

Linear Low Density Polyoxymethylene versus Linear Low Density Polyethylene

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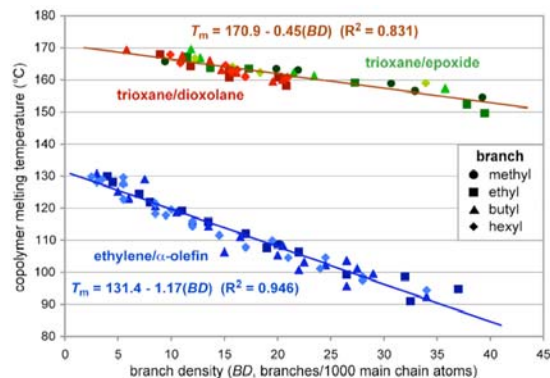
College Station, Texas 77843-3255

Supporting Information

Supporting Information Available: Full synthetic details and copolymer characterization data.

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General Considerations. Boron trifluoride diethyl etherate ($\text{BF}_3\cdot\text{OEt}_2$) and 1,3,5-trioxane were used as received. 1,2-Dichloroethane, cyclohexane, and all epoxides (propylene oxide, 1-butene oxide, 1-hexene oxide, and 1-octene oxide) were purchased and distilled from calcium hydride before use. 4-alkyl-1,3-dioxolanes (4-ethyl-1,3-dioxolane, 4-butyl-1,3-dioxolane, and 4-hexyl-1,3-dioxolane) were synthesized according to literature procedures^{1,2} and distilled from calcium hydride. Dowex 50 was prepared by washing with a 5% HCl solution, followed by continuous washings with water until the effluent was neutral.

Dioxolane Syntheses.

4-Ethyl-1,3-Dioxolane.



In a 200 mL round bottom flask, 30.0 g of 1,2-butane diol (0.33 mol), 9.31 g of paraformaldehyde (0.31 mol), and 5.00 g Dowex 50 were combined. A Dean-Stark condenser was attached and the reaction was heated to 110°C. The reaction was stopped once distillation ceased; about 6 mL of water were collected. The top layer of dioxolane was separated and distilled from calcium hydride. $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ 0.59 (t, $^3J_{\text{HH}} = 3.0$ Hz, 3H, CH_3), 1.09-1.31 (m, 2H, CH_2CH_3), 2.98-3.06 (m, 1H, methine-H), 3.47-3.57 (m, 2H, OCH_2C), 4.43 (s, 1H, OCH_2O), 4.58 (s, 1H, OCH_2O).

4-Butyl-1,3-Dioxolane.



In a 200 mL round bottom flask, 50.0 g of 1,2-hexane diol (0.42 mol), 9.61 g of paraformaldehyde (0.32 mol), and 5.00 g Dowex 50 were combined. A Dean-Stark condenser was attached and the reaction was heated to 120°C. The reaction was stopped once distillation ceased. The top layer of dioxolane was separated and distilled from calcium hydride. $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ 0.69 (t, $^3J_{\text{HH}} = 3.0$ Hz, 3H, CH_3), 1.10-1.42 (m, 6H, $\text{CH}(\text{CH}_2)_3\text{CH}_3$), 3.13-3.20 (m, 1H, methine-H), 3.69-3.72 (m, 2H, OCH_2C), 4.60 (s, 1H, OCH_2O), 4.76 (s, 1H, OCH_2O).

4-Hexyl-1,3-Dioxolane.



In a 200 mL round bottom flask, 50.0 g of 1,2-octane diol (0.34 mol), 9.61 g of paraformaldehyde (0.32 mol), and 5.00 g Dowex 50 were combined. A Dean-Stark condenser was attached and the reaction was heated to 120°C. The reaction was stopped once distillation ceased. The top layer of dioxolane was separated and distilled from calcium hydride. $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ 0.62 (t, $^3J_{\text{HH}} = 3.0$ Hz, 3H, CH_3), 0.98-1.36 (m, 10H, $\text{CH}(\text{CH}_2)_5\text{CH}_3$), 3.03-3.10 (m, 1H, methine-H), 3.58-3.65 (m, 2H, OCH_2C), 4.49 (s, 1H, OCH_2O), 4.65 (s, 1H, OCH_2O).

General Polymerization Procedure. All polymerizations were carried using standard glove box and Schlenk line techniques under a dry nitrogen atmosphere. The epoxide or dioxolane (various feed fractions) was syringed into a solution of trioxane (5.00 g, 55.5 mmol) and 1,2-dichloroethane (5.0 mL) at 42°C under a dry-nitrogen atmosphere, followed by the addition of boron trifluoride diethyl etherate (0.073 g, 0.514 mmol) in cyclohexane (2.5 mL). The polymerization times were adjusted depending on the comonomer feed and corresponding activity. The polymerizations were quenched

with 5% aqueous Na_2CO_3 , washed with copious amounts of water and acetone, and air-dried via suction filtration.

Note that ample evidence suggests that these are indeed copolymers and not blends of POM and other polymers. If the samples were mostly POM homopolymer chains (without incorporated comonomer), then much greater mass loss would be observed via DSC/TGA since such homopolymers would not be stabilized by non-acetal positions along the main chain. Also, the coherent melting point depression observed would be hard to explain if considerable POM homopolymer were present since the melting temperature of such samples would be relatively static and representative of the POM homopolymer itself.

Instrumentation. $^1\text{H NMR}$ spectra of the copolymers were obtained by dissolving ~80 mg of sample in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and employing a Mercury 300 instrument—obtaining a lock with deuterated chloroform at room temperature. The thermal behavior of the copolymers was investigated using a TA Instruments SDT Q600 combination differential scanning calorimeter/thermogravimetric analyzer (DSC/TGA) under an argon atmosphere. The reported melting temperatures were for the cured copolymers and were obtained during the second heating cycle.

NMR Integrations and Assignments. The alkene epoxide mol% incorporation was determined by $^1\text{H NMR}$ according to the following equation:






























$$\text{mol\%} = \frac{I_{\text{CH}_3(\mathbf{b})}/3}{[I_{\text{CH}_2(\mathbf{a})}/6] + [I_{\text{CH}_3(\mathbf{b})}/3]} \times 100$$

The dioxolane mol% incorporation was determined by $^1\text{H NMR}$ according to the following equation:

$$\text{mol\%} = \frac{I_{\text{CH}_3(\mathbf{b})}/3}{\frac{[I_{\text{CH}_2(\mathbf{a})]} - \frac{2}{3}[I_{\text{CH}_3(\mathbf{b})}]}{6} + I_{\text{CH}_3(\mathbf{b})}/3} \times 100$$

The acetal methylene protons (peak **a**) for all copolymers appears as a broad resonance centered near 4.6 or 4.7 ppm. For $n = 0$ (propylene oxide comonomer), peak **b** (the methyl protons) resonates at 0.83-0.84 ppm. For $n = 1$ (butene oxide or ethyldioxolane comonomer), peak **b** resonates at 0.57 to 0.64 ppm. For $n = 3$ (hexene oxide or butyldioxolane comonomer), peak **b** resonates at 0.52 to 0.61 ppm. For $n = 5$ (octene oxide or hexyldioxolane comonomer), peak **b** resonates at 0.50 to 0.55 ppm.

Table 1. Trioxane/Comonomer Copolymerization Results

entry	reference #	comonomer	feed (mol%)	incorp. (mol%) ^a	rel. rate ^b	cure wt. loss (%)	incorp. (mol%) ^c	yield (g)	time (h)	BD ^d	T _m (°C)	density (g/cm ³) ^e
1	ADI II-46	propylene	3.0	4.4	1.48	19.44	5.5	3.23	0.5	9.41	165.8	
2	ADI II-47	oxide	7.4	8.9	1.20	21.65	11.3	4.39	3.0	19.89	163.4	
3	ADI II-58		10.0	8.8	0.88	29.54	12.3	4.79	12.0	21.92	163.0	
4	ADI II-59		15.0	15.8	1.05	6.88	16.9	4.23	24.0	30.67	158.8	
5	ADI II-65		20.0	16.4	0.82	9.32	18.0	4.08	48.0	32.93	156.6	
6	ADI II-66		25.0	17.9	0.72	16.00	21.1	3.55	72.0	39.25	154.6	
7	ADI I-166	1-butene	3.0	4.2	1.40	37.38	6.7	3.89	0.5	11.48	167.1	
8	ADI I-167	oxide	7.4	6.6	0.89	16.34	7.9	4.03	3.0	13.67	163.6	
9	ADI I-168		10.0	8.7	0.87	12.09	9.9	4.22	12.0	17.29	163.5	
10	ADI I-179		15.0	12.8	0.85	15.89	15.1	3.85	24.0	27.28	159.1	
11	ADI I-178		20.0	17.2	0.86	16.17	20.4	2.44	48.0	37.80	152.4	
12	ADI I-169		25.0	17.6	0.70	17.60	21.2	1.31	72.0	39.48	149.6	
13	ADI II-3	1-hexene	3.0	4.7	1.56	33.58	6.9	4.50	0.5	11.84	169.8	
14	ADI II-4	oxide	7.4	6.7	0.90	19.48	7.4	4.46	3.0	12.72	166.9	
15	ADI I-172		10.0	9.5	0.95	21.36	12.1	3.81	12.0	21.50	162.2	
16	ADI I-181		15.0	12.3	0.82	6.05	13.1	3.65	24.0	23.44	161.3	
17	ADI I-182		20.0	14.9	0.74	23.00	19.4	2.25	48.0	35.77	157.6	
18	ADI I-174	1-octene	3.0	4.6	1.54	33.93	7.1	3.38	0.5	12.23	166.7	1.1870
19	ADI I-175	oxide	7.4	6.9	0.94	22.59	9.0	4.19	3.0	15.76	164.1	1.2273
20	ADI I-176		10.0	8.2	0.82	20.95	10.4	4.04	12.0	18.36	162.3	1.2552
21	ADI I-183b		15.0	13.5	0.90	25.50	18.5	2.80	24.0	33.94	159.0	1.1823
22	ADI II-69		20.0	9.7	0.48	15.08	11.5	1.62	48.0	20.30	160.3	1.1500
23	ADI II-53	4-ethyl	3.0	4.4	1.47	16.78	5.3	3.57	0.5	8.95	167.9	
24	ADI II-54	dioxolane	7.4	5.0	0.68	27.90	7.0	3.54	0.5	11.82	164.3	
25	ADI II-55		10.0	7.1	0.71	21.88	9.1	3.69	0.5	15.47	162.9	
26	ADI II-56		15.0	7.4	0.49	18.62	9.1	4.03	0.5	15.45	160.8	
27	ADI II-57		20.0	8.4	0.42	28.24	11.8	5.29	0.5	20.08	160.7	
28	ADI II-61		25.0	10.3	0.41	14.78	12.2	4.59	1.0	20.67	160.2	
29	ADI II-62		30.0	11.2	0.37	8.56	12.3	3.58	1.5	20.84	158.1	
30	ADI II-23	4-butyl	3.0	2.6	0.88	23.66	3.5	5.52	0.5	5.80	169.2	
31	ADI II-24	dioxolane	7.4	4.2	0.57	35.11	6.6	3.72	0.5	11.04	167.7	
32	ADI II-25		10.0	5.3	0.53	32.96	8.1	3.61	0.5	13.62	166.0	
33	ADI II-26		15.0	6.9	0.46	20.28	8.7	5.12	0.5	14.73	163.1	
34	ADI II-28		20.0	8.1	0.41	14.14	9.5	3.25	0.5	16.11	162.3	
35	ADI II-30		25.0	9.1	0.36	23.51	12.0	1.75	1.0	20.46	160.1	
36	ADI II-42		30.0	9.9	0.33	13.33	11.5	1.67	1.5	19.56	159.5	
37	ADI II-34	4-hexyl	3.0	4.4	1.46	24.95	5.9	3.80	0.5	9.91	167.9	1.2235
38	ADI II-35	dioxolane	7.4	4.9	0.66	43.43	8.9	5.78	0.5	15.11	164.6	1.2169
39	ADI II-36		10.0	5.6	0.56	12.27	6.4	3.53	0.5	10.85	165.3	1.2359
40	ADI II-37		15.0	7.9	0.53	16.35	9.6	4.68	0.5	16.21	163.2	1.2439
41	ADI II-39		20.0	7.2	0.36	26.89	10.0	2.32	0.5	16.97	161.0	1.2327
42	ADI II-40		25.0	7.8	0.31	14.40	9.2	4.48	1.0	15.61	162.6	1.2315
43	ADI II-43		30.0	9.5	0.32	21.61	12.3	0.64	1.5	20.93	160.7	1.1959

^aBefore cure by NMR analysis.

^bRelative rate of comonomer incorporation = mol% incorporation/mol% feed.

^cAfter cure. Calculated by NMR/DSC/TGA analysis according to the equation on the following page.

^dBD = branch density, branches per 1000 main chain atoms calculated according to the following equations:

epoxide: $BD = [1000][\text{mol fraction}]/[(3(\text{mol fraction}) + 6(1-\text{mol fraction}))]$

dioxolane: $BD = [1000][\text{mol fraction}]/[(5(\text{mol fraction}) + 6(1-\text{mol fraction}))]$

^eThe density of polyoxymethylene homopolymer is reported as 1.420-1.435.³ Here, specific gravities are measured on plaques (formed by melting under nitrogen gas) according to ASTM D792. See Table 2 below for additional details.

Cure Equation

The mol% of comonomer present following the curing procedure is calculated as follows:

α denotes before cure

ω denotes after cure

$$\text{weight\%}_{\text{comonomer}\alpha} = \frac{(\text{mol\%}_{\text{comonomerNMR}}/100) \times \text{MW}_{\text{comonomer}}}{[(\text{mol\%}_{\text{comonomerNMR}}/100) \times \text{MW}_{\text{comonomer}}] + [(1-\text{mol\%}_{\text{comonomerNMR}})/100] \times \text{MW}_{\text{trioxane}}} \times 100$$

$$\text{weight}_{\text{comonomer}\alpha} = (\text{weight\%}_{\text{comonomer}\alpha}/100) \times \text{sampleweight}_{\text{DSC}}$$

$$\text{weight}_{\text{trioxane}\alpha} = ((1-\text{weight\%}_{\text{comonomer}\alpha})/100) \times \text{sampleweight}_{\text{DSC}}$$

$$\text{weight}_{\text{comonomer}\omega} = \text{weight}_{\text{comonomer}\alpha}$$

$$\text{weight}_{\text{trioxane}\omega} = \text{weight}_{\text{trioxane}\alpha} - (\%\text{weightloss}_{\text{DSC}} \times \text{sampleweight}_{\text{DSC}} / 100)$$

$$\text{mol\%}_{\text{comonomer}\omega} = \frac{\text{weight}_{\text{comonomer}\omega} / \text{MW}_{\text{comonomer}}}{[\text{weight}_{\text{comonomer}\omega} / \text{MW}_{\text{comonomer}}] + [\text{weight}_{\text{trioxane}\omega} / \text{MW}_{\text{trioxane}}]} \times 100$$

Table 2. Density Determination for Selected LLDPOM Samples




The density of polyoxymethylene homopolymer is reported as 1.420-1.435.³ Here, specific gravities are measured on plaques (formed by melting under nitrogen gas) according to ASTM D792. These specific gravities are converted to densities by multiplying by the correct water density factor, which is near 0.9975 because the experiments were performed near 23°C. Note that a green Keck clip (Chemglass #CG-145-05) was employed as the authentic polyoxymethylene (POM) sample. These are made principally from DuPont's Delrin® polyacetal resin.

sample	average density	weight in air	weight in water	water temp. (°C)	water density	sample spec. grav.	sample density	% comon. incorp.
ADI-II-34	1.223540	0.059	0.009	22.9	0.997561	1.180000	1.177121	5.9
		0.048	0.010	22.2	0.997724	1.263157	1.260282	
		0.047	0.009	24.9	0.997069	1.236842	1.233216	
ADI-II-35	1.216898	0.197	0.032	24.9	0.997069	1.193939	1.190439	8.9
		0.191	0.031	22.2	0.997724	1.193750	1.191033	
		0.196	0.042	24.2	0.997246	1.272727	1.269222	
ADI-II-36	1.235939	0.179	0.035	24.9	0.997069	1.243055	1.239412	6.4
		0.180	0.030	22.2	0.997724	1.200000	1.197268	
		0.181	0.039	24.2	0.997246	1.274647	1.271137	
ADI-II-37	1.243934	0.428	0.078	24.9	0.997069	1.222857	1.219272	9.6
		0.437	0.091	24.5	0.997171	1.263005	1.259432	
		0.431	0.088	24.2	0.997246	1.256559	1.253099	
ADI-II-39	1.232685	0.318	0.058	24.9	0.997069	1.223076	1.219492	10.0
		0.312	0.068	22.2	0.997724	1.278688	1.275778	
		0.316	0.054	24.2	0.997246	1.206106	1.202785	
ADI-II-40	1.231483	0.670	0.127	24.9	0.997069	1.233885	1.230269	9.2
		0.677	0.125	22.2	0.997724	1.226449	1.223657	
		0.668	0.131	24.2	0.997246	1.243947	1.240522	
ADI-II-43	1.195916	0.250	0.035	24.2	0.997246	1.162790	1.159588	12.3
		0.252	0.043	22.9	0.997561	1.205741	1.202800	
		0.253	0.047	22.2	0.997724	1.228155	1.225360	
ADI-I-174	1.186955	0.484	0.073	22.9	0.997561	1.177615	1.174743	7.1
		0.485	0.078	22.2	0.997724	1.191646	1.188934	
		0.485	0.081	24.2	0.997246	1.200495	1.197188	
ADI-I-175	1.227281	0.897	0.163	24.9	0.997069	1.222070	1.218488	9.0
		0.897	0.164	22.2	0.997724	1.223738	1.220952	
		0.897	0.177	24.2	0.997246	1.245833	1.242402	
ADI-I-176	1.255249	0.908	0.177	24.5	0.997171	1.242134	1.238620	10.4
		0.904	0.183	24.2	0.997246	1.253814	1.250361	
		0.910	0.199	22.9	0.997561	1.279887	1.276765	
ADI-I-183b	1.182313	0.705	0.108	24.5	0.997171	1.180904	1.177563	18.5
		0.705	0.115	24.2	0.997246	1.194915	1.191624	
		0.700	0.107	22.2	0.997724	1.180438	1.177751	
ADI-I-184	1.150016	0.282	0.036	24.2	0.997246	1.146341	1.143184	32.0
		0.281	0.040	22.9	0.997561	1.165975	1.163131	
		0.282	0.036	22.2	0.997724	1.146341	1.143732	
POM	1.365945	1.224	0.305	24.2	0.997246	1.331882	1.328214	0.0
		1.222	0.339	22.9	0.997561	1.383918	1.380543	
		1.221	0.344	22.2	0.997724	1.392246	1.389077	

Table 3. Ethylene/ α -olefin Copolymerization Data from the Literature

The following data are from Mirabella and Crist and were used to create the LLDPE comparison series in Figure 2 of the manuscript. Note that data from copolymers having more than 40 branches per 1000 main chain atoms were excluded from this analysis because non-linear effects become significant above this threshold.

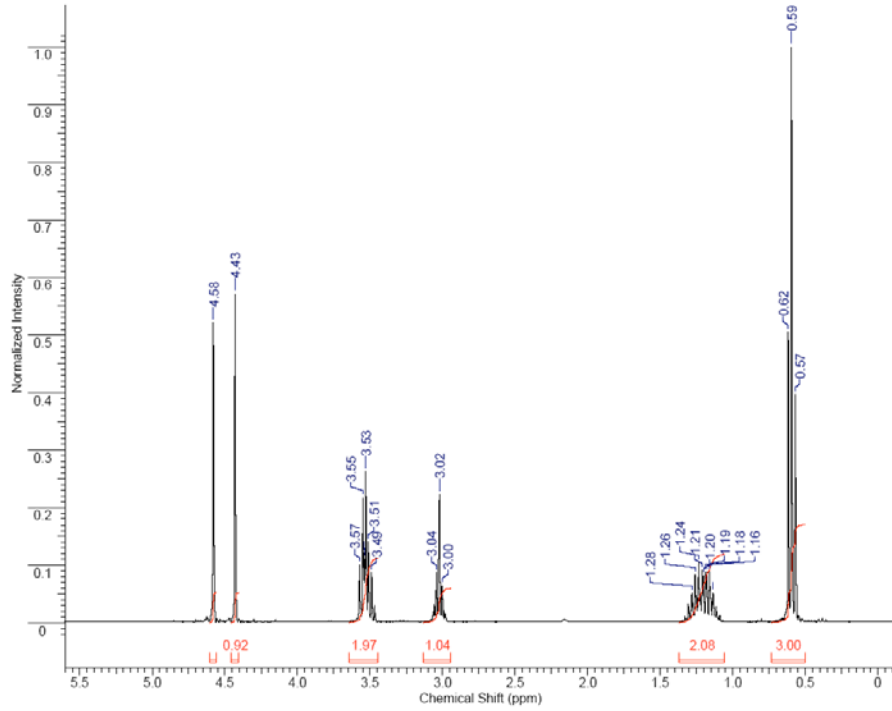
Mirabella, F. M.; Crist, B. *J. Polym. Sci., Part B: Polym. Phys.* **2004**, *42*, 3416-3427.

entry	reference #	comonomer	method	incorp. (mol fraction)	BD^a	T_m (°C)
1	ZN4F4	1-butene	Ziegler-Natta	0.074	37.0	94.7
2	ZN4F5		Ziegler-Natta	0.064	32.0	98.6
3	ZN4F6		Ziegler-Natta	0.044	22.0	106.2
4	ZN4F7		Ziegler-Natta	0.04	20.0	108.7
5	ZN4F8		Ziegler-Natta	0.034	17.0	112.0
6	ZN4F9		Ziegler-Natta	0.027	13.5	115.6
7	ZN4F10		Ziegler-Natta	0.022	11.0	119.1
8	ZN4F11		Ziegler-Natta	0.016	8.0	121.8
9	ZN4F12		Ziegler-Natta	0.014	7.0	124.4
10	ZN4F13		Ziegler-Natta	0.009	4.5	128.1
11	ZN4F14		Ziegler-Natta	0.008	4.0	129.9
12	M4W4		metallocene	0.065	32.5	91.0
13	M4W5		metallocene	0.053	26.5	99.3
14	M4W6		metallocene	0.038	19.0	107.6
15	ZN6F4	1-hexene	Ziegler-Natta	0.058	29.0	99.5
16	ZN6F5		Ziegler-Natta	0.053	26.5	103.7
17	ZN6F6		Ziegler-Natta	0.045	22.5	103.2
18	ZN6F7		Ziegler-Natta	0.041	20.5	108.3
19	ZN6F8		Ziegler-Natta	0.033	16.5	111.0
20	ZN6F9		Ziegler-Natta	0.03	15.0	106.3
21	ZN6F10		Ziegler-Natta	0.021	10.5	118.7
22	ZN6F11		Ziegler-Natta	0.017	8.5	120.6
23	ZN6F12		Ziegler-Natta	0.012	6.0	123.0
24	ZN6F13		Ziegler-Natta	0.011	5.5	128.2
25	ZN6F14		Ziegler-Natta	0.01	5.0	125.2
26	ZN6F15	Ziegler-Natta	0.006	3.0	130.7	
27	M6F1		metallocene	0.04	20.0	105.3
28	M6F2		metallocene	0.027	13.5	114.3
29	M6F3		metallocene	0.024	12.0	116.1
30	M6F4		metallocene	0.015	7.5	129.0
31	M6W1		metallocene	0.068	34.0	92.4
32	M6W2a		metallocene	0.055	27.5	101.2
33	M6W2b		metallocene	0.049	24.5	102.3
34	M6W2c		metallocene	0.044	22.0	100.8
35	M6W3		metallocene	0.053	26.5	95.7
36	ZN8F1	1-octene	Ziegler-Natta	0.068	34.0	94.4
37	ZN8F2		Ziegler-Natta	0.056	28.0	97.5
38	ZN8F3		Ziegler-Natta	0.048	24.0	101.2
39	ZN8F4		Ziegler-Natta	0.042	21.0	104.5
40	ZN8F5		Ziegler-Natta	0.034	17.0	107.8
41	ZN8F6		Ziegler-Natta	0.029	14.5	111.5
42	ZN8F7		Ziegler-Natta	0.024	12.0	114.2
43	ZN8F8		Ziegler-Natta	0.019	9.5	117.7
44	ZN8F9		Ziegler-Natta	0.017	8.5	118.2
45	ZN8F10		Ziegler-Natta	0.011	5.5	122.7
46	ZN8F11		Ziegler-Natta	0.006	3.0	128.1
47	ZN8F12	Ziegler-Natta	0.005	2.5	129.8	
48	M8aF1		metallocene	0.056	28.0	98.6
49	M8aF2		metallocene	0.02	10.0	119.5
50	M8aF3		metallocene	0.007	3.5	129.0
51	M8bF1		metallocene	0.039	19.5	109.9
52	M8bF2		metallocene	0.017	8.5	121.4
53	M8bF3		metallocene	0.011	5.5	129.6
54	M8cF1		metallocene	0.049	24.5	104.6
55	M8cF2		metallocene	0.024	12.0	115.9
56	M8cF3		metallocene	0.011	5.5	127.5

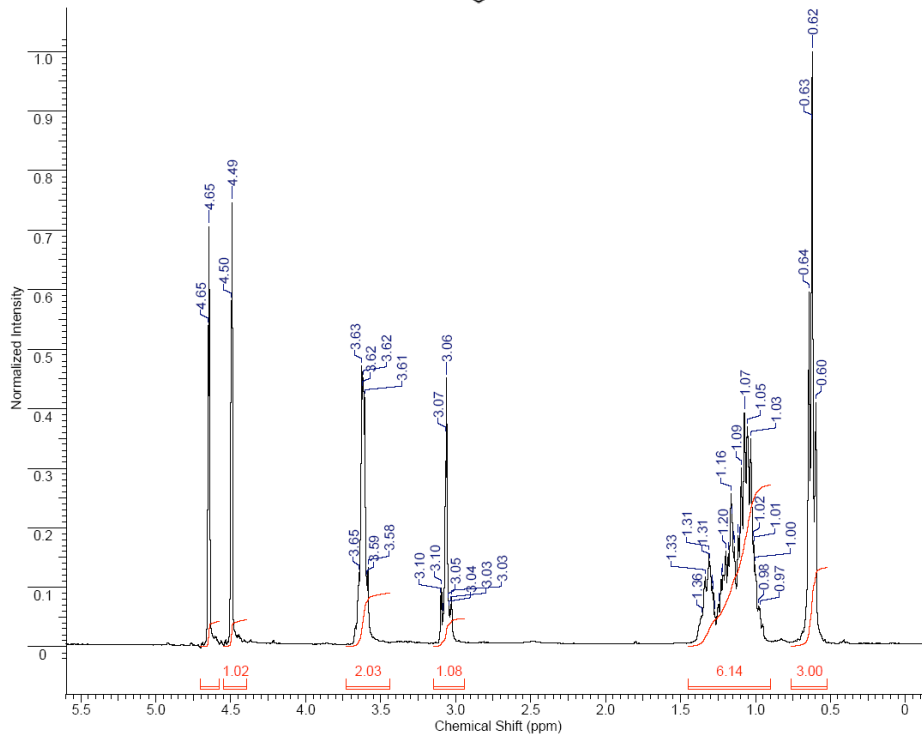
$$^aBD = [1000][\text{mol fraction}]/[(2(\text{mol fraction}) + 2(1-\text{mol fraction})) = [1000][\text{mol fraction}]/[2]$$

Monomer ¹H NMR Data

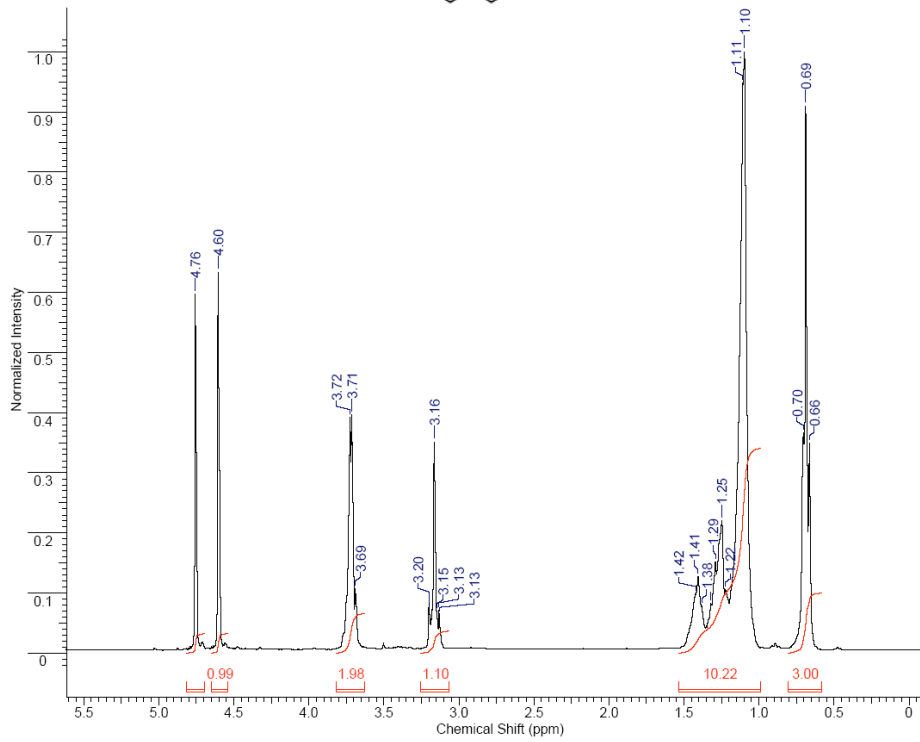
4-ethyl-1,3-dioxolane



4-butyl-1,3-dioxolane

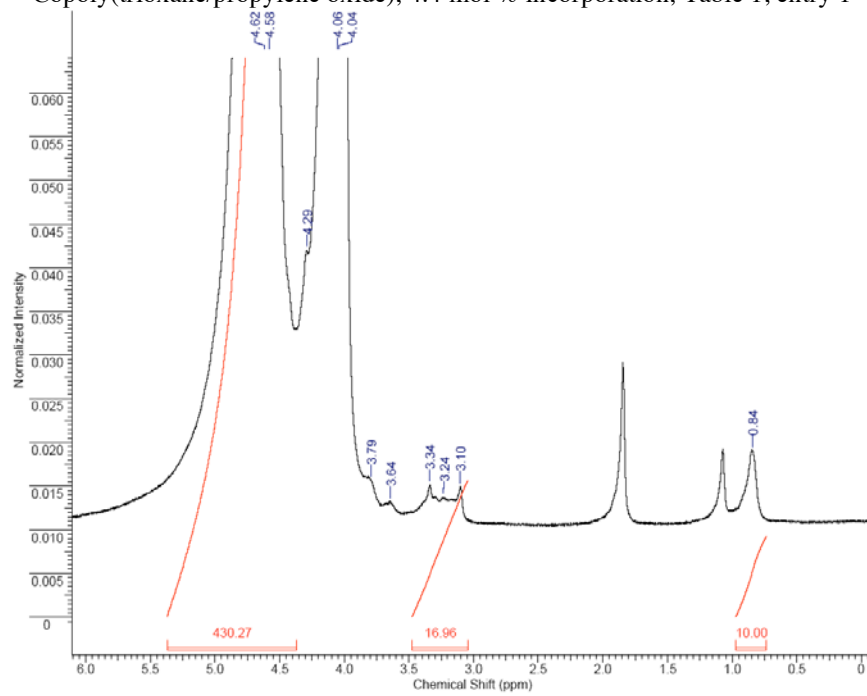


4-hexyl-1,3-dioxolane

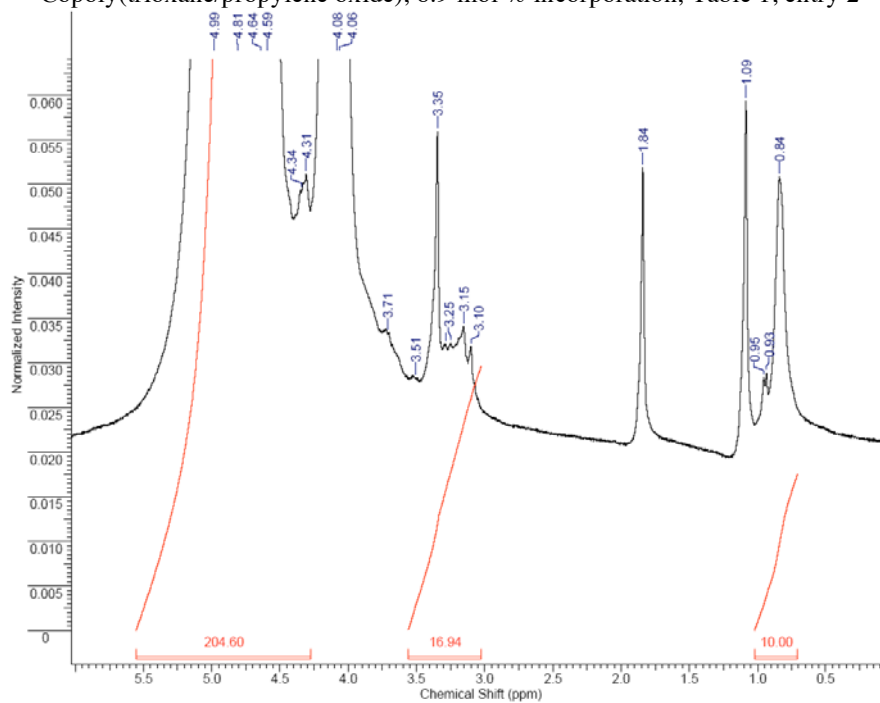


Copolymer ^1H NMR Data

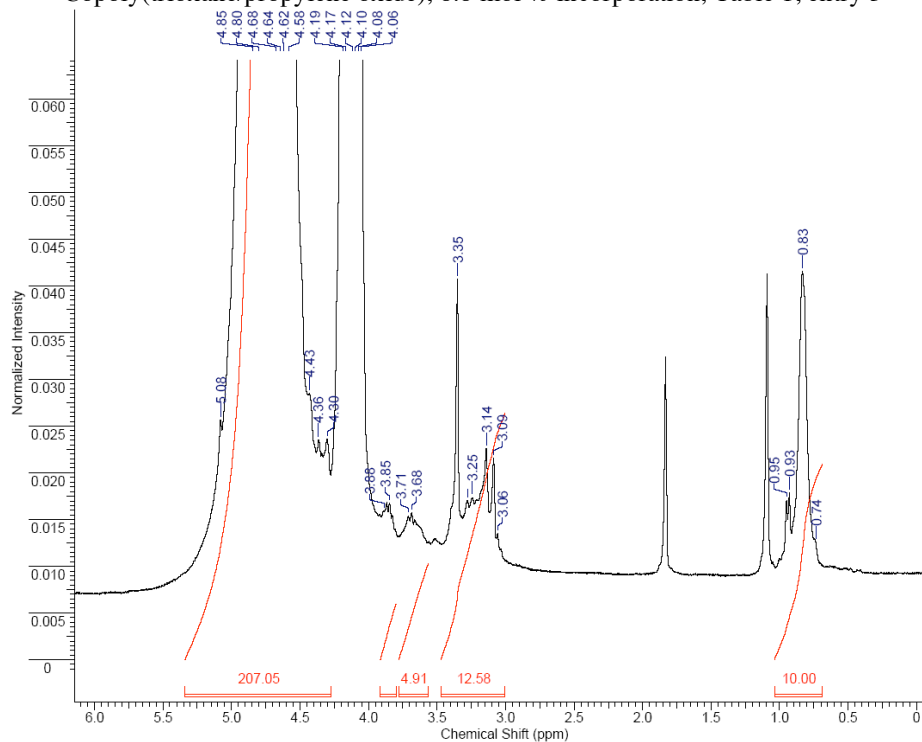
Copoly(trioxane/propylene oxide), 4.4 mol % incorporation, Table 1, entry 1



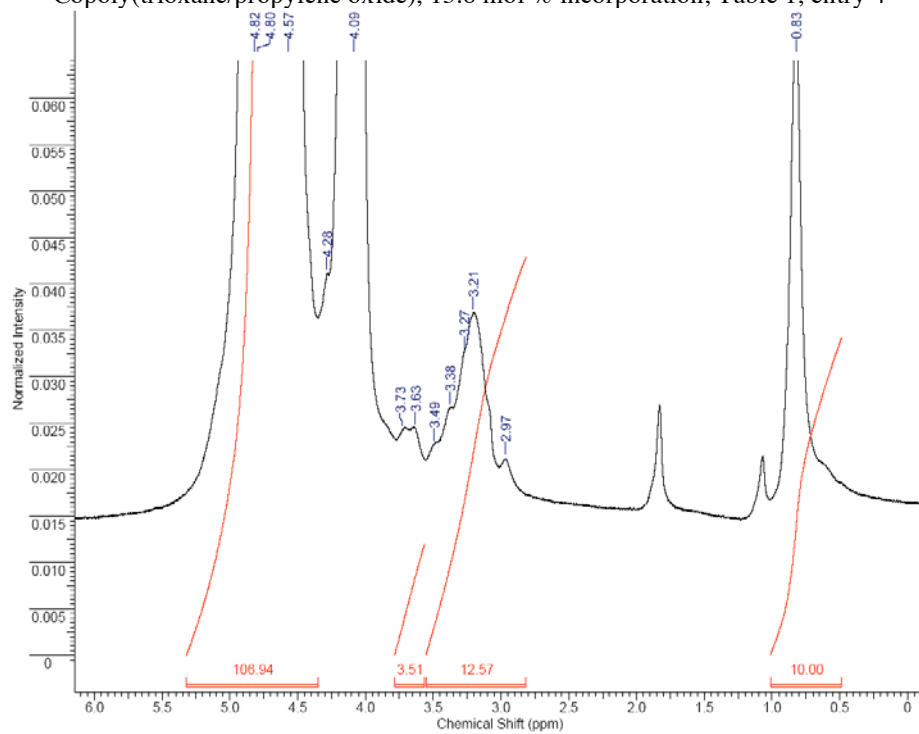
Copoly(trioxane/propylene oxide), 8.9 mol % incorporation, Table 1, entry 2



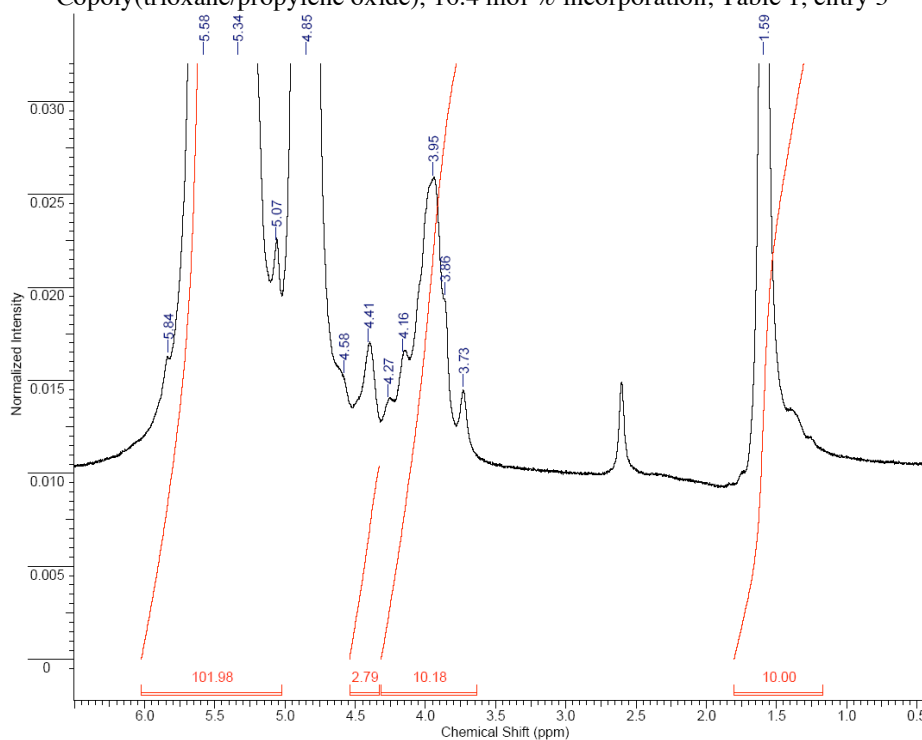
Copoly(trioxane/propylene oxide), 8.8 mol % incorporation, Table 1, entry 3



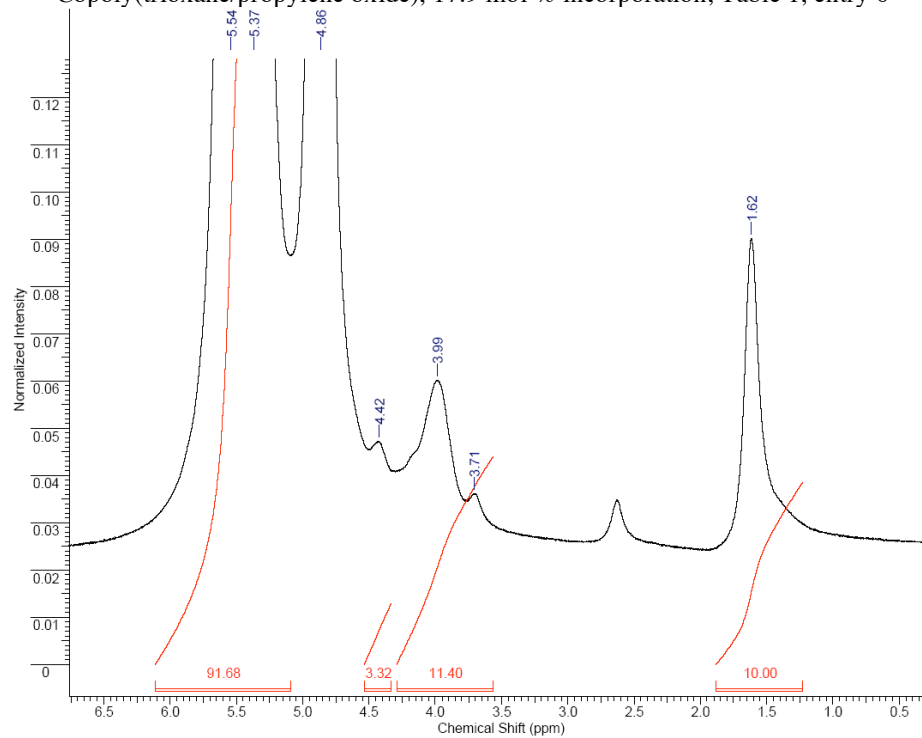
Copoly(trioxane/propylene oxide), 15.8 mol % incorporation, Table 1, entry 4



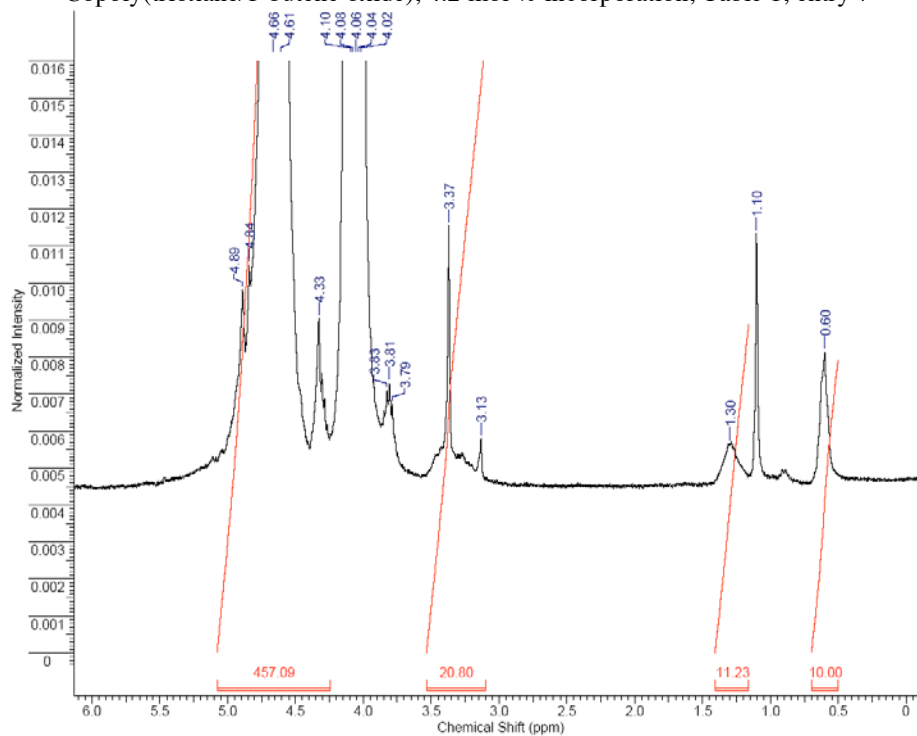
Copoly(trioxane/propylene oxide), 16.4 mol % incorporation, Table 1, entry 5



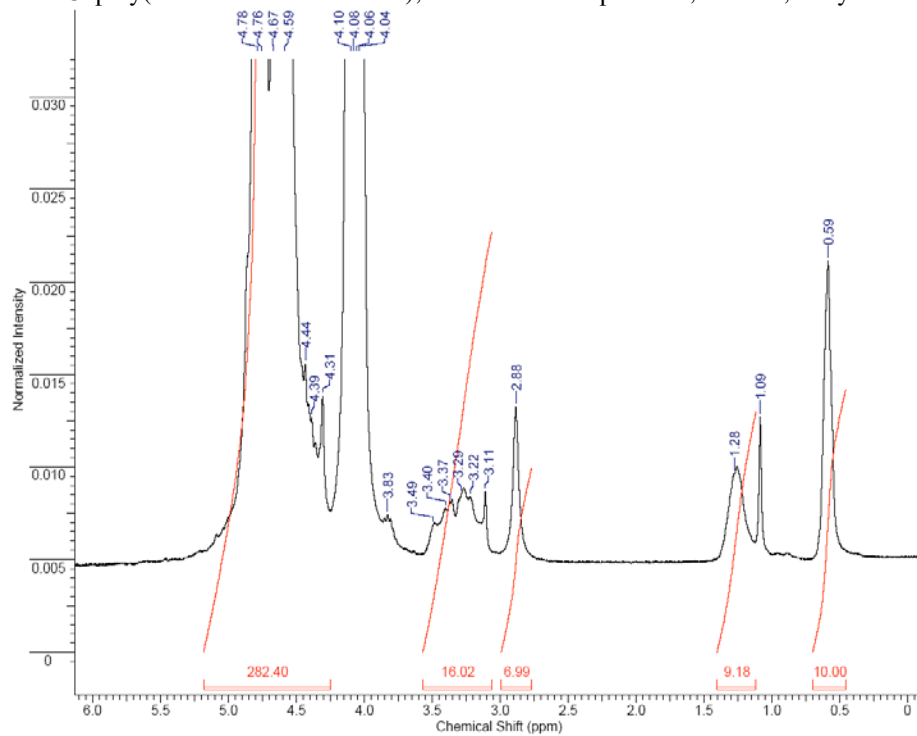
Copoly(trioxane/propylene oxide), 17.9 mol % incorporation, Table 1, entry 6



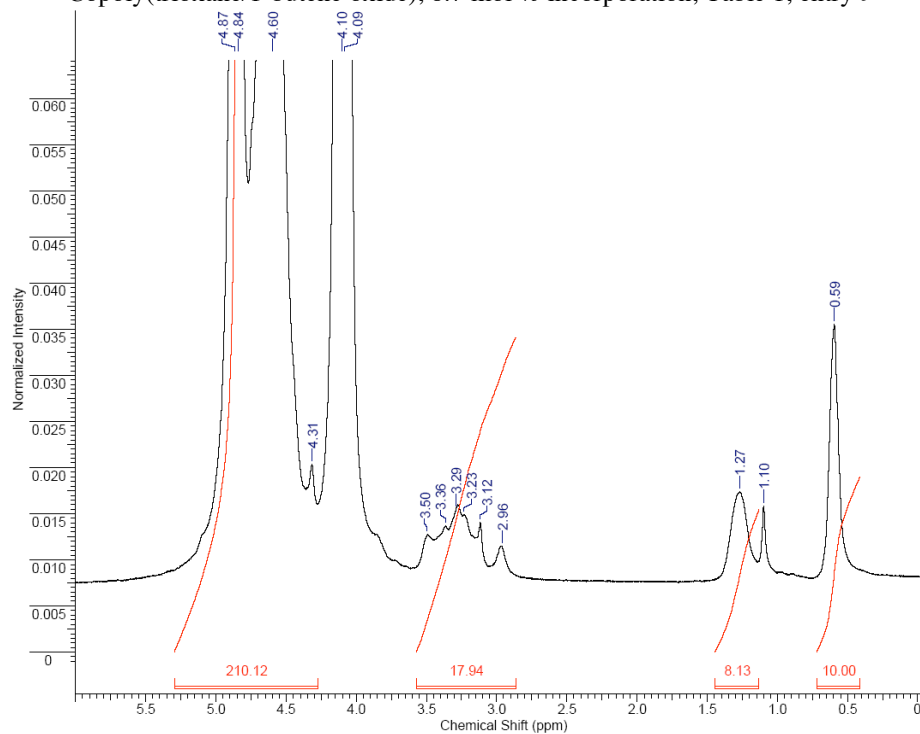
Copoly(trioxane/1-butene oxide), 4.2 mol % incorporation, Table 1, entry 7



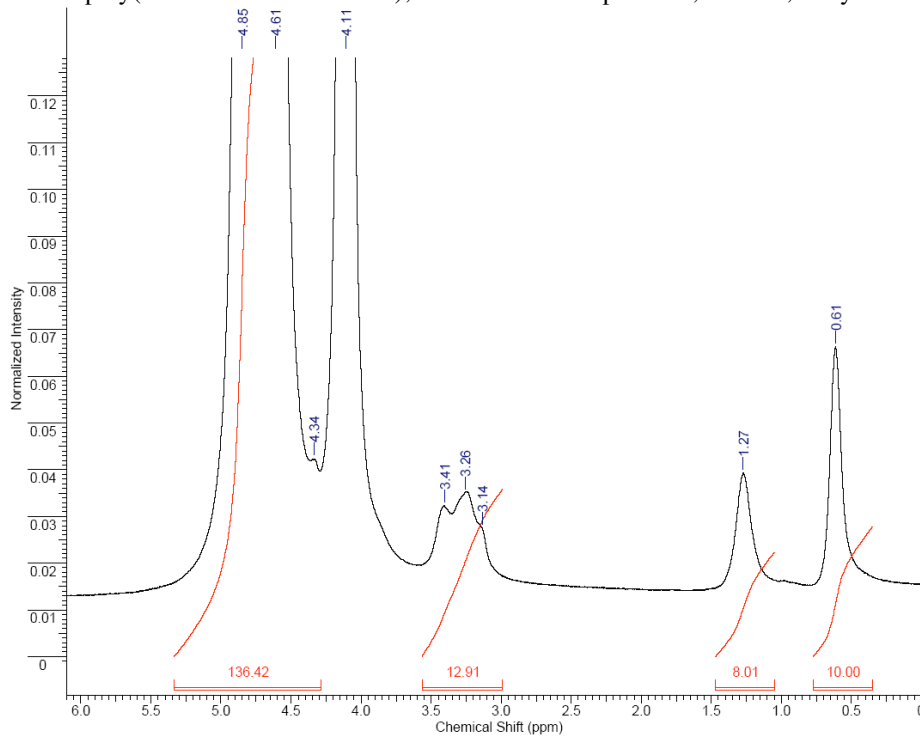
Copoly(trioxane/1-butene oxide), 6.6 mol % incorporation, Table 1, entry 8



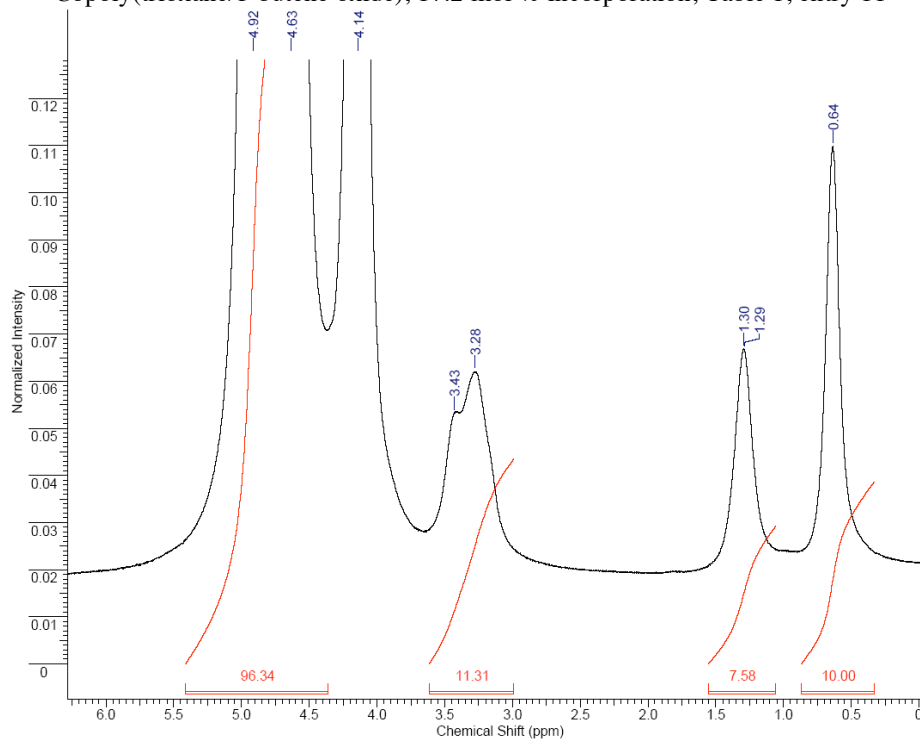
Copoly(trioxane/1-butene oxide), 8.7 mol % incorporation, Table 1, entry 9



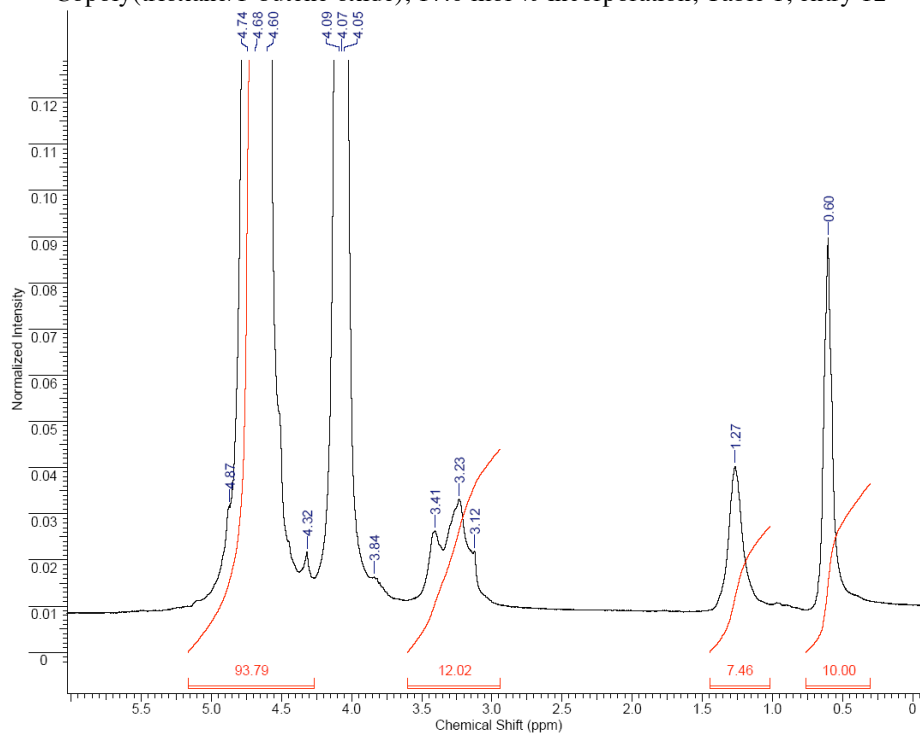
Copoly(trioxane/1-butene oxide), 12.8 mol % incorporation, Table 1, entry 10



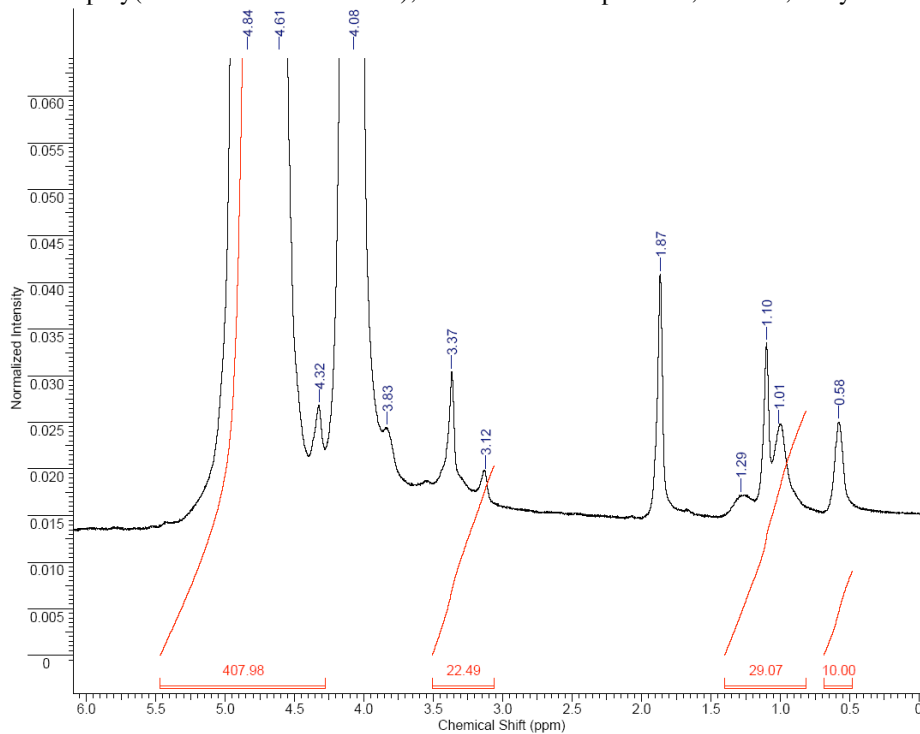
Copoly(trioxane/1-butene oxide), 17.2 mol % incorporation, Table 1, entry 11



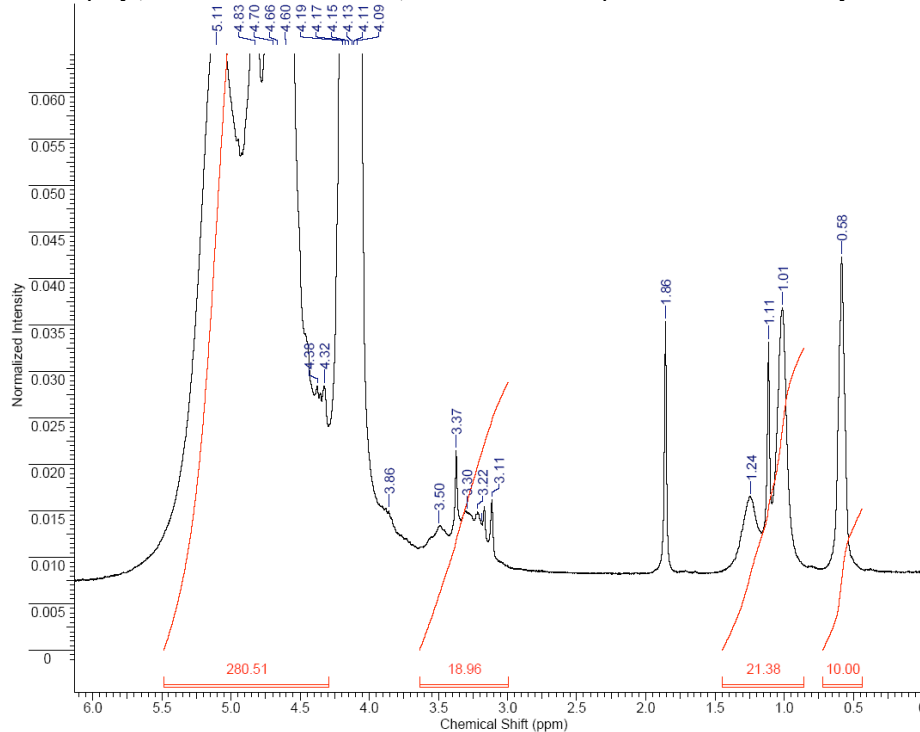
Copoly(trioxane/1-butene oxide), 17.6 mol % incorporation, Table 1, entry 12



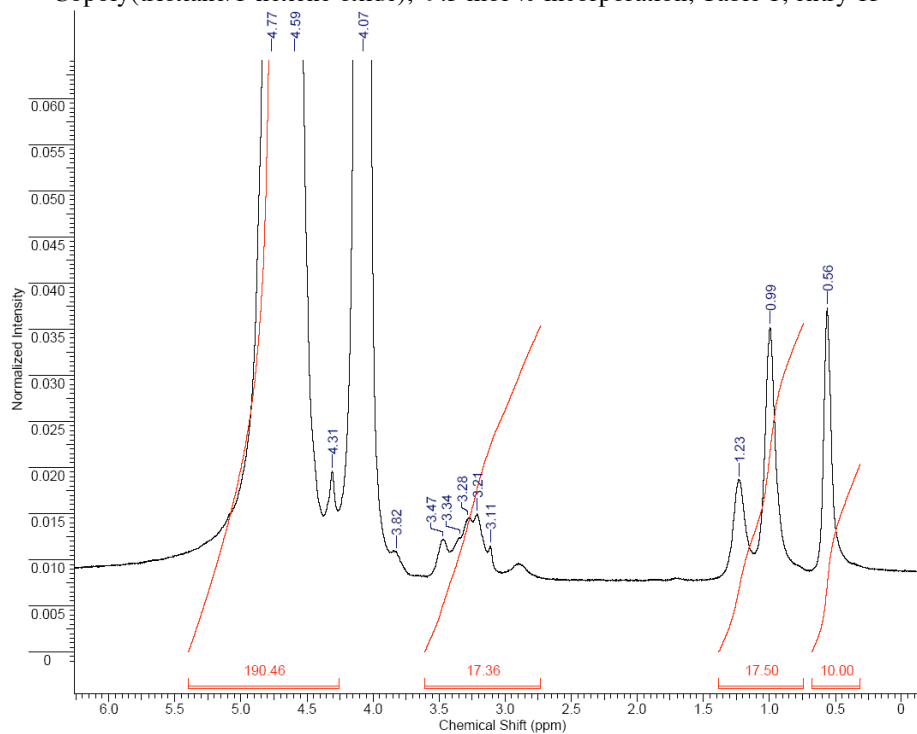
Copoly(trioxane/1-hexene oxide), 4.7 mol % incorporation, Table 1, entry 13



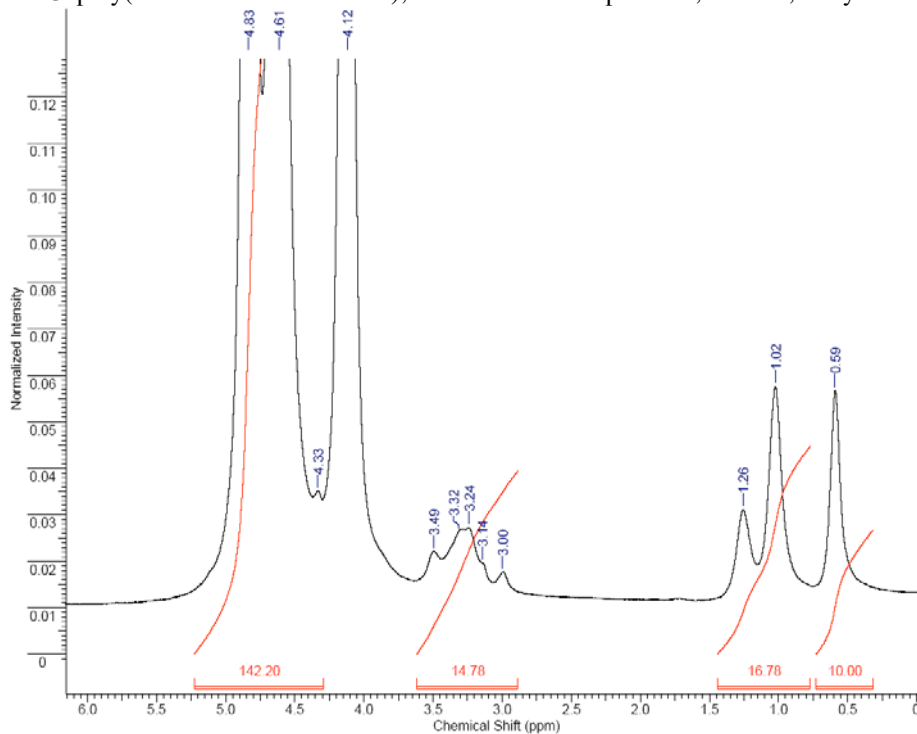
Copoly(trioxane/1-hexene oxide), 6.7 mol % incorporation, Table 1, entry 14



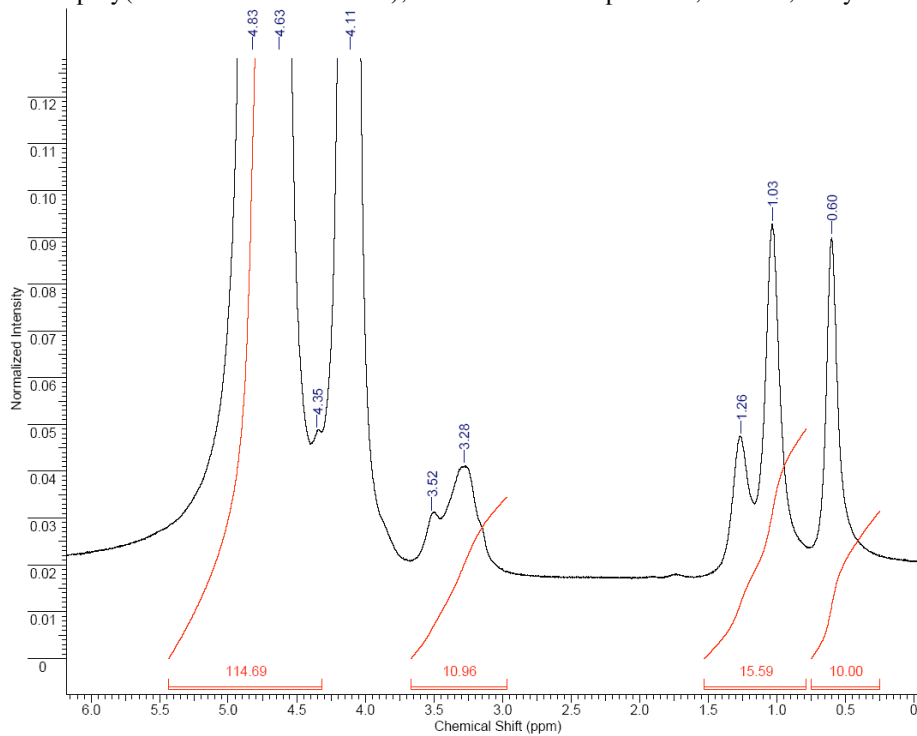
Copoly(trioxane/1-hexene oxide), 9.5 mol % incorporation, Table 1, entry 15



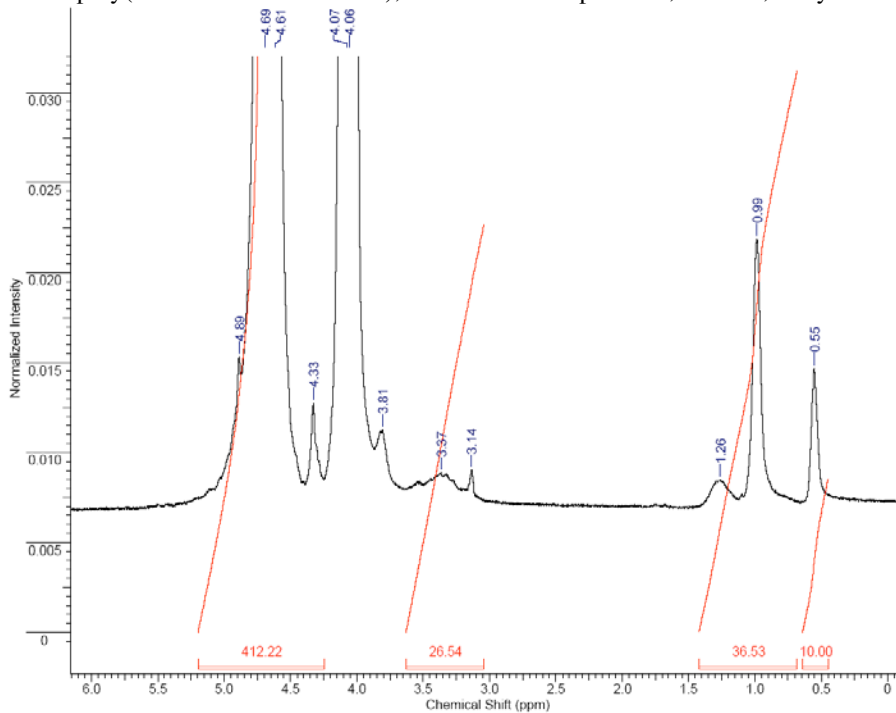
Copoly(trioxane/1-hexene oxide), 12.3 mol % incorporation, Table 1, entry 16



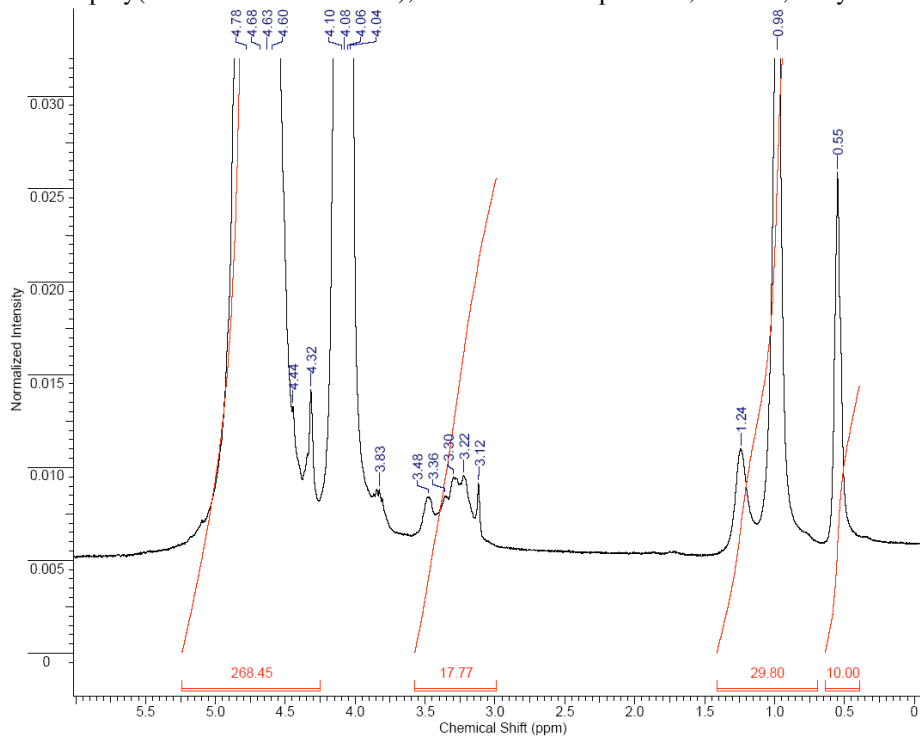
Copoly(trioxane/1-hexene oxide), 14.9 mol % incorporation, Table 1, entry 17



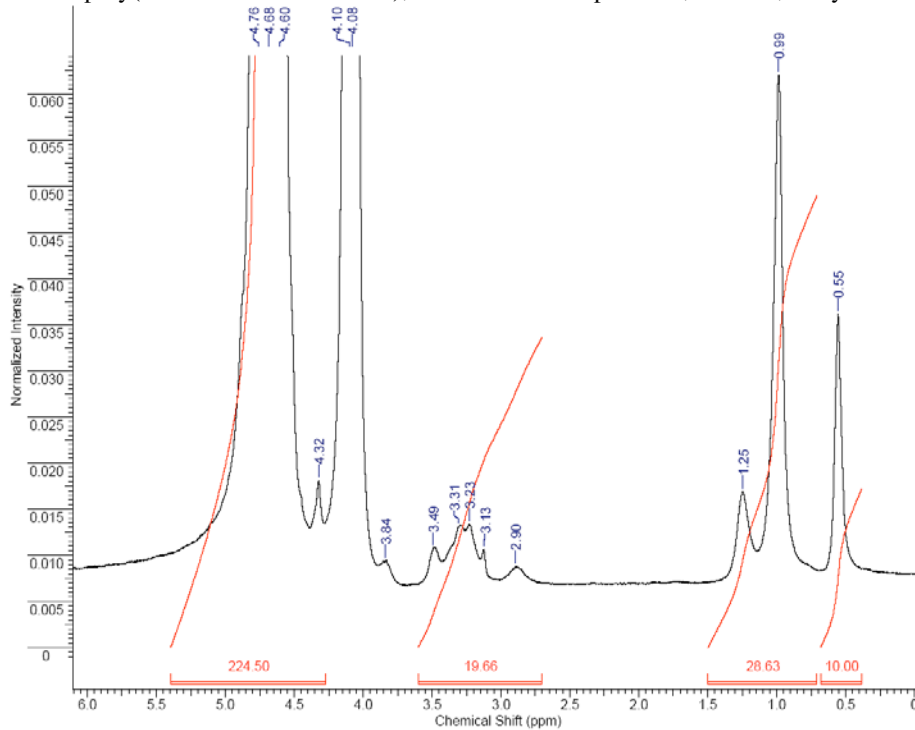
Copoly(trioxane/1-octene oxide), 4.6 mol % incorporation, Table 1, entry 18



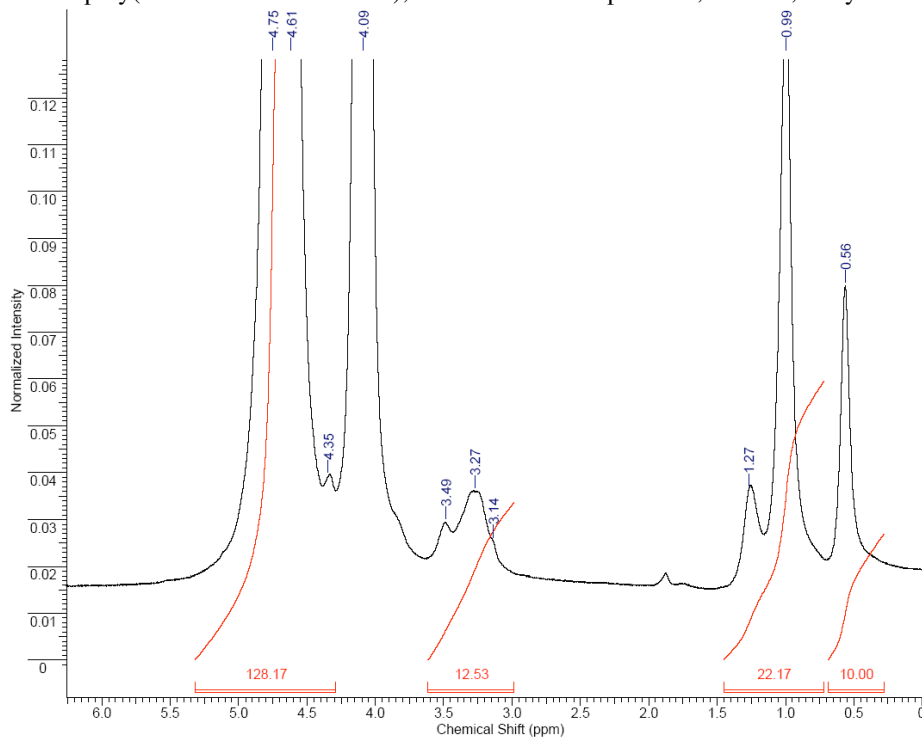
Copoly(trioxane/1-octene oxide), 6.9 mol % incorporation, Table 1, entry 19



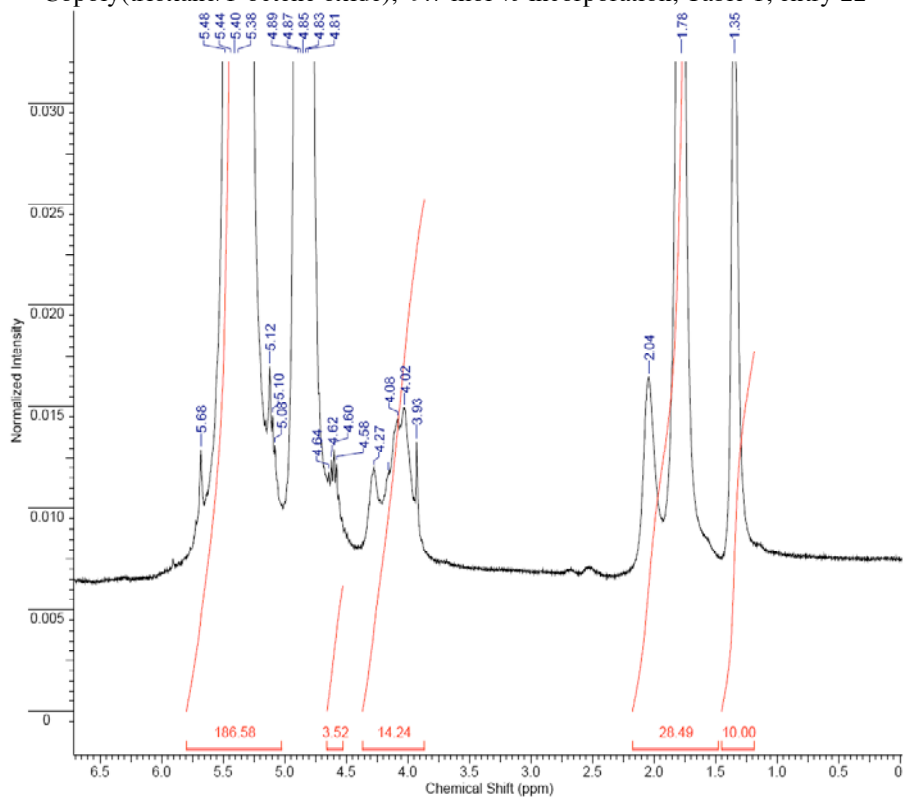
Copoly(trioxane/1-octene oxide), 8.2 mol % incorporation, Table 1, entry 20



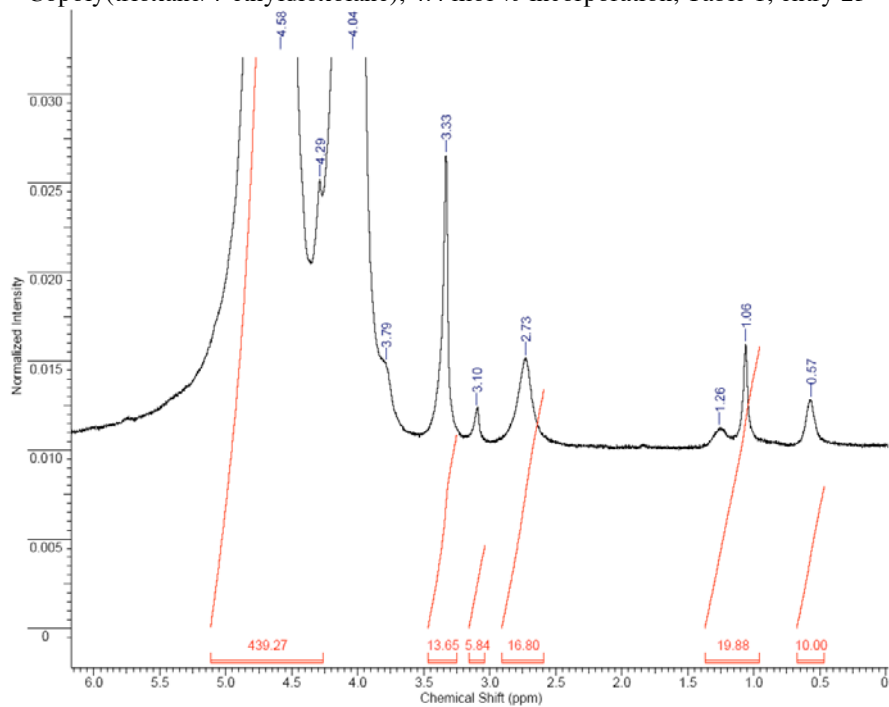
Copoly(trioxane/1-octene oxide), 13.5 mol % incorporation, Table 1, entry 21



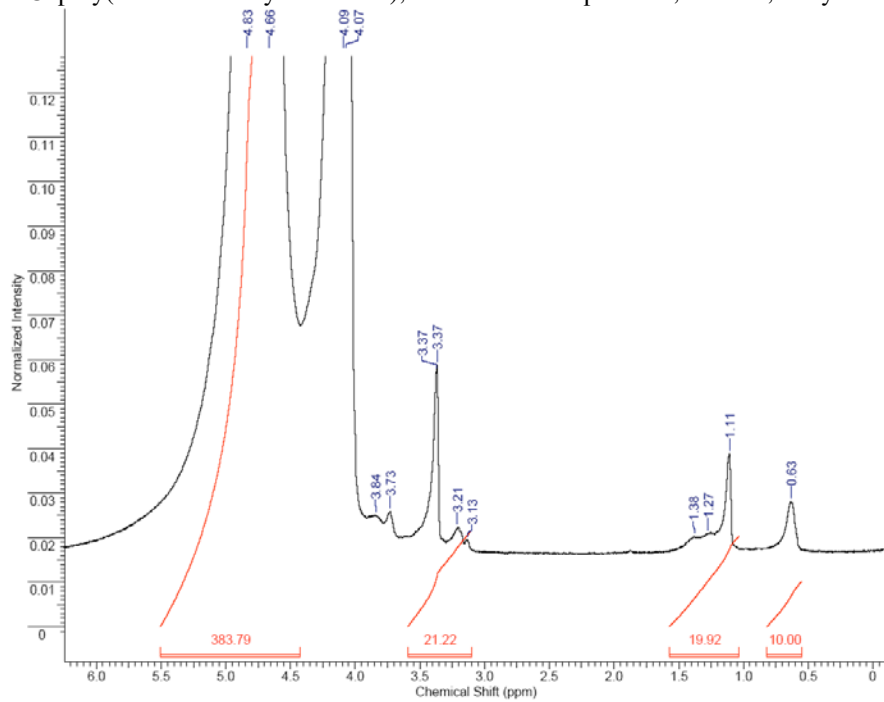
Copoly(trioxane/1-octene oxide), 9.7 mol % incorporation, Table 1, entry 22



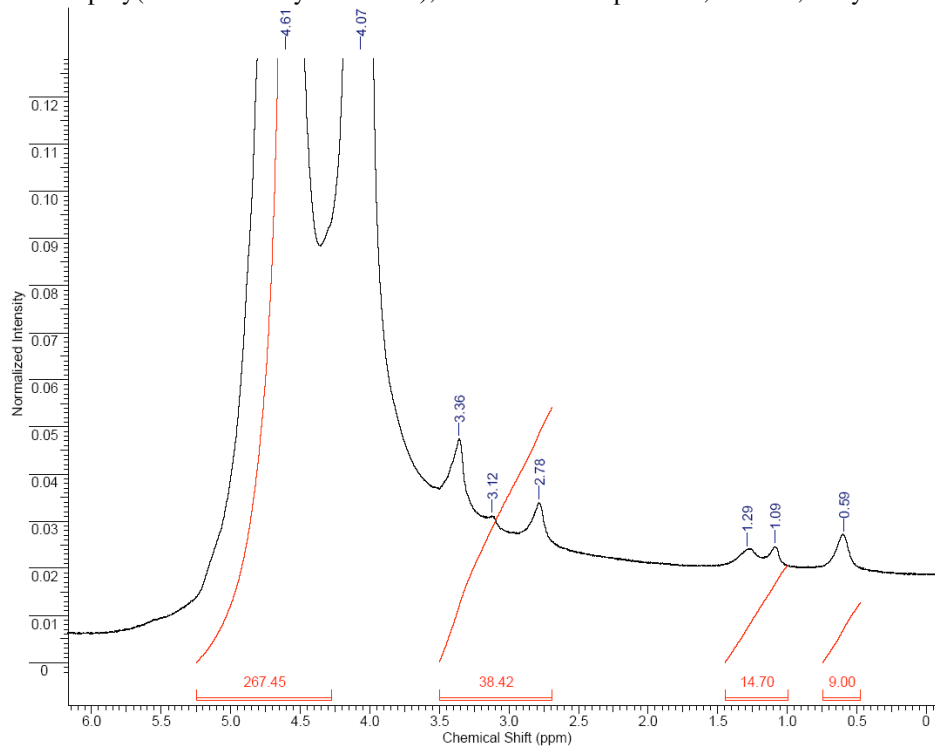
Copoly(trioxane/4-ethyldioxolane), 4.4 mol % incorporation, Table 1, entry 23



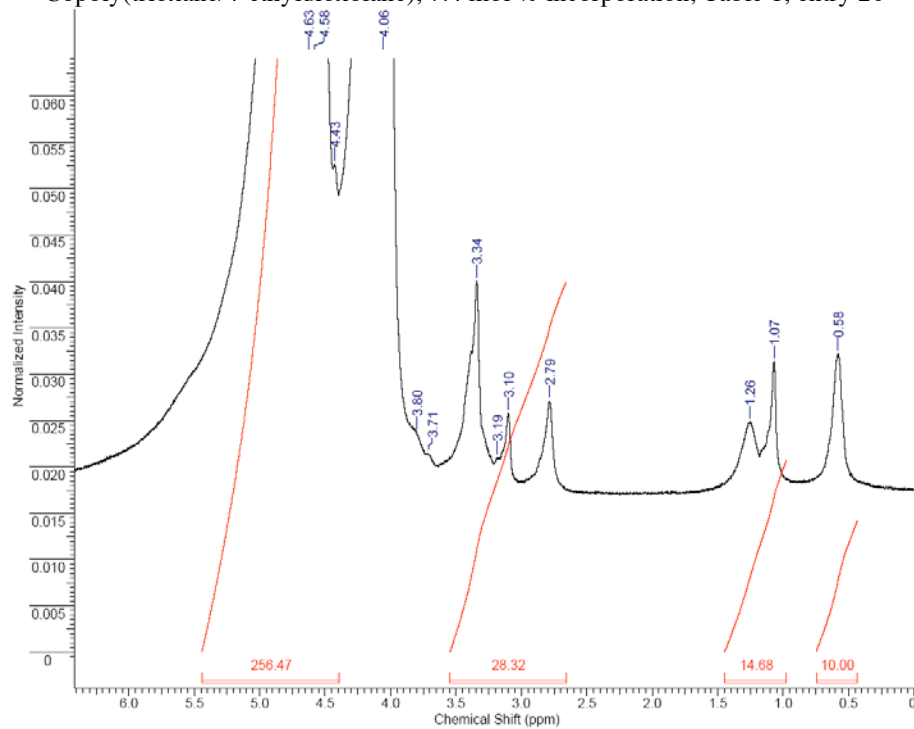
Copoly(trioxane/4-ethyldioxolane), 5.0 mol % incorporation, Table 1, entry 24



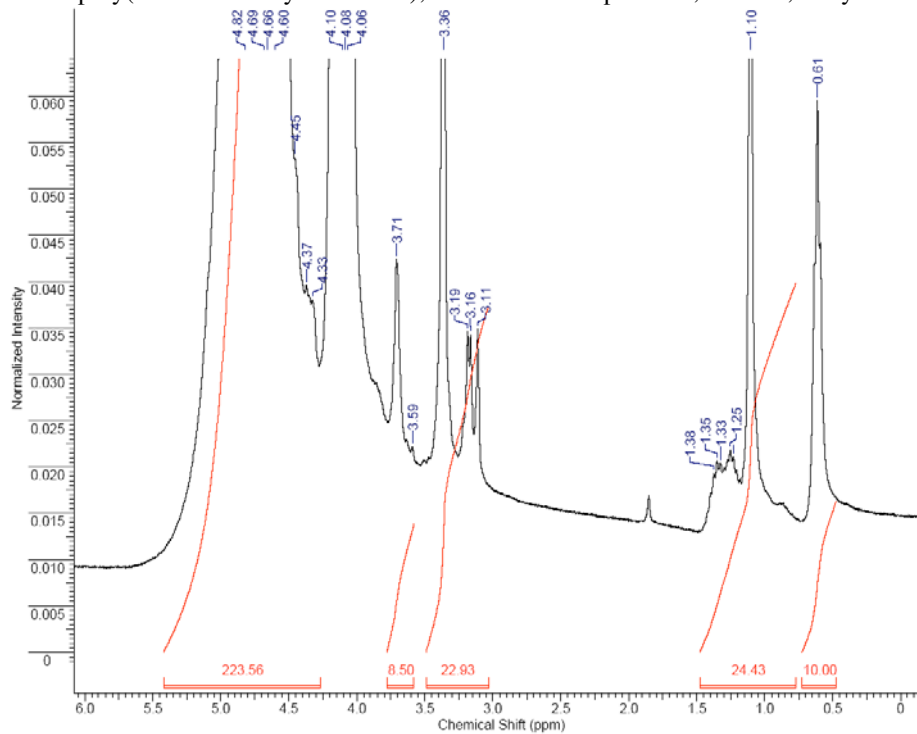
Copoly(trioxane/4-ethyldioxolane), 7.1 mol % incorporation, Table 1, entry 25



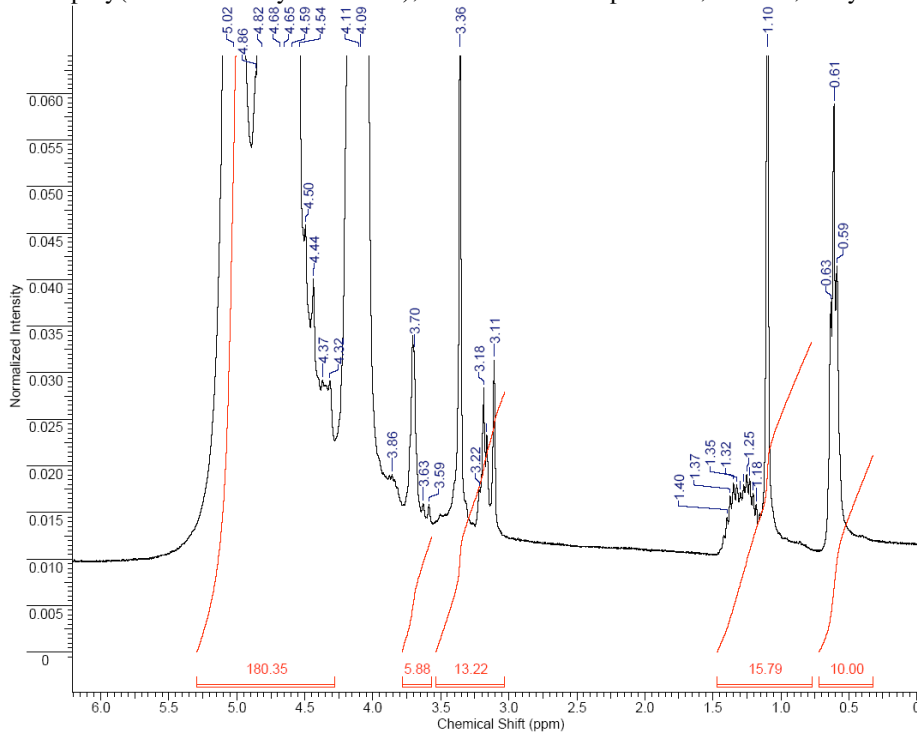
Copoly(trioxane/4-ethyldioxolane), 7.4 mol % incorporation, Table 1, entry 26



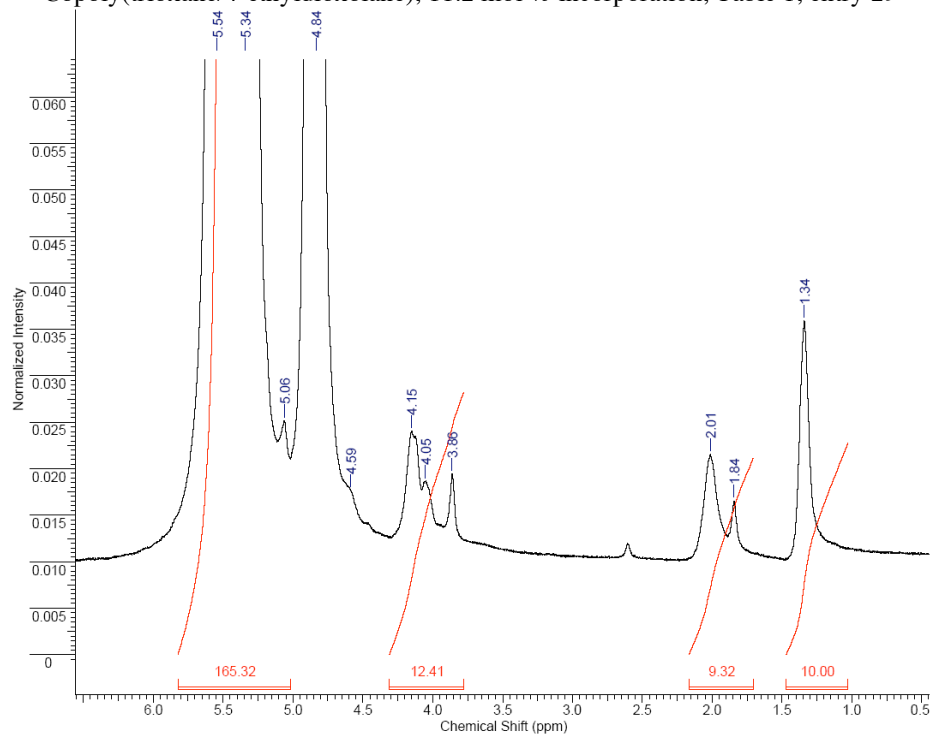
Copoly(trioxane/4-ethyldioxolane), 8.4 mol % incorporation, Table 1, entry 27



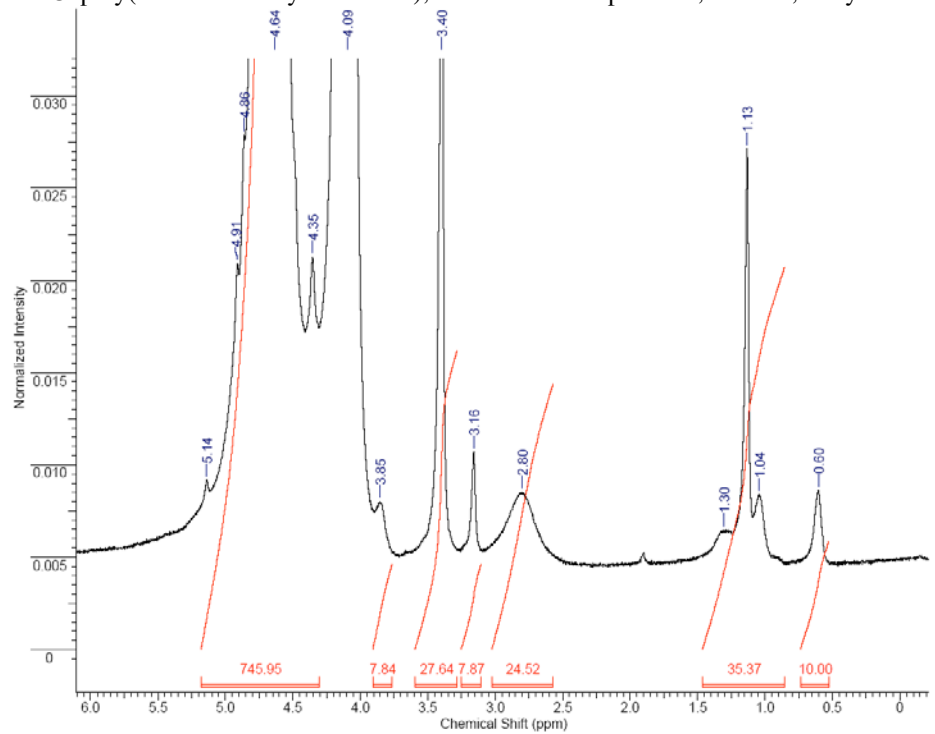
Copoly(trioxane/4-ethyldioxolane), 10.3 mol % incorporation, Table 1, entry 28



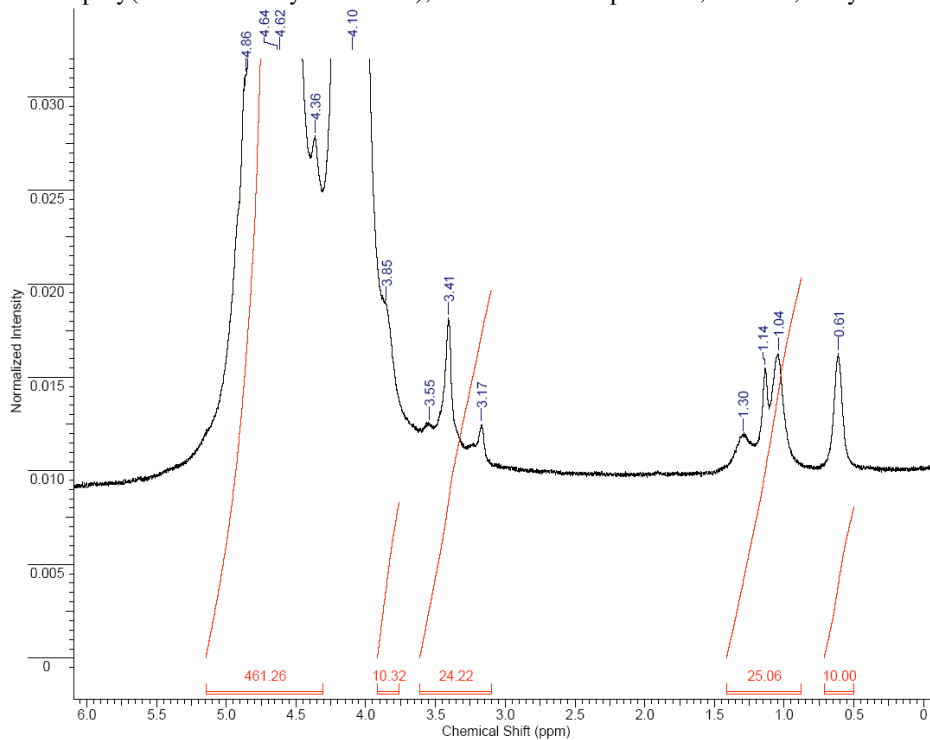
Copoly(trioxane/4-ethyldioxolane), 11.2 mol % incorporation, Table 1, entry 29



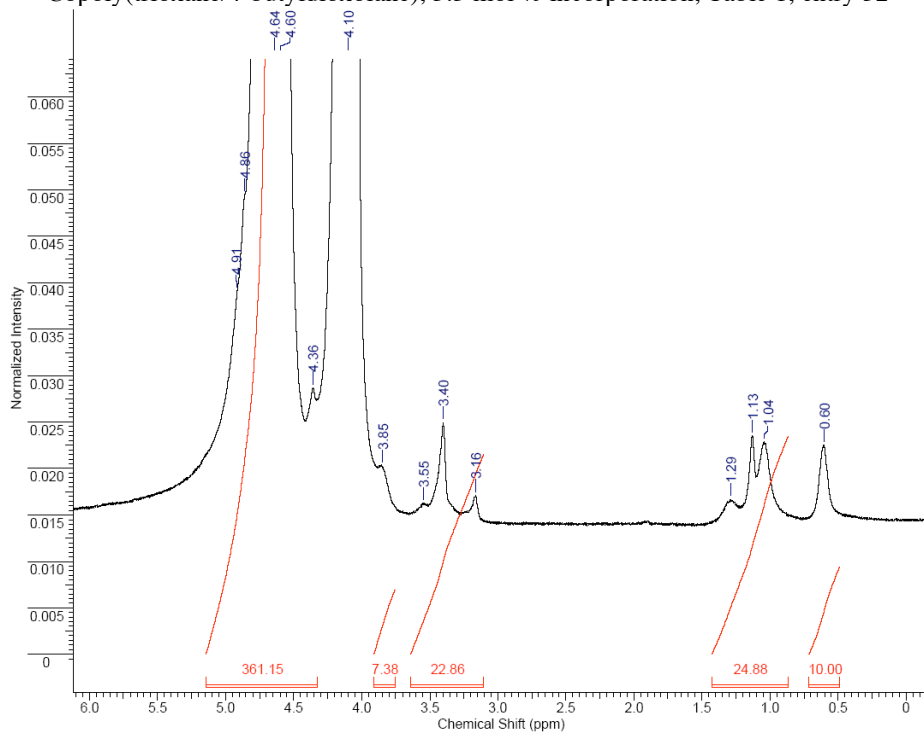
Copoly(trioxane/4-butyldioxolane), 2.6 mol % incorporation, Table 1, entry 30



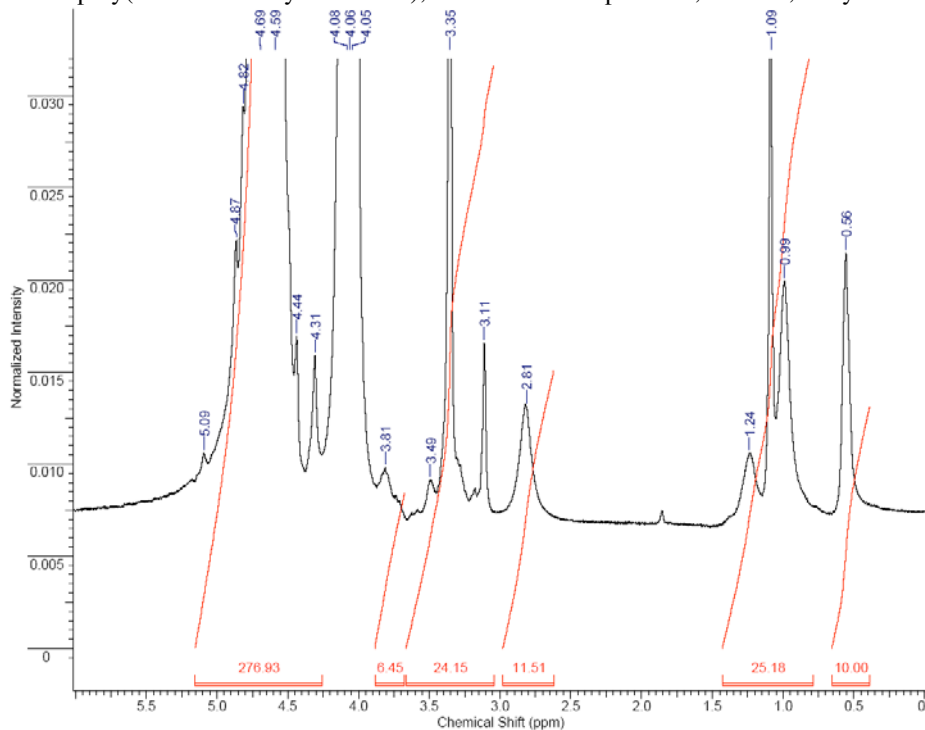
Copoly(trioxane/4-butyldioxolane), 4.2 mol % incorporation, Table 1, entry 31



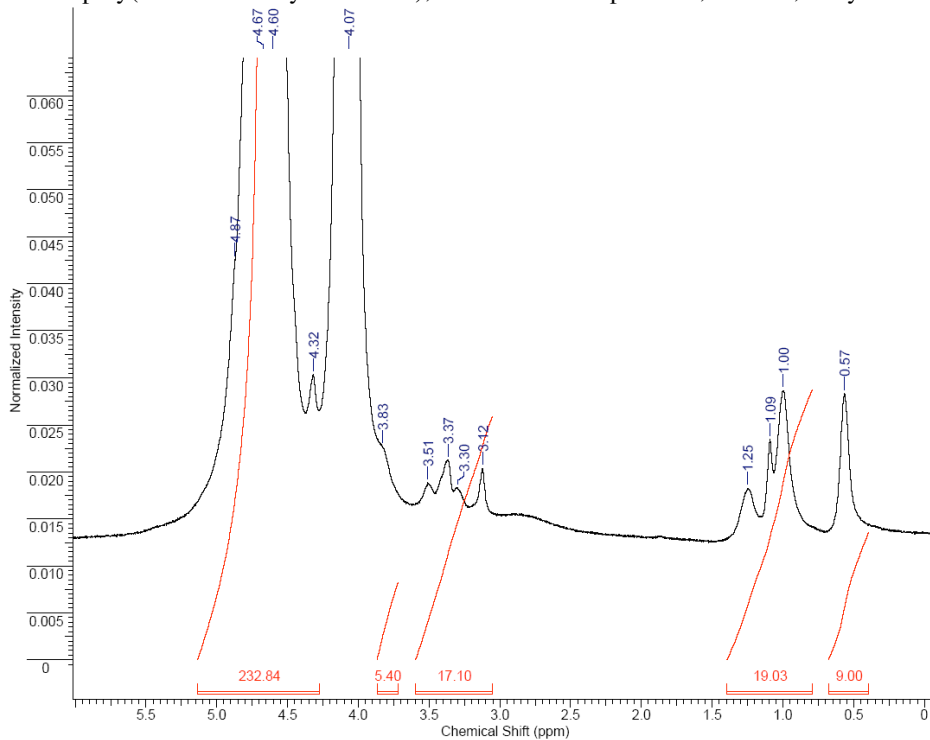
Copoly(trioxane/4-butyldioxolane), 5.3 mol % incorporation, Table 1, entry 32



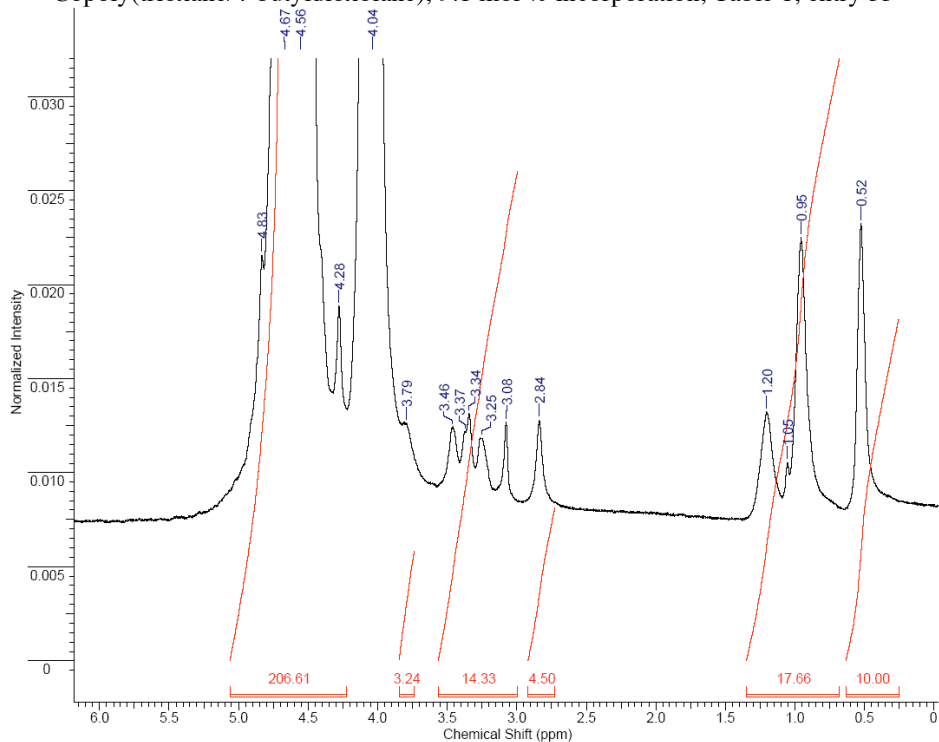
Copoly(trioxane/4-butyldioxolane), 6.9 mol % incorporation, Table 1, entry 33



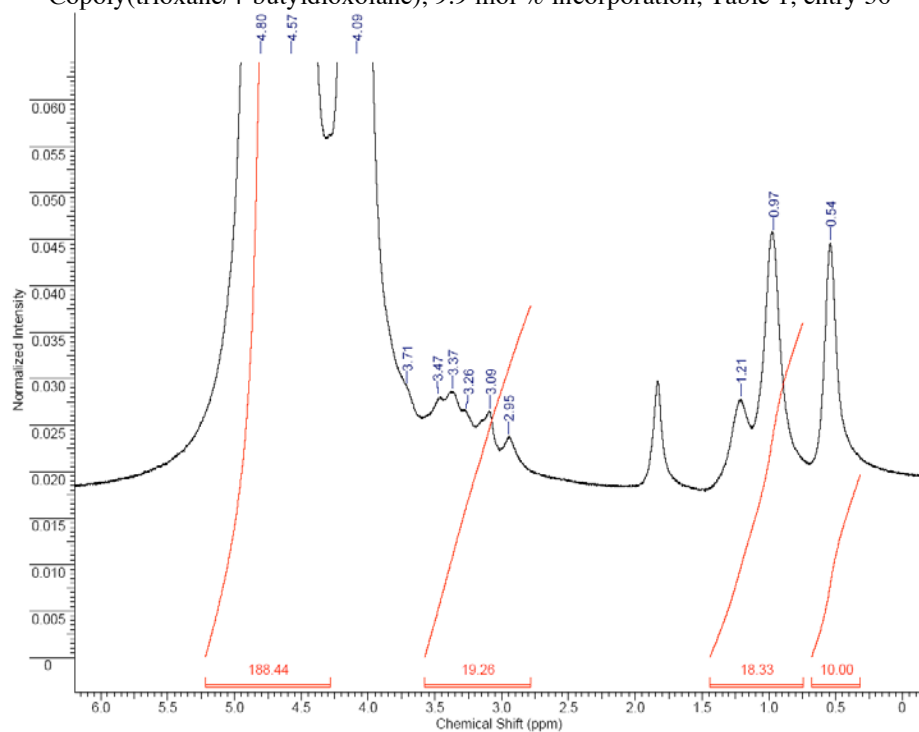
Copoly(trioxane/4-butyldioxolane), 8.1 mol % incorporation, Table 1, entry 34



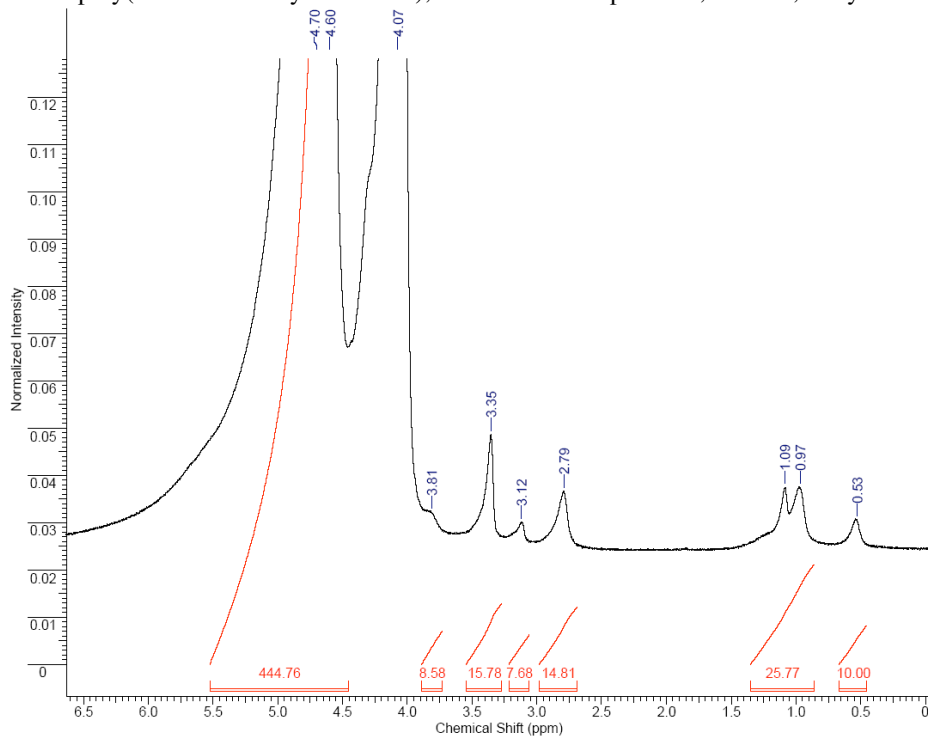
Copoly(trioxane/4-butyldioxolane), 9.1 mol % incorporation, Table 1, entry 35



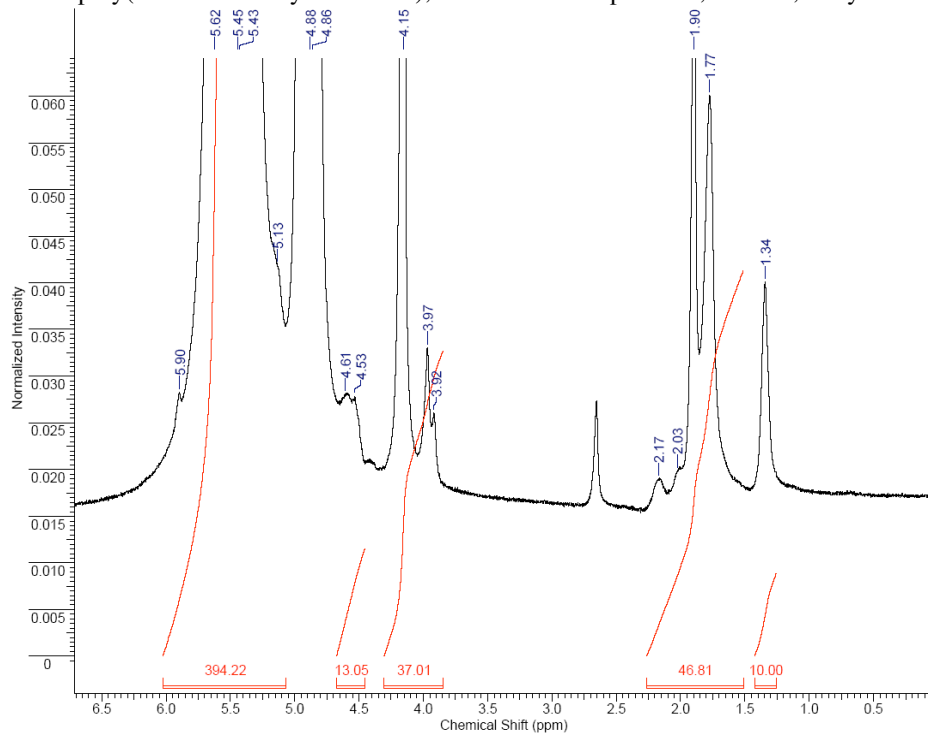
Copoly(trioxane/4-butyldioxolane), 9.9 mol % incorporation, Table 1, entry 36



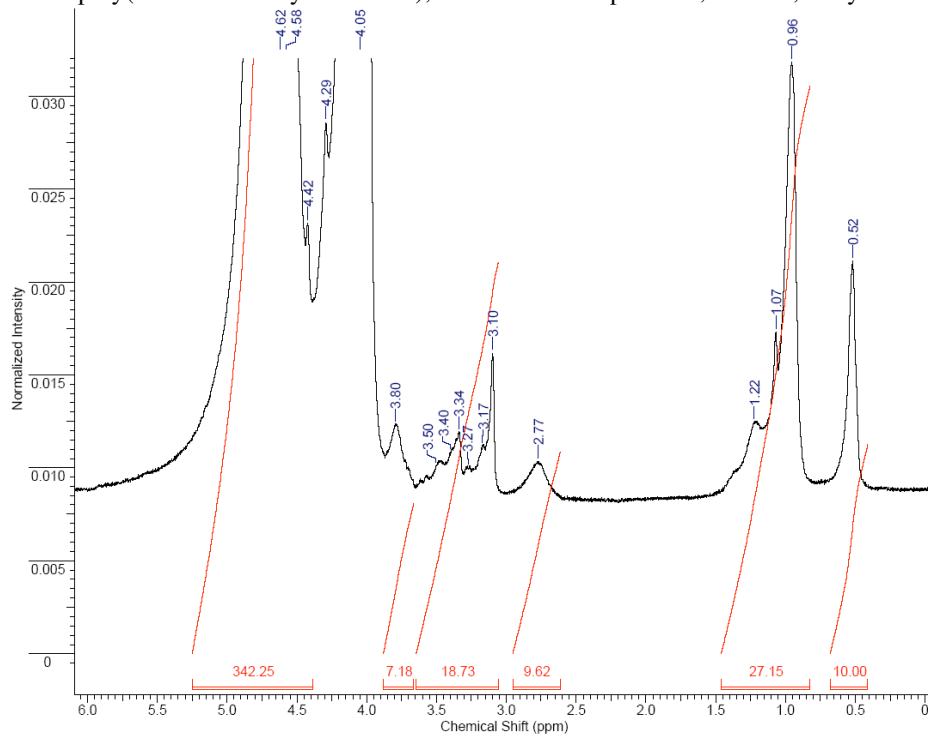
Copoly(trioxane/4-hexyldioxolane), 4.4 mol % incorporation, Table 1, entry 37



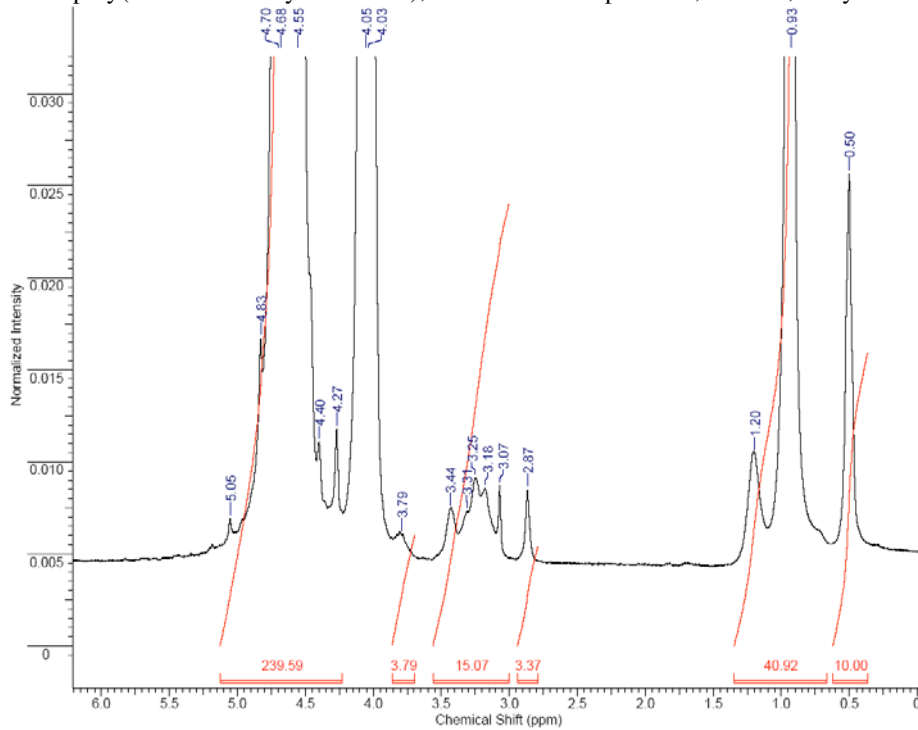
Copoly(trioxane/4-hexyldioxolane), 4.9 mol % incorporation, Table 1, entry 38



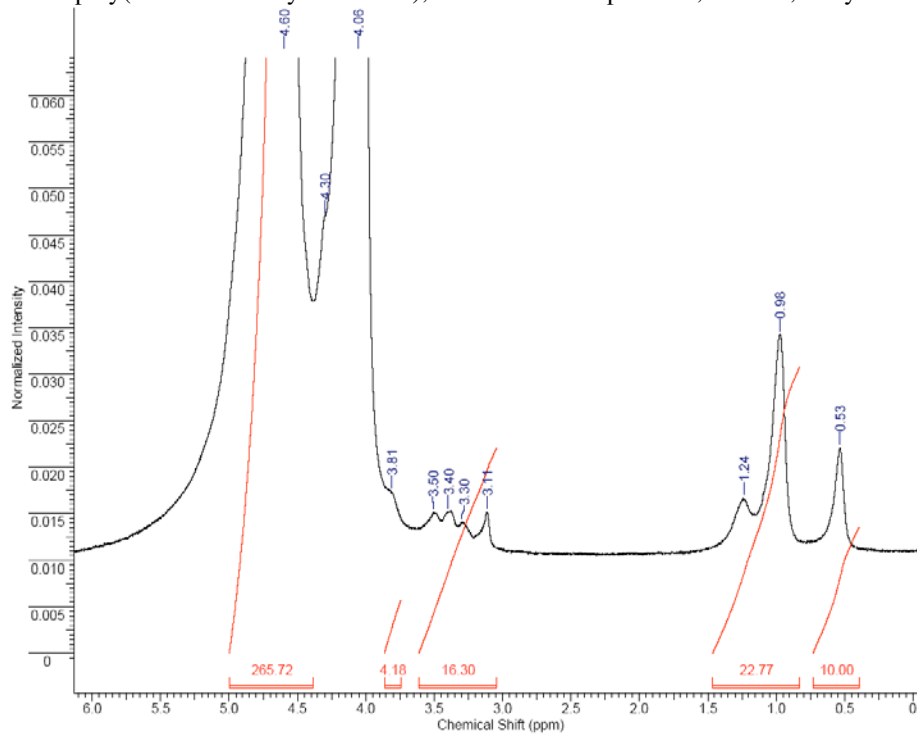
Copoly(trioxane/4-hexyldioxolane), 5.6 mol % incorporation, Table 1, entry 39



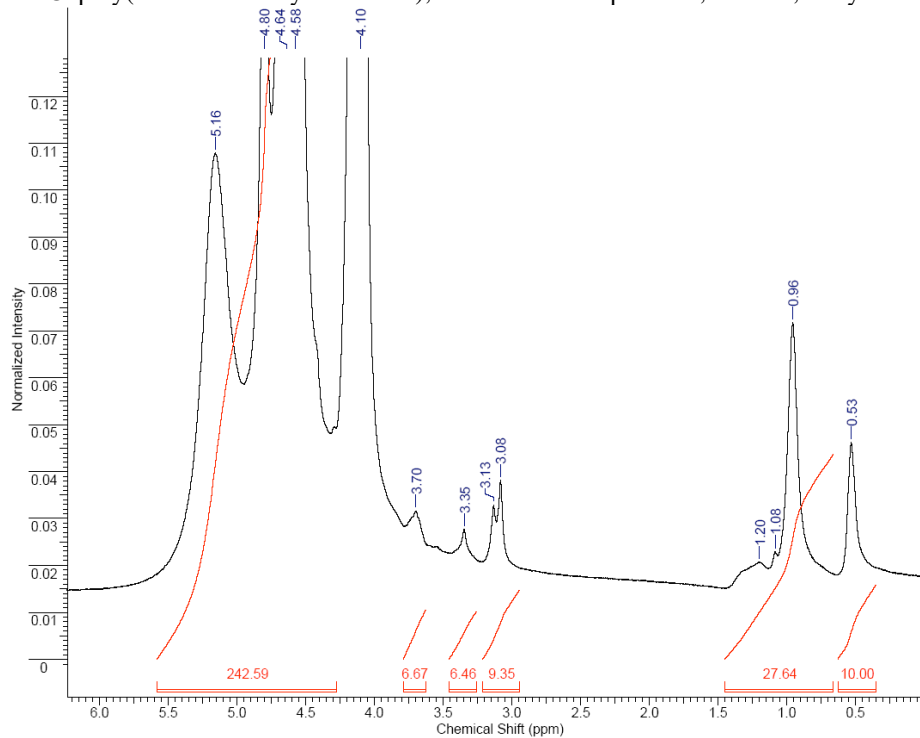
Copoly(trioxane/4-hexyldioxolane), 7.9 mol % incorporation, Table 1, entry 40



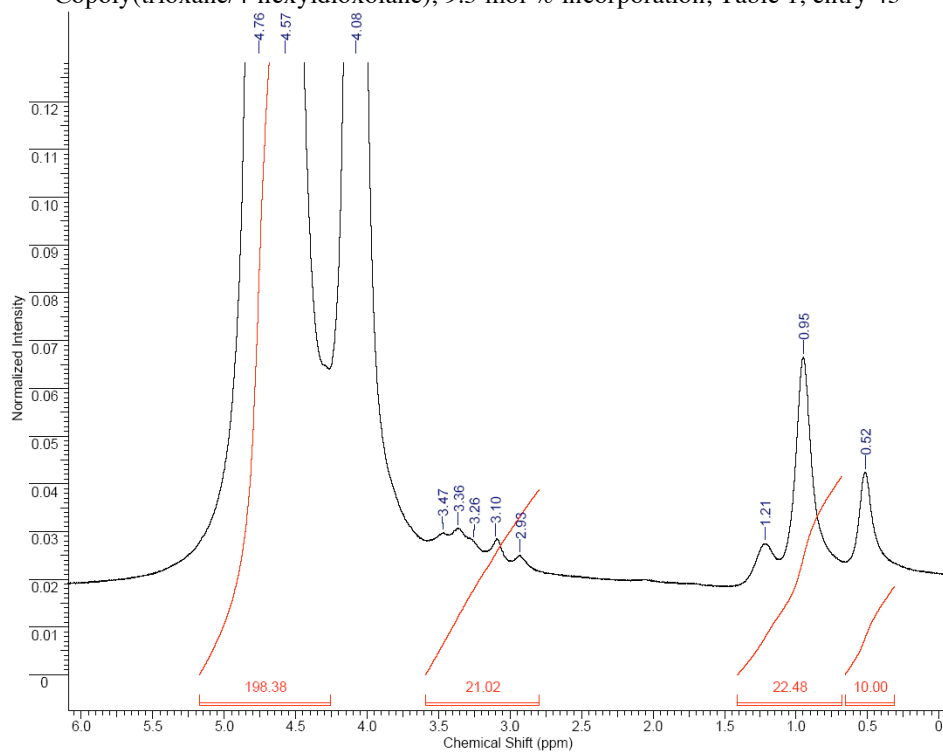
Copoly(trioxane/4-hexyldioxolane), 7.2 mol % incorporation, Table 1, entry 41



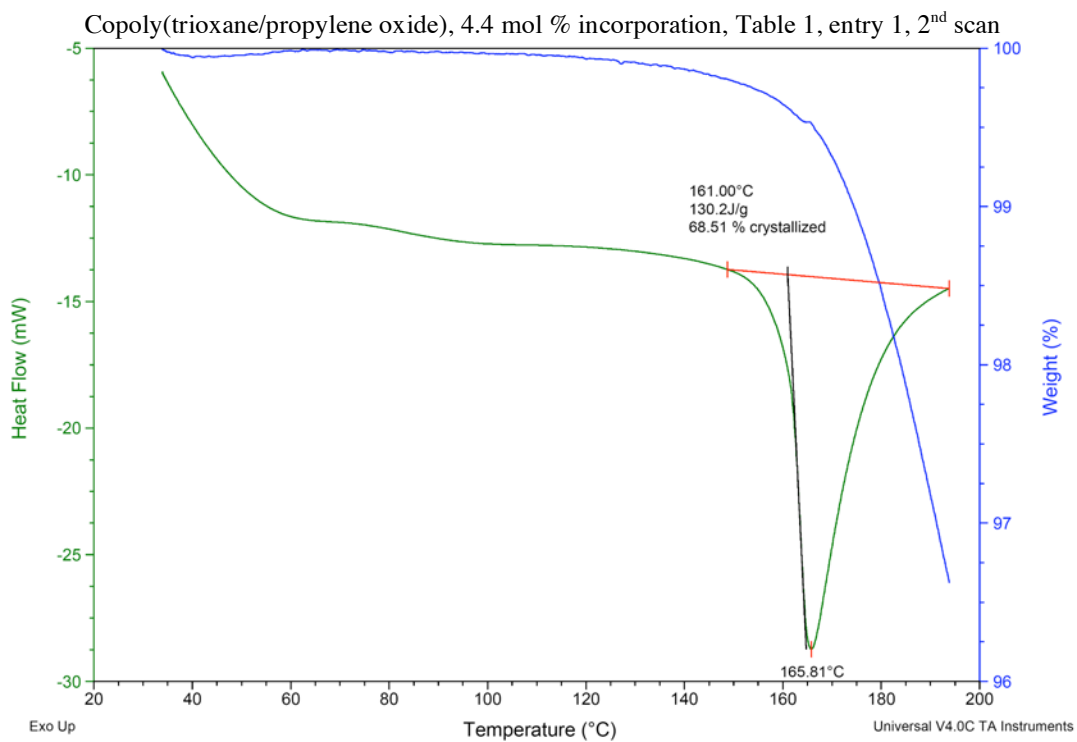
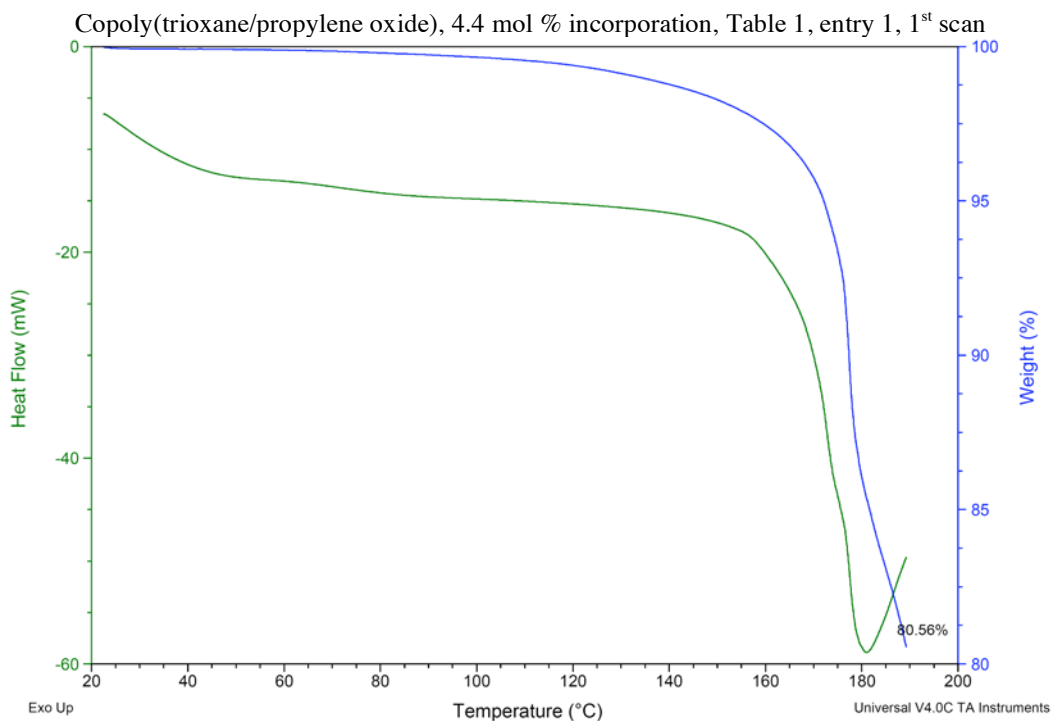
Copoly(trioxane/4-hexyldioxolane), 7.8 mol % incorporation, Table 1, entry 42

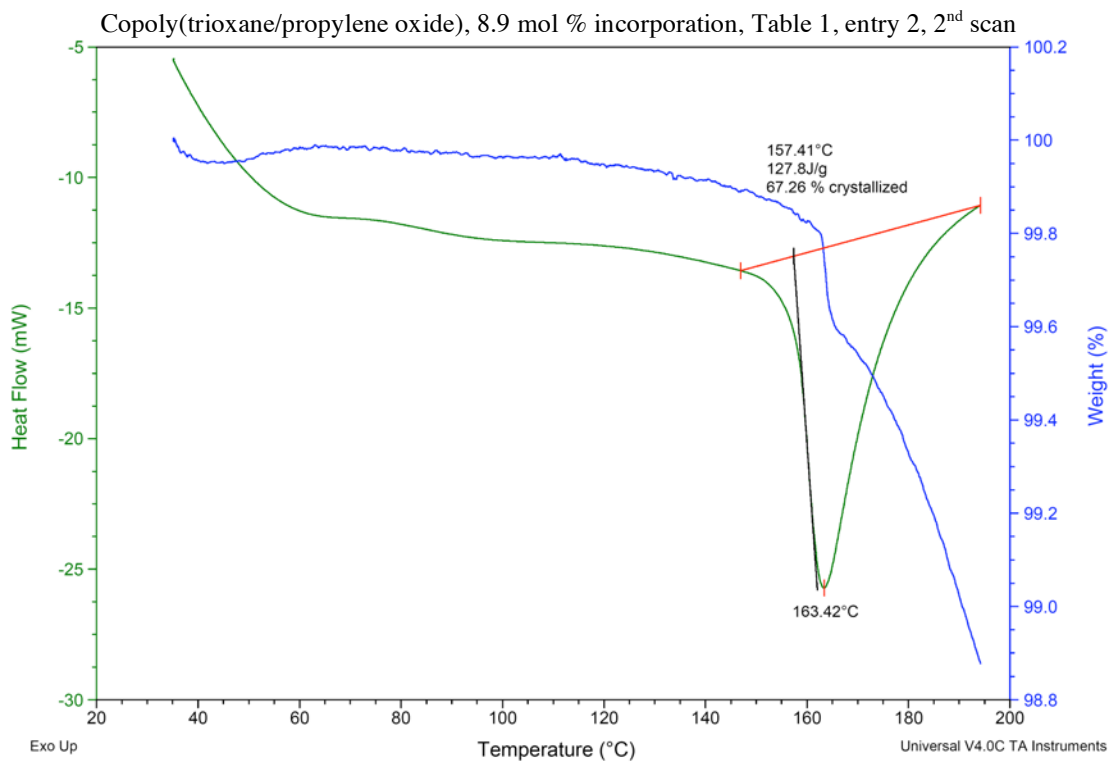
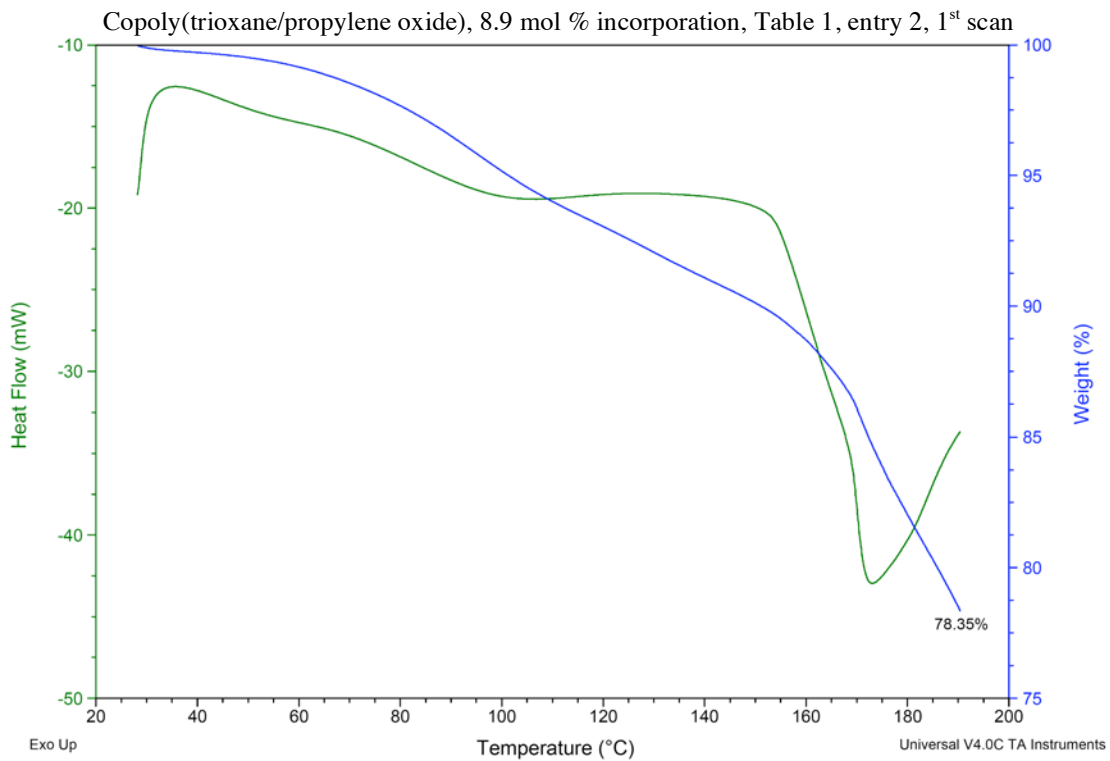


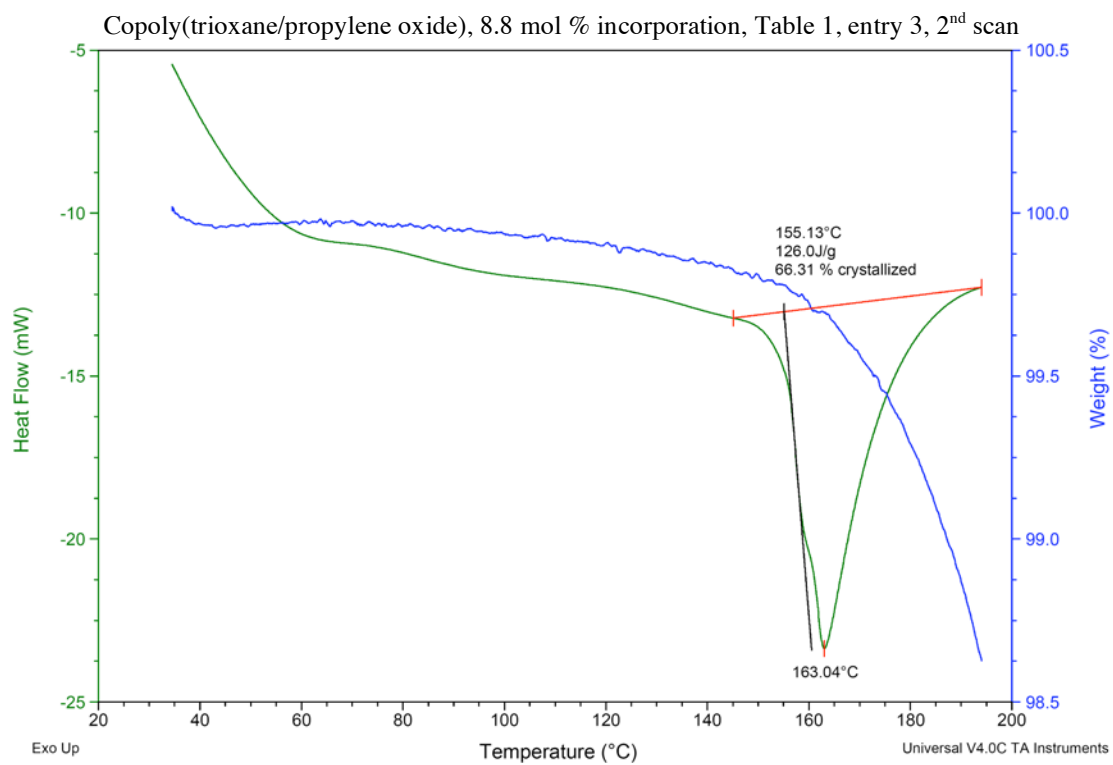
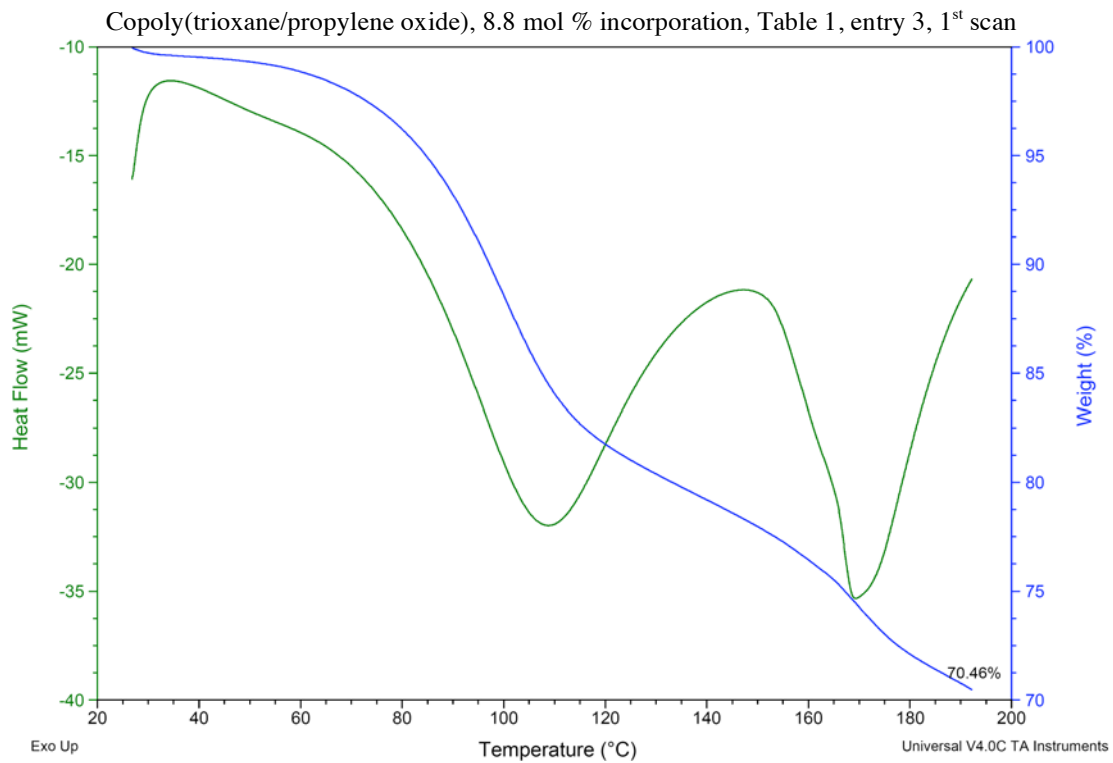
Copoly(trioxane/4-hexyldioxolane), 9.5 mol % incorporation, Table 1, entry 43

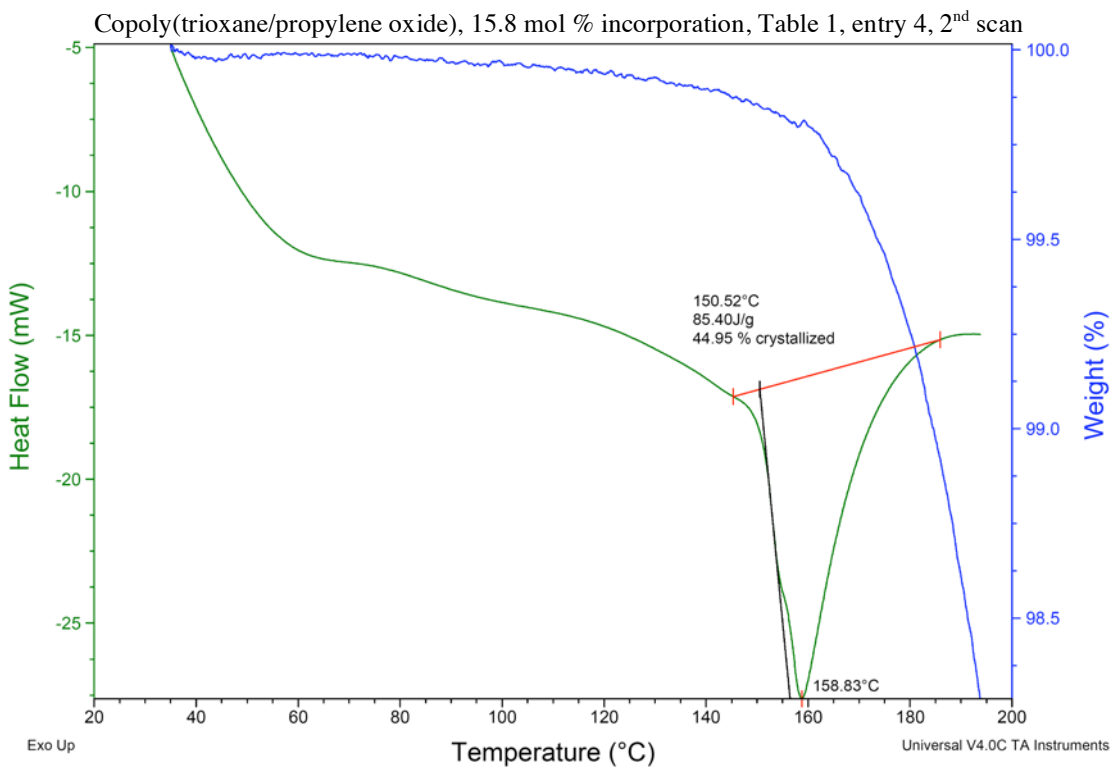
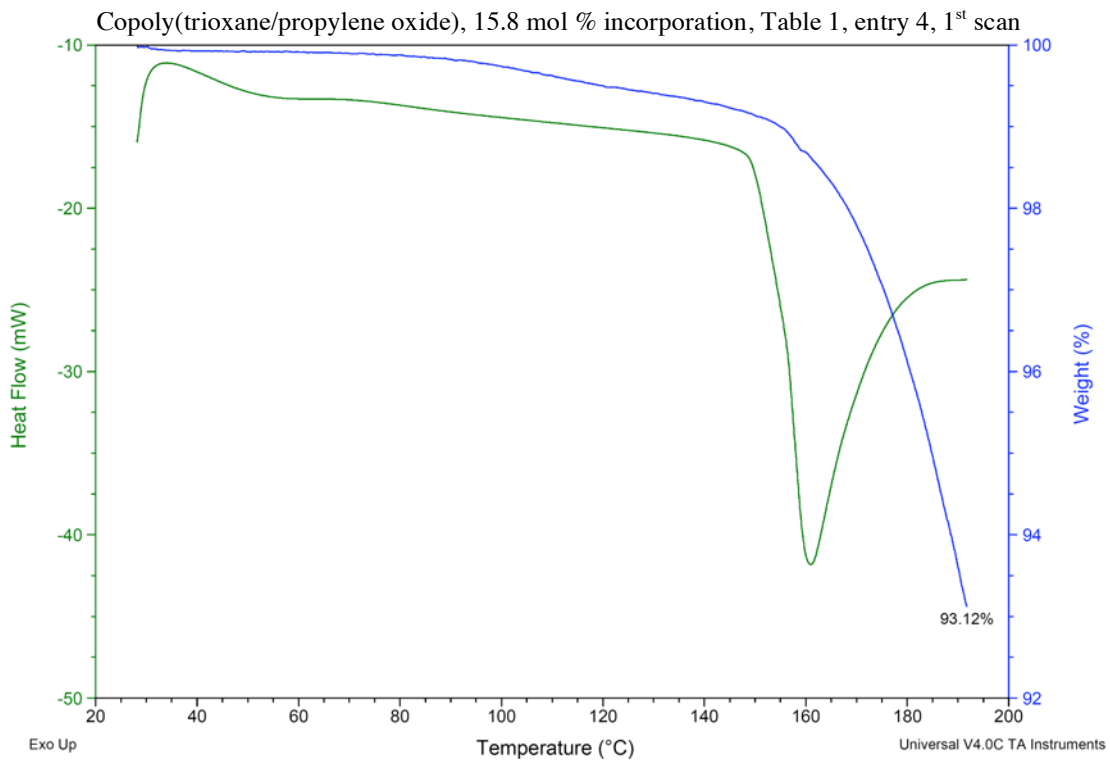


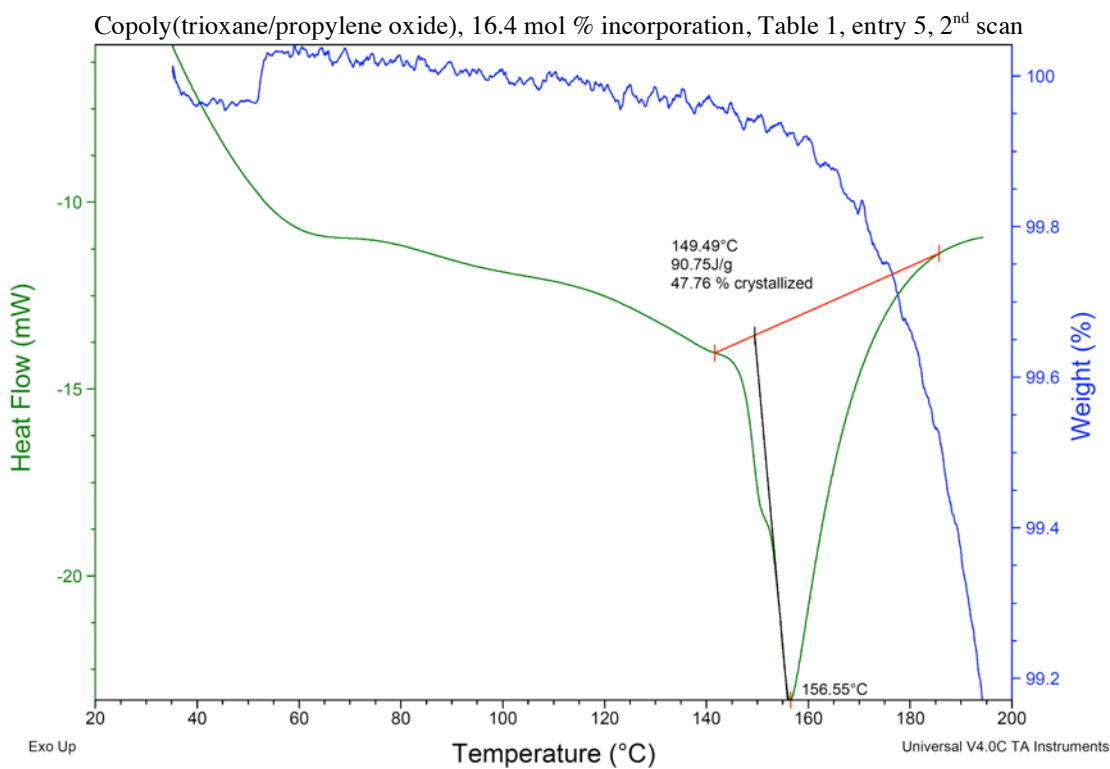
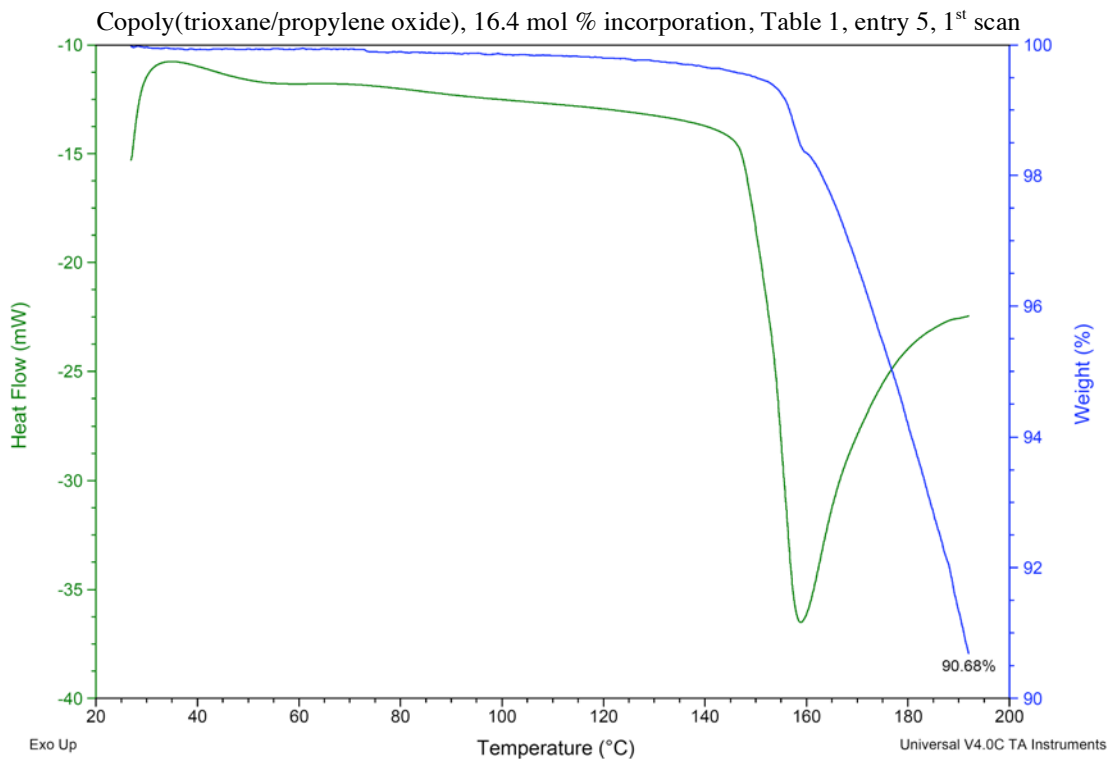
Differential Scanning Calorimetry/Thermal Gravimetric Analysis Data

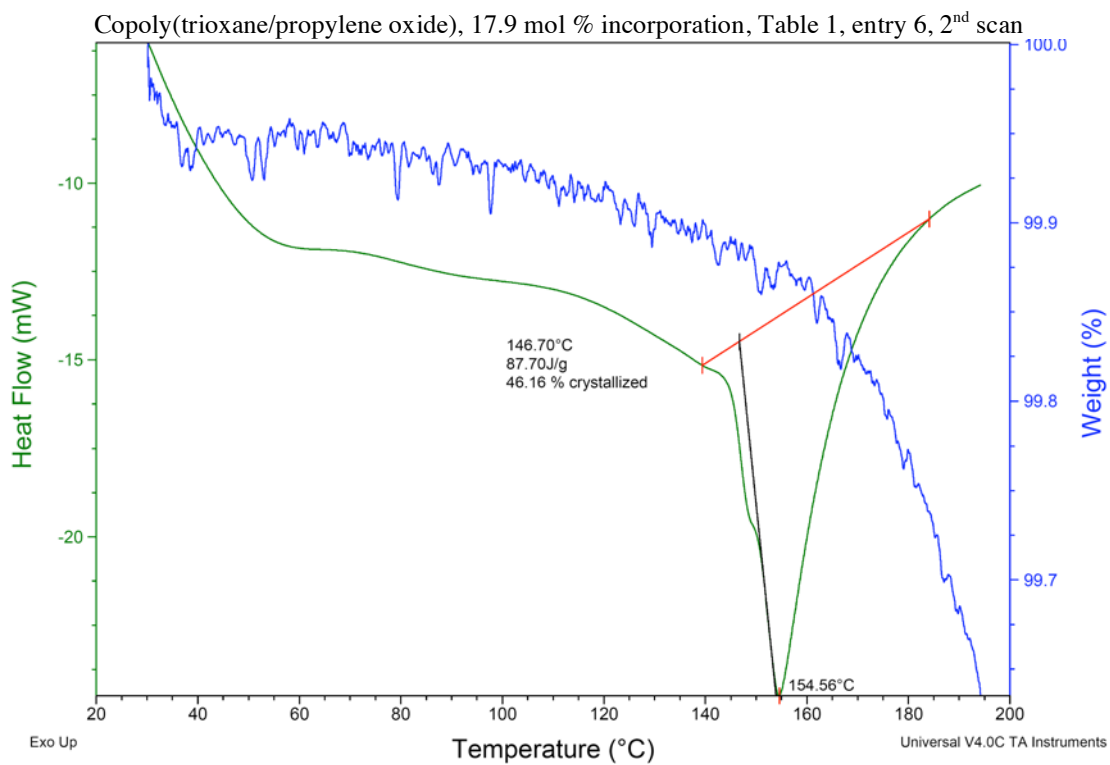
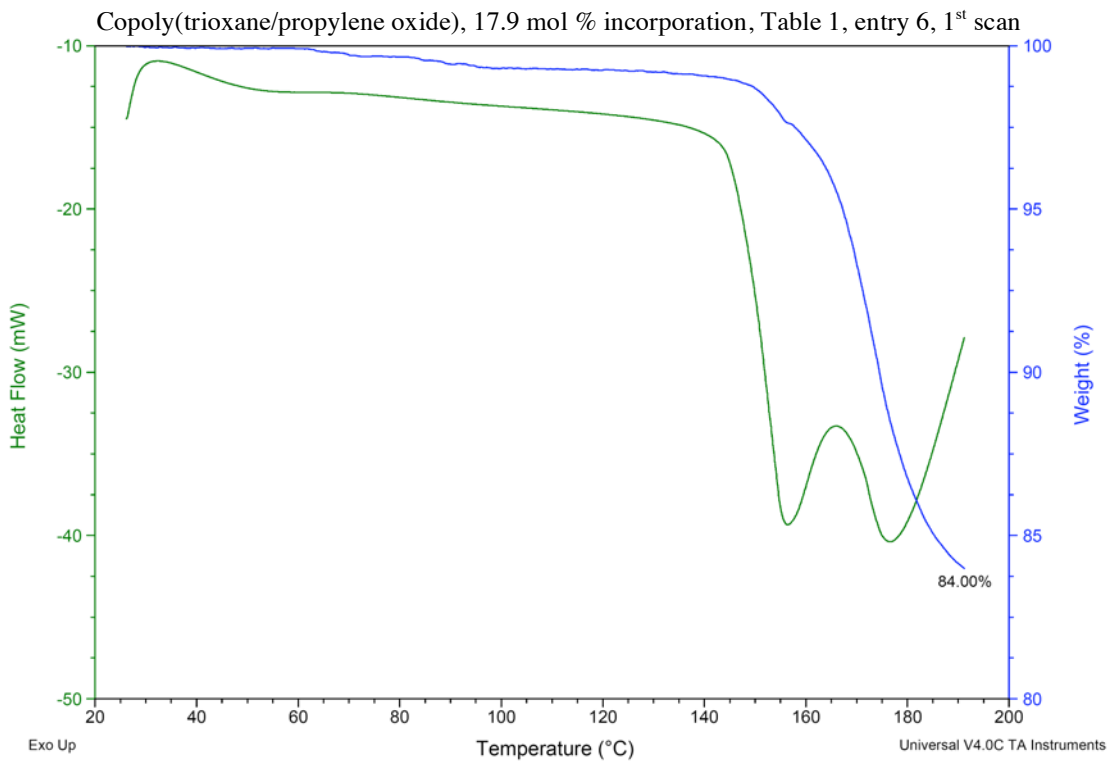


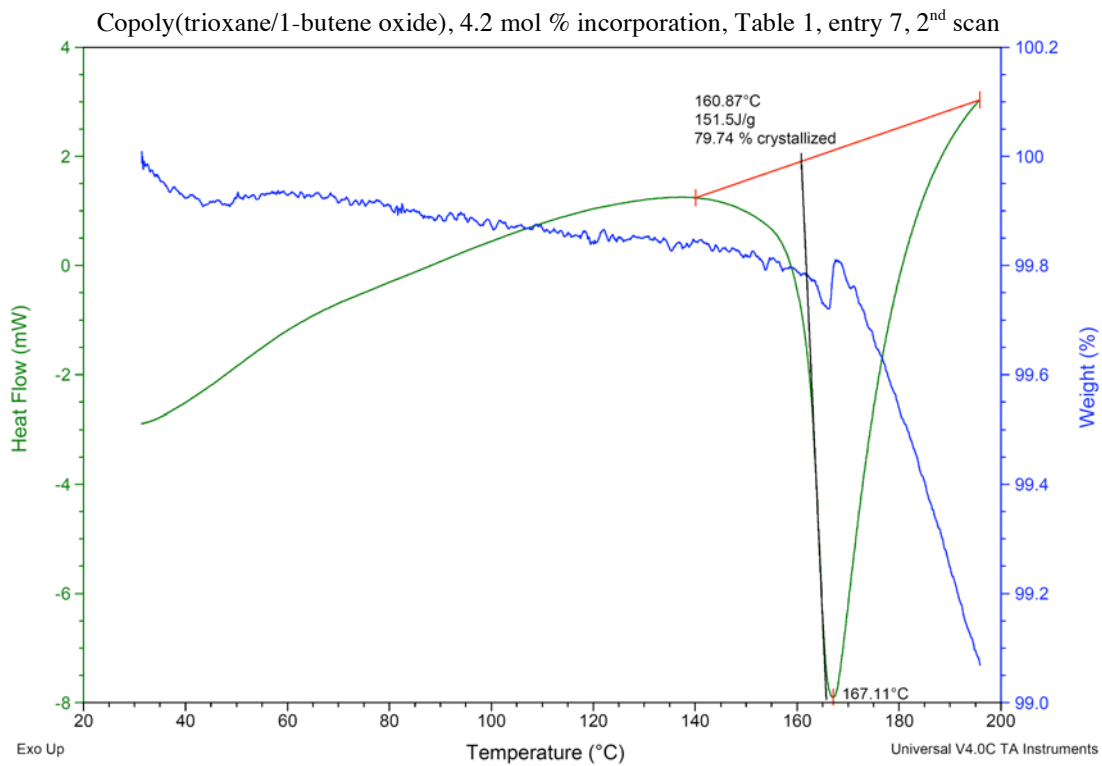
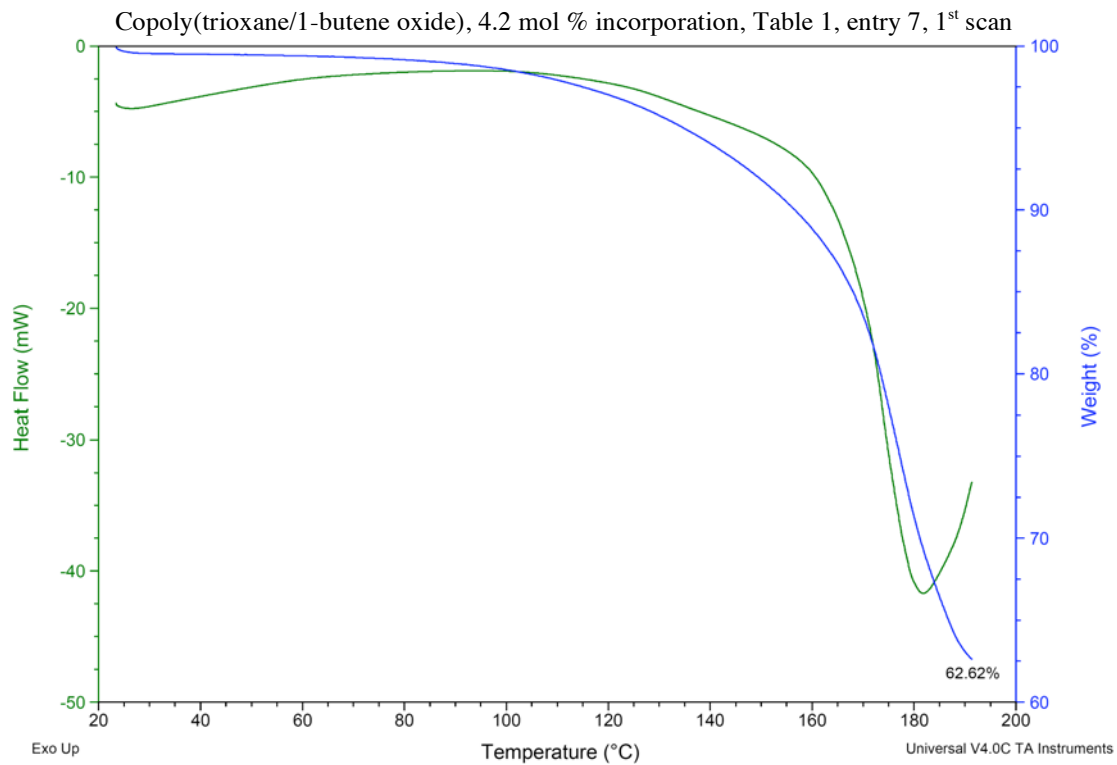


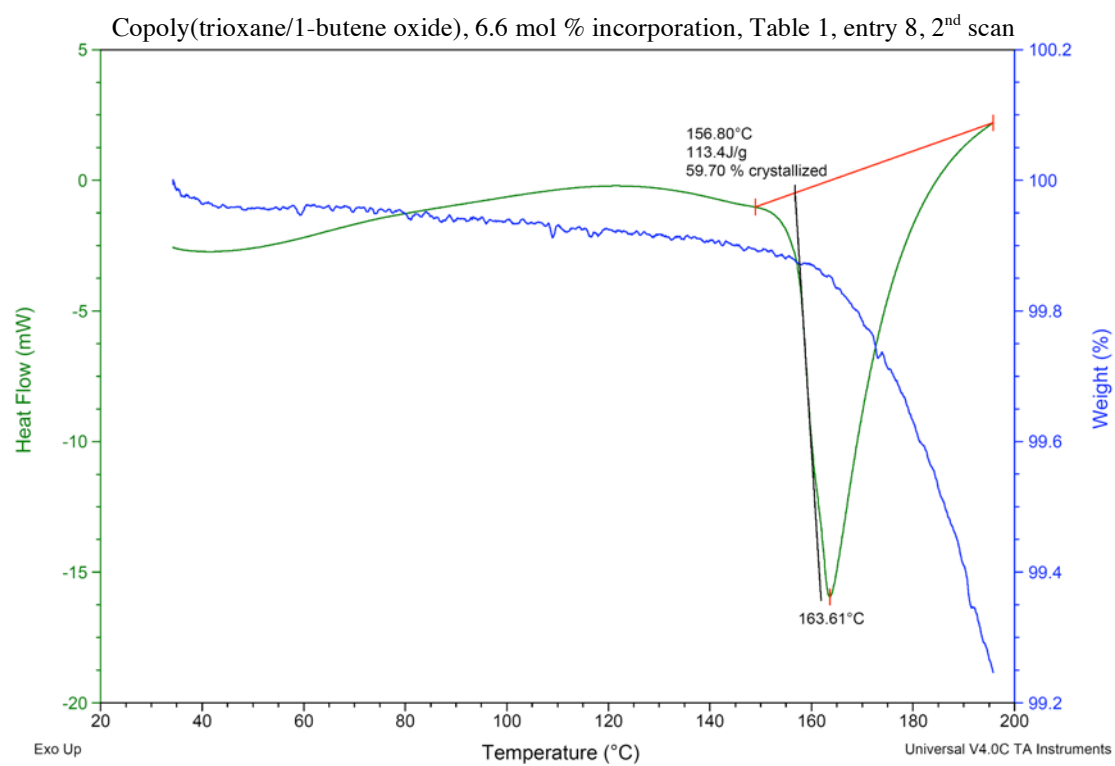
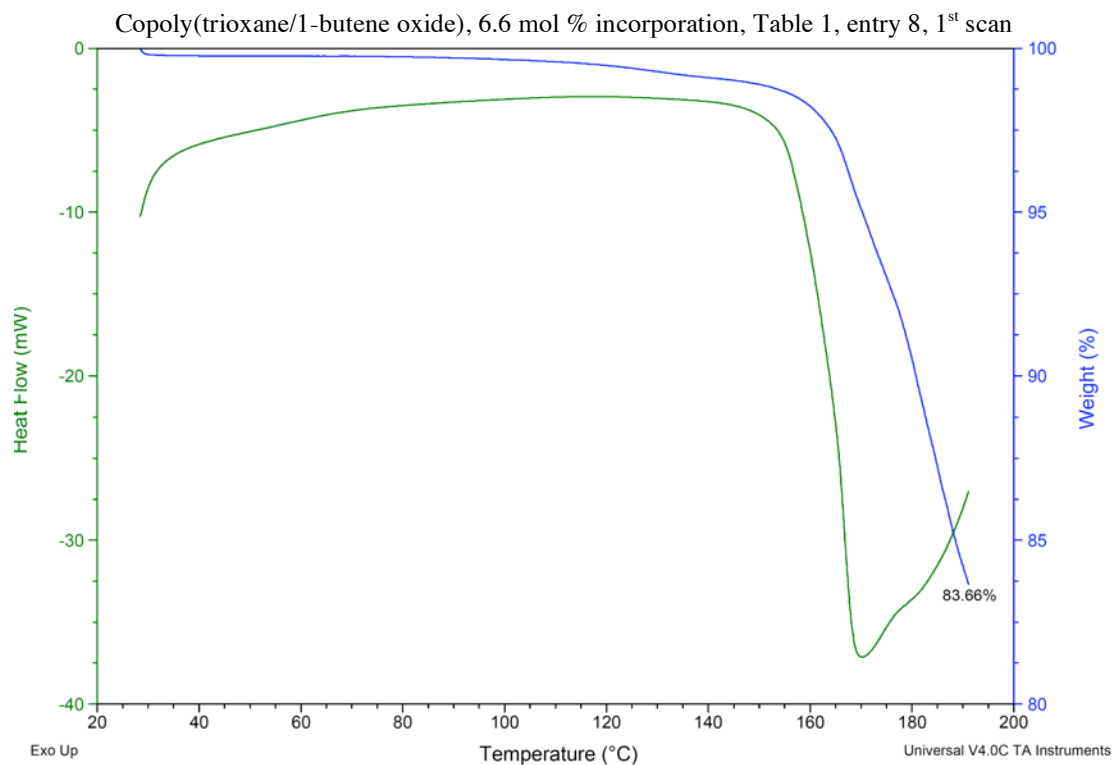


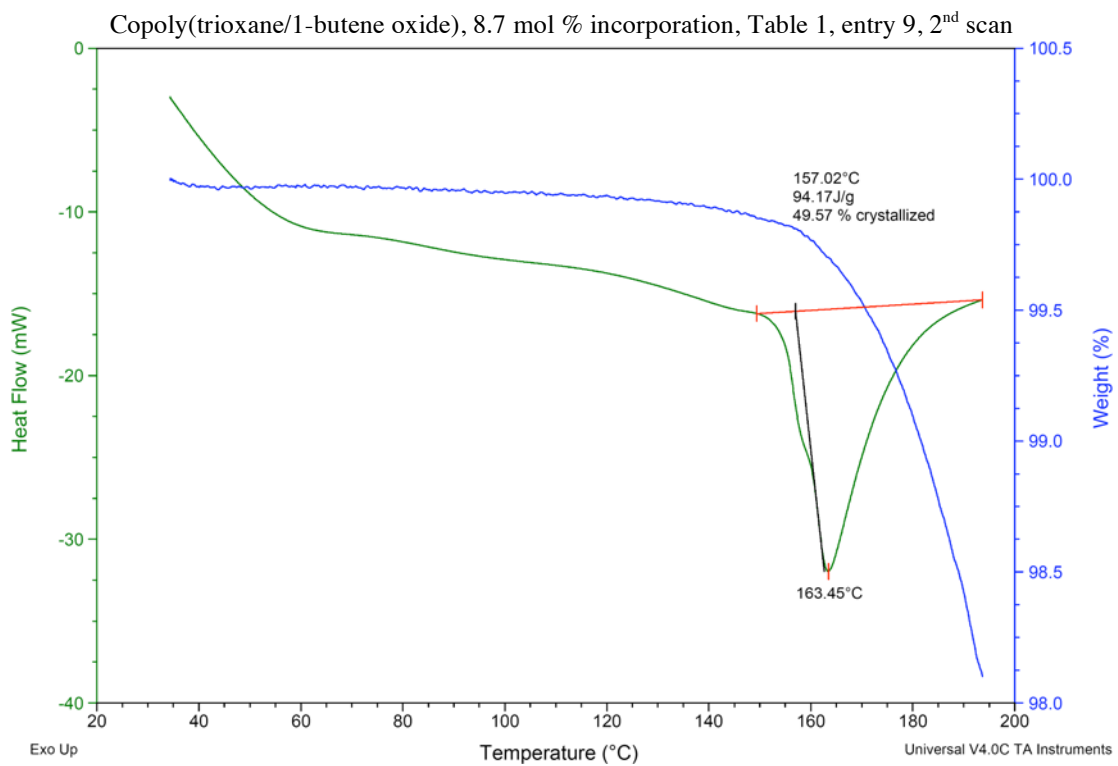
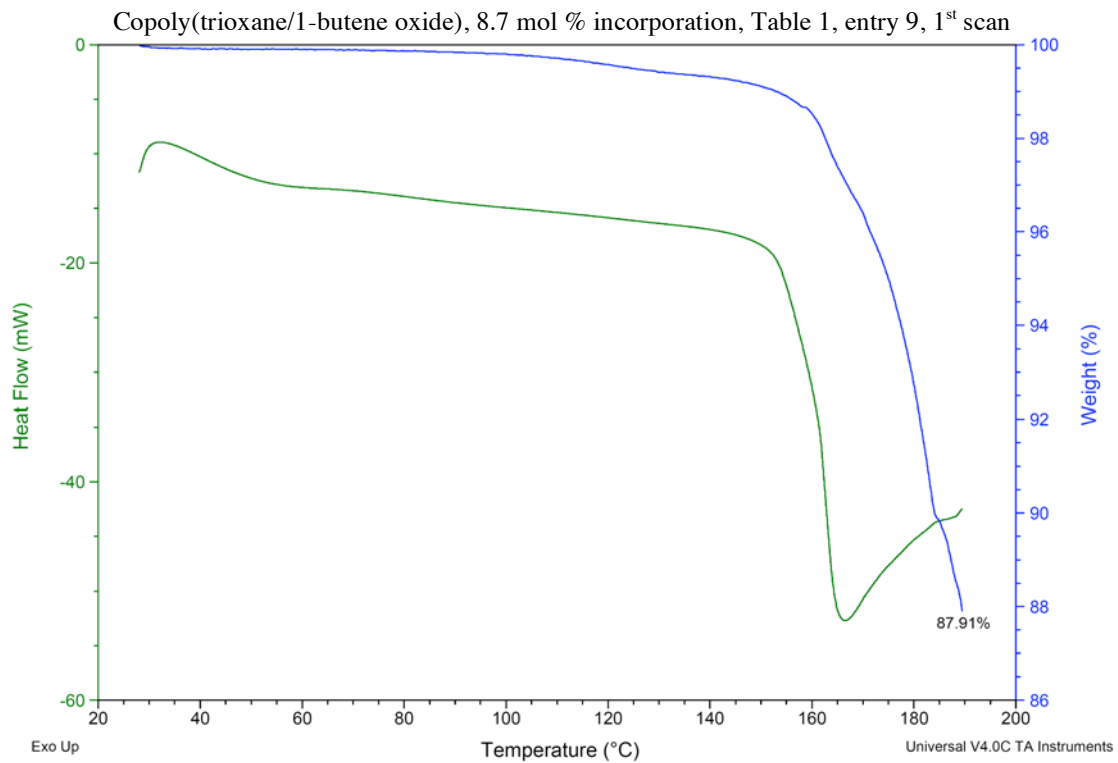


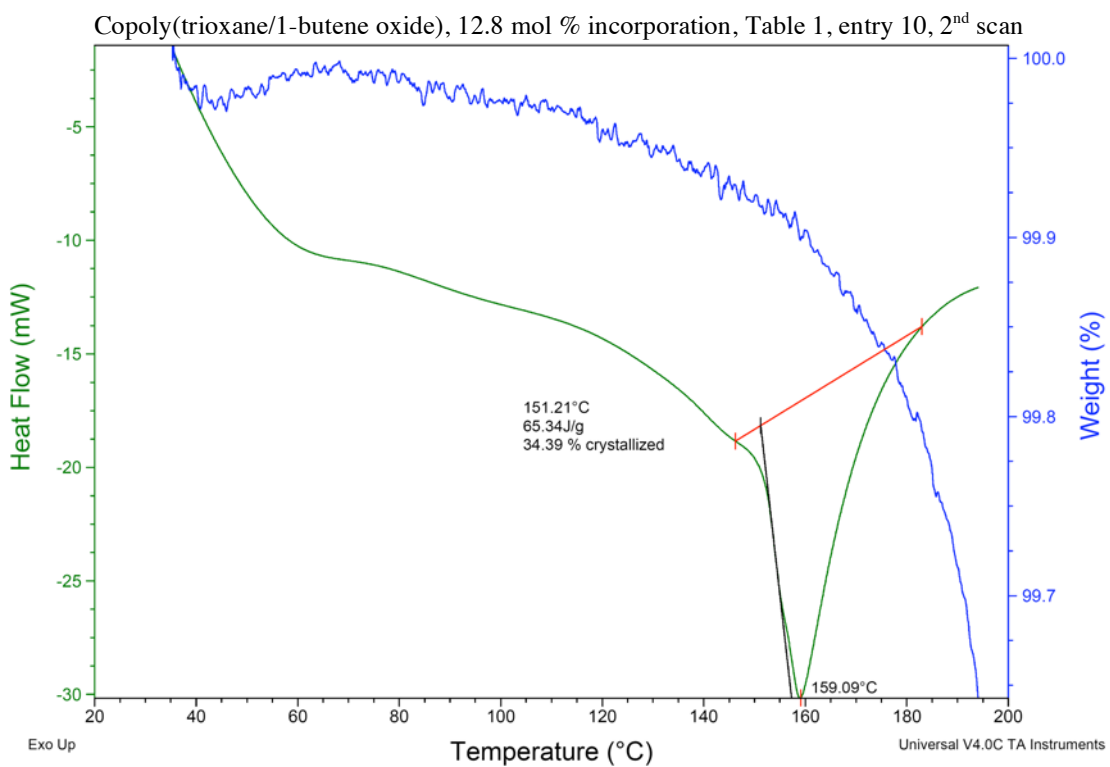
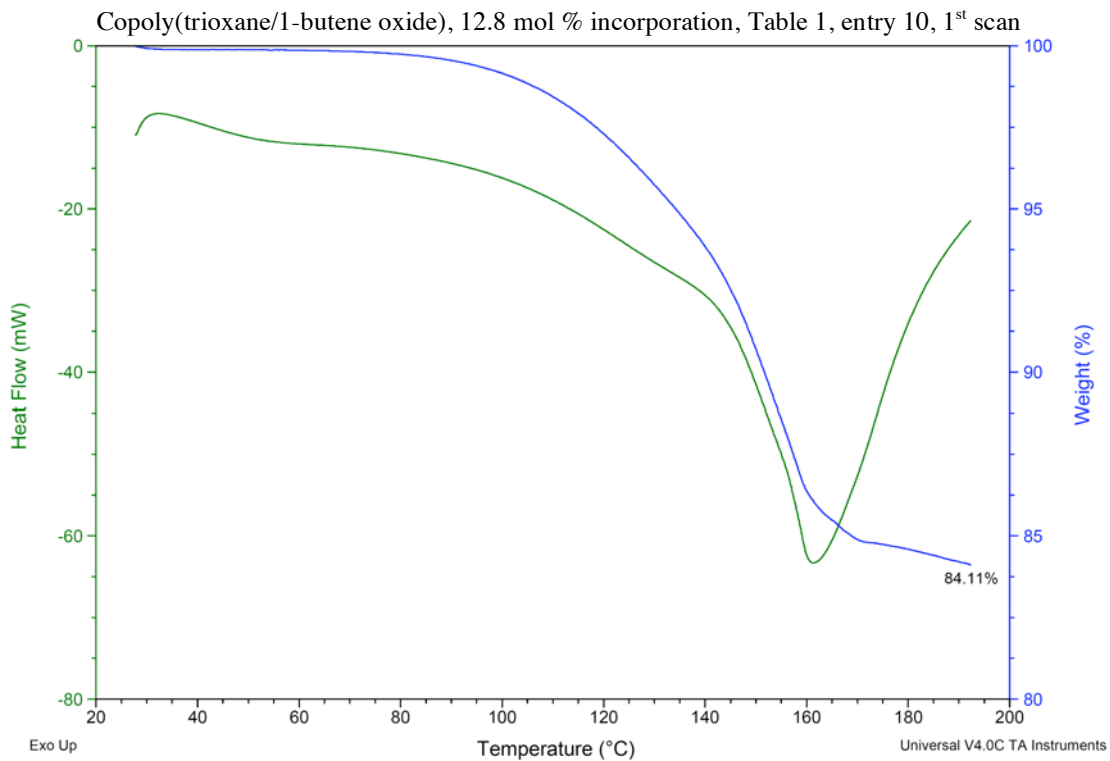


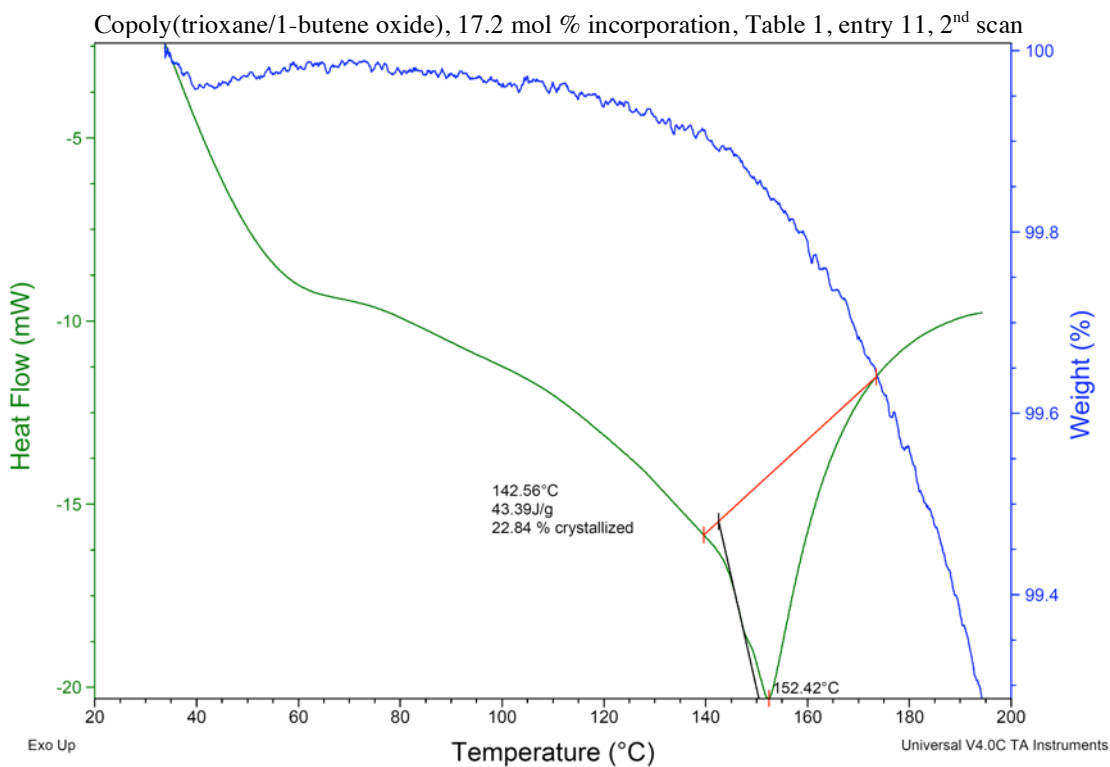
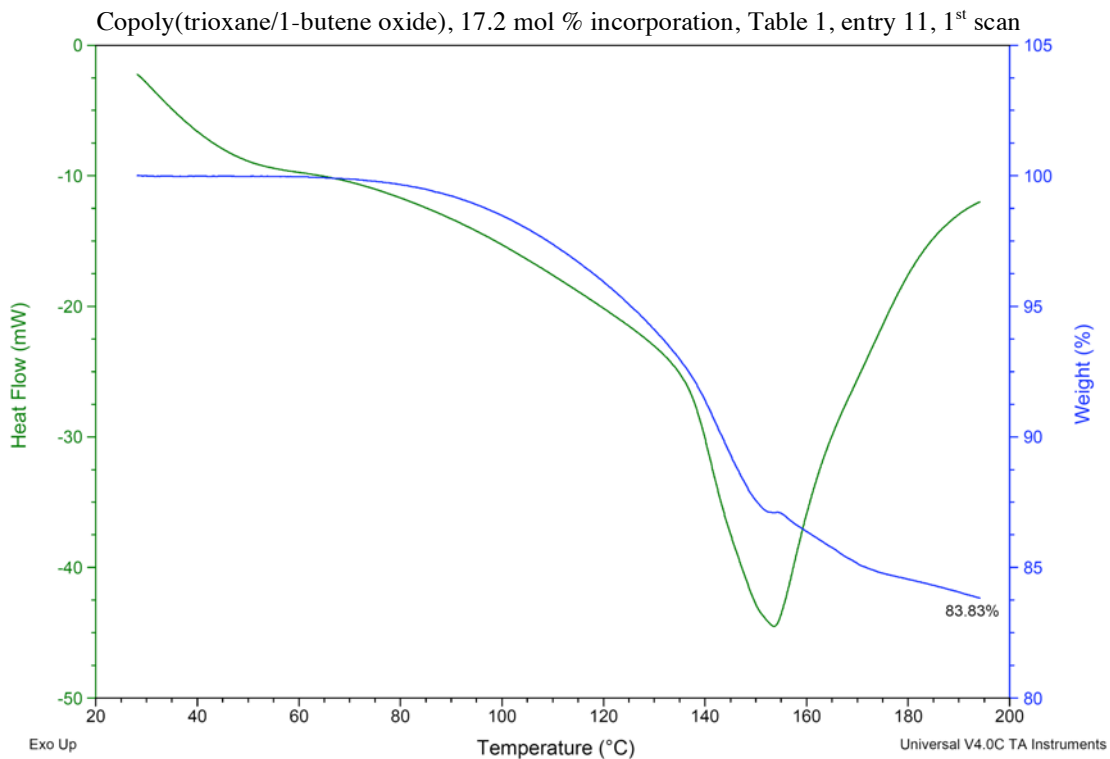


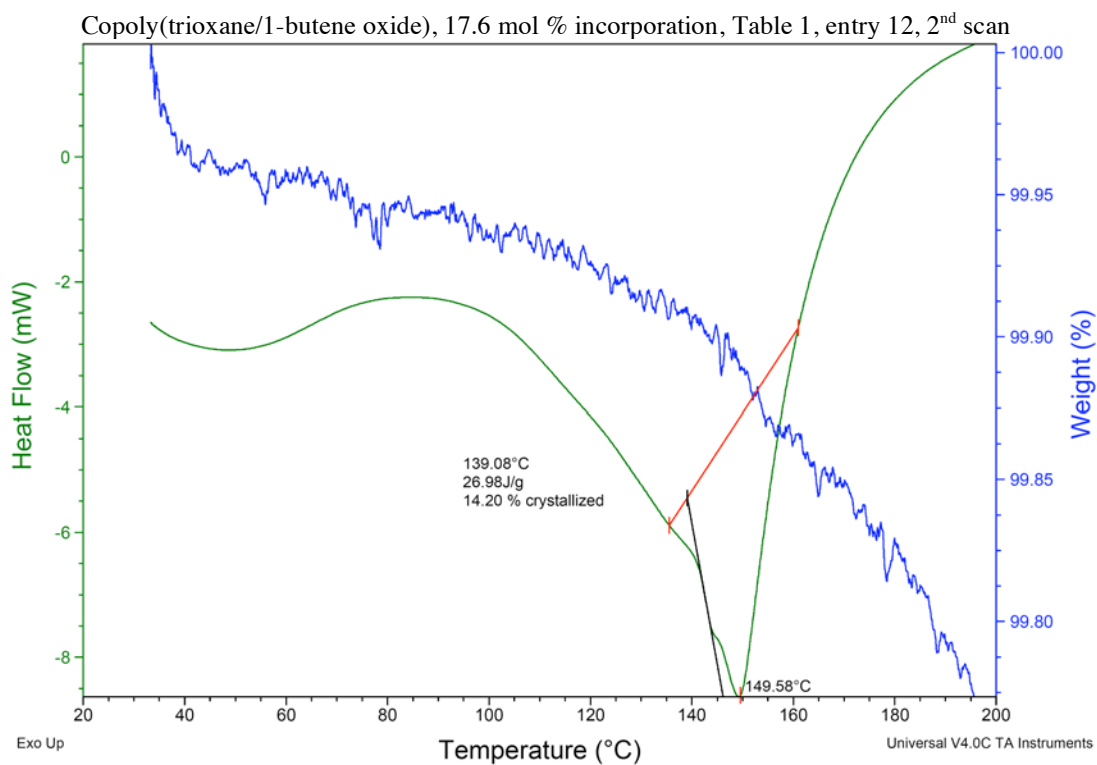
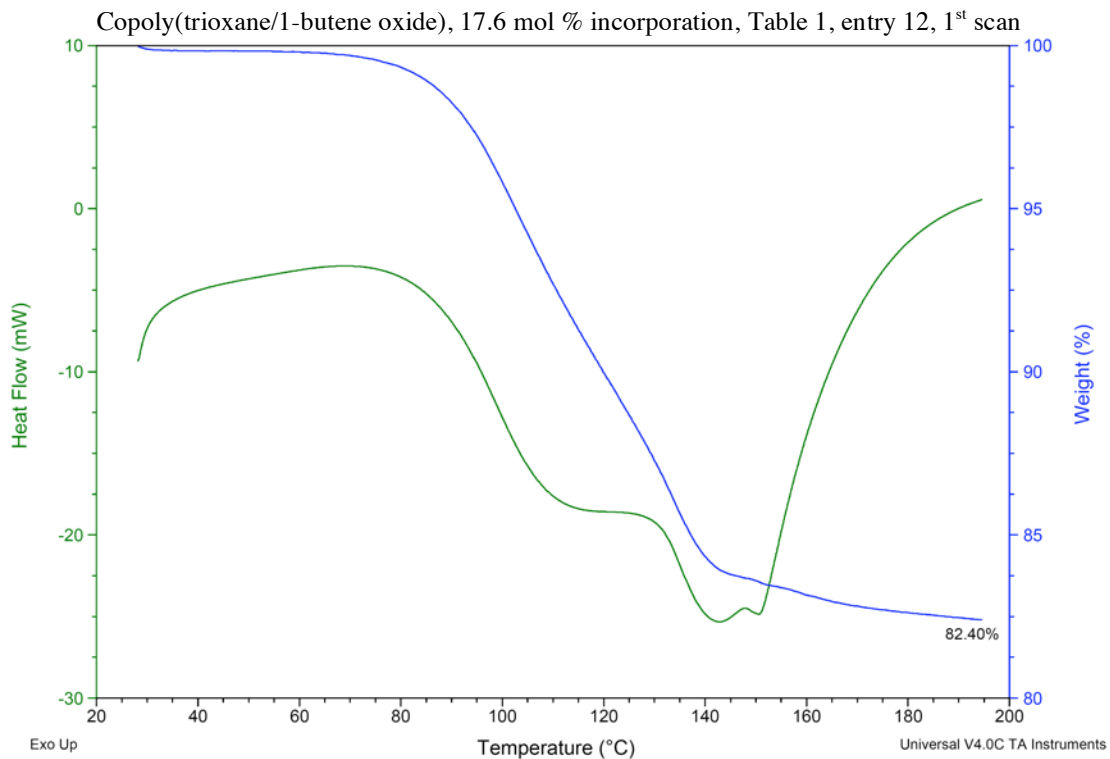


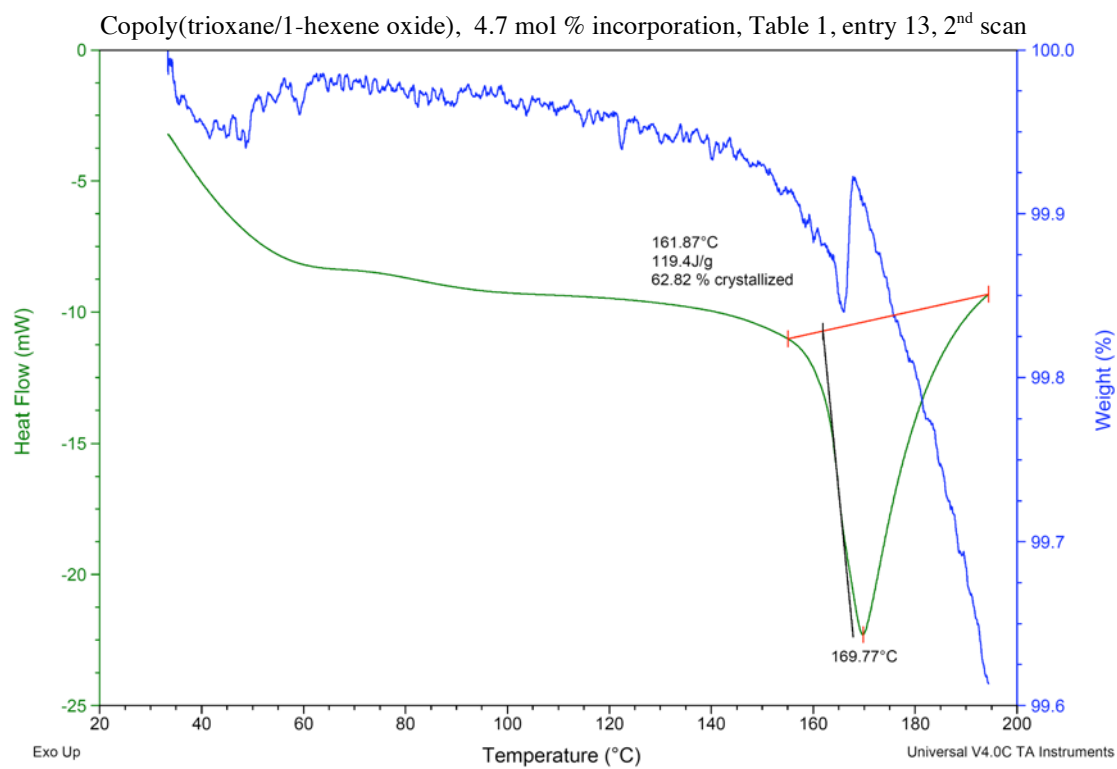
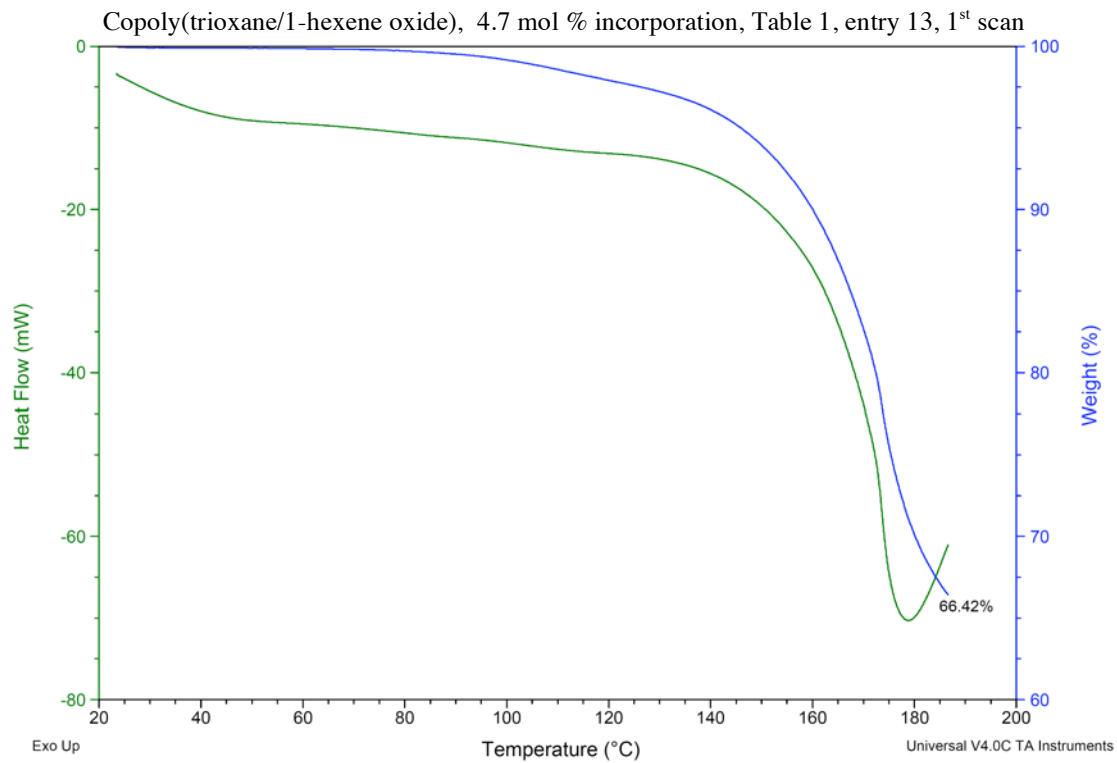


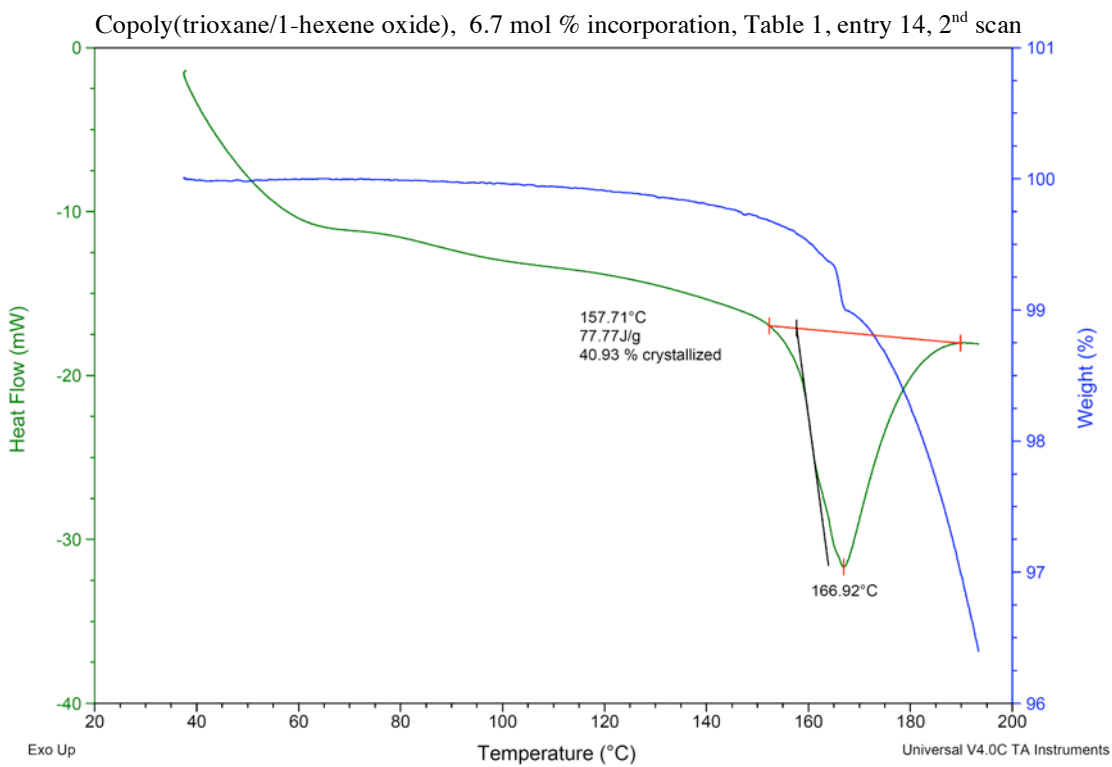
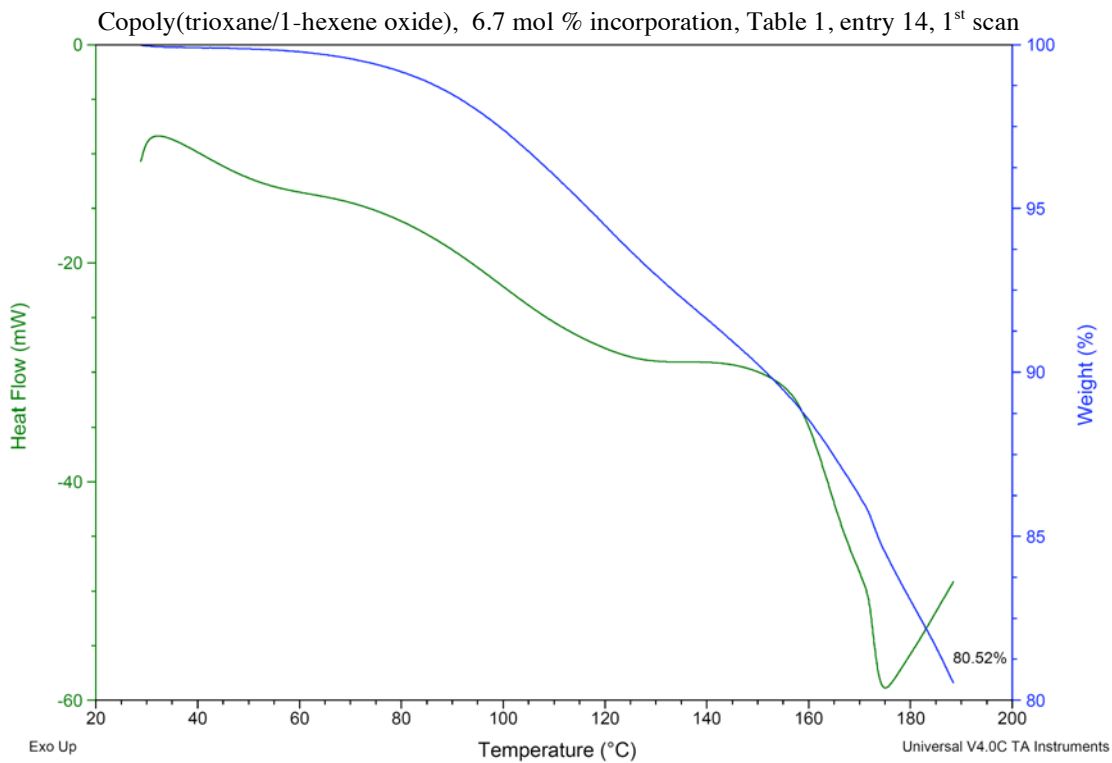


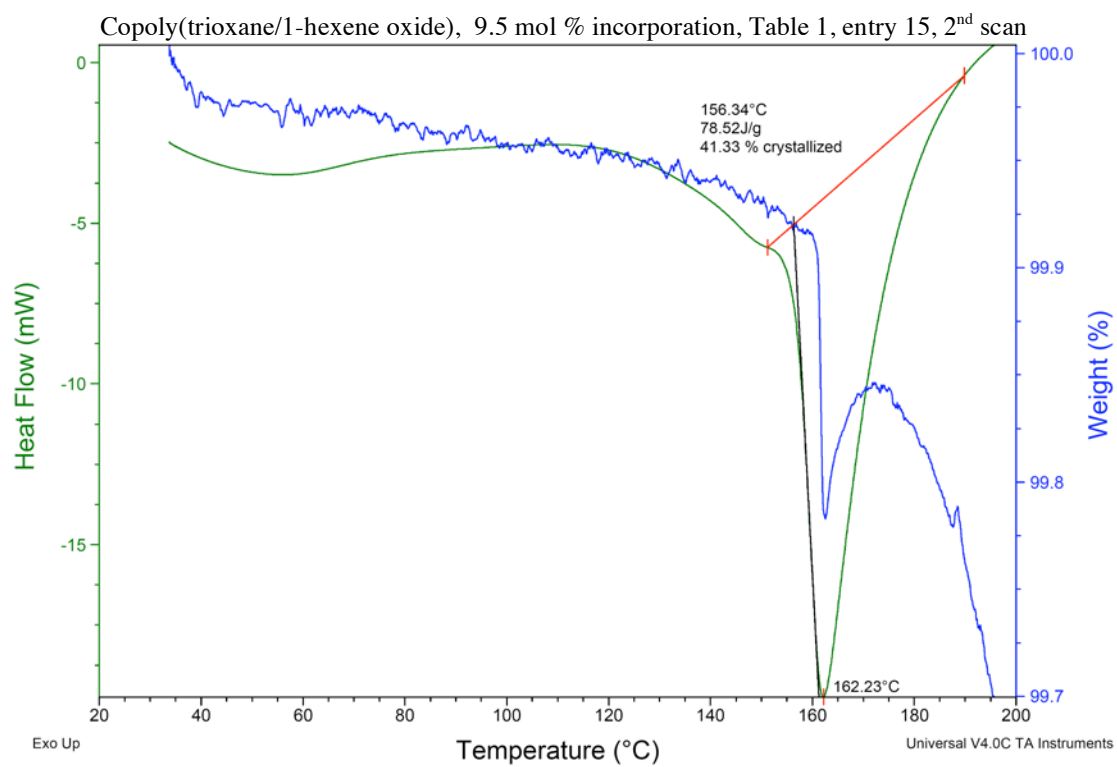
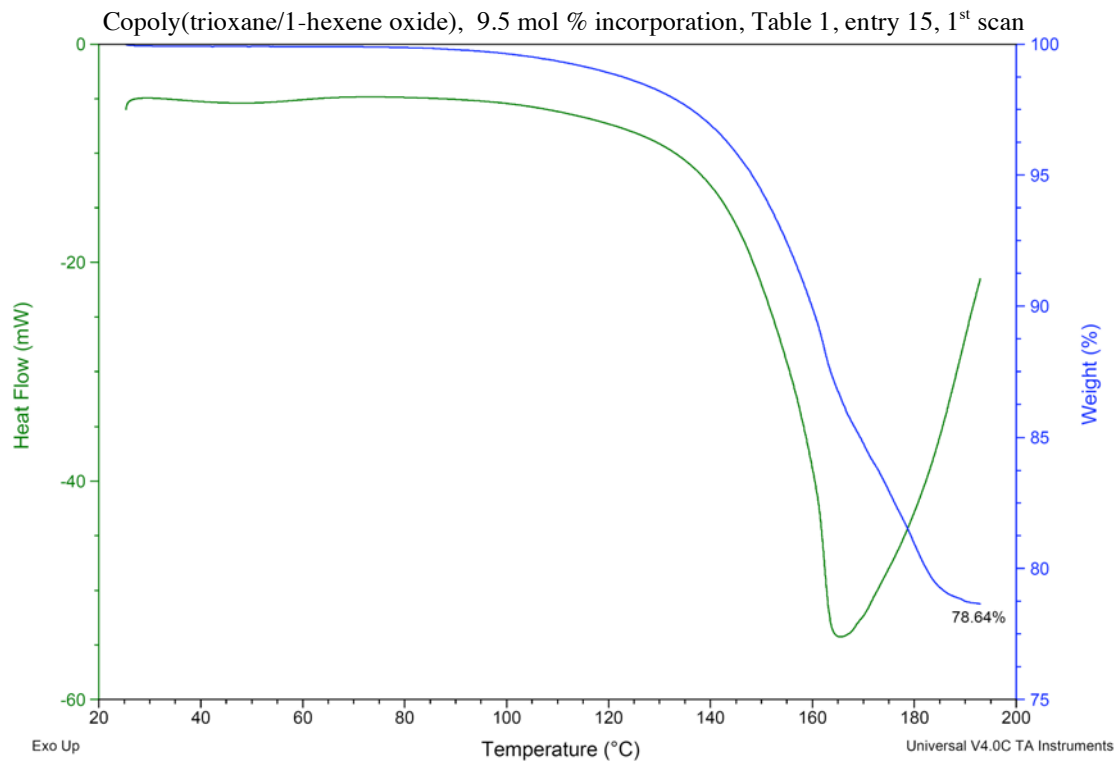


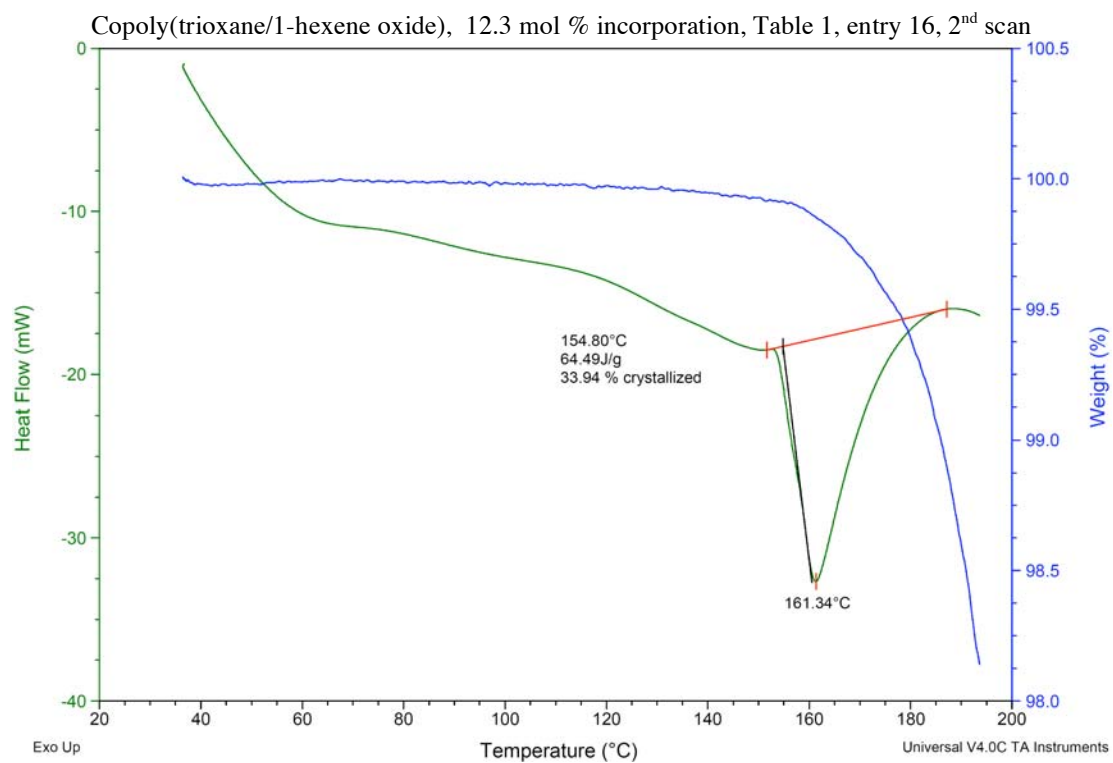
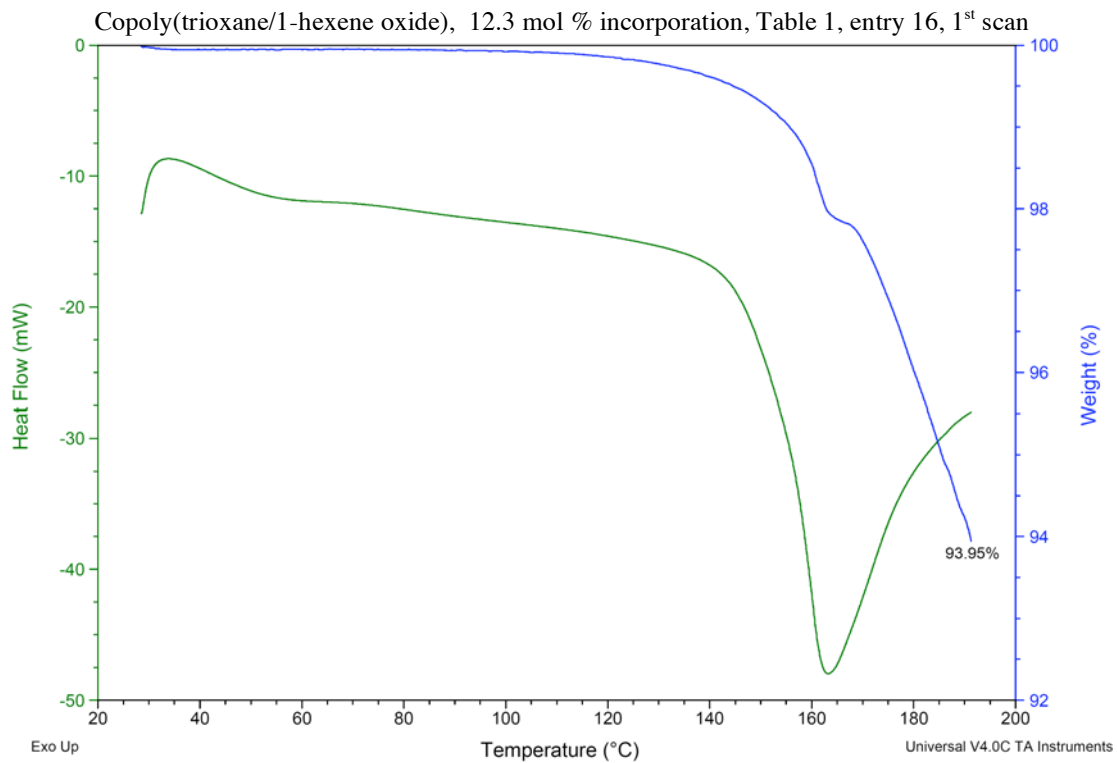


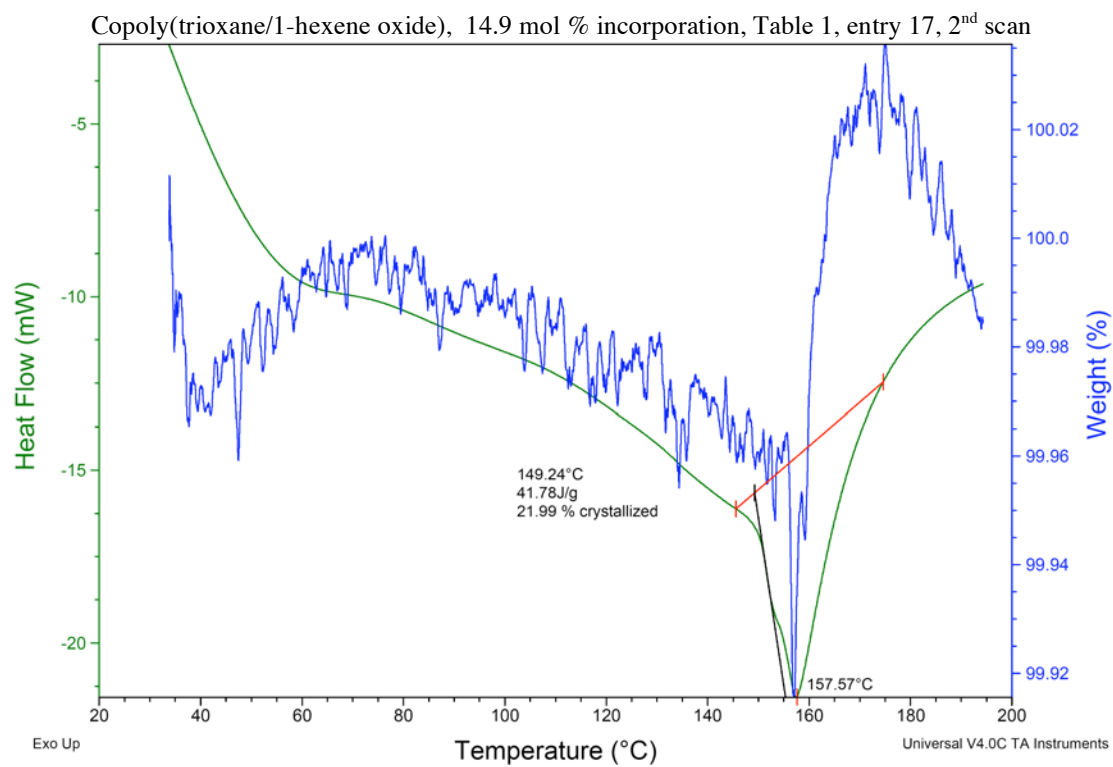
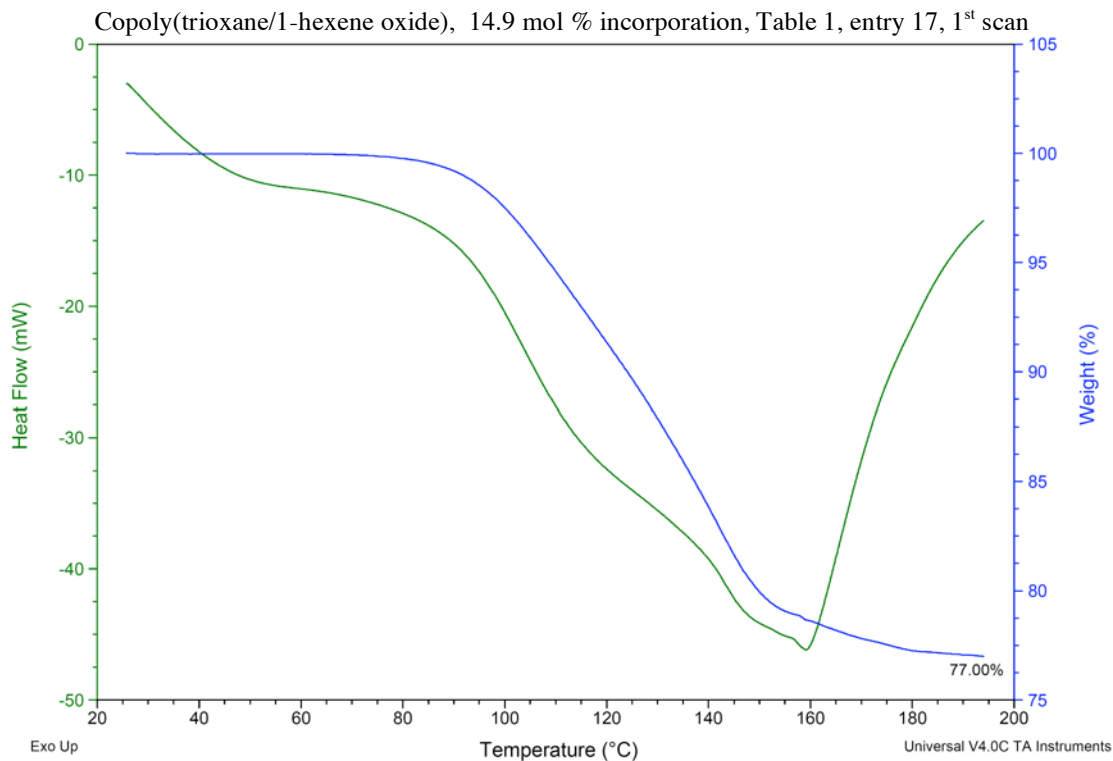


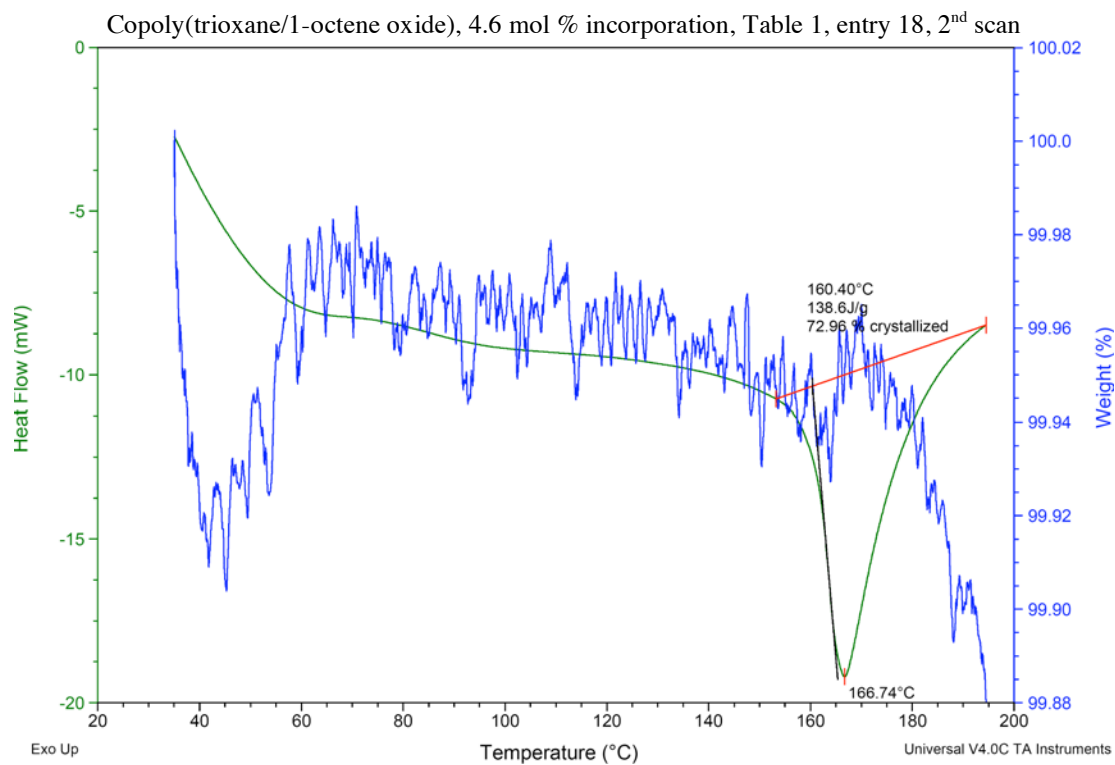
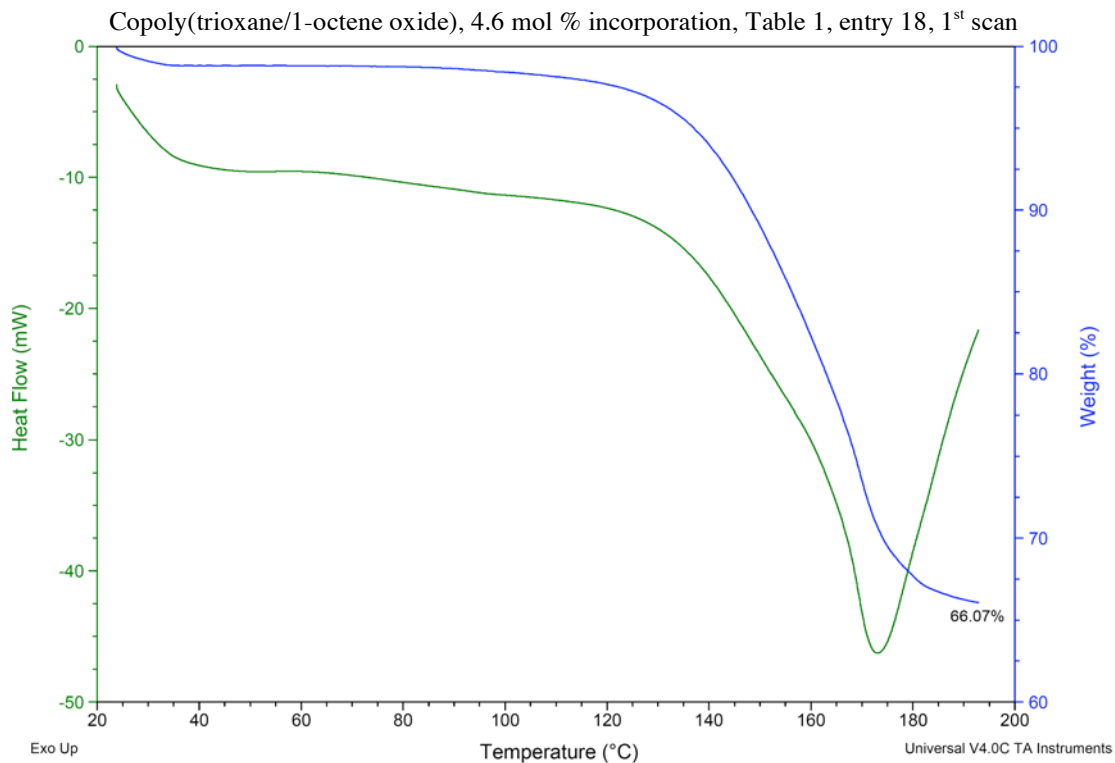


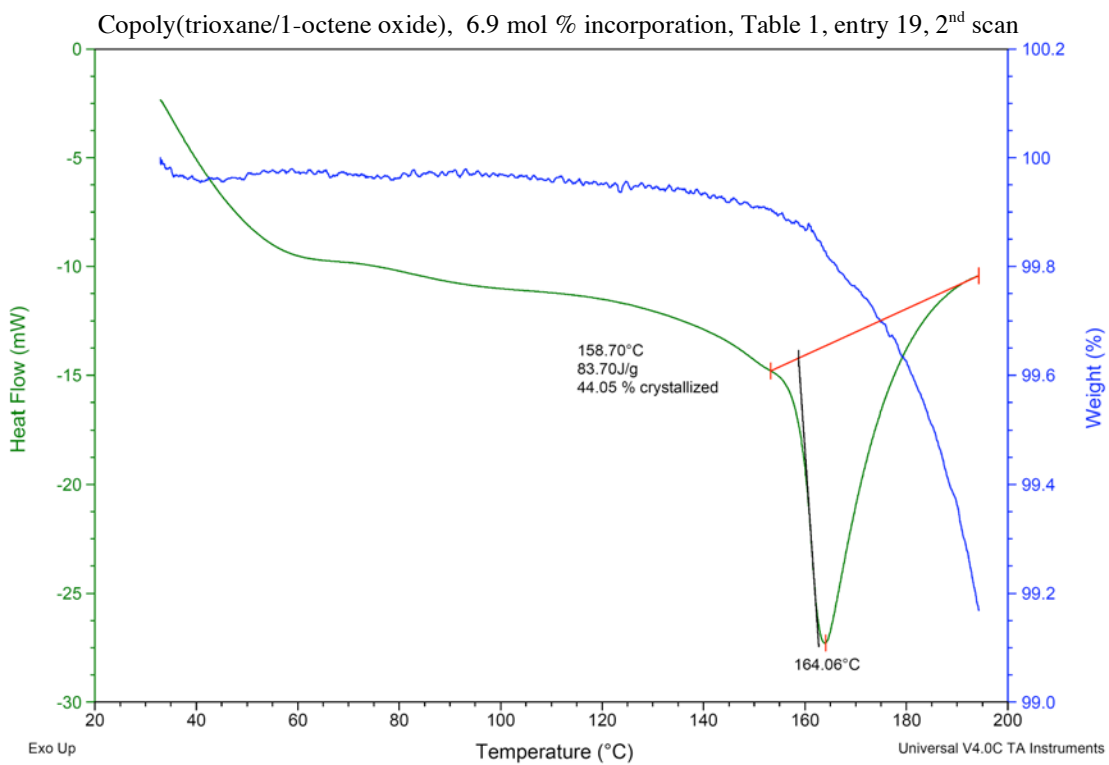
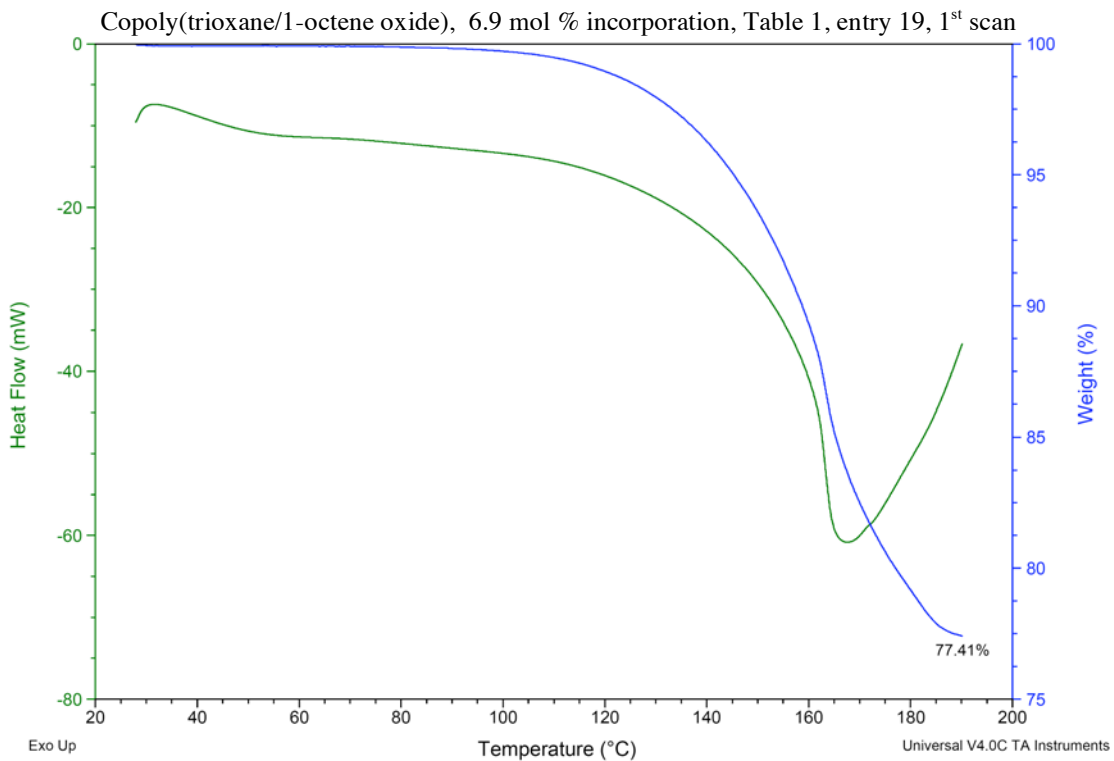


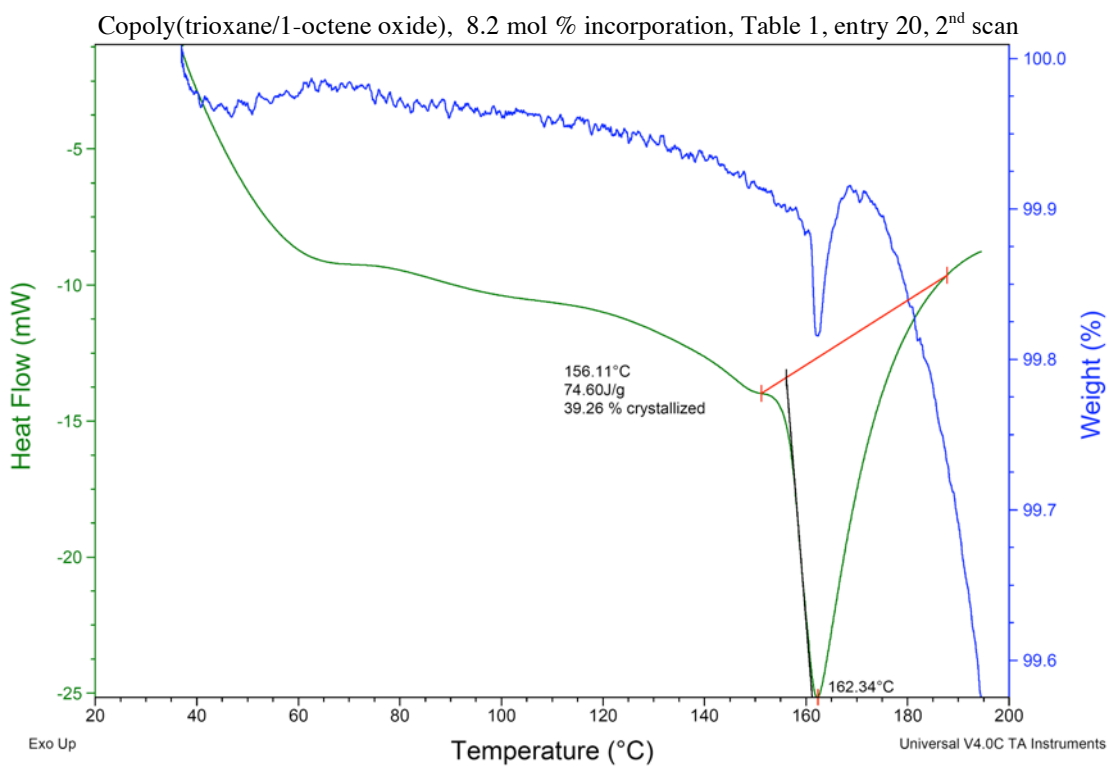
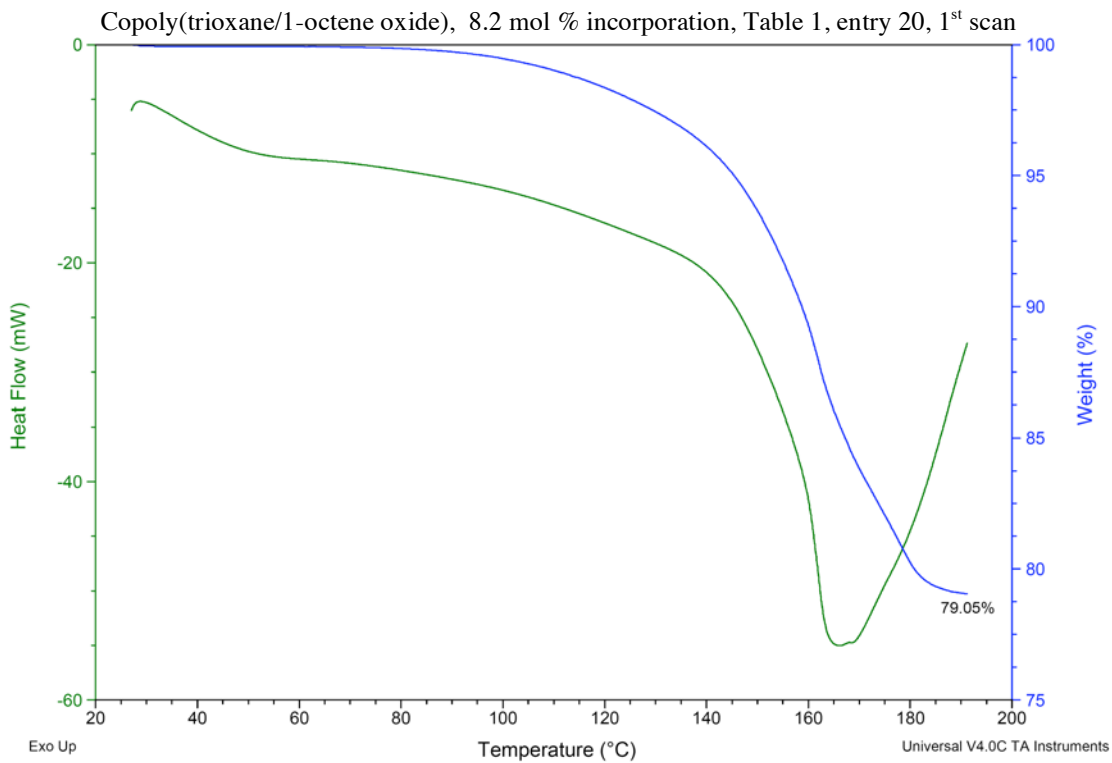


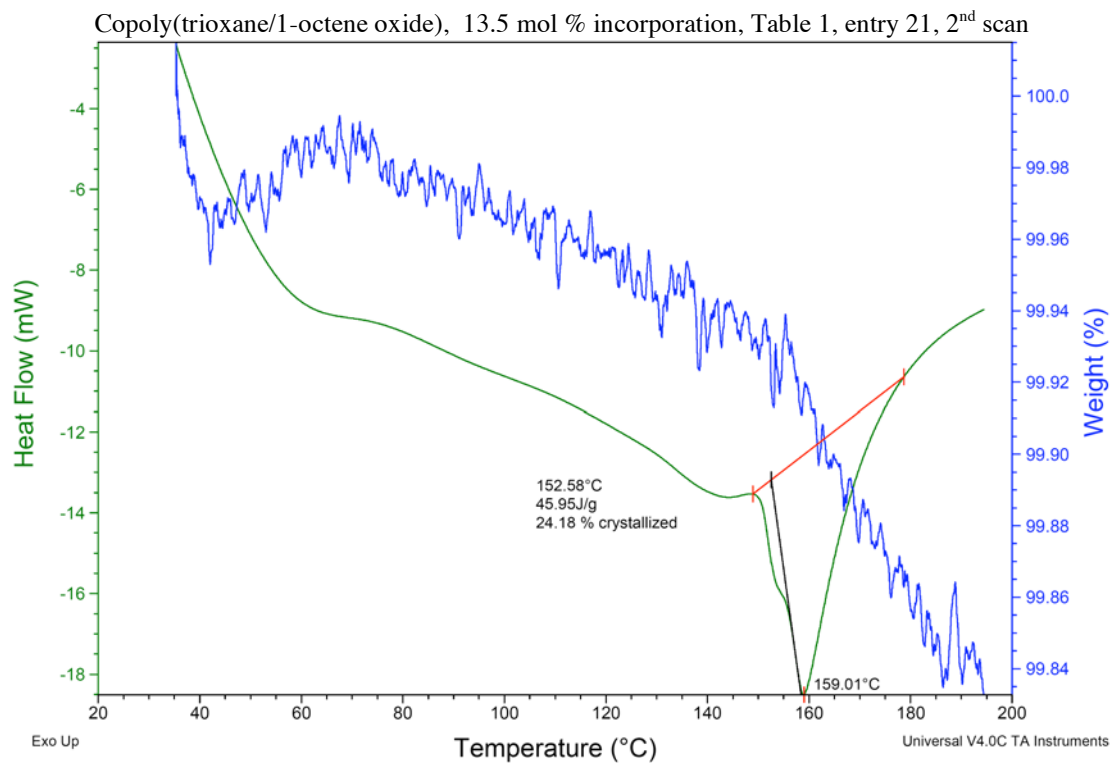
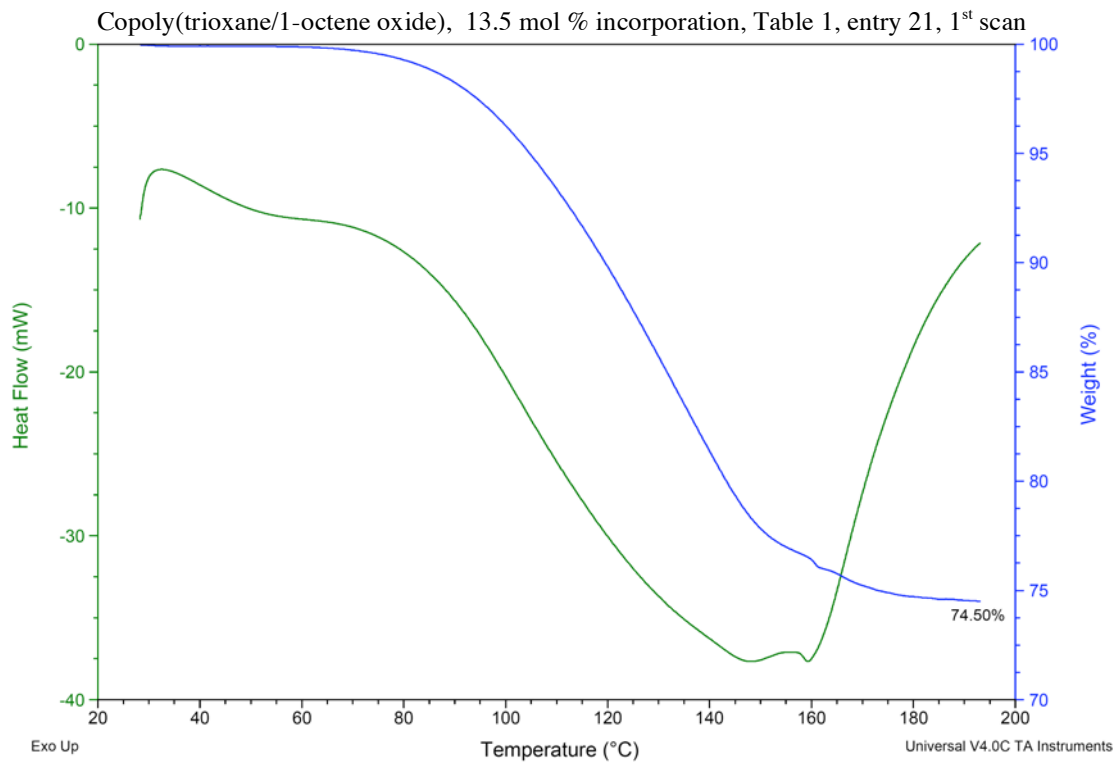




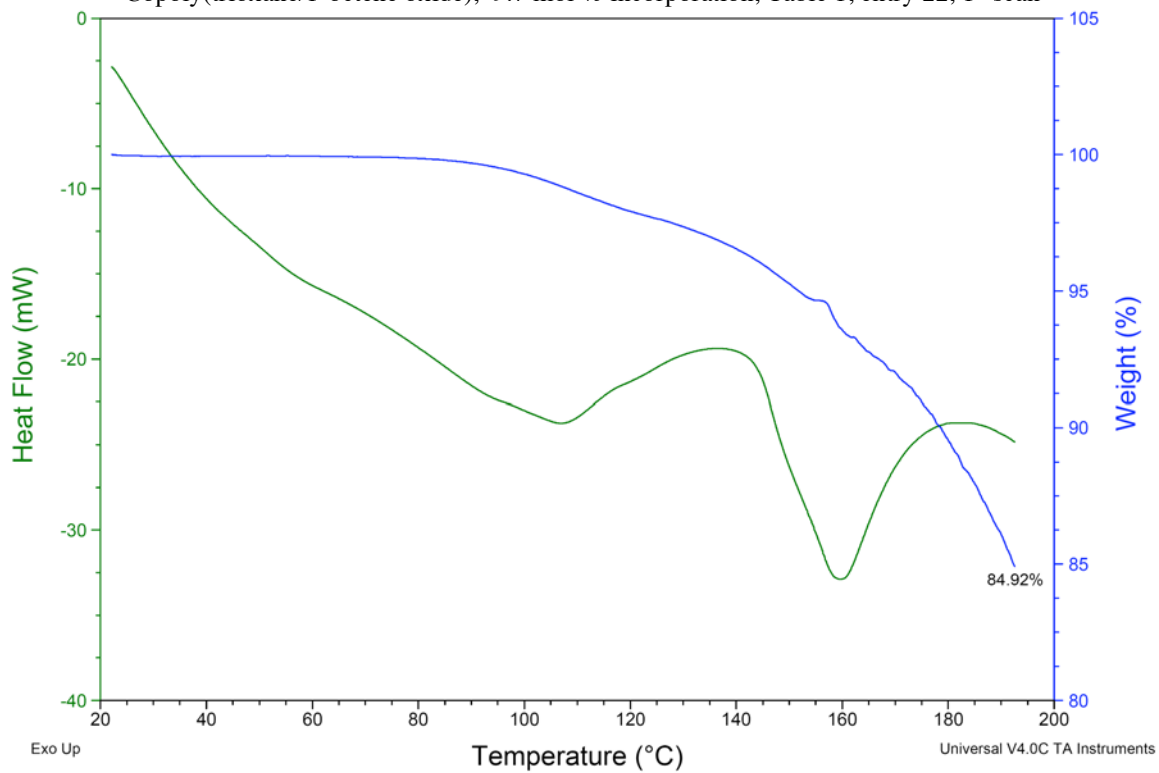




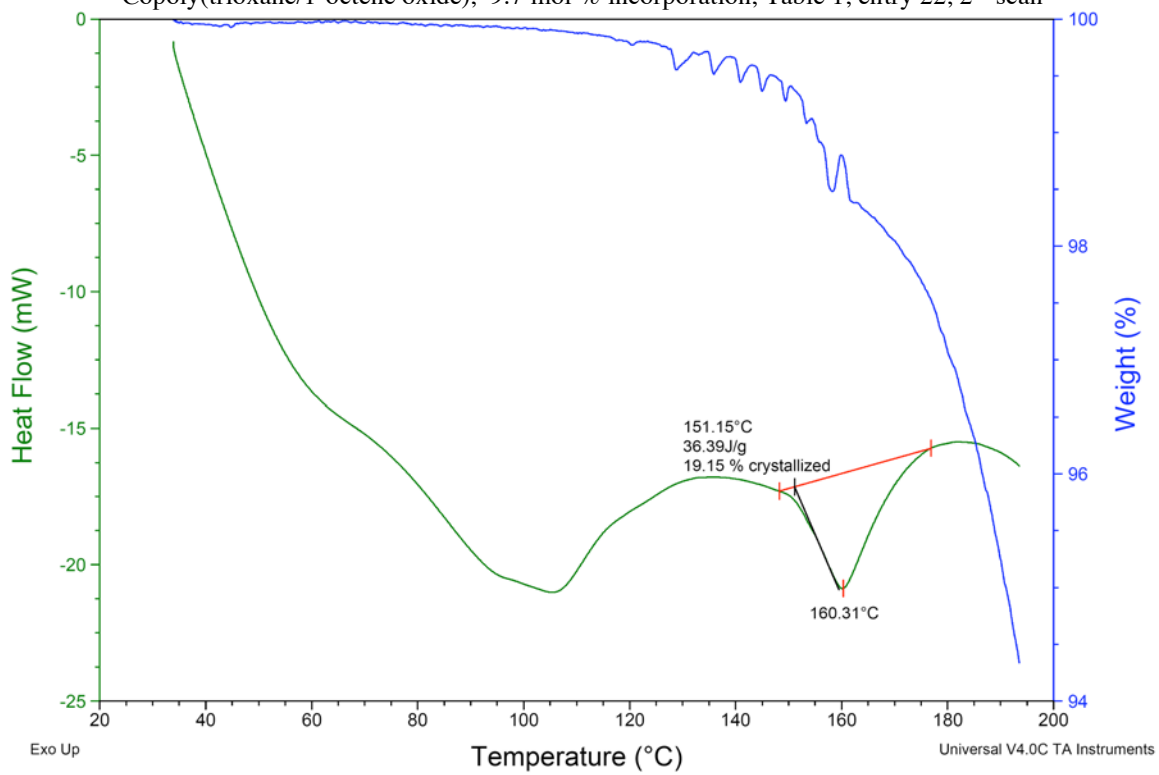


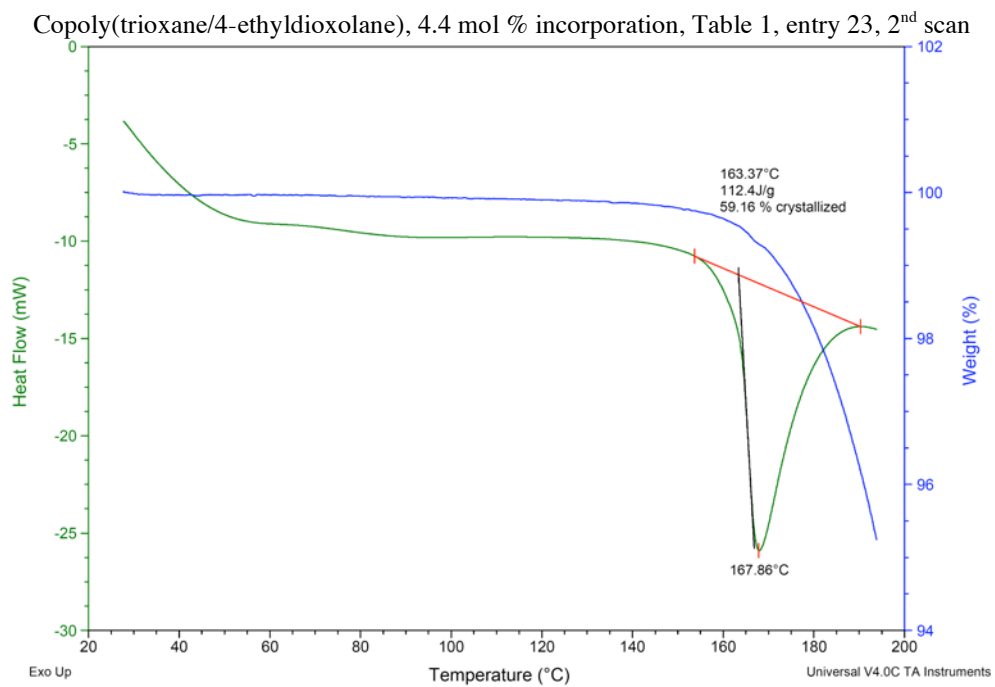
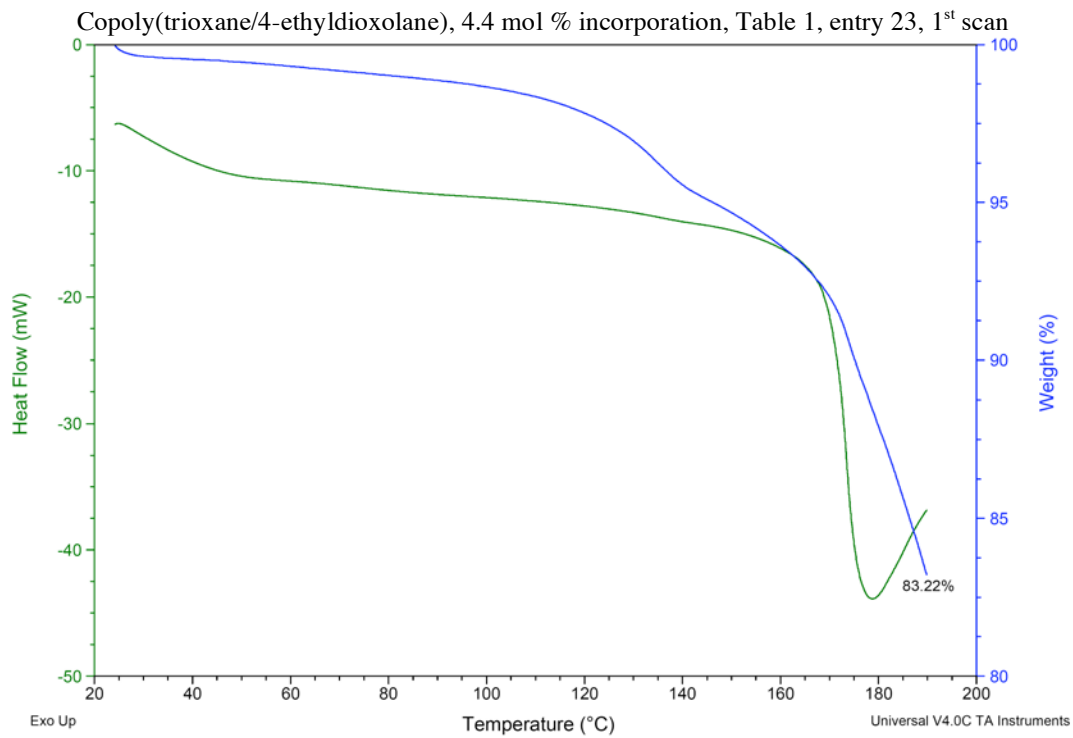


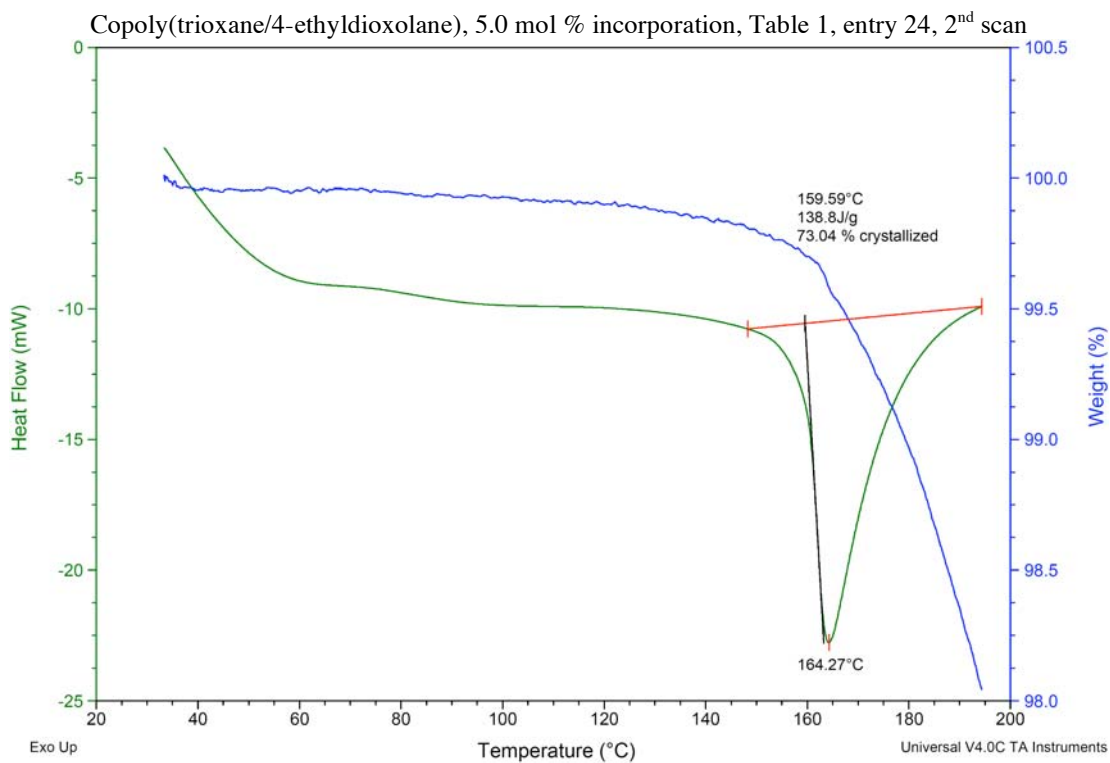
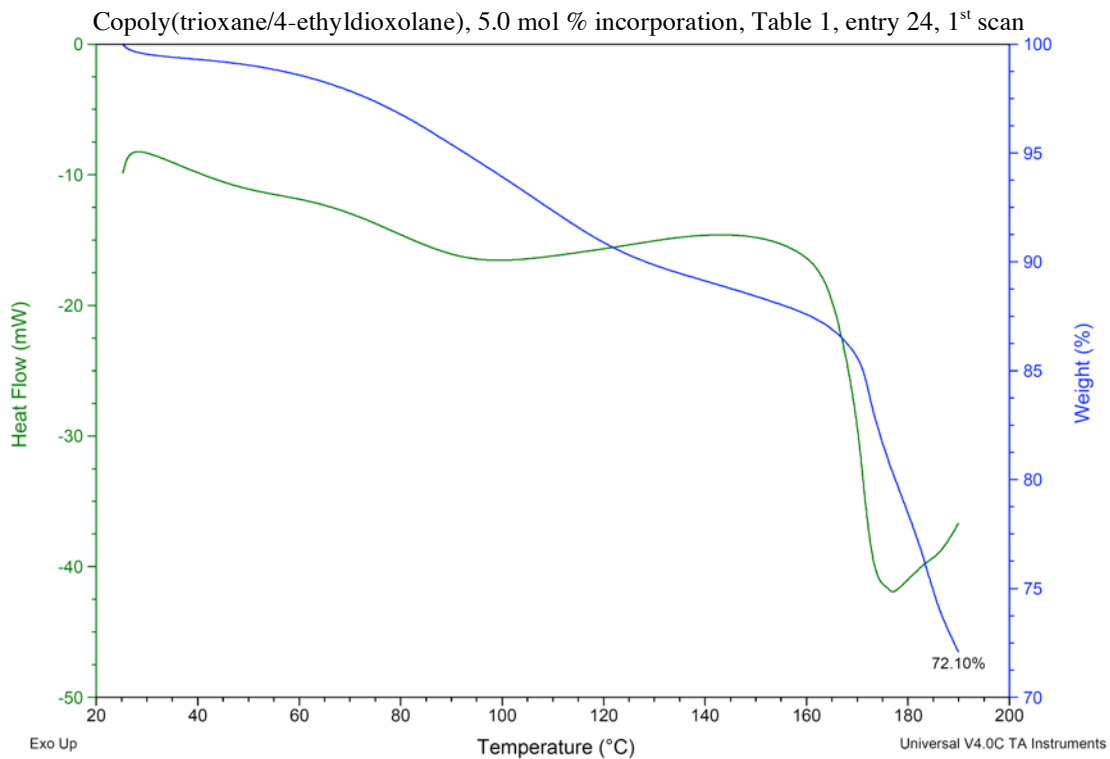
Copoly(trioxane/1-octene oxide), 9.7 mol % incorporation, Table 1, entry 22, 1st scan

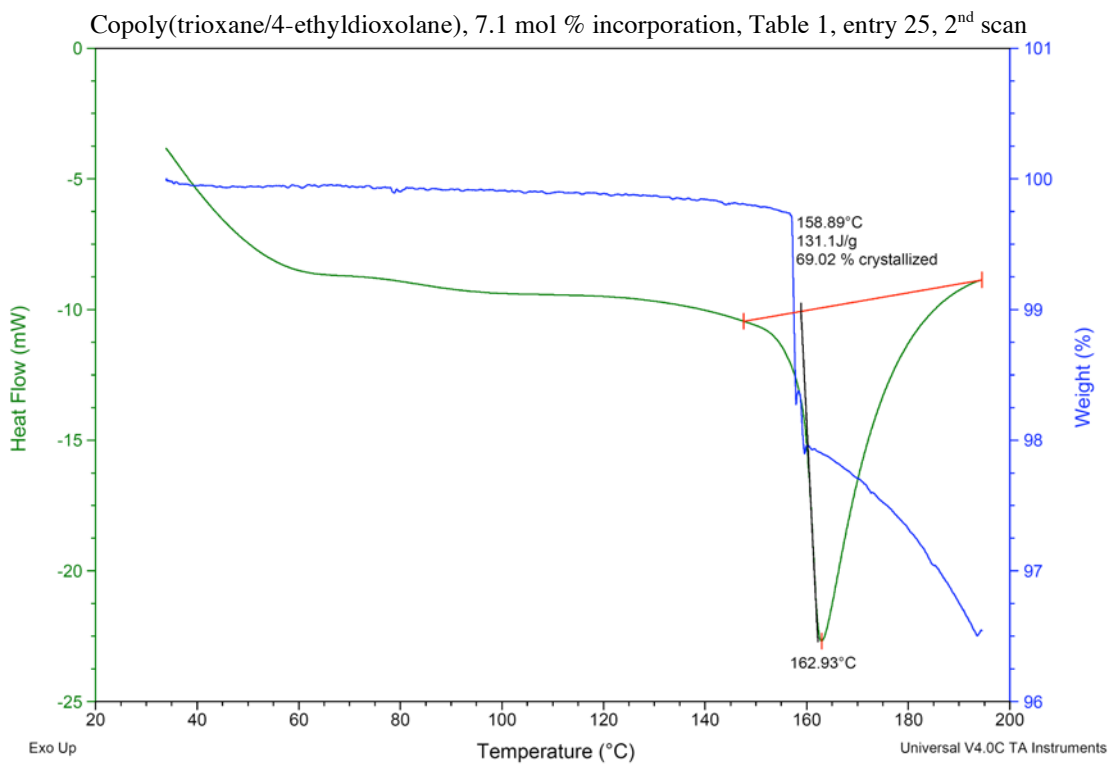
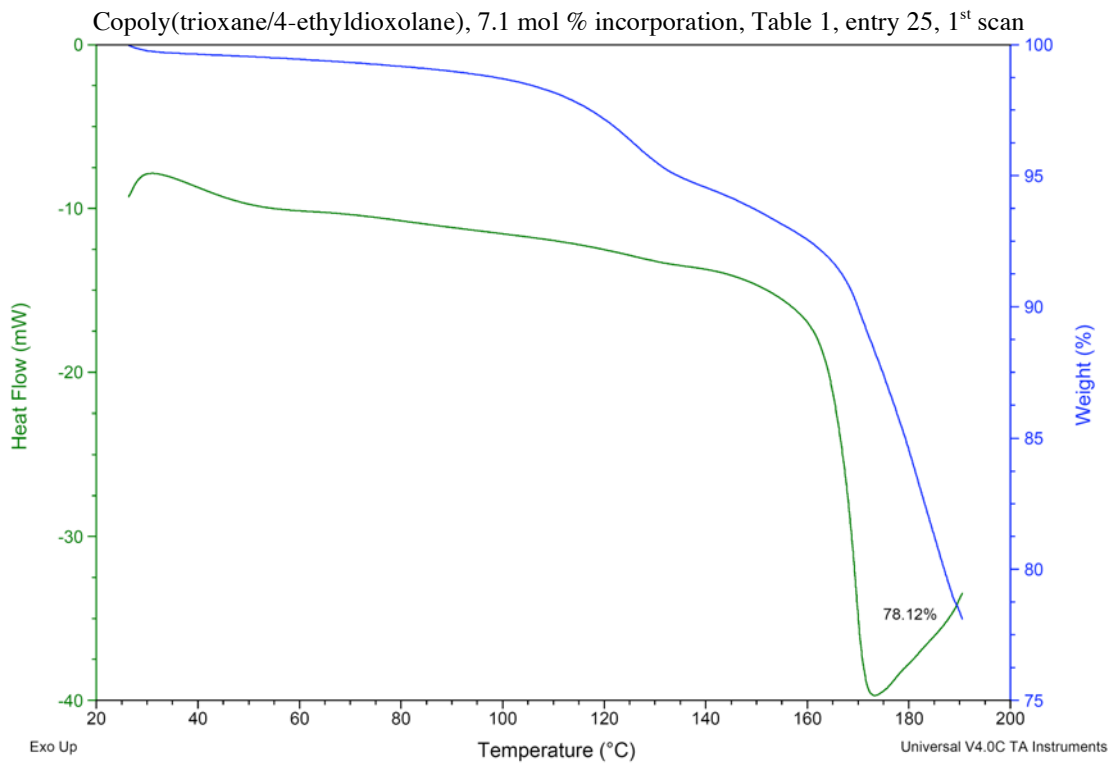


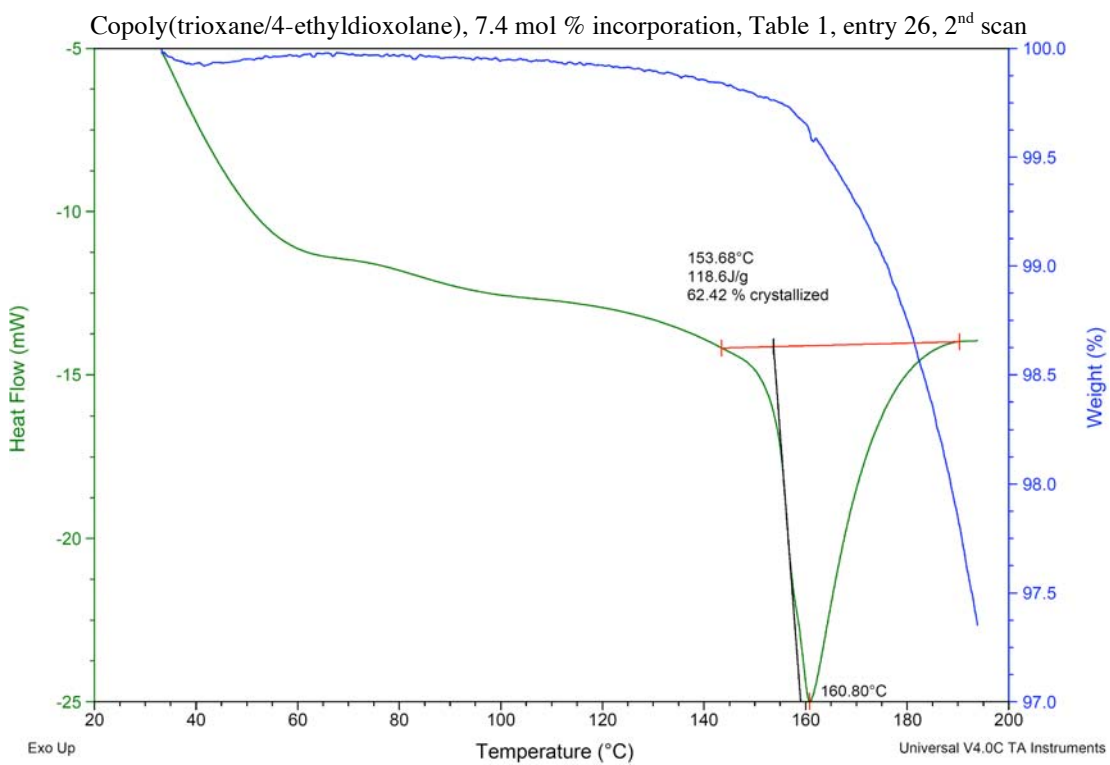
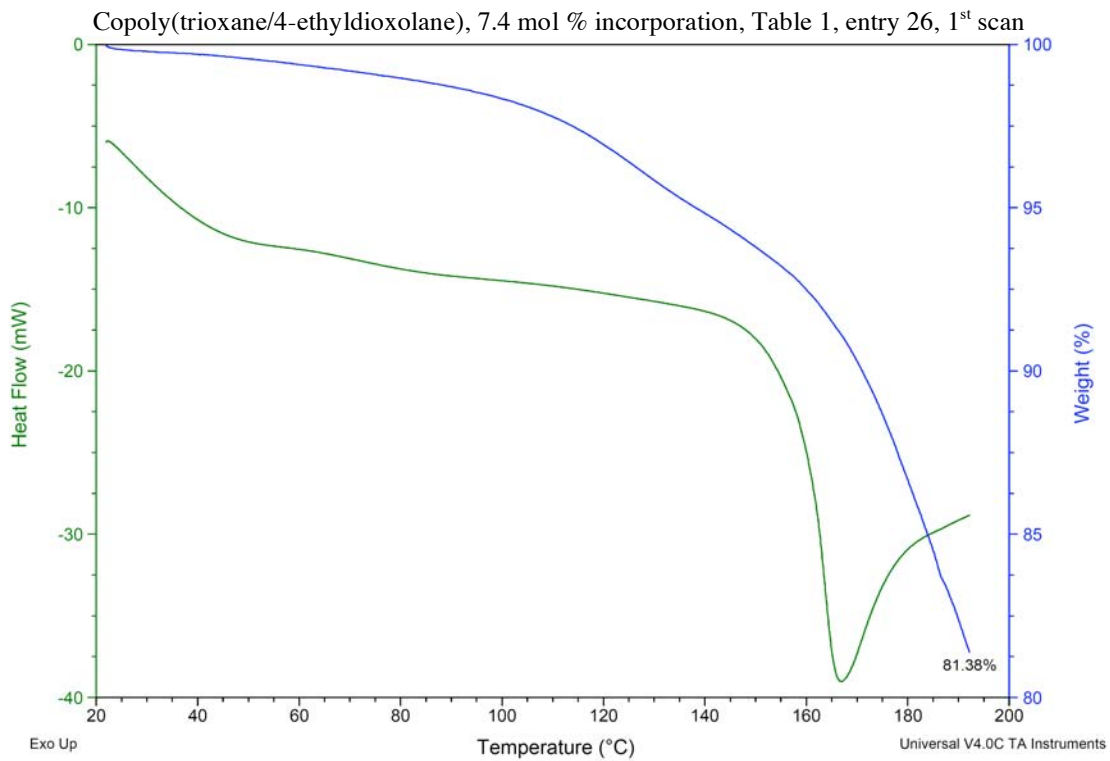
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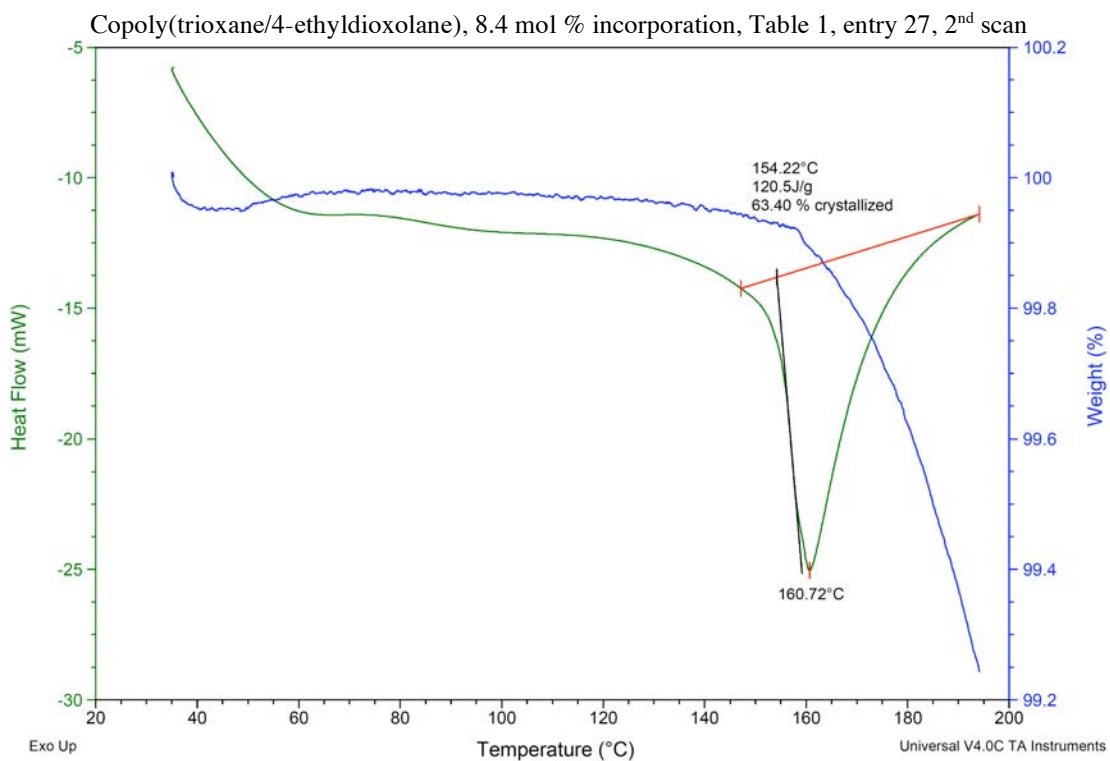
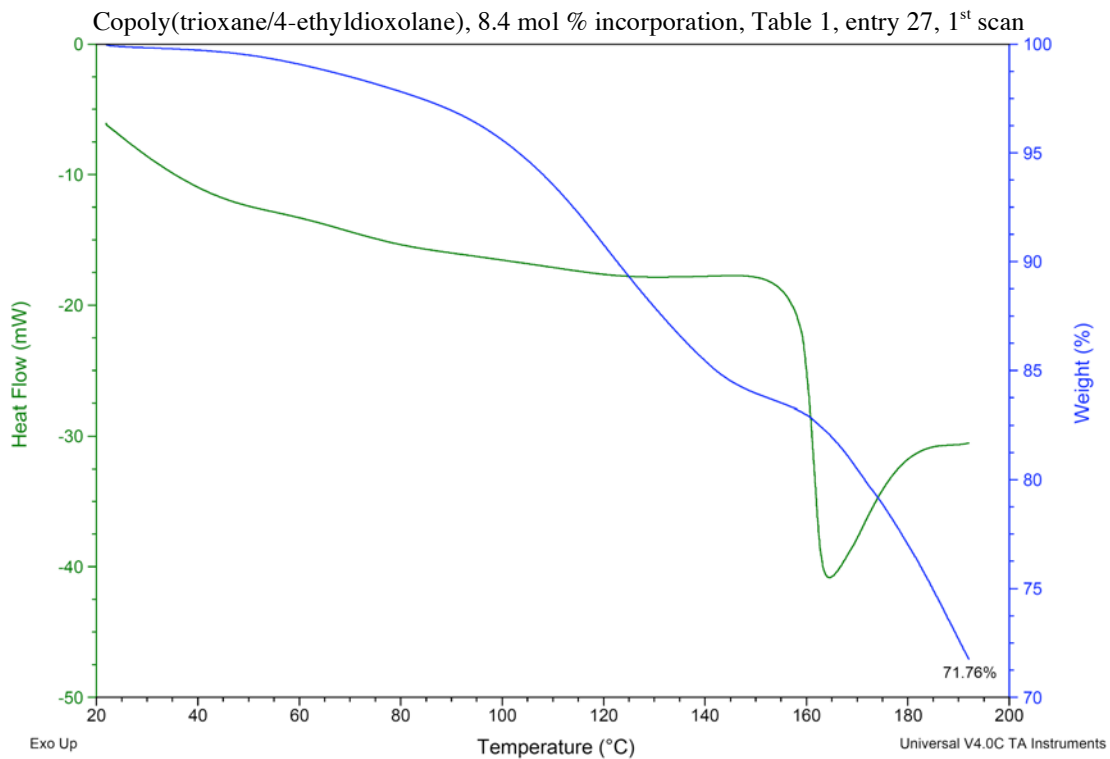


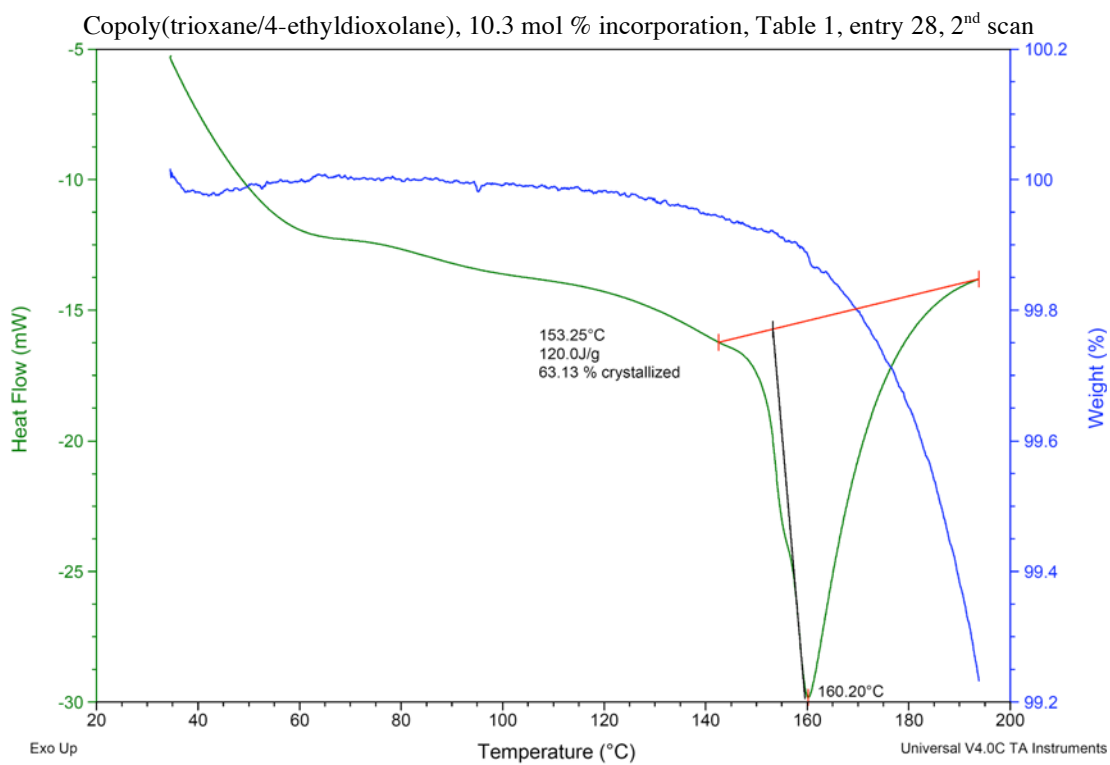
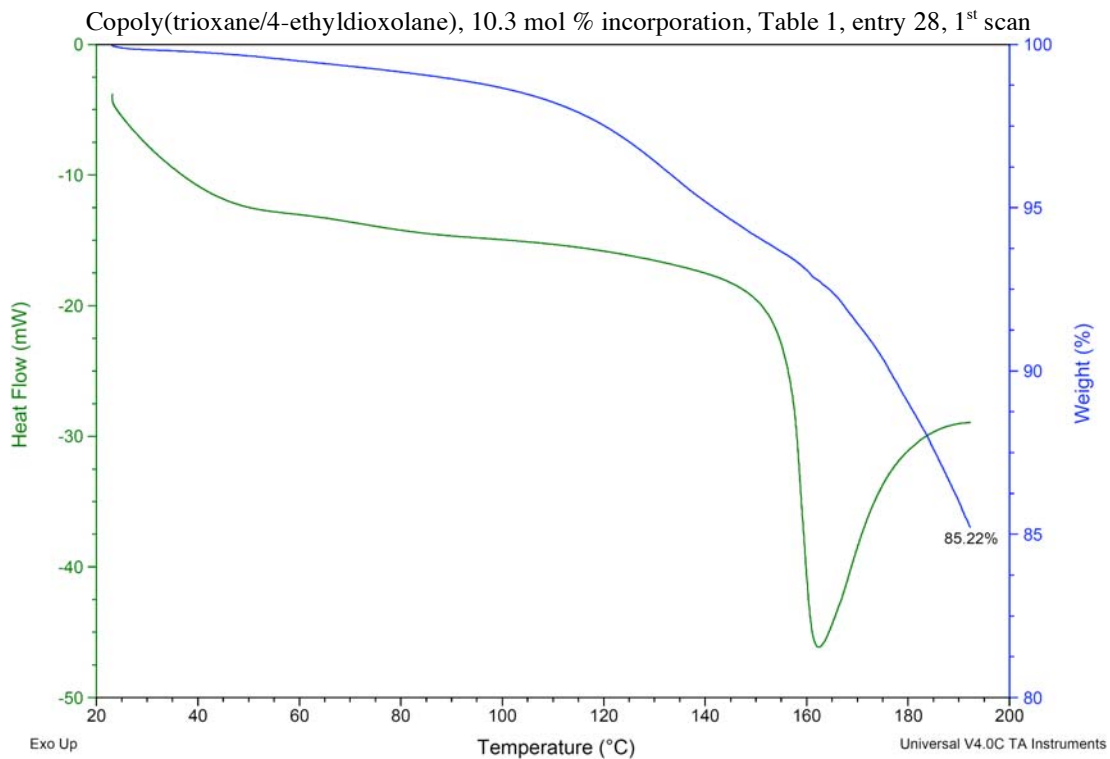


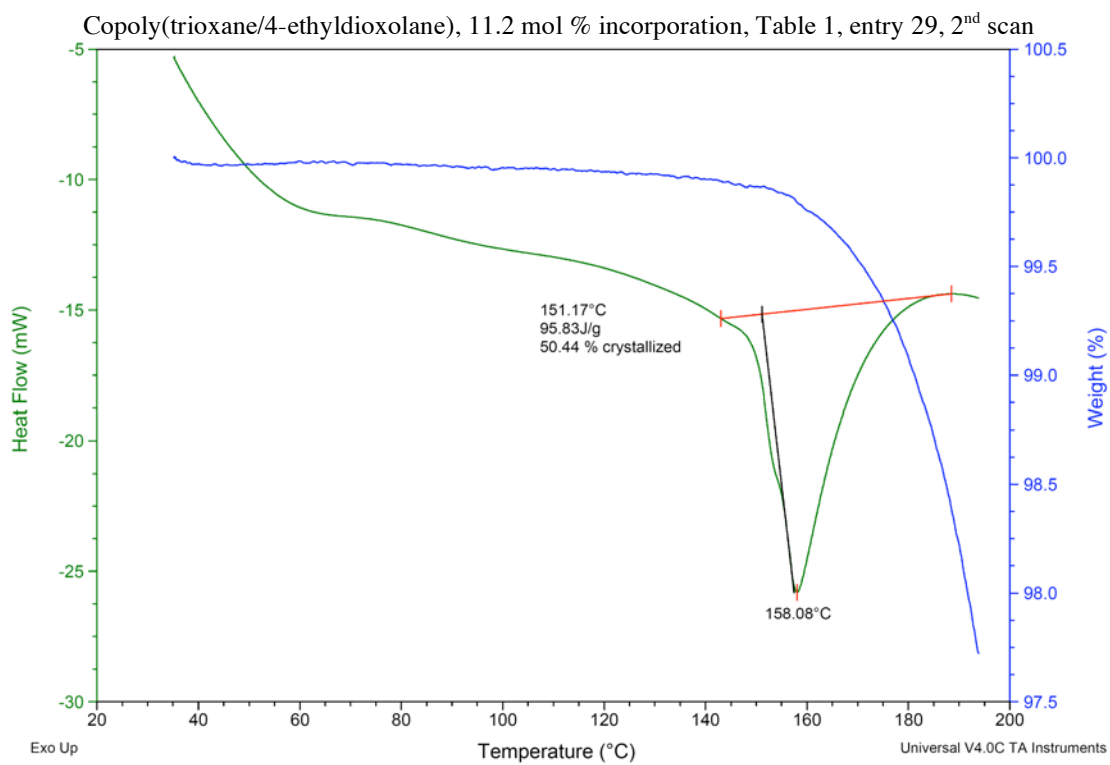
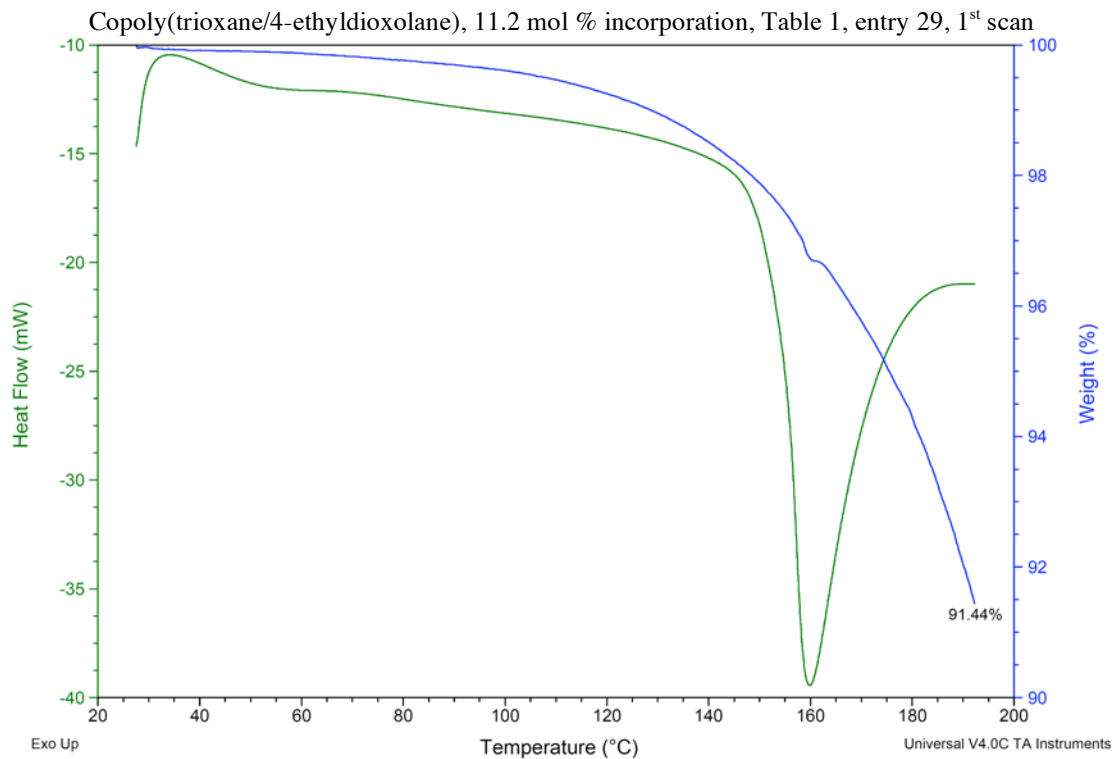


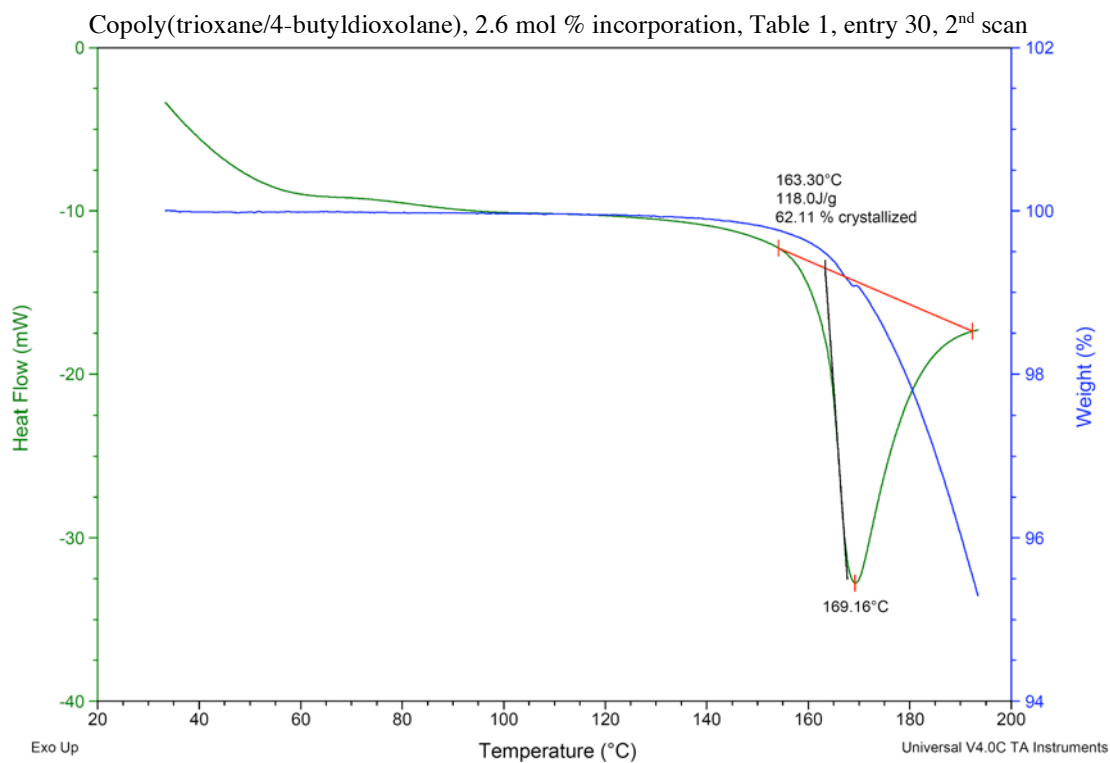
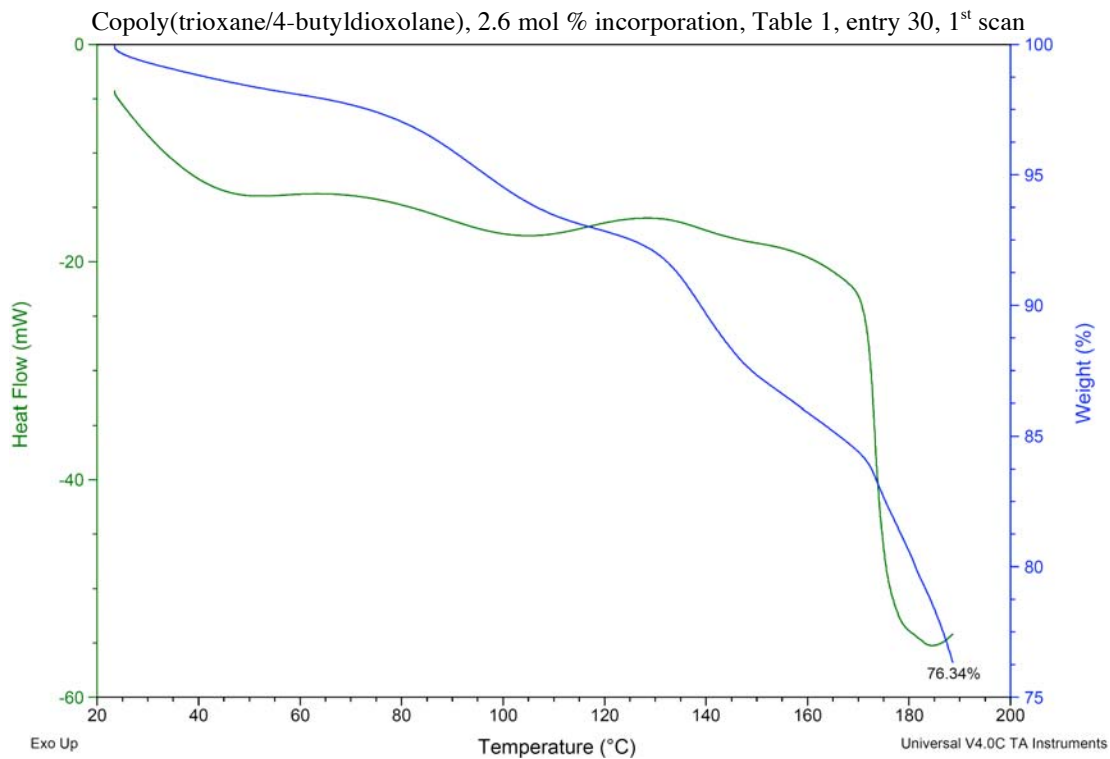


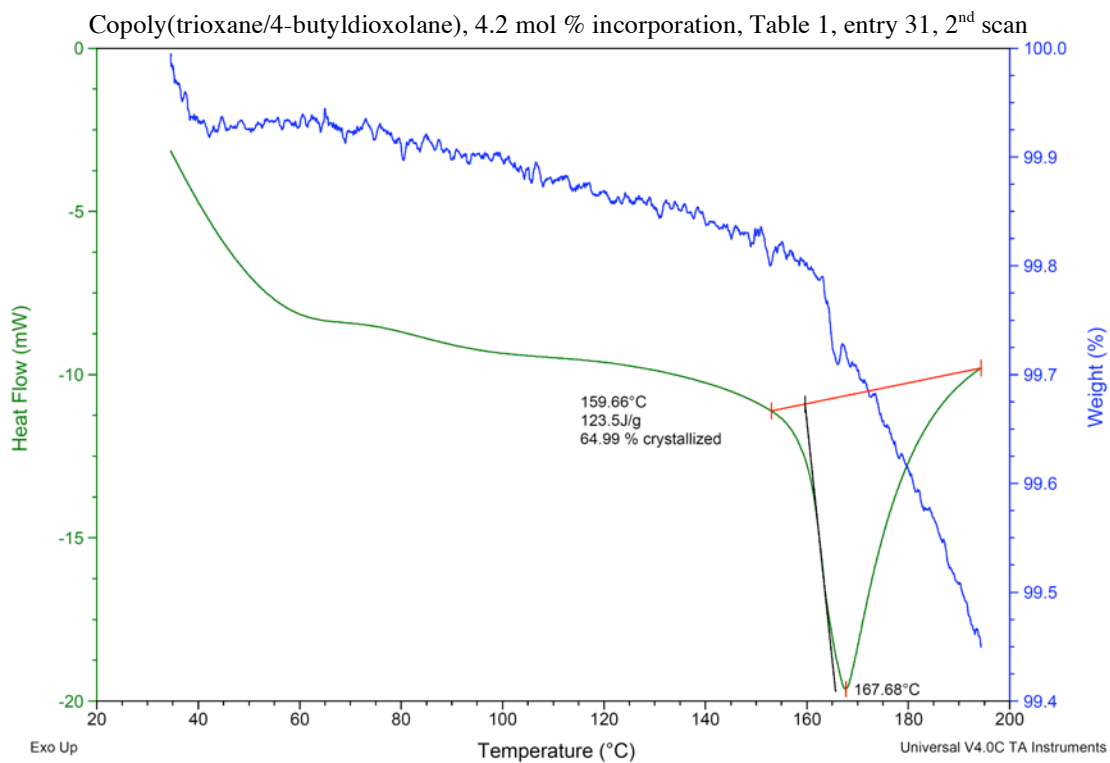
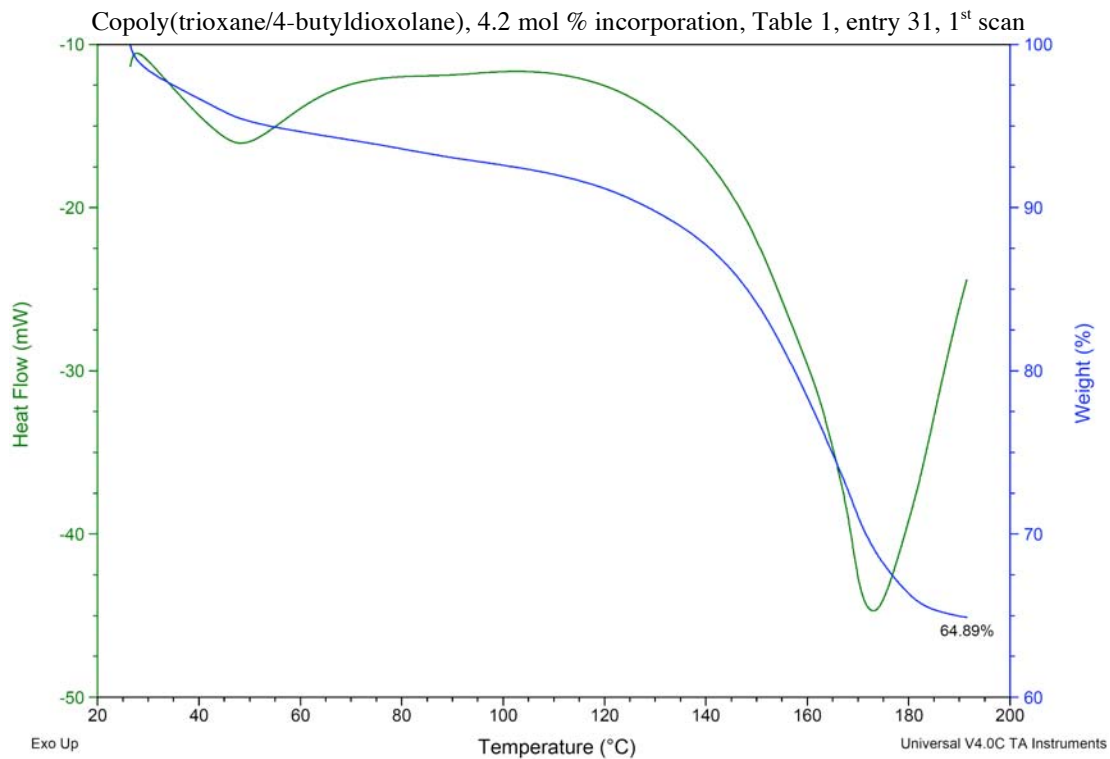


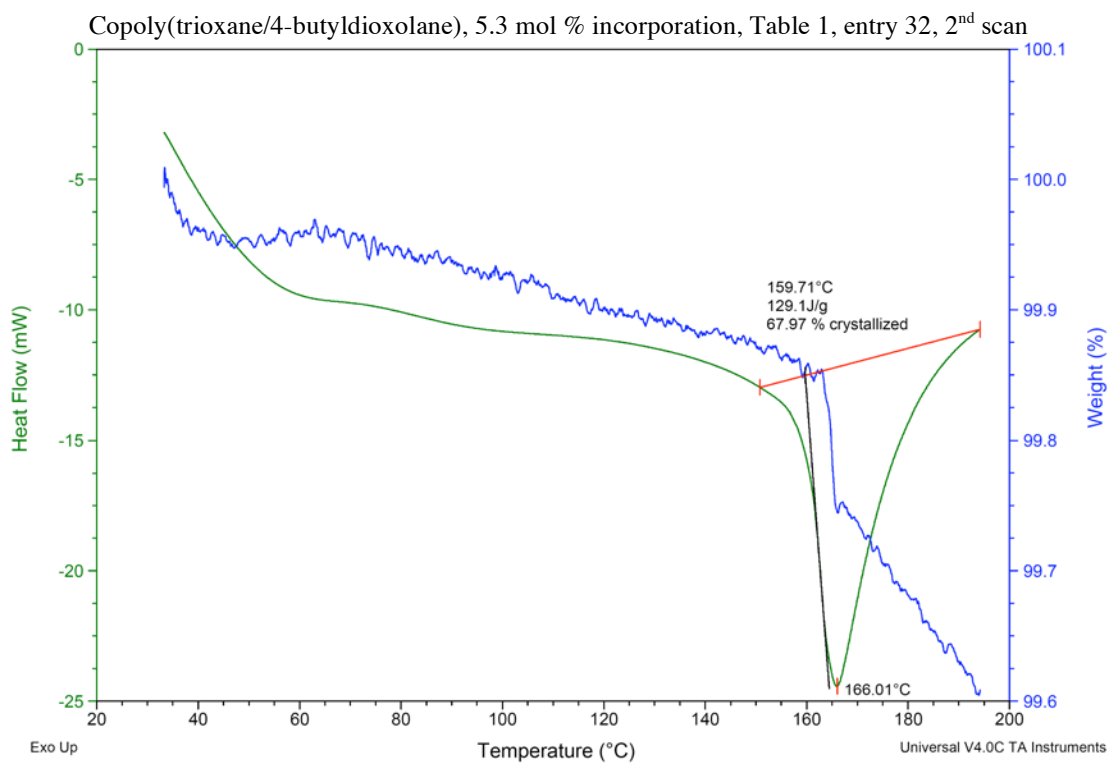
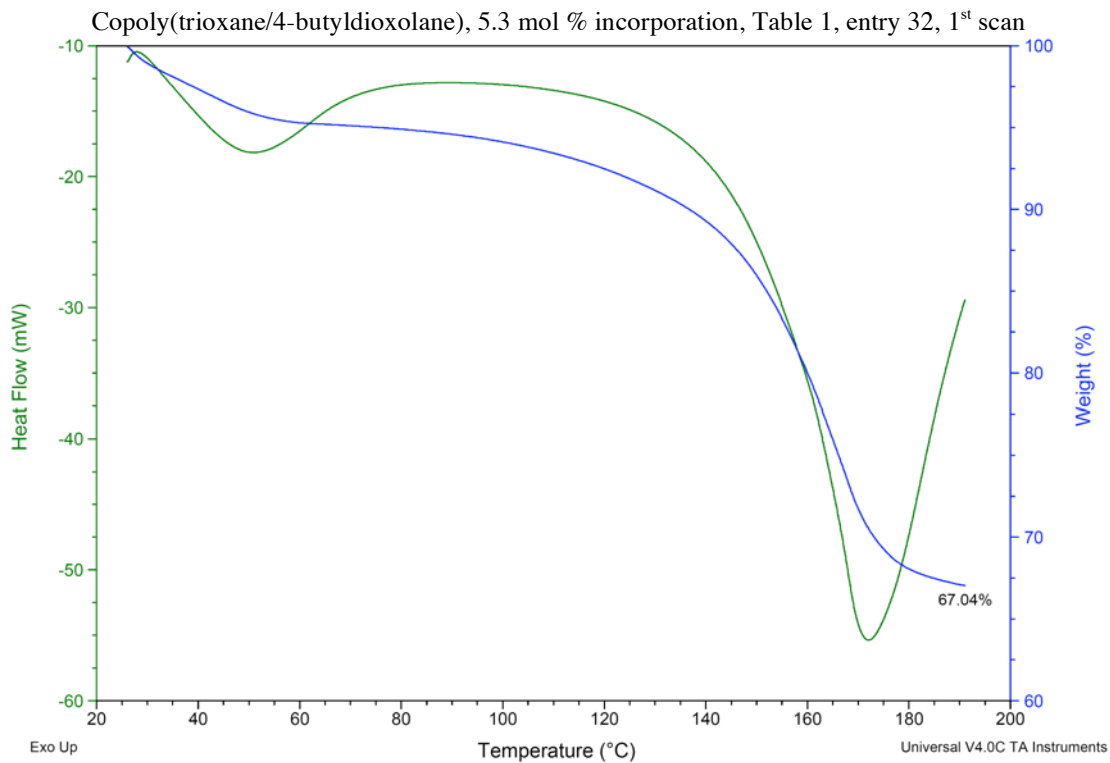


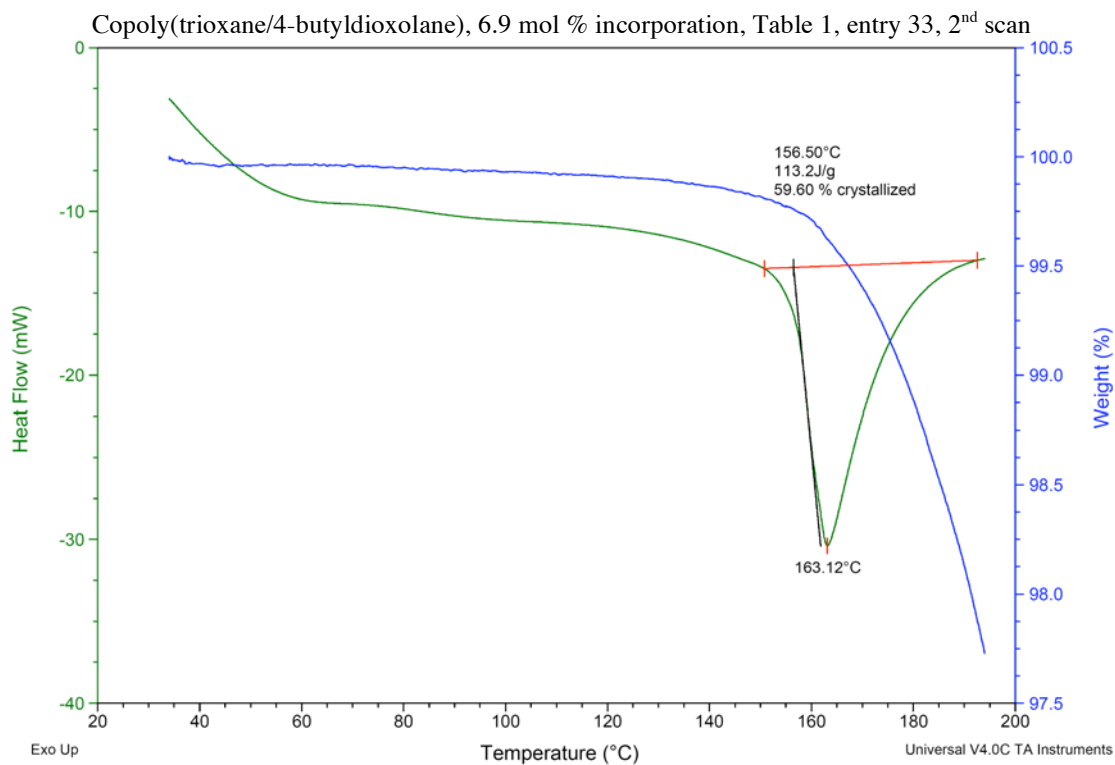
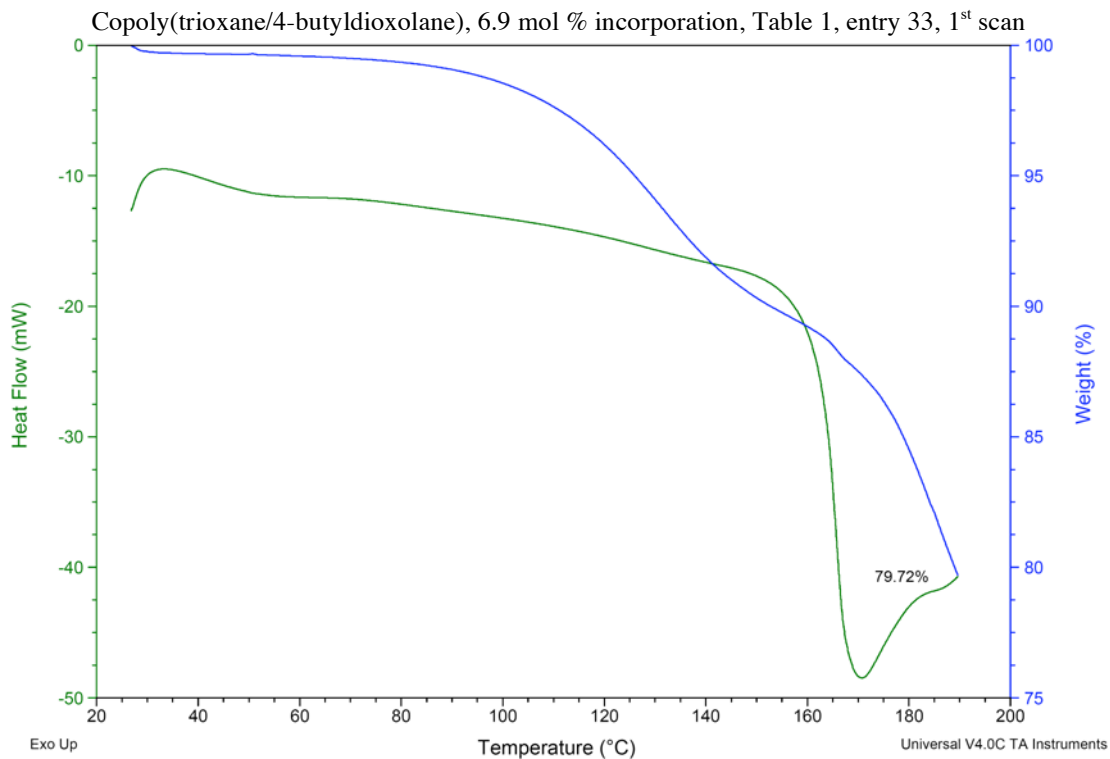


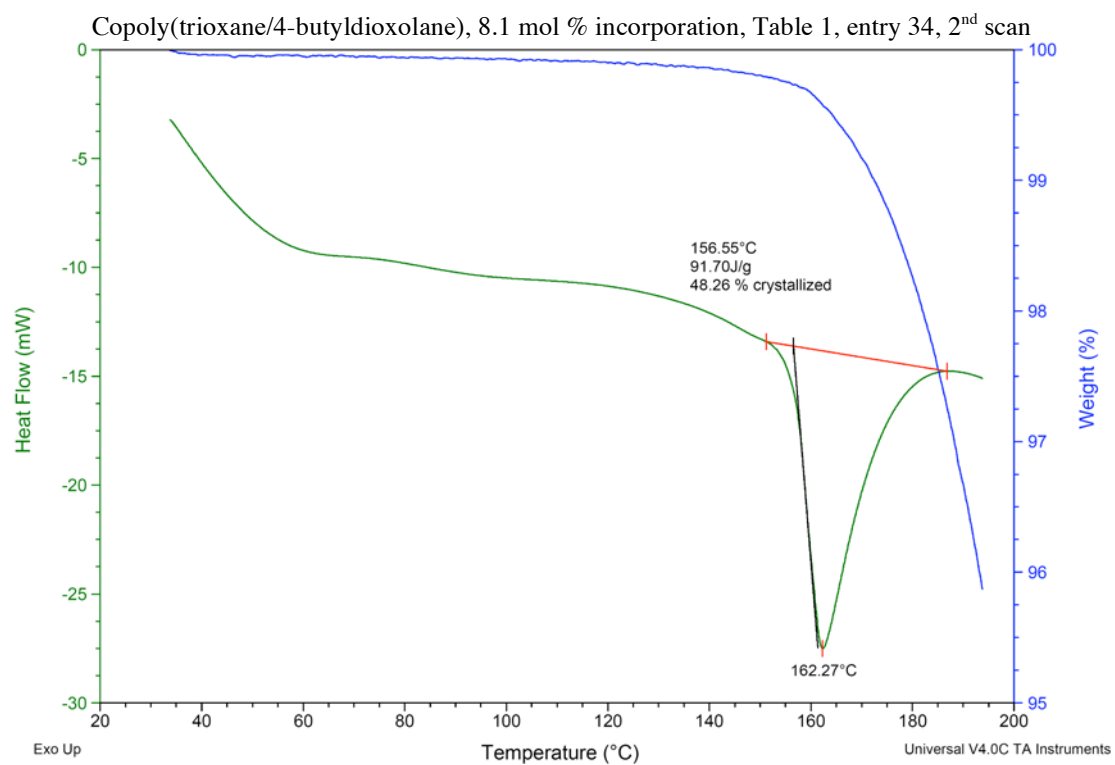
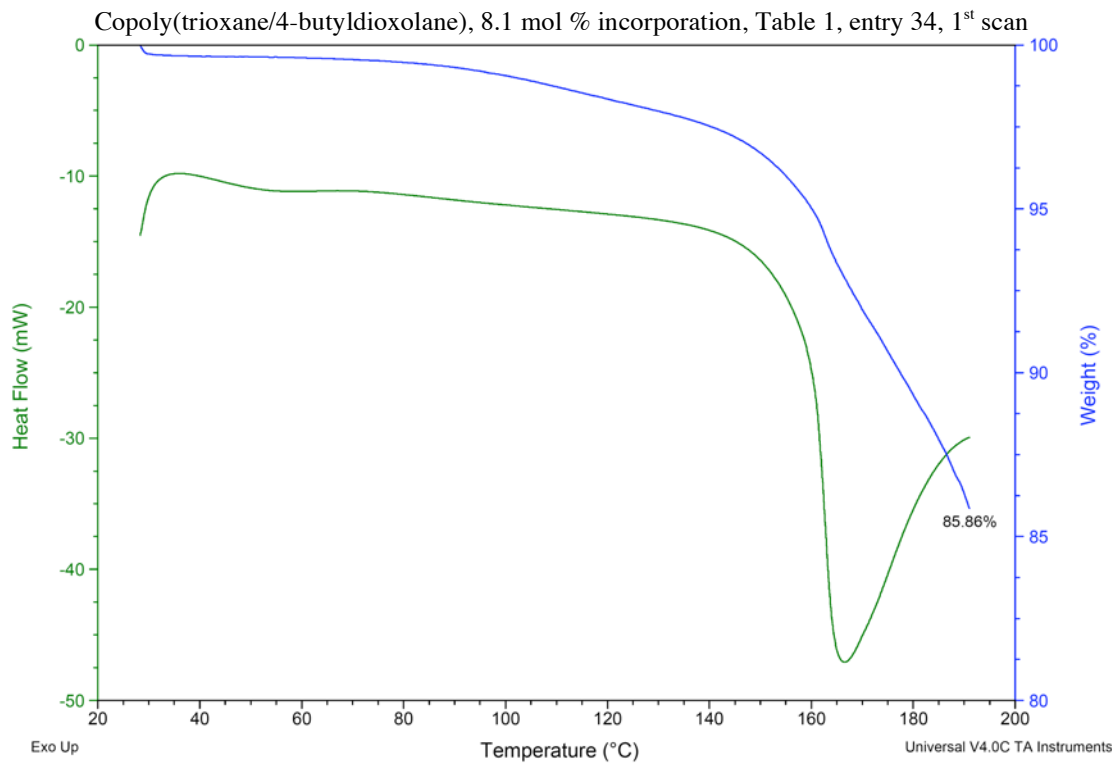


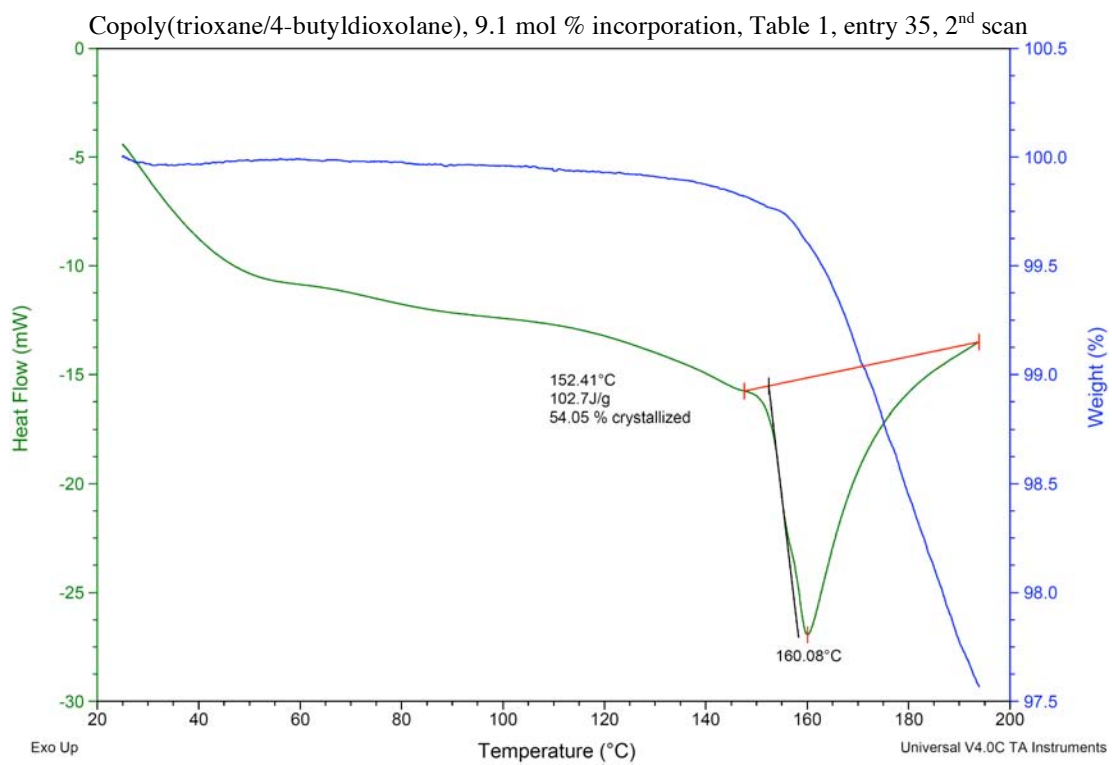
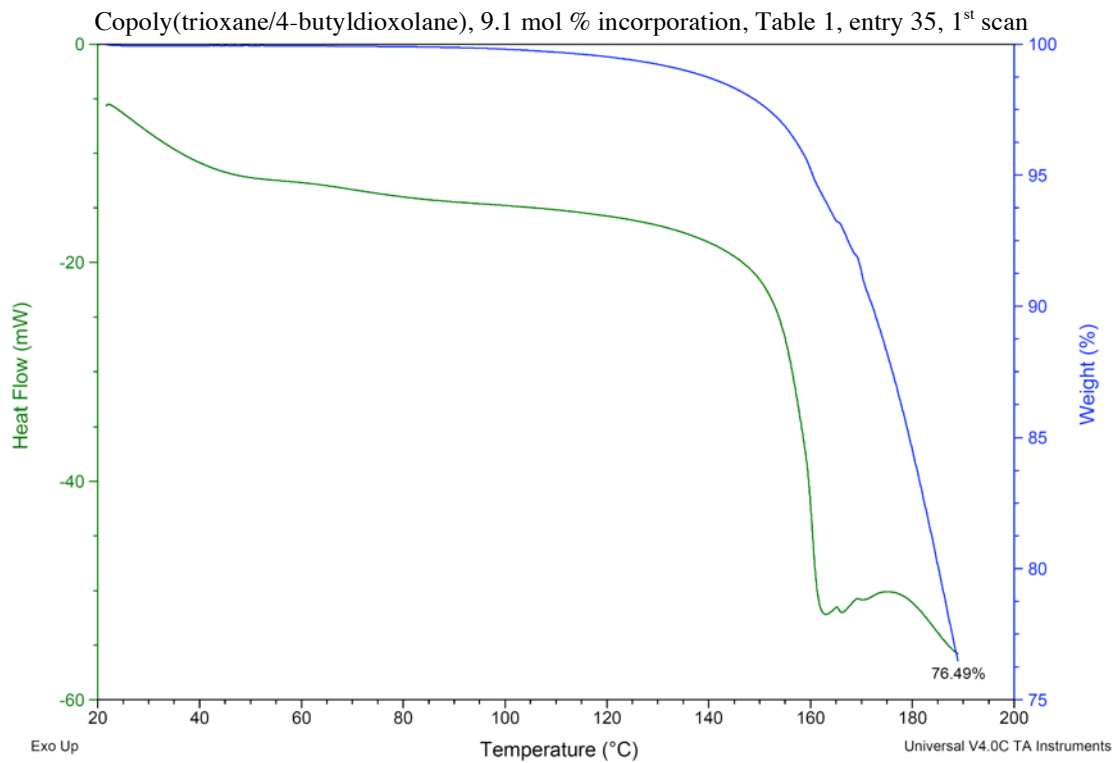


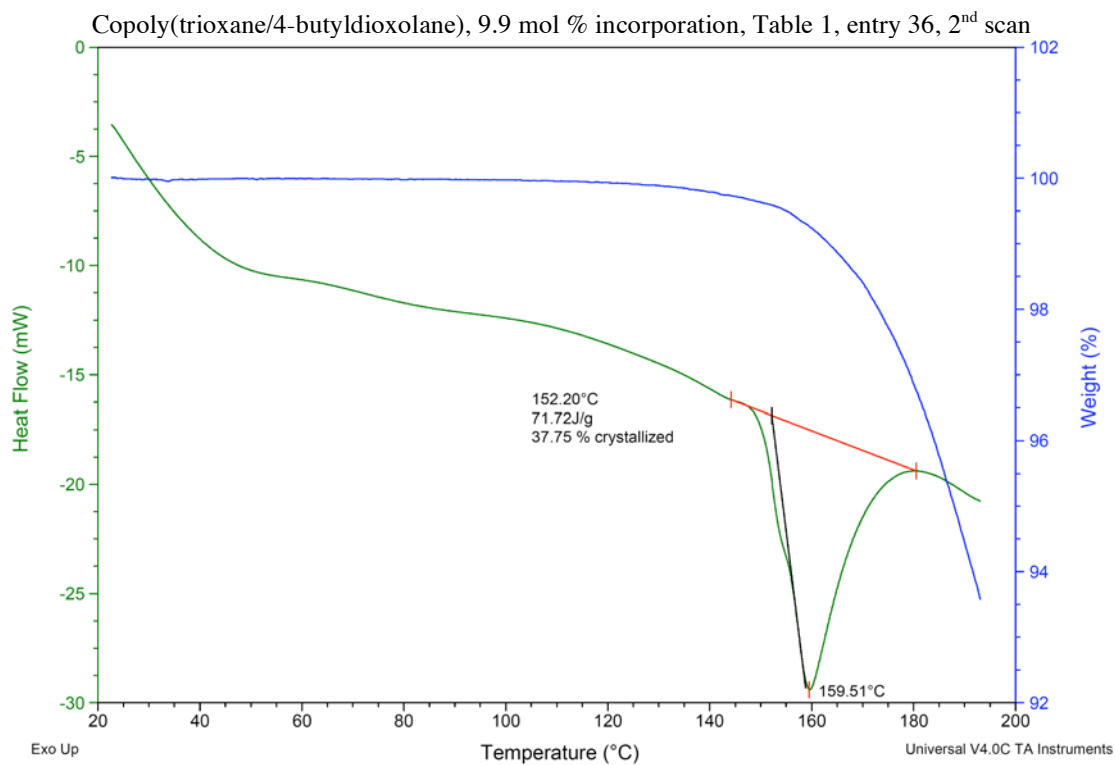
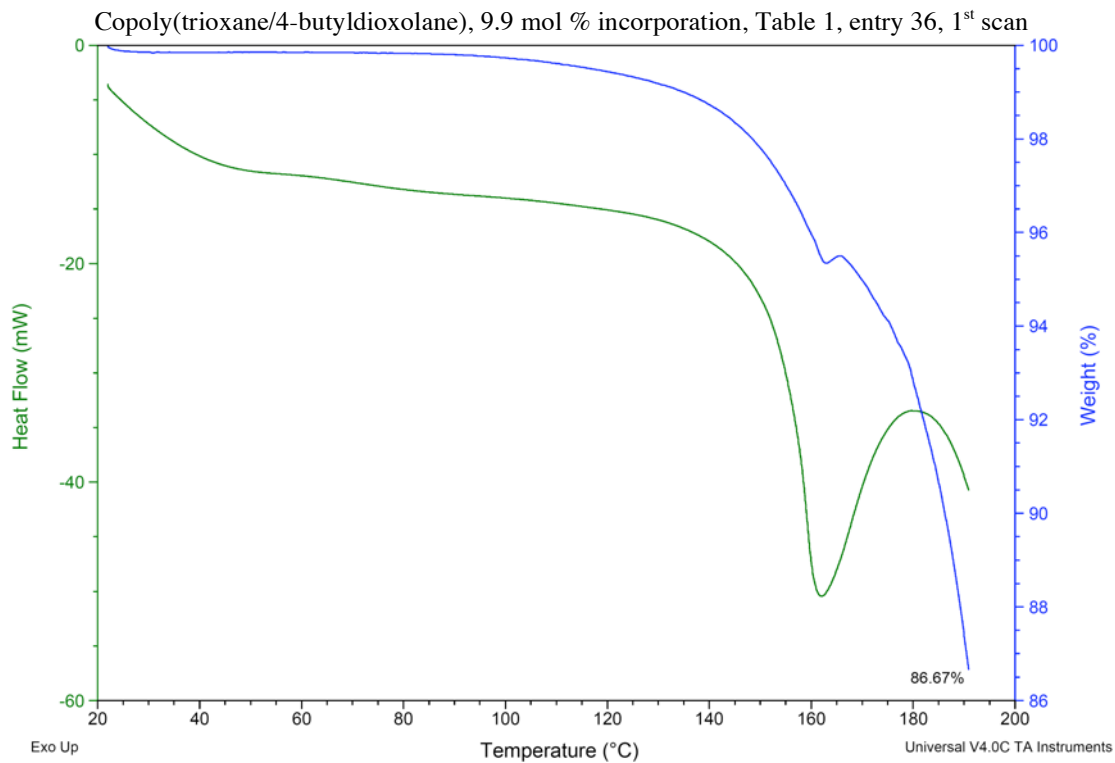


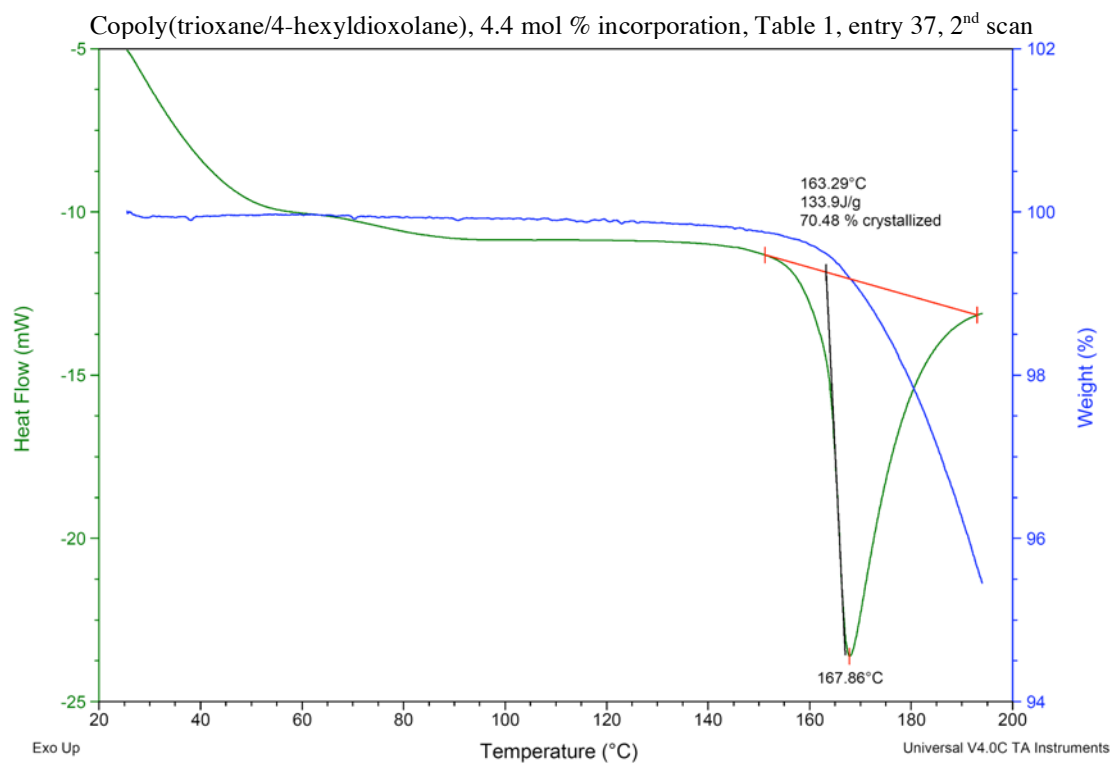
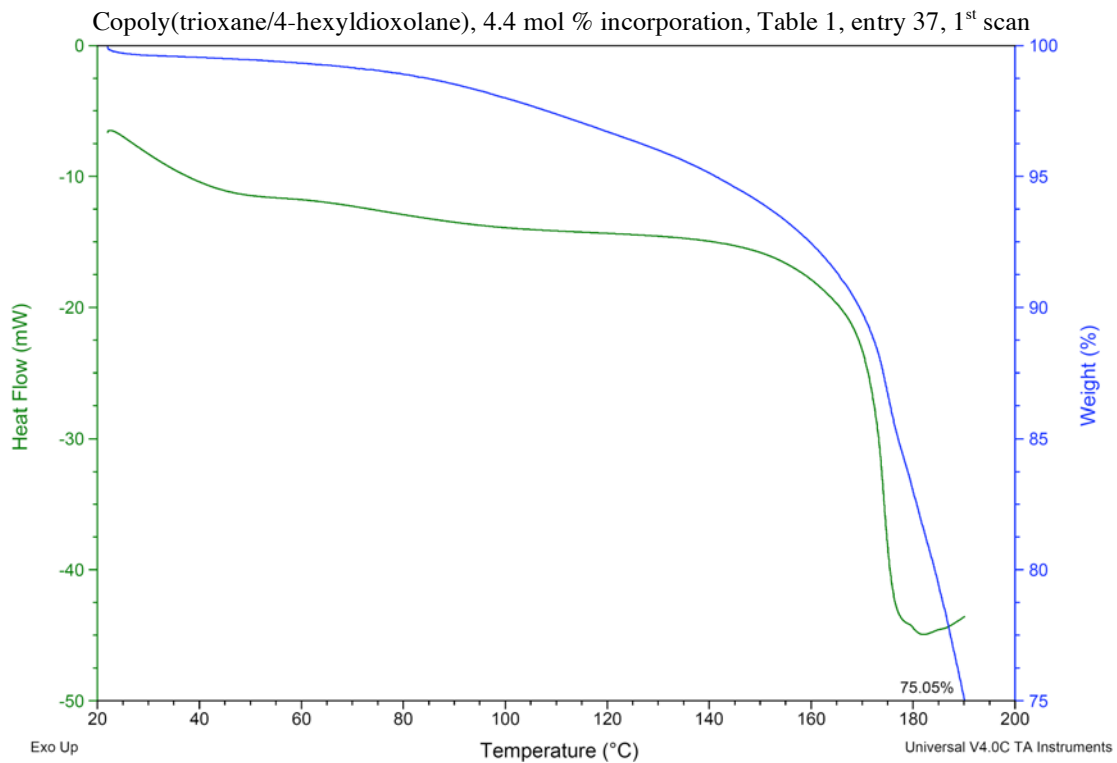


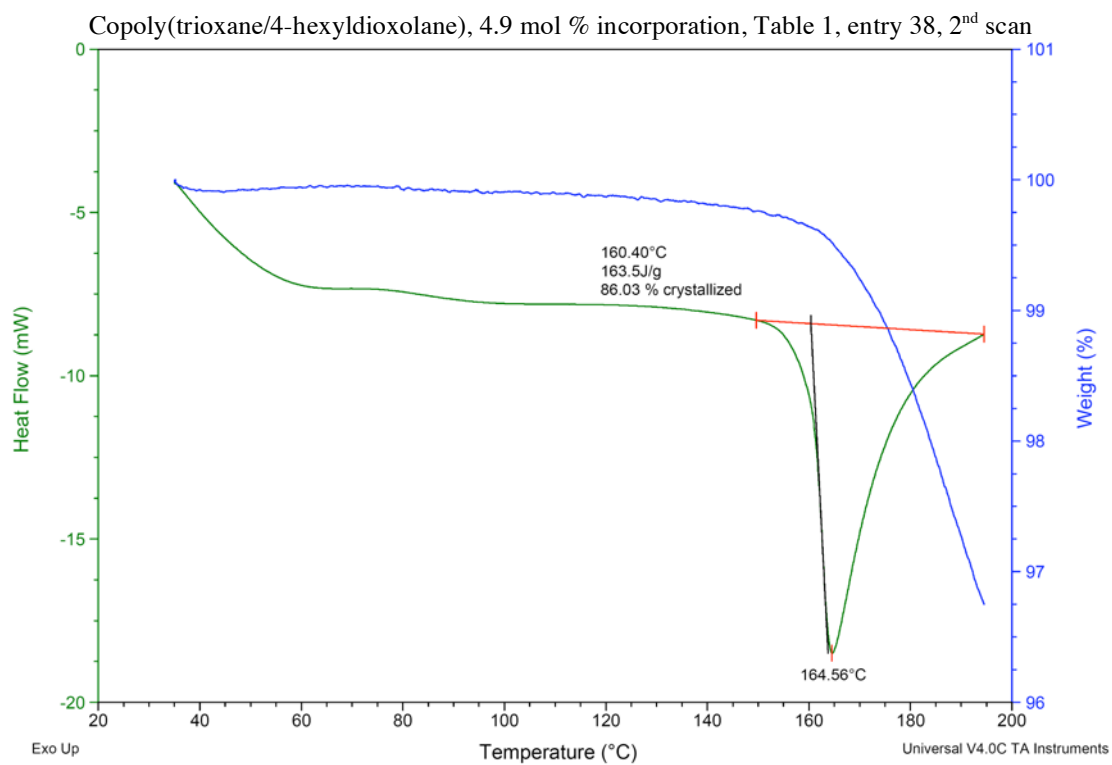
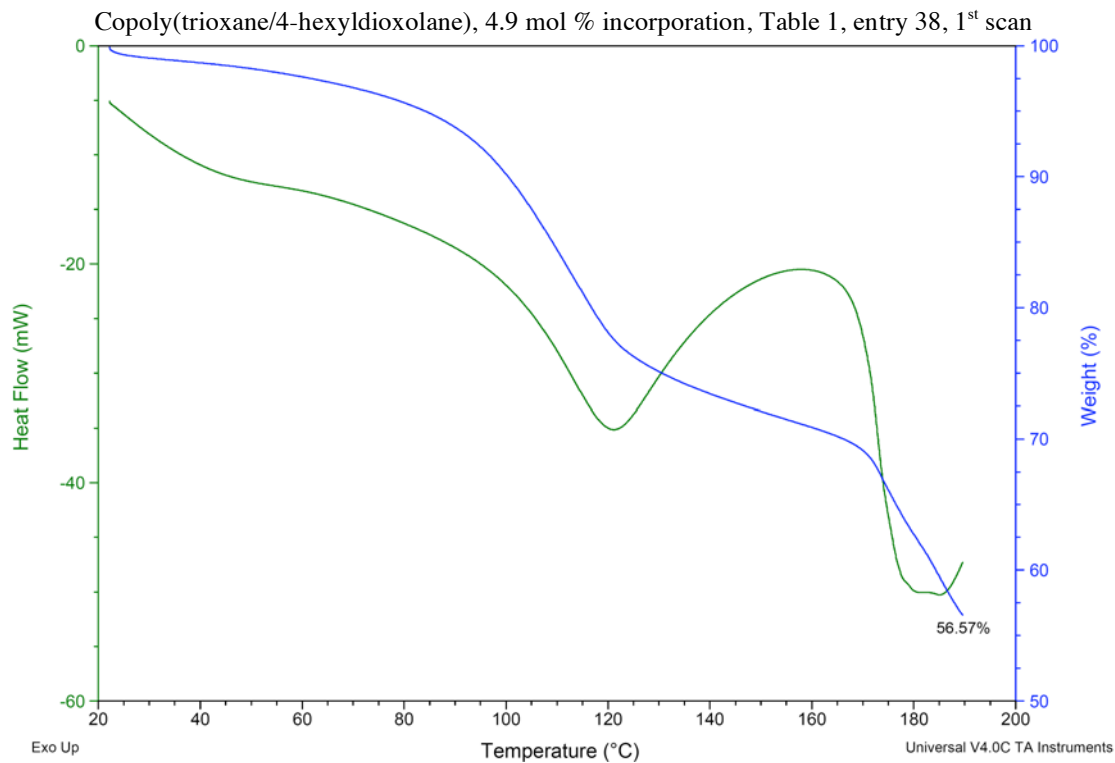


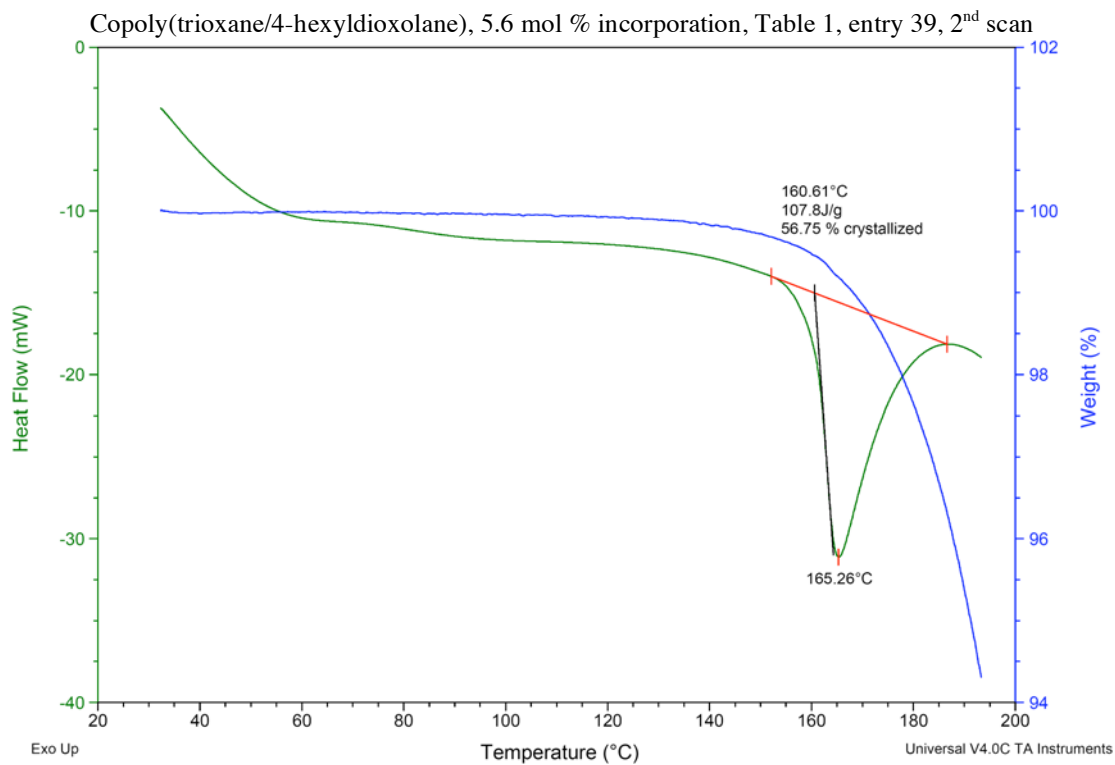
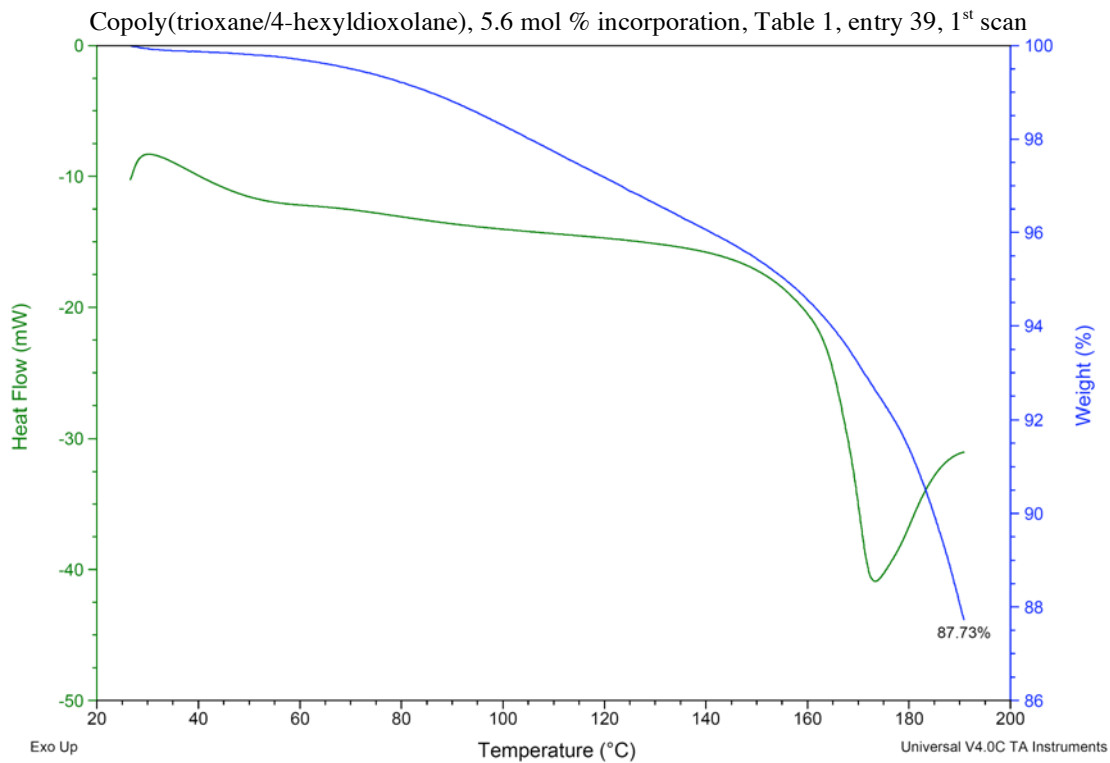


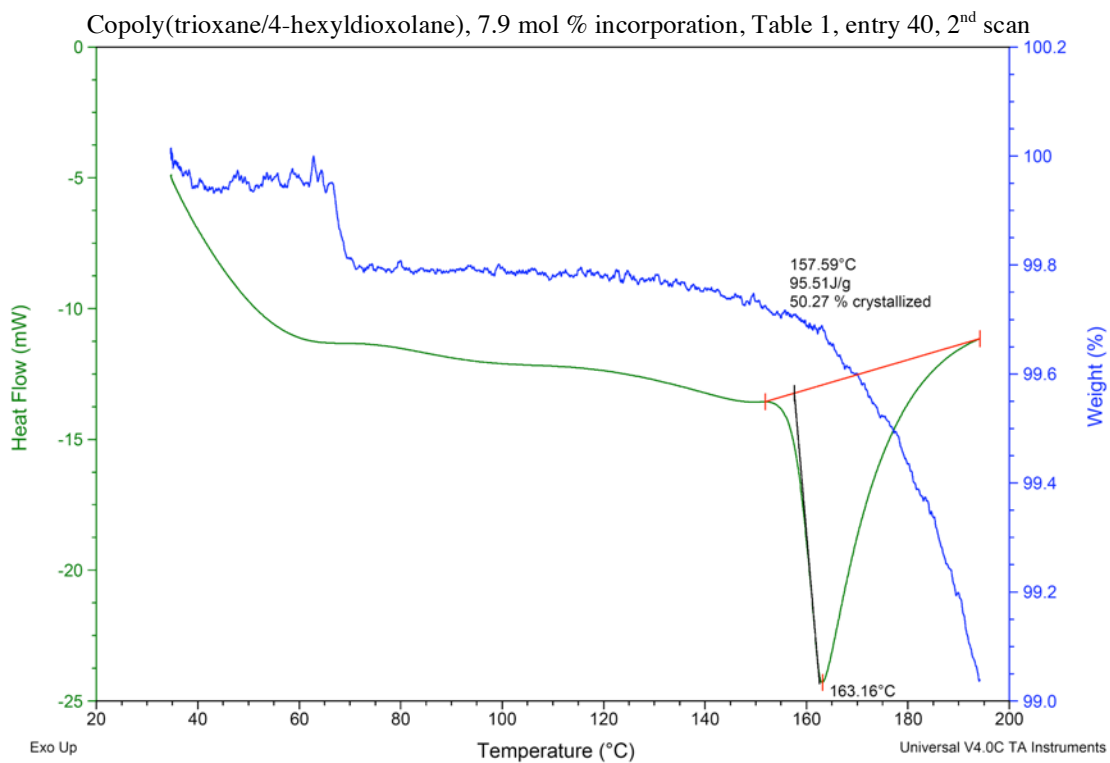
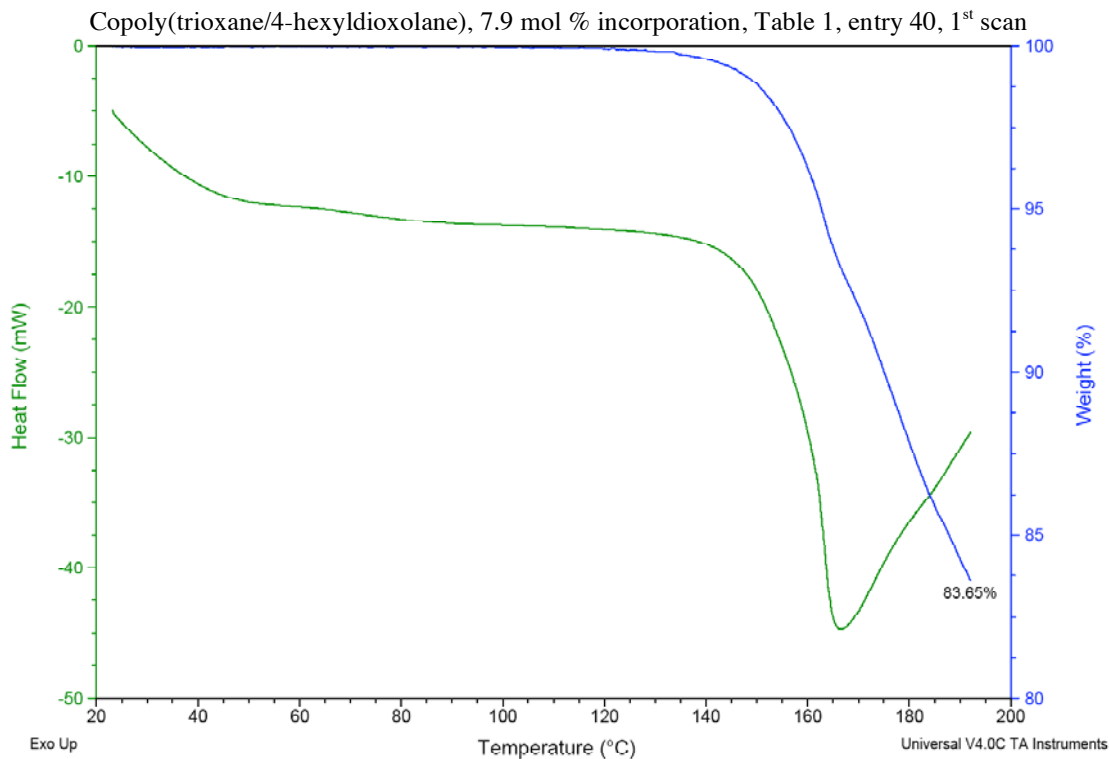


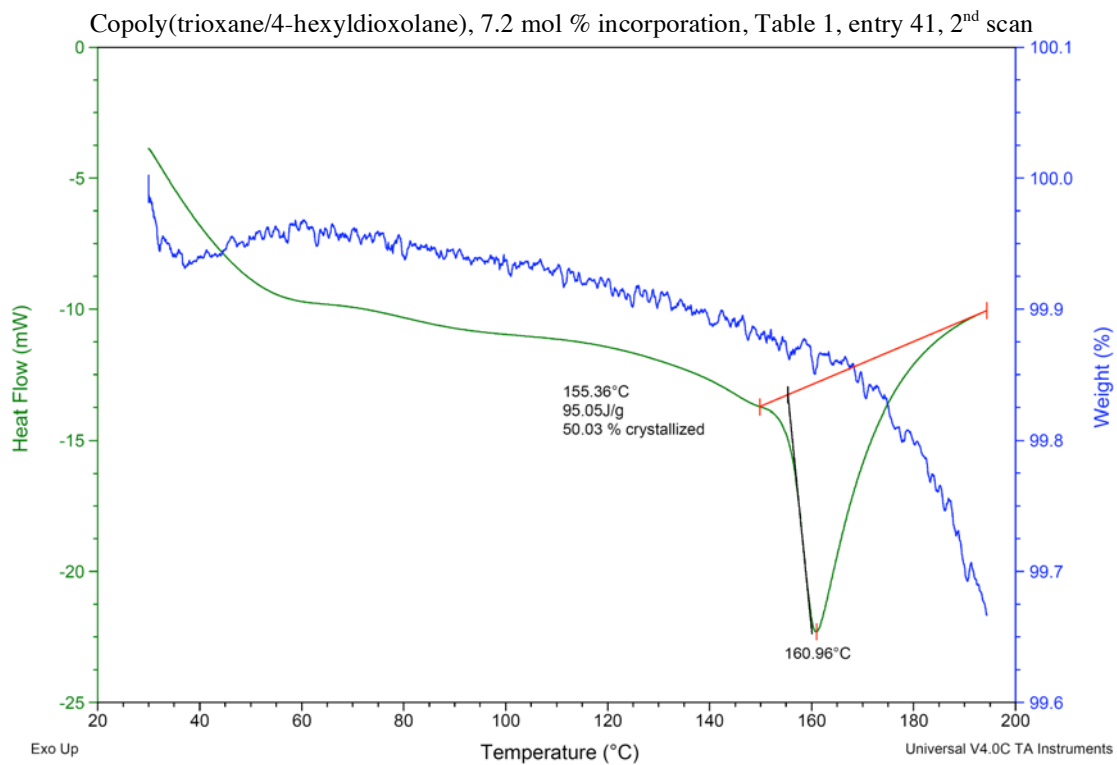
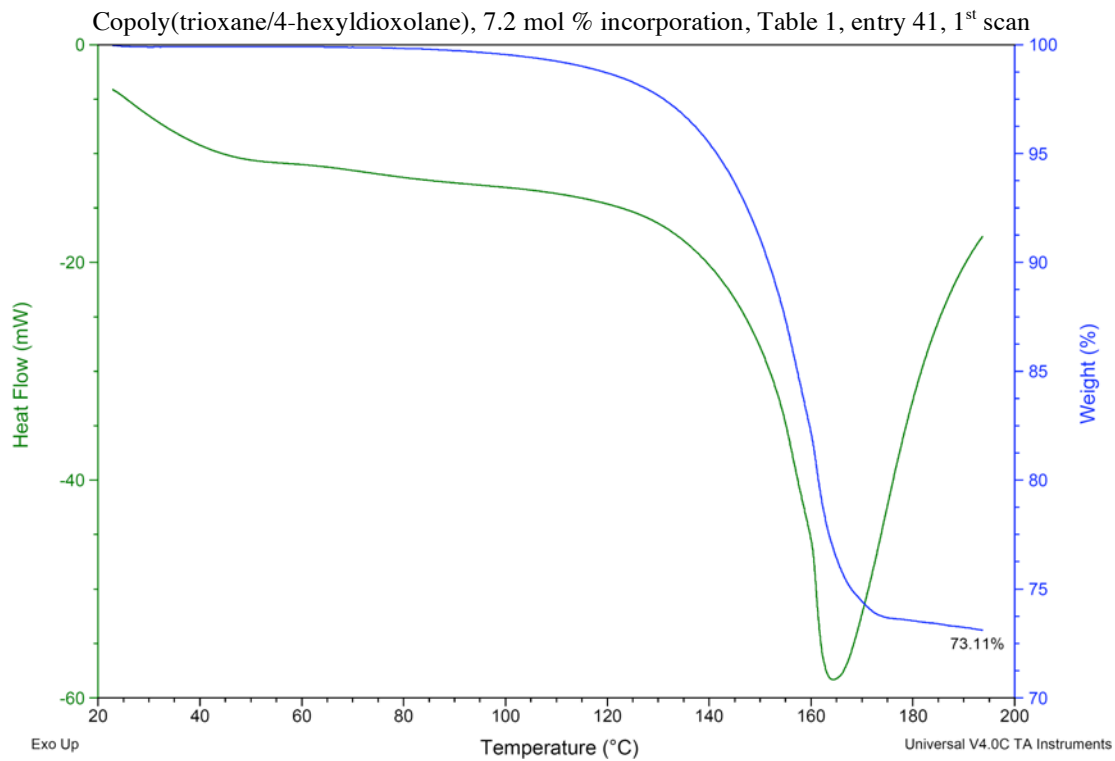


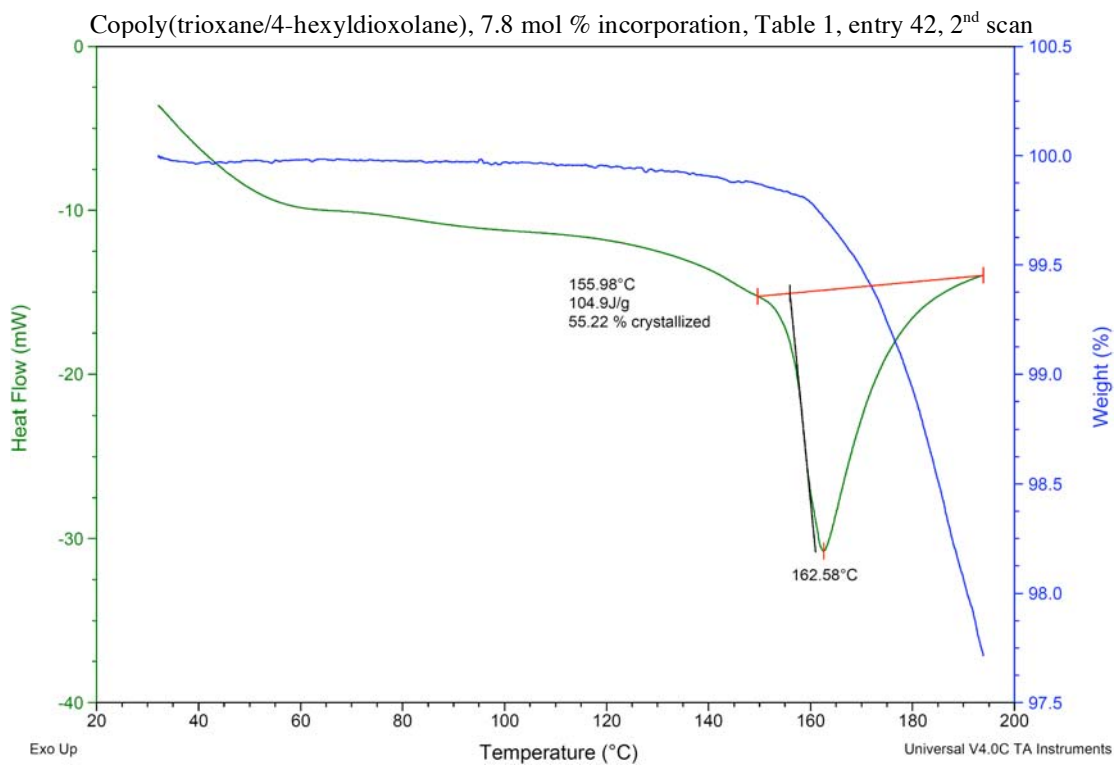
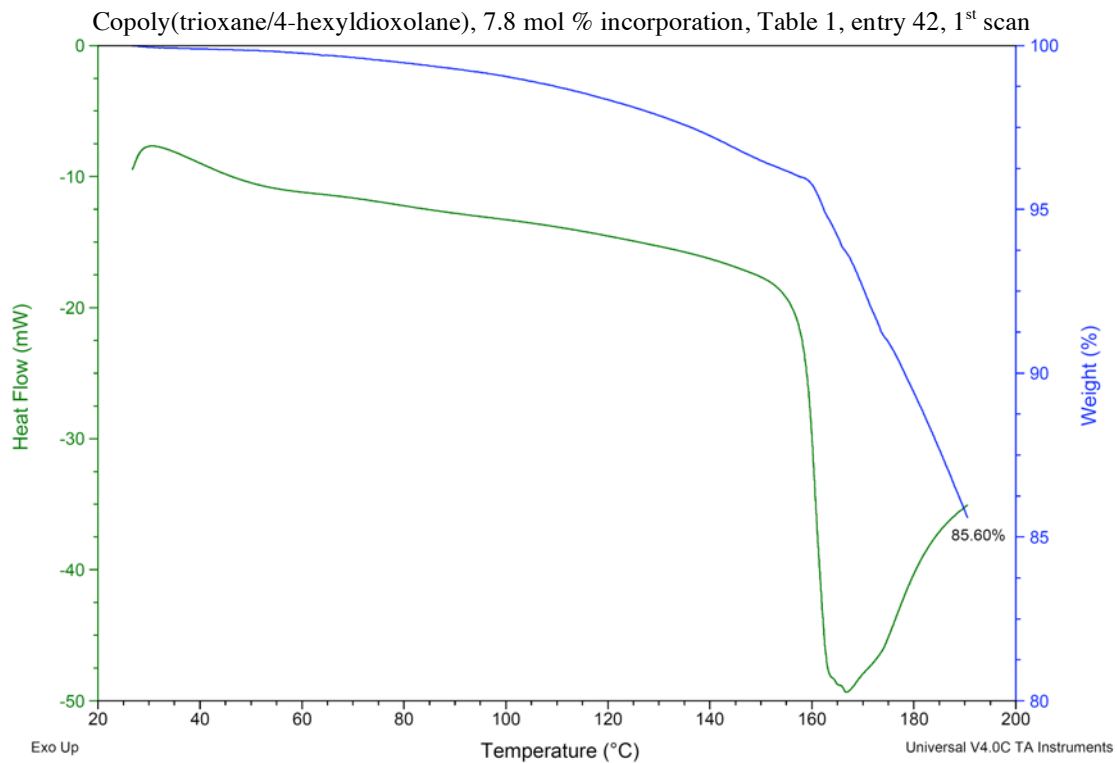


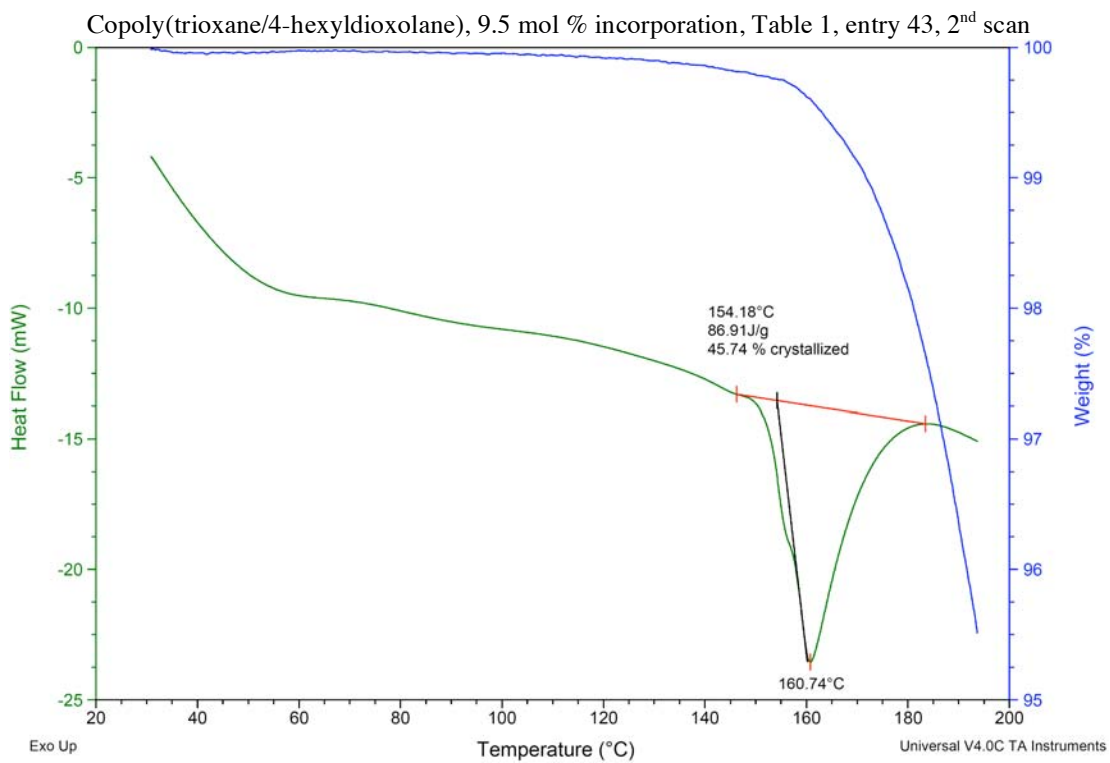
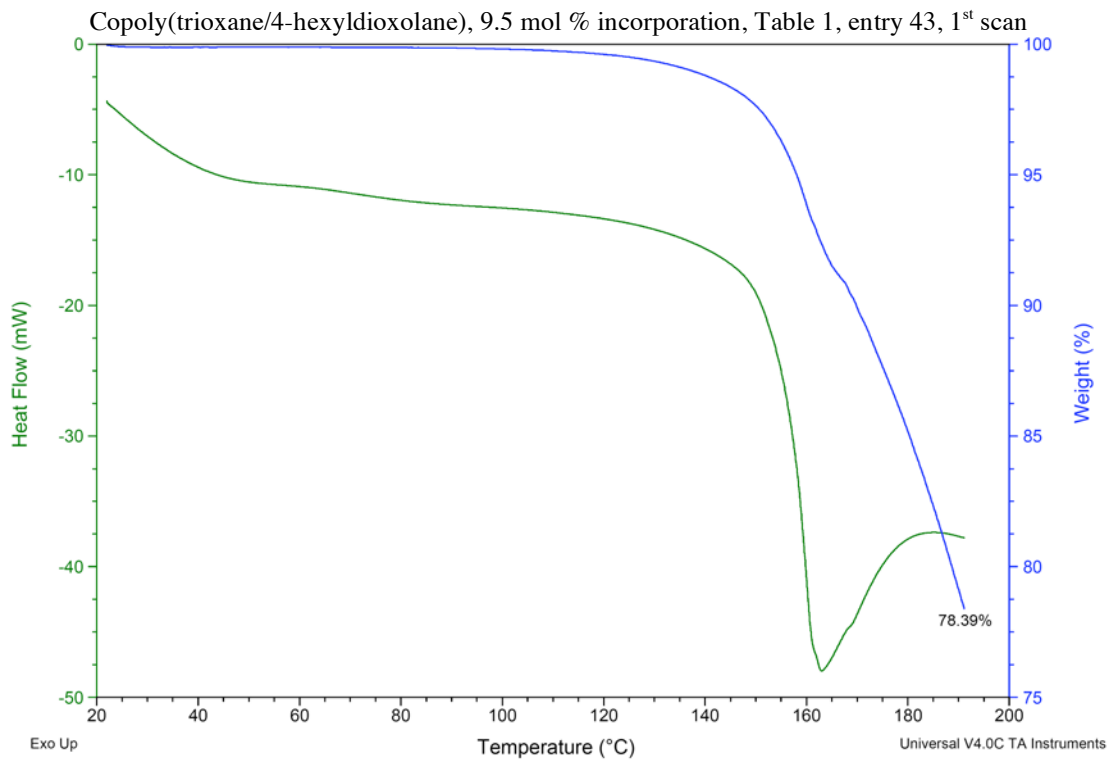












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- (2) Astle, M. J.; Zaslowsky, J. A.; Lafyatis, P. G. *Ind. Eng. Chem.* **1954**, 46, 787-791.
- (3) Mück, K.-F. "Physical Constants of Poly(oxymethylene) in *Polymer Handbook*, 4th Edition; Brandup, J.; Immergut, E. H.; Grulke, E. A., Eds.; Wiley-Interscience: New York, **1999**, Section V, pp. 97-112.