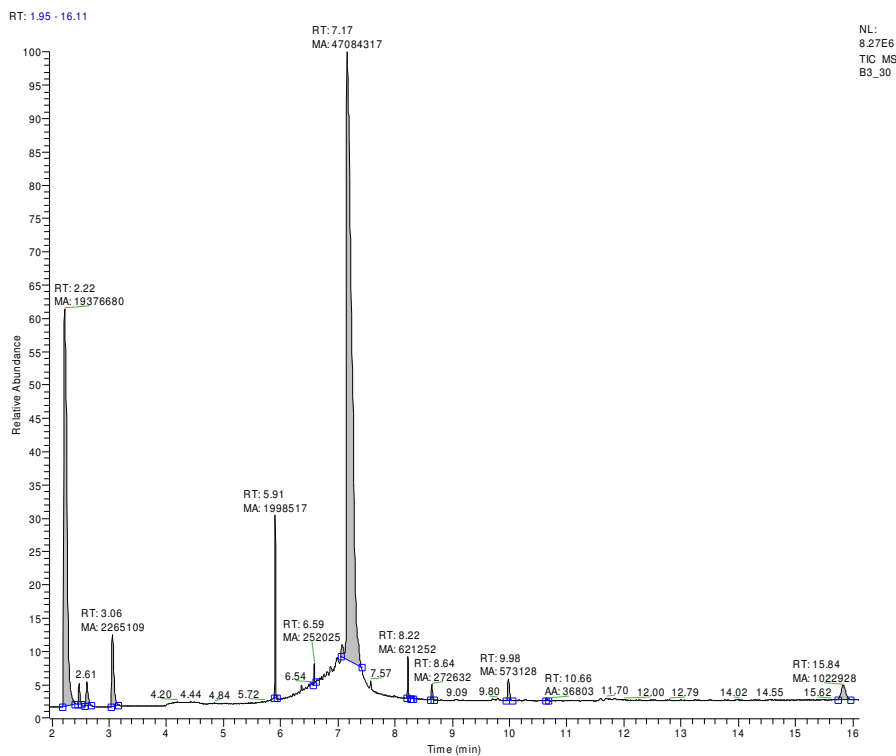


Figure 36. TIC of volatile components in pre-polymer HTPE 27B aged at 200°C for 30 min

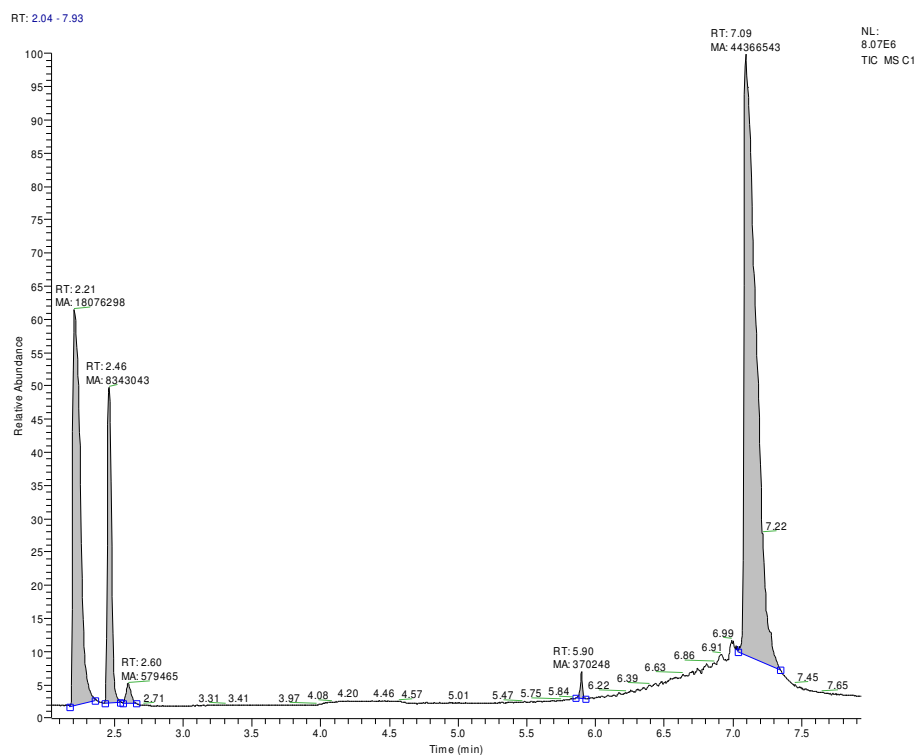


Figure 37. TIC of volatile components in binder network 16N27B aged at 100°C for 30 min

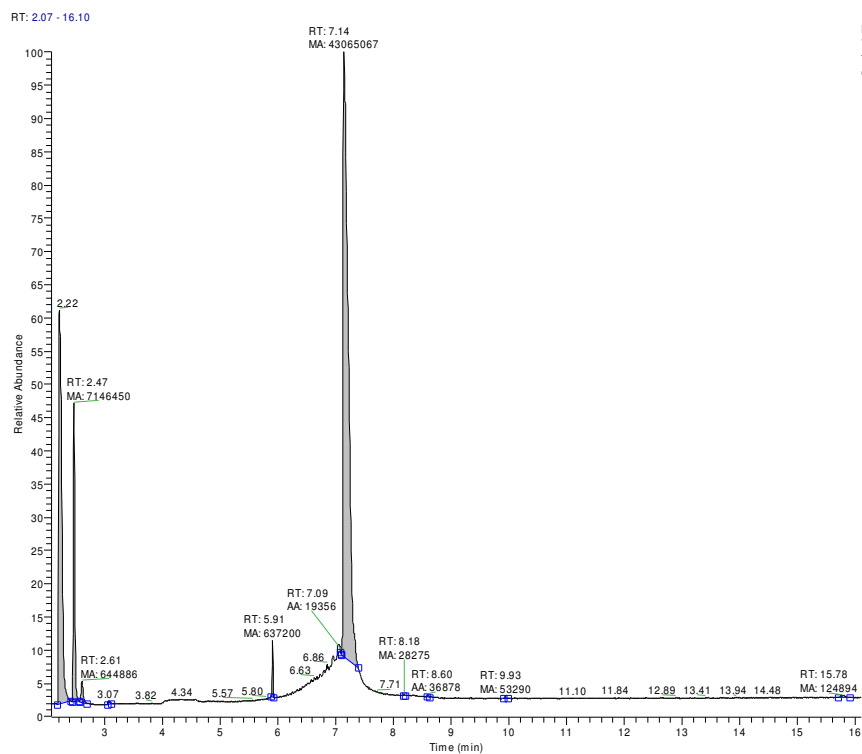


Figure 38. TIC of volatile components in binder network 16N27B aged at 150°C for 30 min

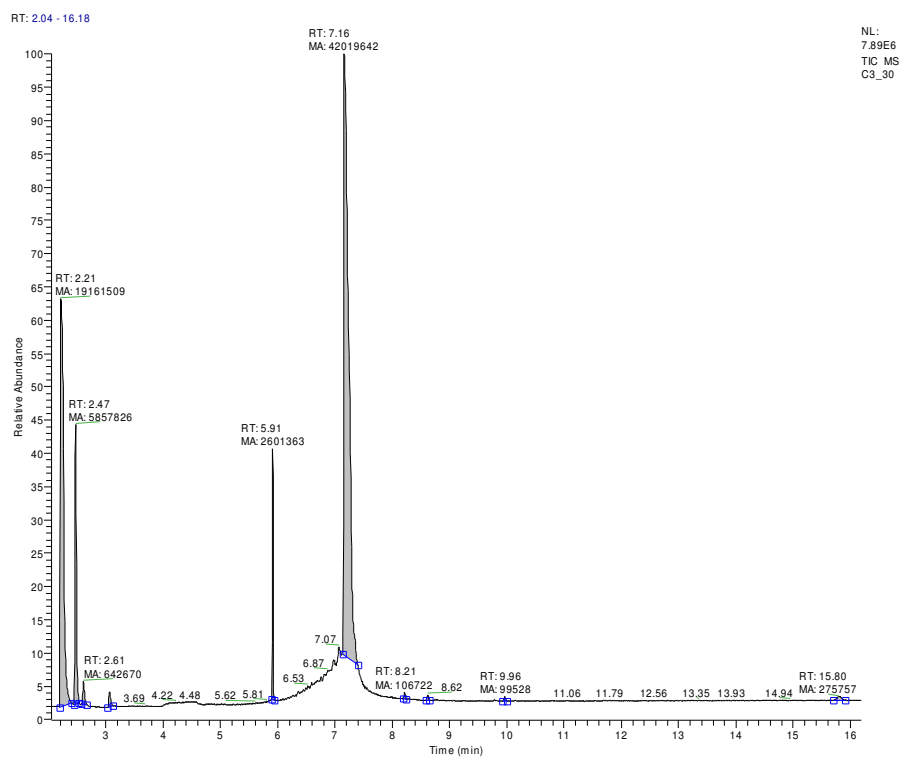


Figure 39. TIC of volatile components in binder network 16N27B aged at 200°C for 30 min

APPENDIX H

n-BuNENA

SYNTHESIS AND CHARACTERISATION

1.1 Introduction

As stated in Chapter I, n-butyl-2-nitratoethylnitramine (n-BuNENA), an energetic plasticizer, is part of the HTPE propellant formulation. Because it was not possible to obtain samples commercially the compound was synthesized in the Department of Environmental and Ordnance Systems, DCMT by Dr Alistair MacCuish. The resulting product was characterised by FTIR, NMR, DSC, HPLC and density analysis. Figure 1 shows the n-BuNENA molecular structure.

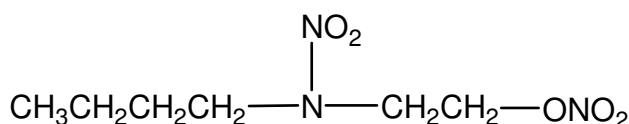


Figure 1. n-Butyl-2-nitratoethyl-nitramine

1.2 Synthesis of n-BuNENA

A sample of n-BuNENA was synthesized by modifying the experimental procedure described by Zhen [1996] and by Kala [2004], as described below. Table 1 shows the reagents used for the n-BuNENA synthesis.

Table 1. Reagents Used in n-BuNENA Synthesis

Reagent name	supplier	Amount
Nitric acid	Aldrich	40 cm ³
2-(butylamino)ethanol	Aldrich	46.8g
Acetic anhydride	Aldrich	96 cm ³
Zinc chloride	Aldrich	1.0g
Sodium carbonate	Aldrich	2.0g
Chloroform	Aldrich	25 cm ³
Sodium sulphate	Aldrich	54g

99.5% Nitric acid (40 cm³) was placed in a 250 cm³ 3-necked flask equipped with a condenser, thermometer and dropping funnel with extended delivery tube (terminating below the surface of the nitric acid). The nitric acid was cooled in an ice bath and stirred magnetically during the slow addition of 2-(butylamino)ethanol (46.8 g). The rate of addition was such that the temperature remained below 22°C.

Following completion of the addition, the reaction mixture was stirred at room temperature for a further 25 min. A dropping funnel containing acetic anhydride (96 cm³) and zinc chloride (1.0 g) was fitted to the flask and this solution was added slowly to the reaction mixture whilst the temperature was kept between 25°C and 30°C by means of an ice bath. The solution was stirred for one hour at room temperature after completion of the addition. (Note: the temperature must be monitored very carefully

after removal from the ice bath due to the danger of an exothermic reaction; it must be returned to the ice bath immediately if it shows signs of rising rapidly or rises to a temperature above ambient). The solution was then poured onto 500 cm³ of crushed ice and allowed to stand until most of the ice had melted. A light yellow liquid formed at the bottom; this was collected by pipette and transferred to a separating funnel where it was washed with water, sodium carbonate solution and then water again. It was diluted with chloroform (approx 25 cm³) and then dried over sodium sulphate. Filtration and evaporation of the solvent gave a yellowish liquid (54 g).

1.3 Characterisation of n-BuNENA

After the synthesis, n-BuNENA was characterised by several techniques and the results were compared with the data presented by Rao [2004], Shen [1996], Chakraborty [2004], Sitzmann [2006] and the ICI technical data for n-BuNENA [ICI, RXL 647].

1.3.1 FTIR analysis and results

Fourier Transform Infrared spectroscopy was performed as stated in Chapter 2, Section 2.3.5. Figure 2 shows the infra red spectrum for the n-BuNENA and Table 2 gives a summary of the main peaks.

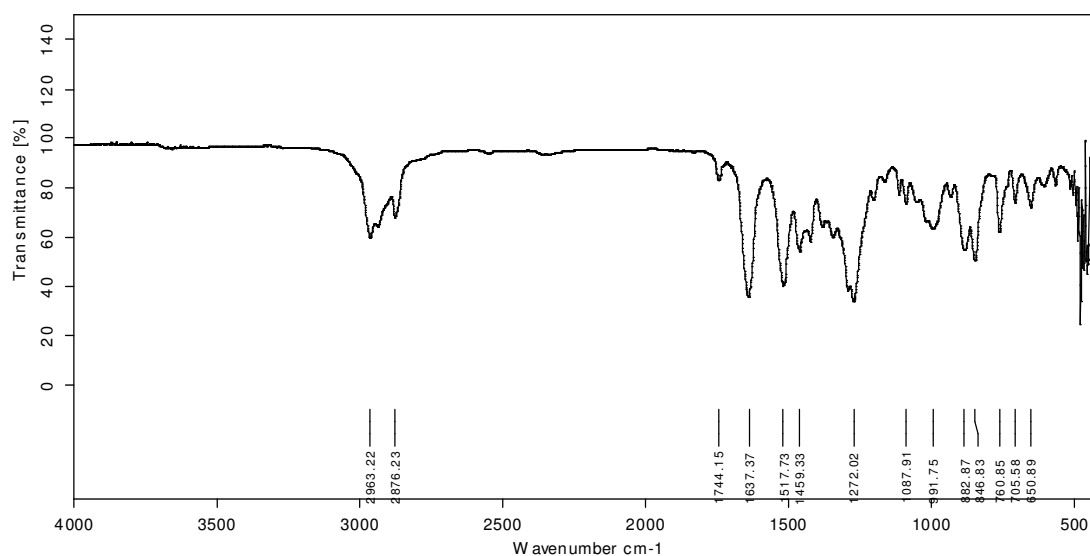


Figure 2. FTIR spectrum of n-BuNENA

Table 2. Main Characteristic Infrared Peaks of n-BuNENA

[Nakanishi, 1964]

Wave Number (cm ⁻¹)	Assignment	
2963	Alkane group	CH ₂ CH ₂
1745	Carbonyl group stretch	C=O
1637	Asymmetric Stretching of nitrates	ONO ₂
1518	Asymmetric Stretching of nitramines	NNO ₂
1272	Symmetric Stretching of nitramines	NNO ₂
882	Nitro group	O-N

1.3.2 NMR analysis and results

In order to validate *n*-BuNENA molecular structure, proton nuclear magnetic resonance spectroscopy was performed as stated in Chapter 2, Section 2.3.3. Deuterated chloroform (CDCl_3) was used as a solvent and tetramethylsilane (TMS) as reference. Figure 3 shows the *n*-BuNENA ^1H NMR spectrum.

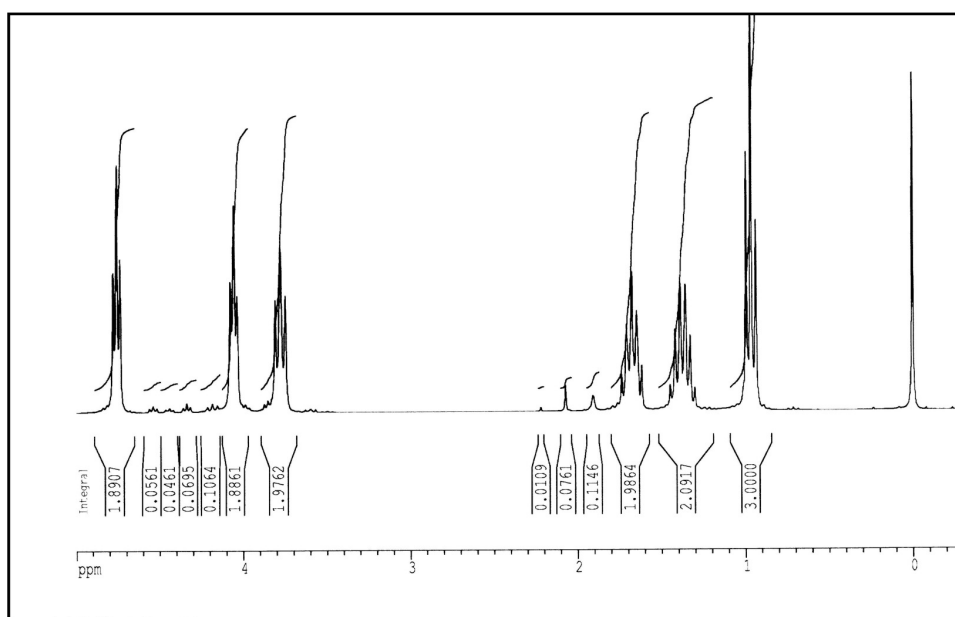


Figure 3. ^1H NMR spectrum of *n*-BuNENA sample 2B

1.3.3 Water content determination in *n*-BuNENA

The quantitative determination of the water content was performed using a 684 Karl Fischer (KF) coulometer. The water content for the different *n*-BuNENA batches is presented in Table 3.

Table 3. Water Content Results for *n*-BuNENA Batches

Batch	Water content, ppm	Water content, %
01/10/2005	42.27	0.0042
17/11/2005	111.0	0.0111

1.3.4 DSC analysis and results

In order to determine the *n*-BuNENA glass transition temperature (T_g), melting point and thermal decomposition, differential scanning calorimetry was performed as described in Chapter 2, Section 2.3.4. Sample weights were around 8 mg. For the T_g determination the samples were heated at a rate of 2°C per min from -100 to $+30^\circ\text{C}$ and for thermal decomposition they were heated at a rate of 10°C per min from 30 to $+300^\circ\text{C}$. A nitrogen atmosphere was maintained during the analyses.

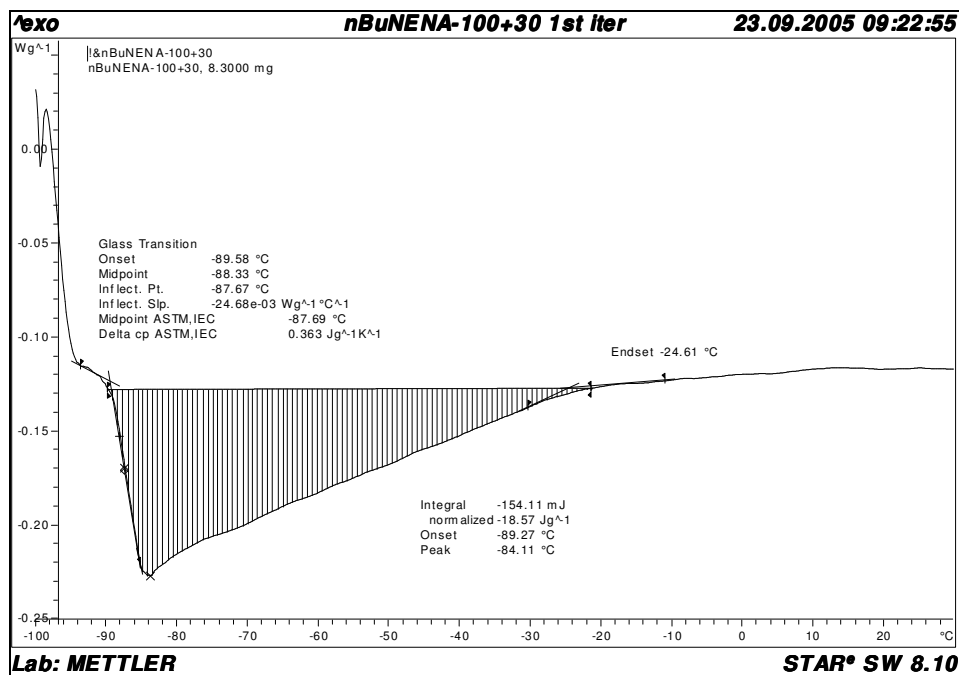


Figure 4. DSC Tg thermogram of n-BuNENA

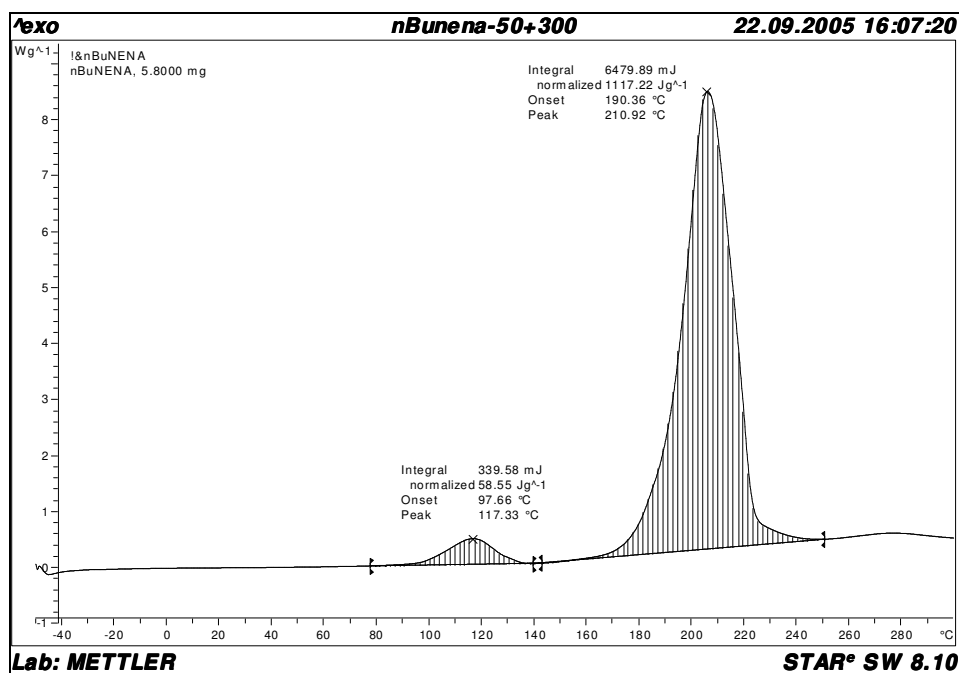


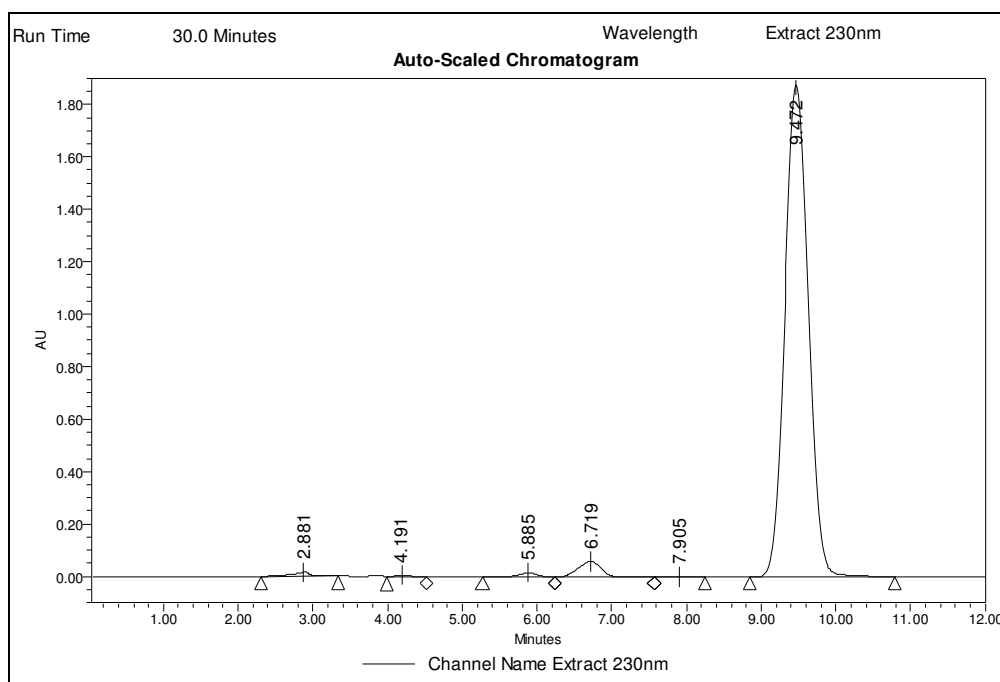
Figure 5. DSC thermogram of n-BuNENA

In Table 4 are presented glass transition temperatures and decomposition peak and heat output results. Figure 4 shows a DSC thermogram for the n-BuNENA obtained in the temperature range -100 to 30°C. The DSC thermal decomposition thermogram in the temperature range 30 to 300°C is shown in Figure 5.

Table 4. Results of DSC and TGA analysis of n-BuNENA

Batch. No	Glass Transition Temperature (°C)	Decomposition temperature (°C)	Heat of Decomposition (J g ⁻¹)
01/10/05	-87.67	210.92	1117
14/02/05	Not measured	211.36	1280
17/02/06	Not measured	212.50	1014

1.3.5 Purity determination by HPLC

**Figure 6. HPLC Chromatogram of a sample of n-BuNENA**

In order to determine the percentage purity of the product, high performance liquid chromatography (HPLC) was performed using a Waters HPLC model 2695 separation module interfaced to a Waters photodiode array detector model 996. The HPLC equipment was controlled via a PC running Empower Pro Window 2000 software from Waters Corporation. An Inertsil column 5 μ m ODS 2-2 of dimensions 250 x 4.6 mm was used. The mobile phase was methanol 60% and water 40%. A small quantity of the sample was diluted in 10 parts of methanol and then placed in a sample vial. The loaded vial was placed in the autoinjector and maintained at 100°C for 2 min before being sampled and an injection made. A characteristic chromatogram of the sample is presented in Figure 6.

1.3.6 Density determination

Density determinations at 25°C were performed using an AccuPyc 1330 Pycnometer for 1 cm³ samples from Micromeritics, as described in Chapter II Section 2.3.7. The density measurements are presented in Table 5.

Table 5. Results of Density Measurements on n-BuNENA

Run	Density (g cm ⁻³)	Density standard deviation (g cm ⁻³)	Sample weight (g)	Volume (cm ³)	Volume standard deviation (cm ³)
1	1.2227	0.0032	0.6300	0.5153	-0.0013
2	1.2206	0.0011	0.6300	0.5161	-0.0005
3	1.2178	-0.0017	0.6300	0.5173	0.0007
4	1.2182	-0.0013	0.6300	0.5172	0.0006
5	1.2182	-0.0013	0.6300	0.5172	0.0005
Average	1.2195	0.0021	0.6300	0.5166	0.0009

1.4 Discussion of Results

The IR spectrum presented in Figure 2, together with data from Table 2, show a band at 1637 cm⁻¹, which is assigned to a nitrate group. Bands at 1518 and 1272 cm⁻¹ are assigned to nitramine groups and the band at 882 cm⁻¹ is assigned to a nitro group. These bands are in good agreement with those in the infra red spectra presented by Shen [1996] and Rao [2004] and with the information presented by Sitzmann [2006], indicating that the spectrum corresponds to that of *n*-butyl-2-nitratoethylnitramine (*n*-BuNENA). A small band at 1744 cm⁻¹ was also present in the sample prepared by Shen [1996] and was assigned to an ester carbonyl group within a by-product that Sitzmann [2006] later identified as *n*-Butyl-N-Nitroethanolamine acetate. The peak at 650 cm⁻¹ possibly corresponds to contamination by chloroform, from the final extraction process.

The ¹H NMR spectrum obtained from the product and presented in Figure 3 was compared against the spectra presented by Rao [2004] and Sitzmann [2006]. From the comparison it was established that the product obtained corresponds to *n*-butyl-2-nitratoethylnitramine (*n*-BuNENA). As stated by Rao [2004], from Figure 3 the triplets at 0.96 ppm can be assigned to methyl protons. The methylene protons attached to O-NO₂ and N-CH₂ appear as triplets in the region 3.8 to 4.77 ppm. The sextet and pentate at 1.4 and 1.7 ppm are assigned to the two methylene protons attached to the methyl group.

The glass transition temperature of *n*-BuNENA was found to be at -88°C and the thermal decomposition (exothermic) peak was found at 211°C, which is in agreement with the information presented by Chakraborty [2004]. Another small exothermic peak was found at 117 °C. It is believed that this peak is part of an impurity, possibly *n*-Butyl-N-Nitroethanolamine acetate as suggested by Sitzmann [2006]. In the FTIR spectrum the peak at 1745 cm⁻¹ can be assigned to a carbonyl C=O group.

The purity of the product was obtained from HPLC analysis and was found to be around 95% (main peak at retention time 9.47 min), as can be seen from Figure 6. The purity is similar to that reported by Chakraborty [2004] 94 to 96%, slightly higher than that of Sitzmann [2006], 93%, and lower than that reported by Shen [1996], 98%, and Rao, > 99%. The main impurity is present at retention time 6.7 min and amounts to around 3%. Possibly it is related to the exothermic peak in the DSC thermogram at 117 °C. A comprehensive study of *n*-BuNENA and the by-products identified in its synthesis was

presented by Sitzmann [2006]. Density was determined as 1.21 g cm^{-3} , which agrees with the information presented by Chakraborty [2004].

1.5 Conclusions

A sample of n-butyl-2-nitratoethylnitramine, (n-BuNENA), was synthesized and characterized. The characterization shows that the measured properties of the product are in agreement with those reported in the literature and that the product was the same as the material used as the energetic plasticizer in the HTPE propellant manufacture.

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ICI Explosives (RXL, 647), Technical Data, Butyl NENA, PB NO.211.

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