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Supporting information

Isosorbide monoacrylate: a sustainable monomer for the production of fully biobased polyacrylates and thermosets.

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Experimental section

Synthesis of 4-hydroxyhexahydrofurane-1-yl-acrylate (isosorbide monoacrylate (IMA))

A mixture of acrylic acid (1 eq, 0.23 mol, 16.6 g), dry isosorbide (1.5 eq, 0.35 mol, 50 g) in dry acetonitrile (500 mL) was bubbled under nitrogen during 30 min under stirring. Then catalyst ($Sc(OTf)_3$; $ZnCl_2$; HCl or H_2SO_4 - 1.23 eq) was added dropwise and the mixture was stirred at 40°C under nitrogen overnight. Ethyl acetate was added and the organic was washed with a saturated solution of sodium bicarbonate and water successively. The resulting organic phase was dried over $MgSO_4$, evaporated and subjected to column chromatography (SiO_2: dichloromethane/ethyl acetate (7:3)) to furnish endo/exo-substituted Isosorbide mono-acrylates as a light-yellow liquid (Yield:17%).

Exo: *NMR ^1H, 300 MHz, 25 °C, $CDCl_3$ (δ=ppm)*: δ= 3.59 (1H, dd, 6 Hz, 9.51 Hz) ; 3.91 (1H, dD, 6 Hz, 9.51 Hz) ; 4.07 (2H, m) ; 4.32 (1H, m) ; 4.53 (1H, d, 4.41 Hz) ; 4.66 (1H, t, 4.90 Hz) ; 5.32 (1H, s) ; 5.89 (1H, dD, 1.40 Hz, 10.45 Hz) ; 6.13 (1H, dD, 10.45 Hz, 17.20 Hz) ; 6.45 (1H, dD, 1.40 Hz, 17.20 Hz). *NMR ^{13}C, 75 MHz, 25 °C, $CDCl_3$ (δ=ppm)*: δ= 72.4; 73.4; 73.6; 78.7; 82.3; 85.9; 128.1; 132.1; 165.2

Endo: *NMR ^1H, 300 MHz, 25°C, $CDCl_3$ (δ=ppm)*: δ= 3.90 (4H , m) ; 4.35 (1H, m) ; 4.43 (1H, d, 5.05Hz) ; 4.90 (1H, m), 5.24 (1H, q, 5.48 Hz) ; 5.89 (1H, dD, 1.40 Hz, 10.40 Hz) ; 6.18 (1H, dD, 10.40 Hz, 17.33 Hz) ; 6.48 (dD, 1.40 Hz, 17.33 Hz). *NMR ^{13}C, 75 MHz, 25 °C, $CDCl_3$ (δ=ppm)*: δ= 70.4; 74.4; 75.7; 76.2; 80.5; 88.3; 127.8; 131.8; 165.7

General procedure for conventional free radical polymerizations

All the polymerizations were made with the same protocol: reagents (IMA, AIBN) and solvents (anhydrous dimethylformamide (DMF), anhydrous dimethyl sulfoxide (DMSO) or a mixture of anhydrous isopropanol and anhydrous dioxane) were added in a Schlenk and three freeze-pump-thaw cycles were made. Then the mixture was stirred at 90°C under nitrogen. All quantities are shown in the Tables S1 and S2.

General procedure for the formation of thermosets

In an aluminum mold, 1 g of PIMA were dissolved in 2 g of dry *N,N*-dimethylformamide. 10 mol% (26.4 mg) of succinic anhydride were added and the mixture was heating at 120°C overnight. Then a post-curing was made during 2h hours at 190°C. The piece was removed from the mold, cut and analyzed by DSC and DMA.

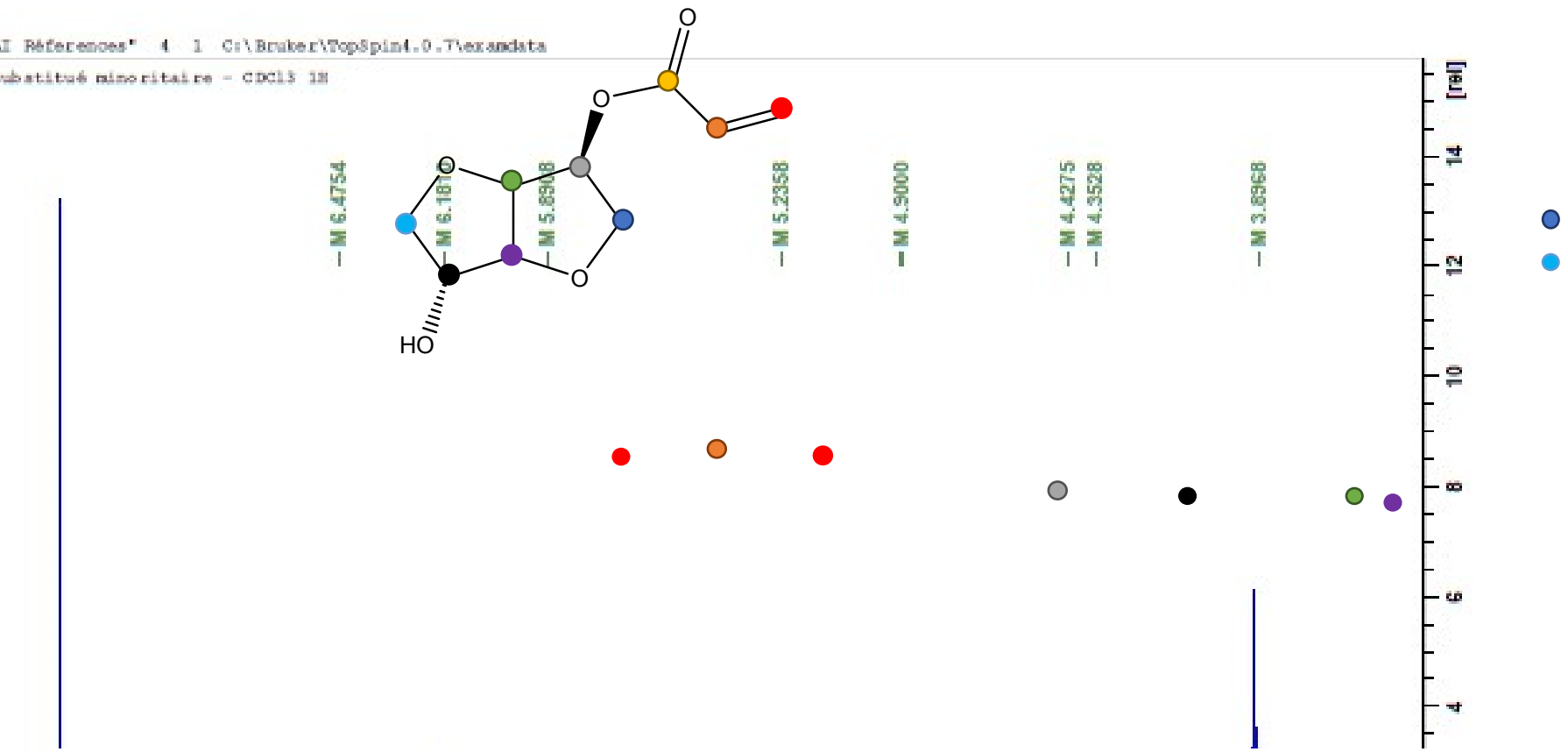
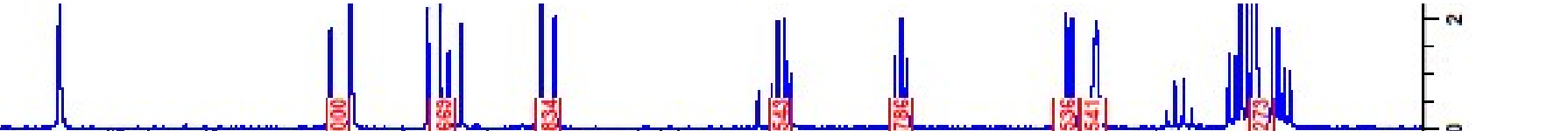


Figure S 1 : NMR ^{1}H, $CDCl_3$ of IMA endo



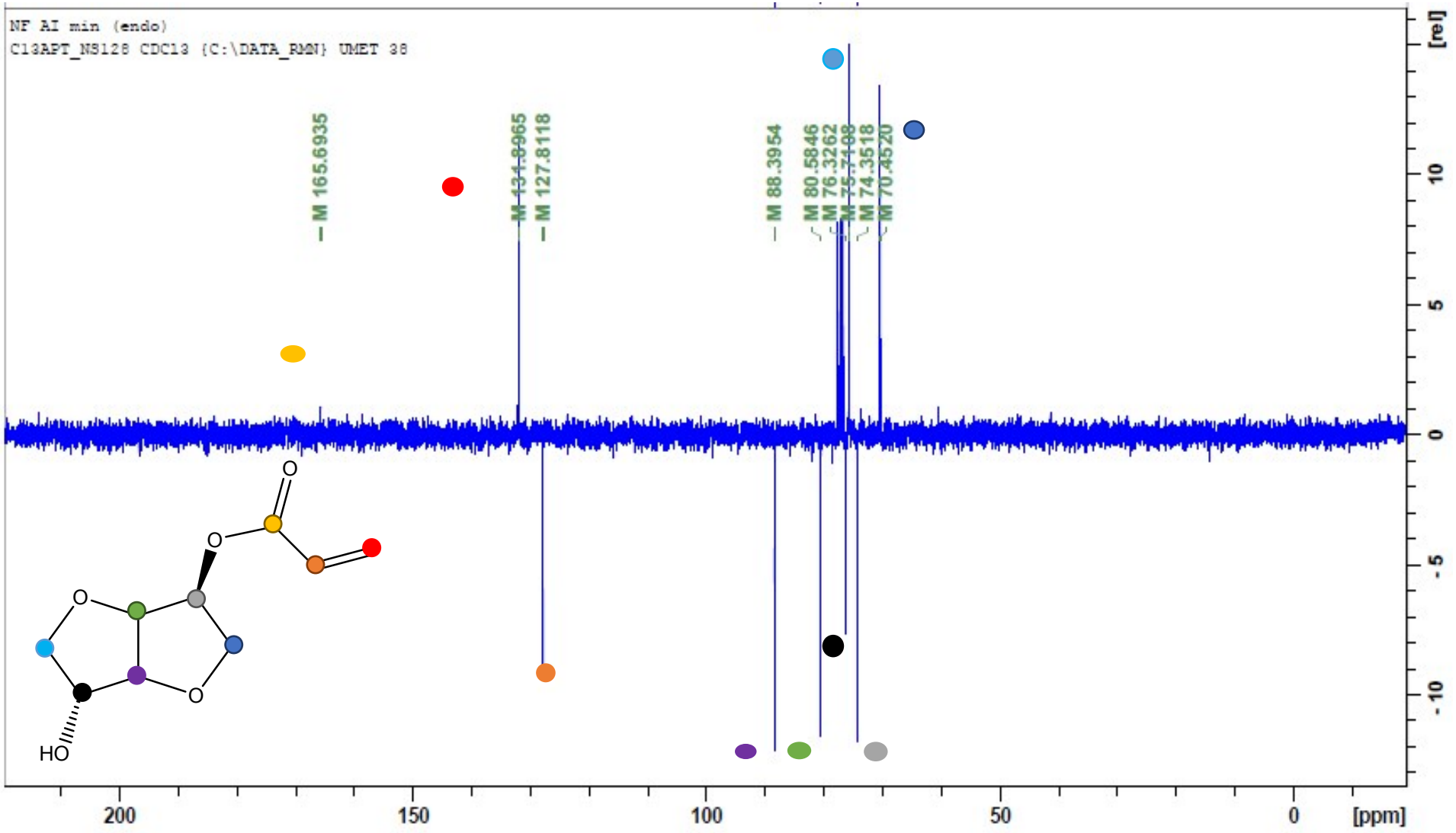


Figure S 2 : NMR ^{13}C Jmod, $CDCl_3$ of IMA endo

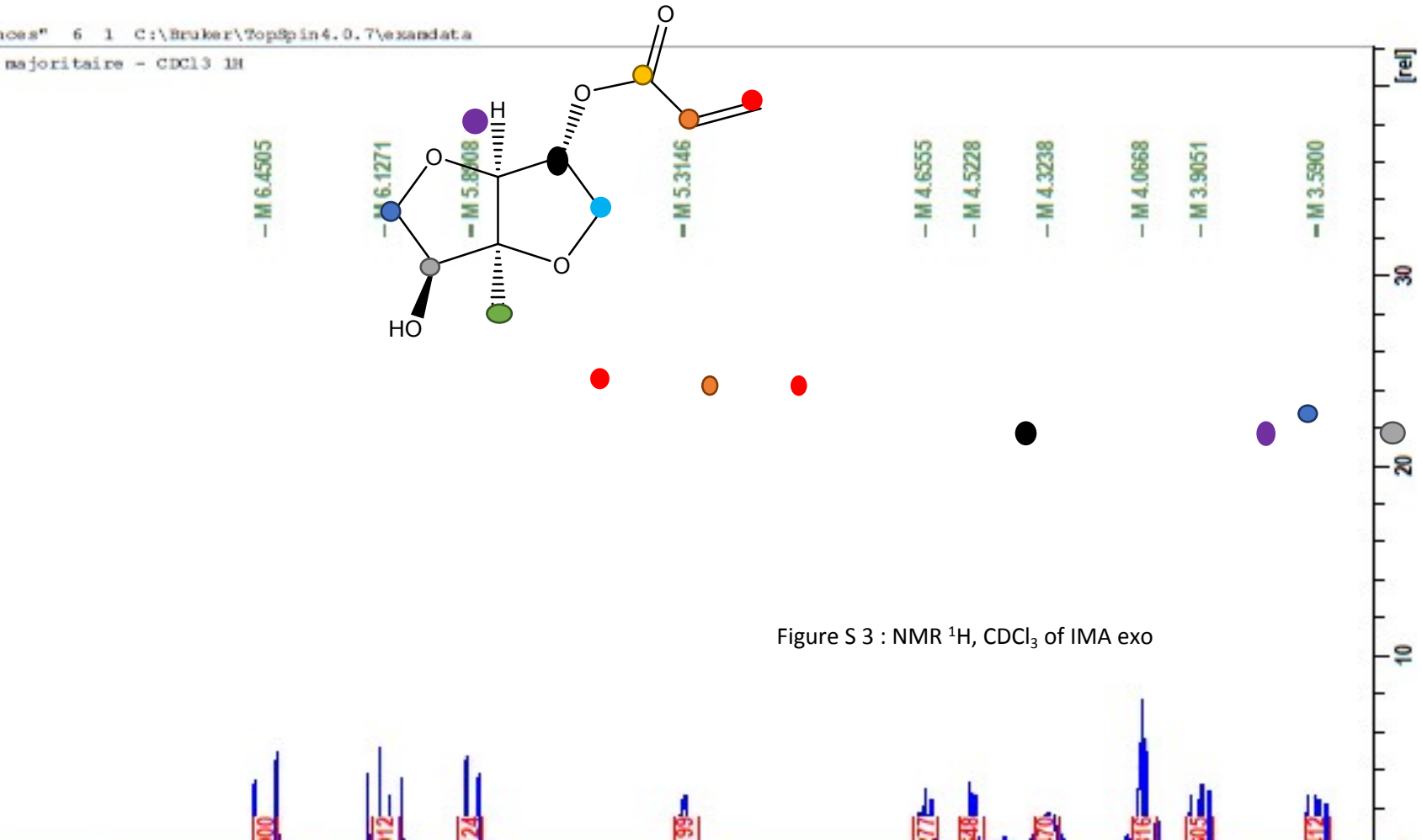


Figure S 3 : NMR ^{1}H, $CDCl_3$ of IMA exo

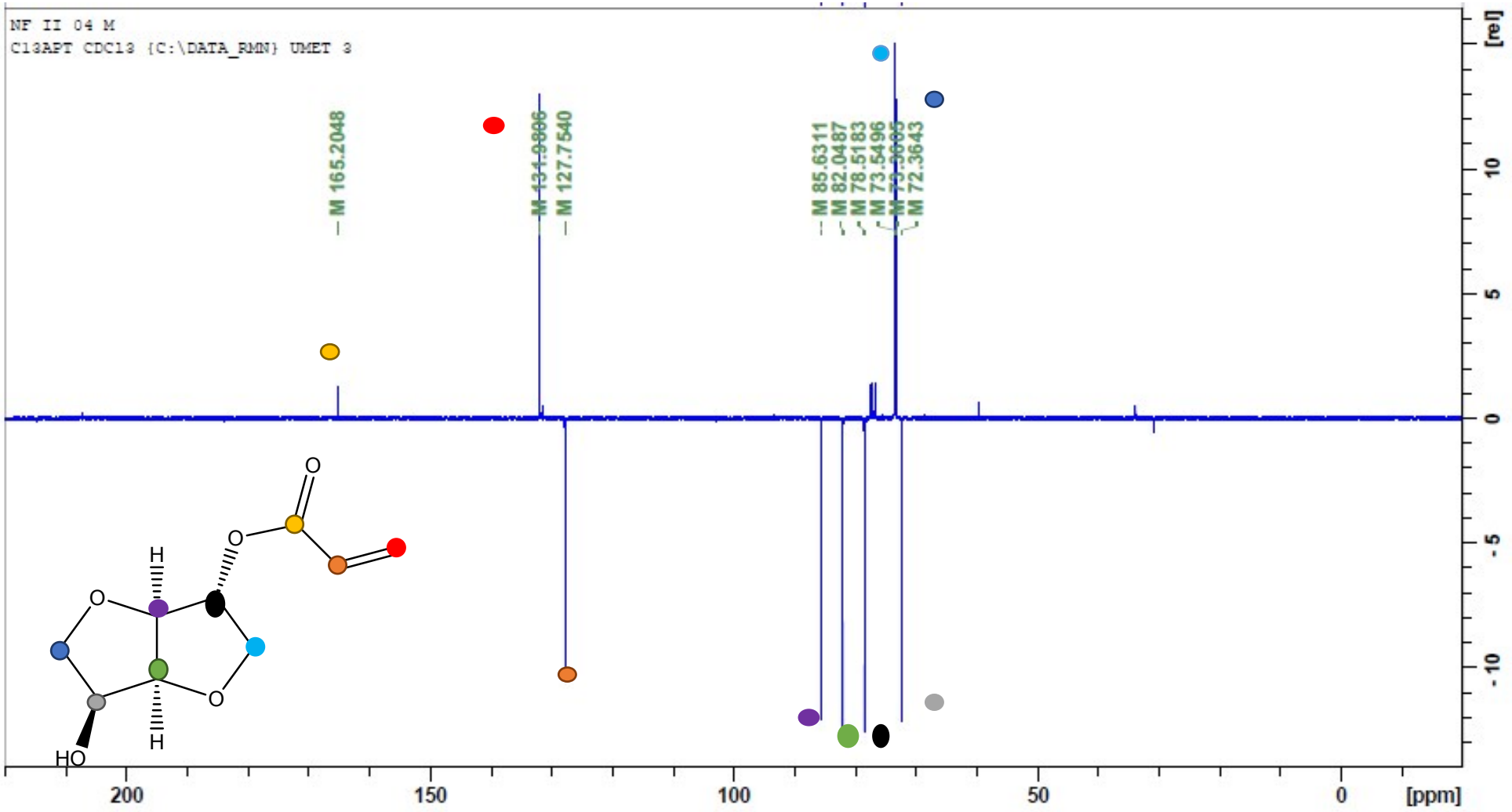


Figure S 4 : NMR 13C Jmod, CDCl3 of IMA exo

Table S 1 : Free radical polymerization of isosorbide monoacrylate.

[AI]/[AIBN]	Monomer	AIBN	Solvents	[Solvent]/[AI]
100	500 mg, 2.5 mmol	2.1 mg, $1.28x10^{-2}$ mmol	Isopropanol 1 (250 mg, 4.17 mmol) Dioxane 6 (1500 mg, 17 mmol)	8,468
200	500 mg, 2.5 mmol	1.1 mg, $6.4x10^{-3}$ mmol	Isopropanol 1 (250 mg, 4.17 mmol) Dioxane 6 (1500 mg, 17 mmol)	8,468
500	500 mg, 2.5 mmol	$4.2x10^{-1}$ mg, $2.6x10^{-1}$ mmol	Isopropanol 1 (250 mg, 4.17 mmol) Dioxane 6 (1500 mg, 17 mmol)	8,468
1000	500 mg, 2.5 mmol	$2.1x10^{-1}$ mg, $1.28x10^{-3}$ mmol	Isopropanol 1 (250 mg, 4.17 mmol) Dioxane 6 (1500 mg, 17 mmol)	8,468
5000	500 mg, 2.5 mmol	$4.2x10^{-2}$ mg, $2.6x10^{-2}$ mmol	Isopropanol 1 (250 mg, 4.17 mmol) Dioxane 6 (1500 mg, 17 mmol)	8,468
10000	500 mg, 2.5 mmol	$2.1x10^{-2}$ mg, $1.28x10^{-4}$ mmol	Isopropanol 1 (250 mg, 4.17 mmol) Dioxane 6 (1500 mg, 17 mmol)	8,468
100	500 mg, 2.5 mmol	2.1 mg, $1.28x10^{-2}$ mmol	Isopropanol 1 (875 mg, 14.6 mmol) Dioxane 1 (875 mg, 9.9 mmol)	9,8
100	500 mg, 2.5 mmol	2.1 mg, $1.28x10^{-2}$ mmol	Isopropanol 1 (438 mg, 7.30 mmol) Dioxane 3 (1313 mg, 14.9 mmol)	8,88
100	500 mg, 2.5 mmol	2.1 mg, $1.28x10^{-2}$ mmol	DMF (1650 mg, $2.26x10^{-2}$ mol)	9,04
100	500 mg, 2.5 mmol	2.1 mg, $1.28x10^{-2}$ mmol	DMSO (1958 mg, $2,51x10^{-2}$ mol)	10,04

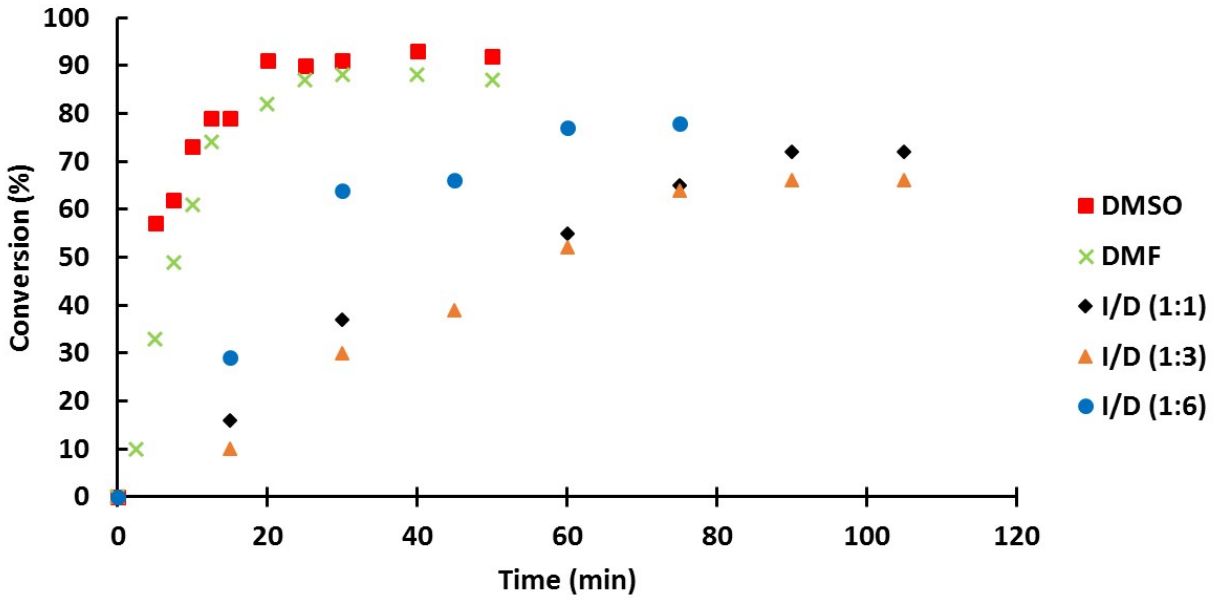


Figure S 5: Evolution of IMA conversion in different solvents ([IMA]/[AIBN]) =100) at 90 °C

Table S 2 Study of influence of [solvent]/[IMA] ratio on polymerization of IMA.

[IMA]/[AIBN]	Monomer	AIBN	Solvents	[Solvent]/[IMA]
100	1000 mg, 5 mmol	4.2 mg, $2.56x10^{-2}$ mmol	Isopropanol 1 (250 mg, 4.17 mmol) Dioxane 6 (1500mg, 17 mmol)	4,234
100	1000 mg, 5 mmol	4.2 mg, $2.56x10^{-2}$ mmol	DMF (1650 mg, $2.26x10^{-2}$ mol)	4,52
100	1000 mg, 5 mmol	4.2 mg, $2.56x10^{-2}$ mmol	DMSO (1958 mg, $2,51x10^{-2}$ mol)	5,02
100	750 mg, 3.75 mmol	3.2 mg, $1,92x10^{-2}$ mmol	Isopropanol 1 (250 mg, 4.17 mmol) Dioxane 6 (1500 mg, 17 mmol)	5,6453
100	750 mg, 3.75 mmol	3.2 mg, $1,92x10^{-2}$ mmol	DMF (1650 mg, $2.26x10^{-2}$ mol)	6,0267
100	750 mg, 3.75 mmol	3.2 mg, $1,92x10^{-2}$ mmol	DMSO (1958 mg, $2,51x10^{-2}$ mol)	6,693
100	250 mg, 1.25 mmol	1 mg, $6.4x10^{-3}$ mmol	Isopropanol 1 (250 mg, 4.17 mmol) Dioxane 6 (1500 mg, 17 mmol)	16,936
100	250 mg, 1.25 mmol	1 mg, $6.4x10^{-3}$ mmol	DMF (1650 mg, $2.26x10^{-2}$ mol)	18,08
100	250 mg, 1.25 mmol	1 mg, $6.4x10^{-3}$ mmol	DMSO (1958 mg, $2,51x10^{-2}$ mol)	20,08
100	100 mg, 0.5 mmol	0.4 mg, $2.56x10^{-3}$ mmol	Isopropanol 1 (250 mg, 4.17 mmol) Dioxane 6 (1500 mg, 17 mmol)	42,34
100	100 mg, 0.5 mmol	0.4 mg, $2.56x10^{-3}$ mmol	DMF (1650 mg, $2.26x10^{-2}$ mol)	45,2
100	100 mg, 0.5 mmol	0.4 mg, $2.56x10^{-3}$ mmol	DMSO (1958 mg, $2,51x10^{-2}$ mol)	50,2

Table S 3 : Data for Mayo plot at 2 min.

Isopro/Dioxane			DMF			DMSO		
DPn	**1/DPn**	**[S]/[M]**	**DPn**	**1/DPn**	**[S]/[M]**	**DPn**	**1/DPn**	**[S]/[M]**
300	0,00333333	4,234	401	0,00249377	4,52	560	0,00178571	5
204	0,00490196	5,645	253	0,00395257	6,02	491	0,00203666	6,7
135	0,00740741	8,468	215	0,00465116	9,04	405	0,00246914	10
96	0,01041667	16,936	147	0,00680272	18,08	225	0,00444444	20,1
50	0,02	30	88	0,01136364	32	175	0,00571429	34
38	0,02631579	42,34	67	0,01492537	45,2	125	0,008	50,7

Table S 4 : Data for Mayo plot at 5 min.

Isopro/Dioxane			DMF			DMSO		
DPn	**1/DPn**	**[S]/[M]**	**DPn**	**1/DPn**	**[S]/[M]**	**DPn**	**1/DPn**	**[S]/[M]**
213	0,00469484	4,234	305	0,00327869	4,52	894	0,00111857	5
147	0,00680272	5,645	170	0,00588235	6,02	327	0,0030581	6,7
92	0,01086957	8,468	164	0,00609756	9,04	255	0,00392157	10
72	0,01388889	16,936	82	0,01219512	18,08	175	0,00571429	20,1
40	0,025	42,34	67	0,01492537	45,2	181	0,00552486	50,7

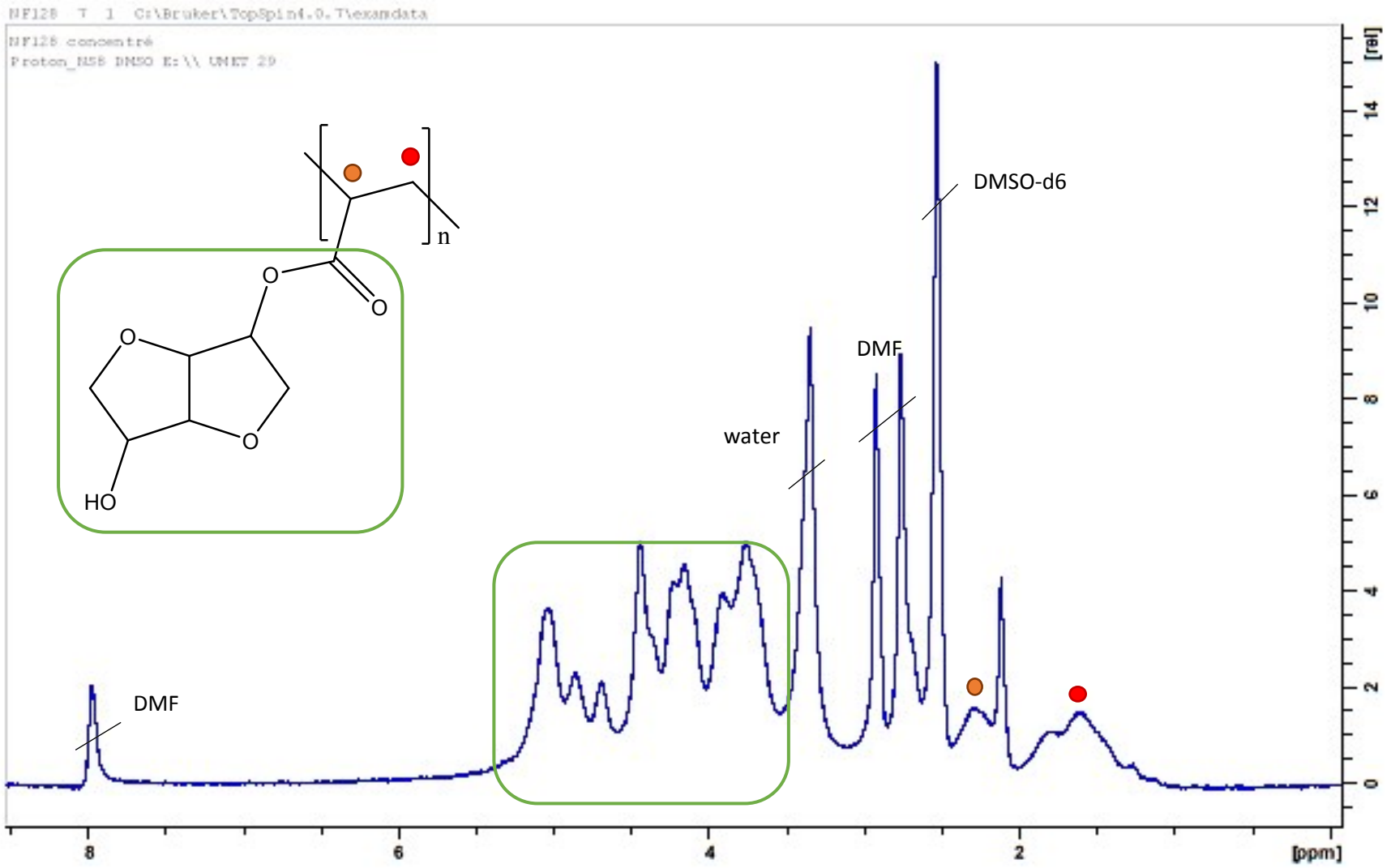


Figure S 6 : NMR 1H of PIMA in DMSO-d6.

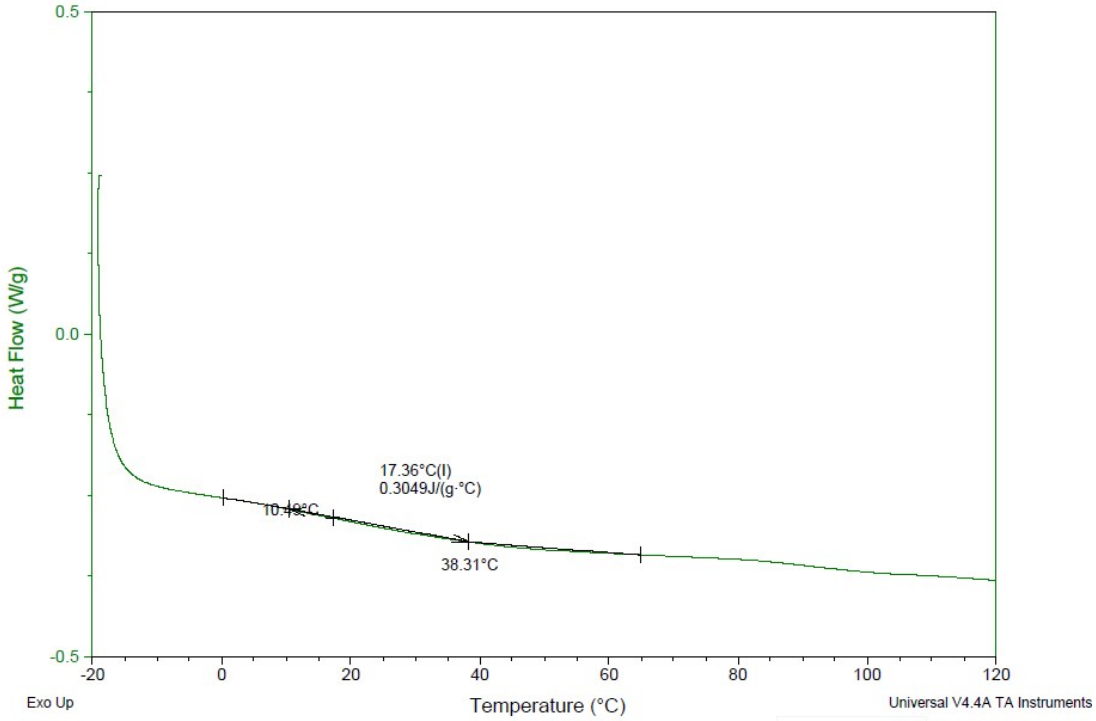


Figure S 7 : DSC thermogram of PIMA 2000 g/mol

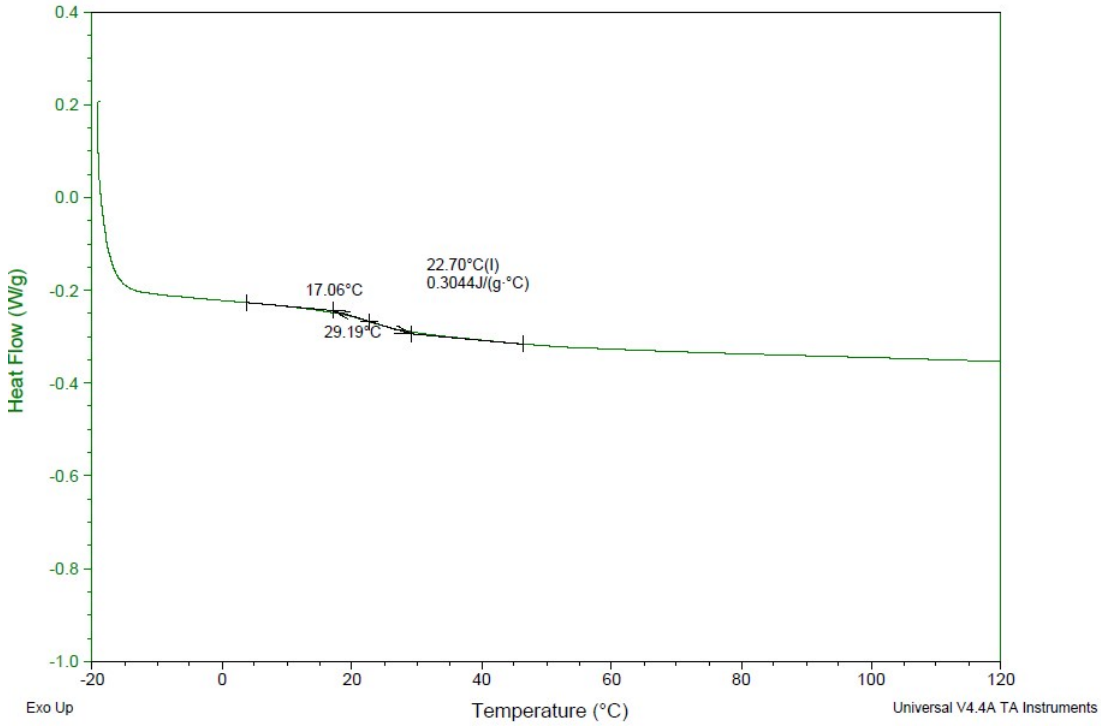


Figure S 8 : DSC thermogram of PIMA 3200 g/mol

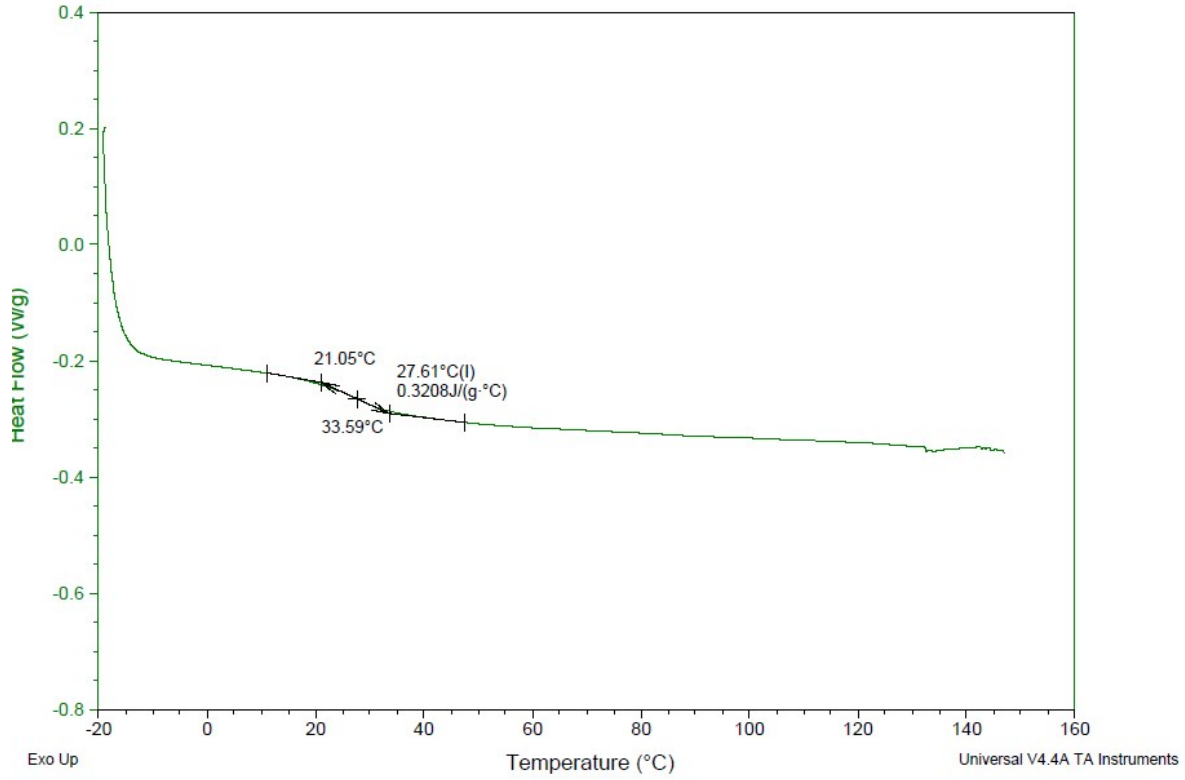


Figure S 9 : DSC thermogram of PIMA 4200 g/mol

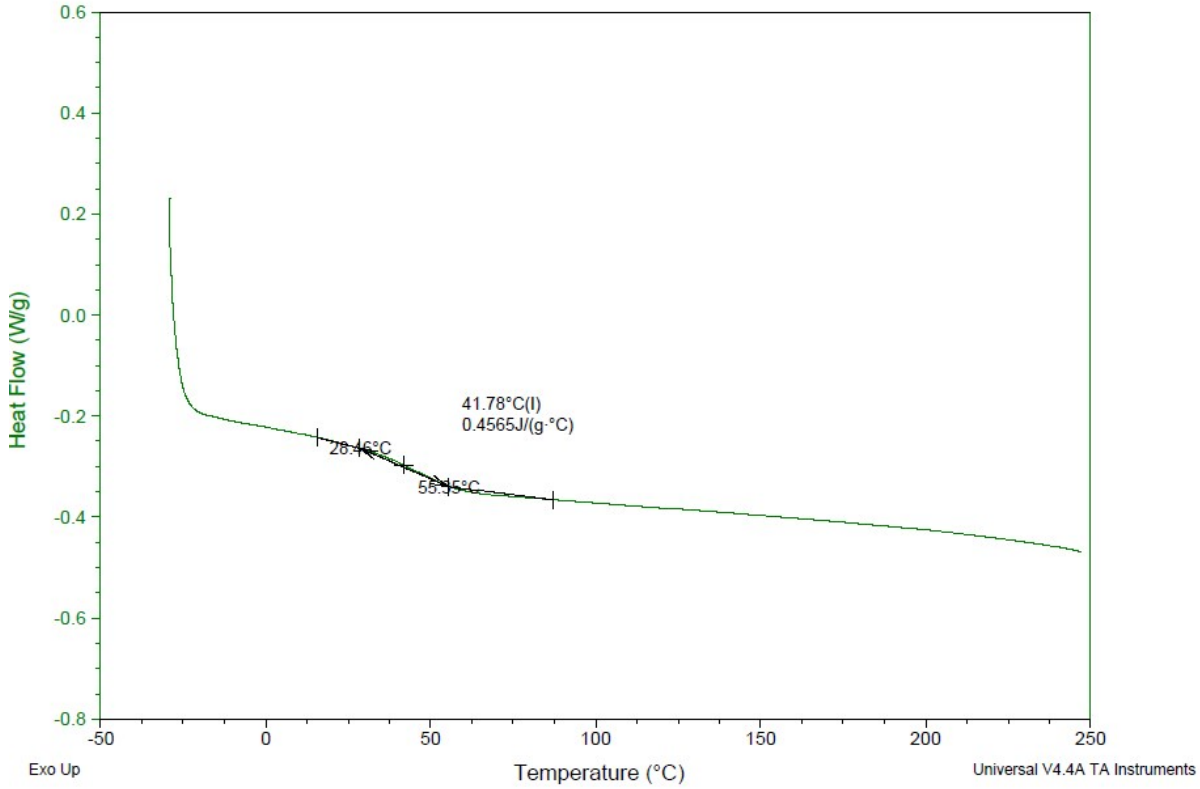


Figure S 10 : DSC thermogram of PIMA 7200 g/mol

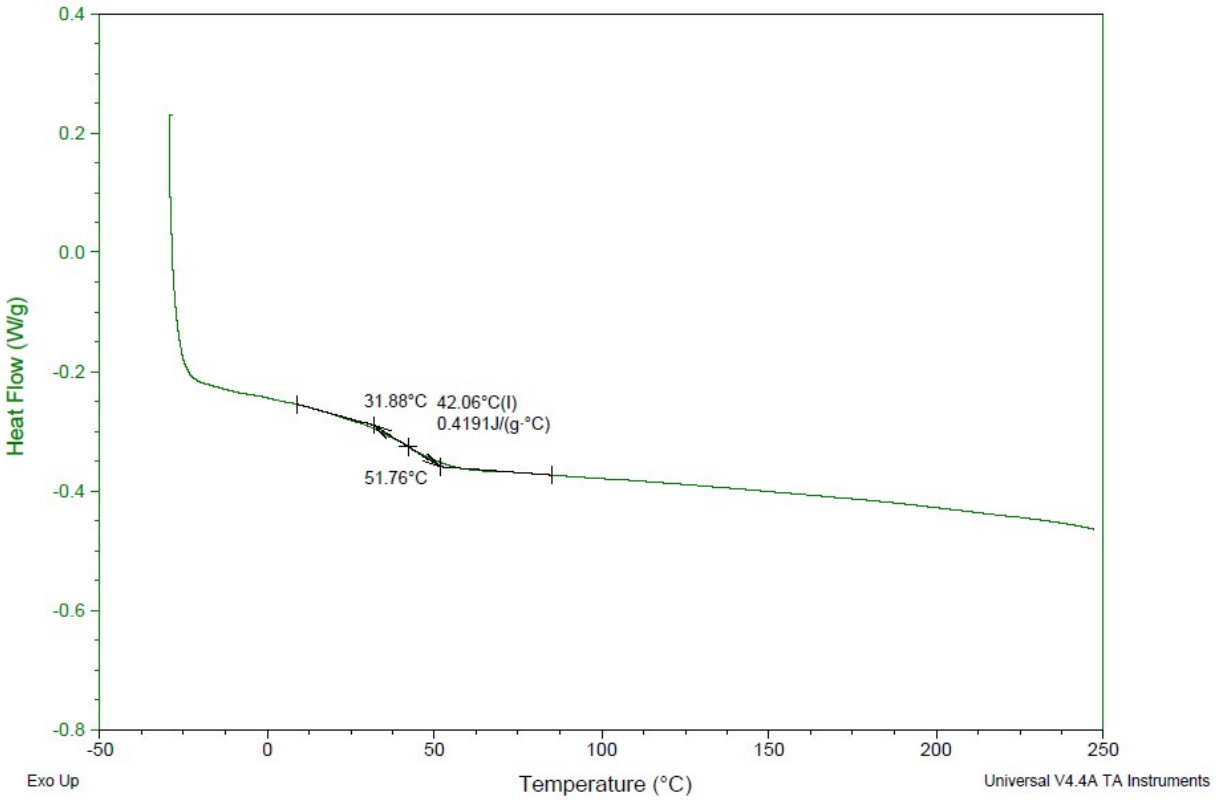


Figure S 11 : DSC thermogram of PIMA 7700 g/mol

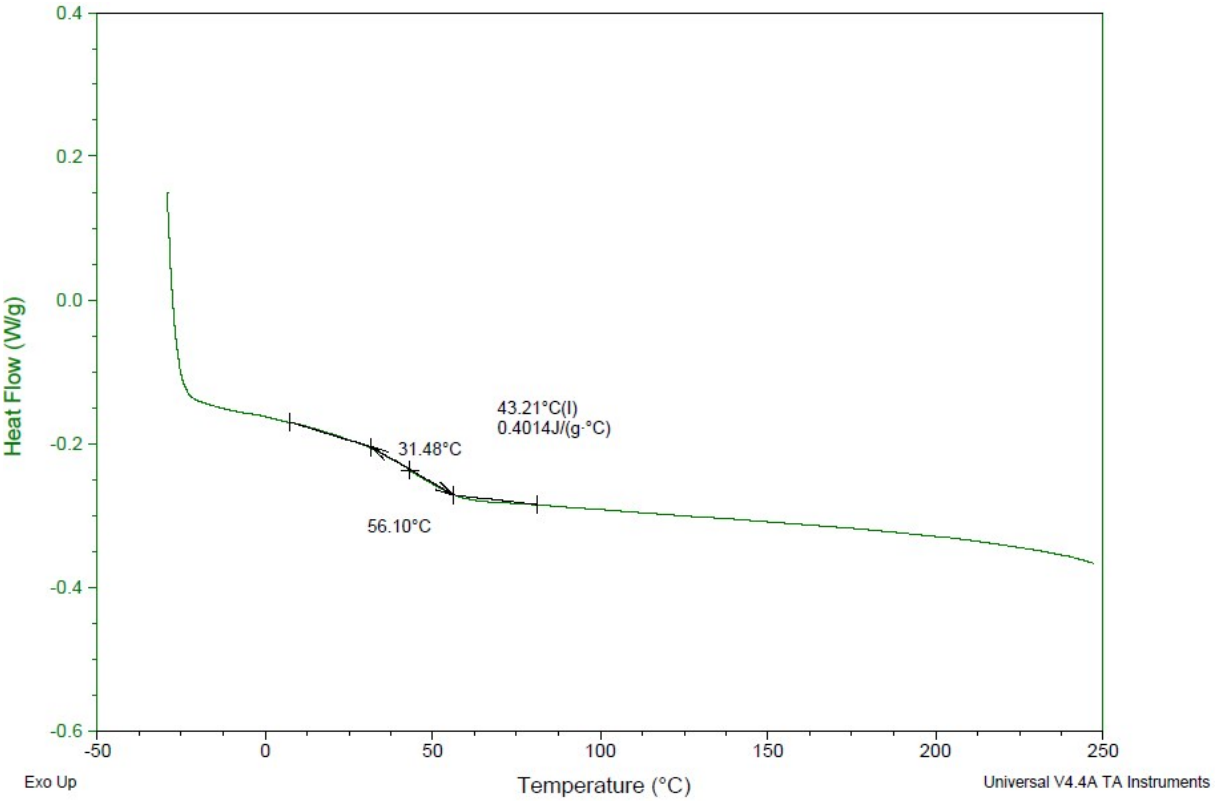


Figure S 12 : DSC thermogram of PIMA 9000 g/mol

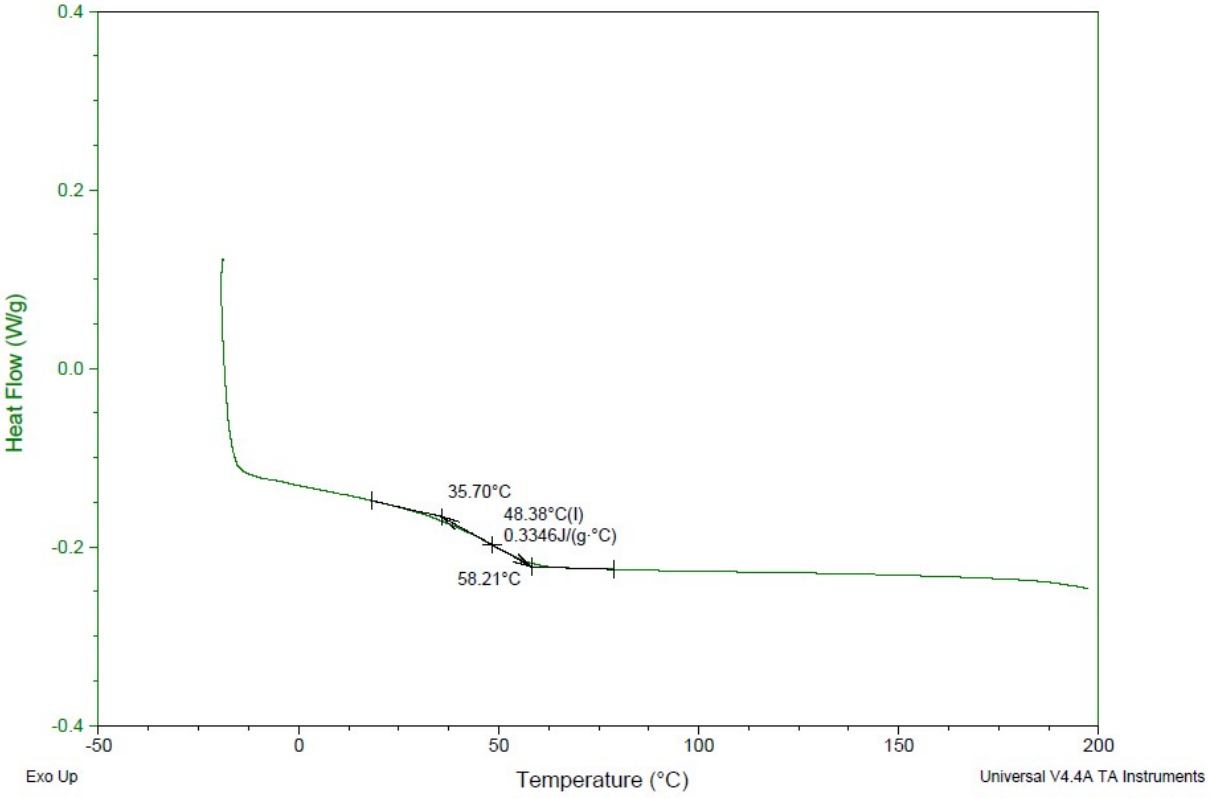


Figure S 13 : DSC thermogram of PIMA 12100 g/mol

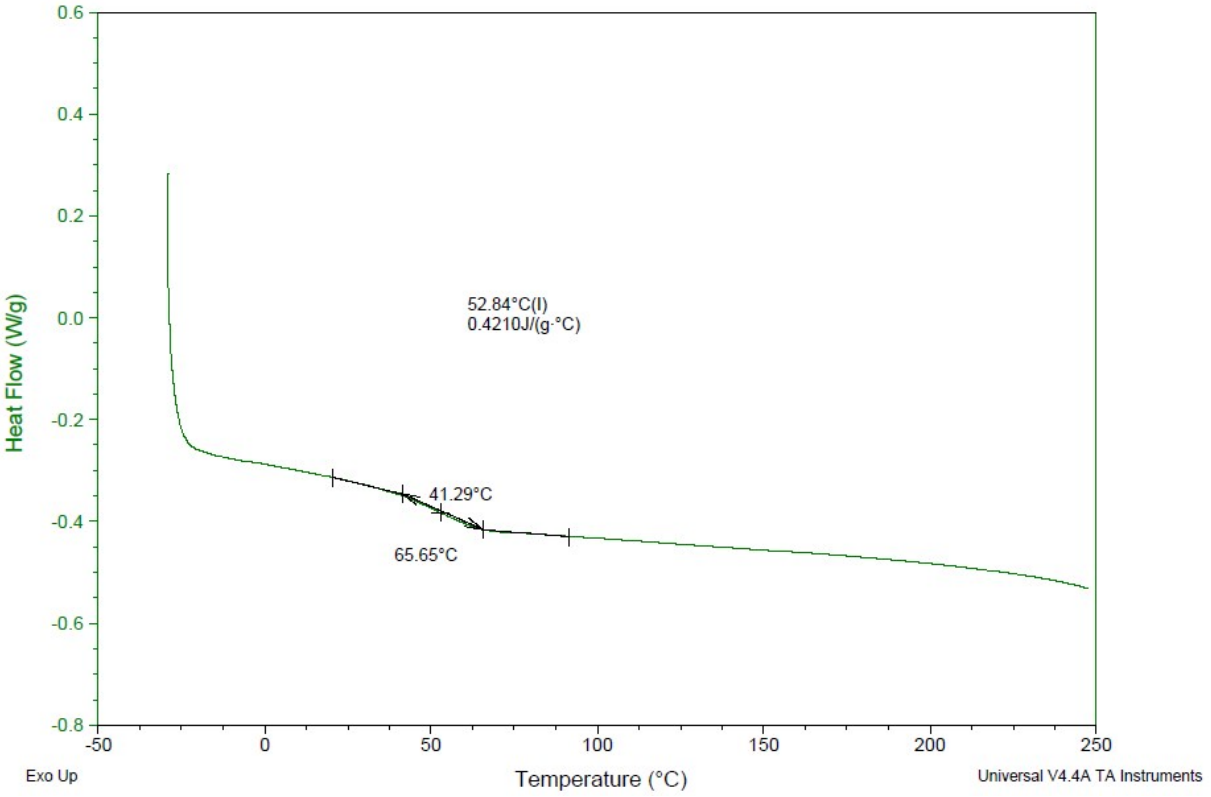


Figure S 14 : DSC thermogram of PIMA 12700 g/mol

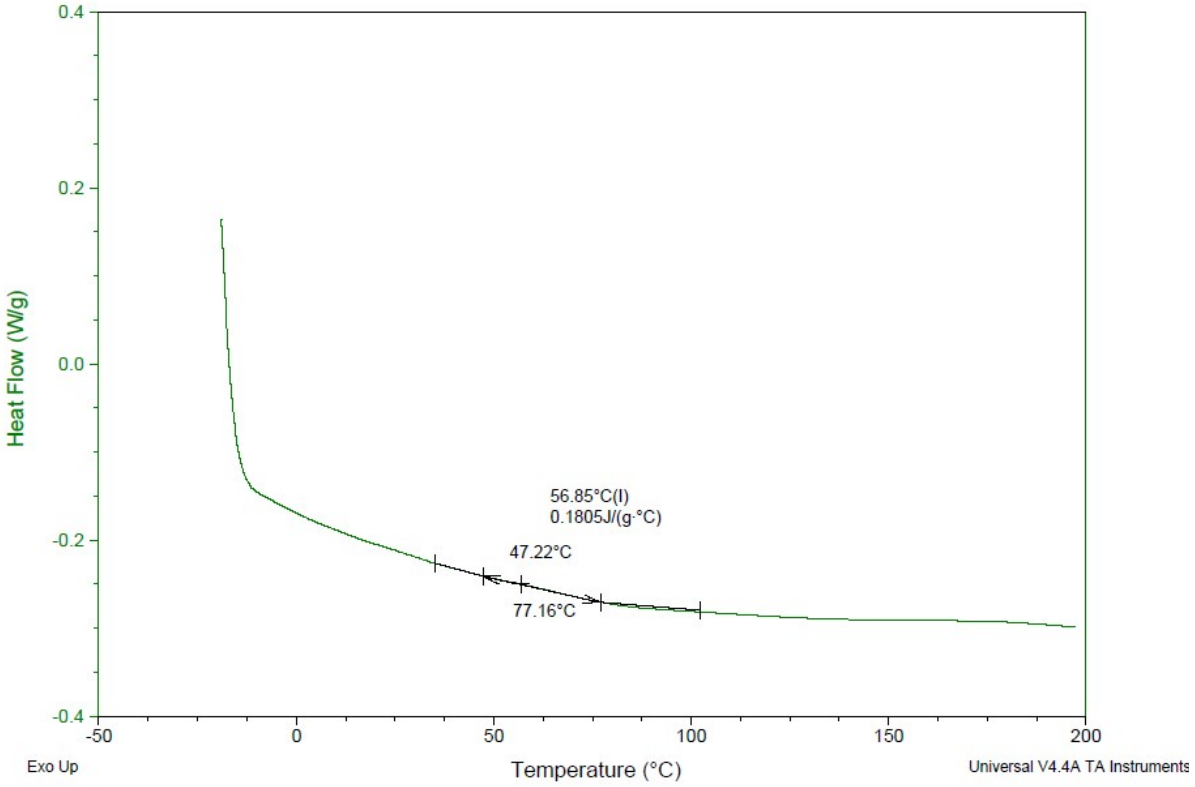


Figure S 15 : DSC thermogram of PIMA 13200 g/mol

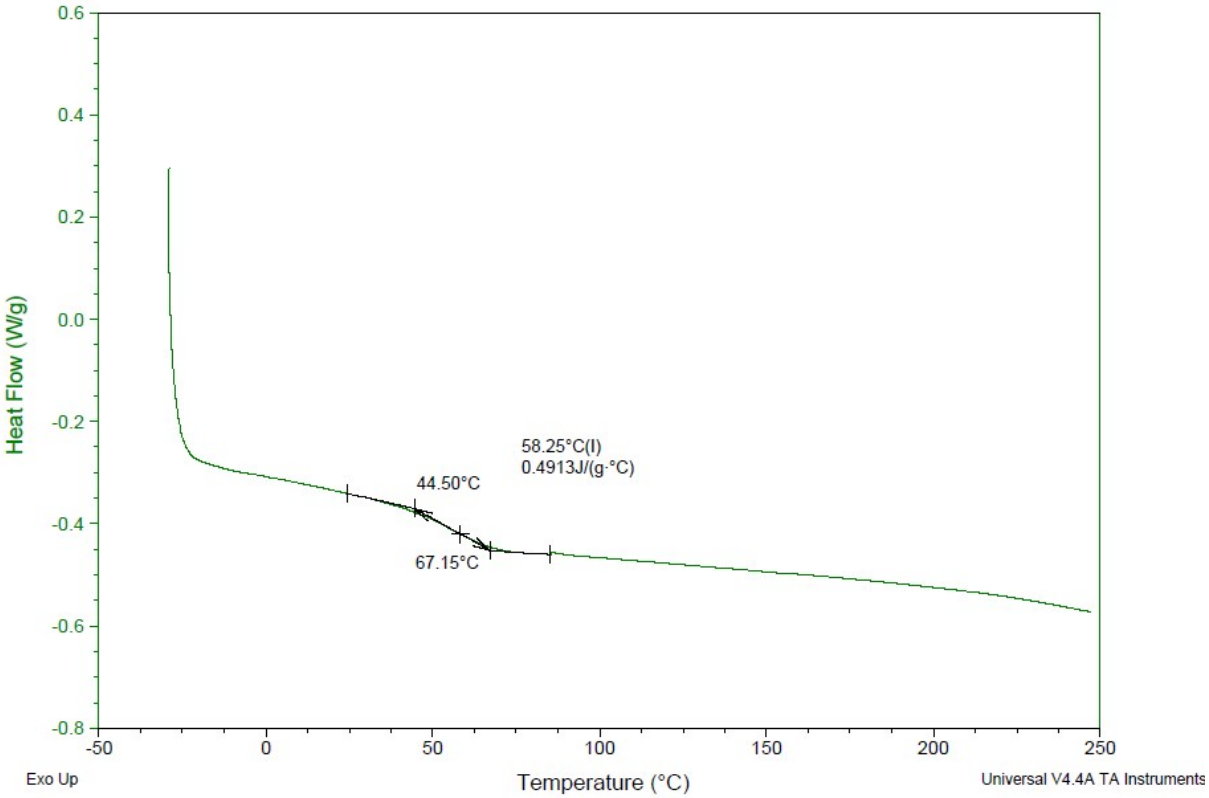


Figure S 16 : DSC thermogram of PIMA 25900 g/mol

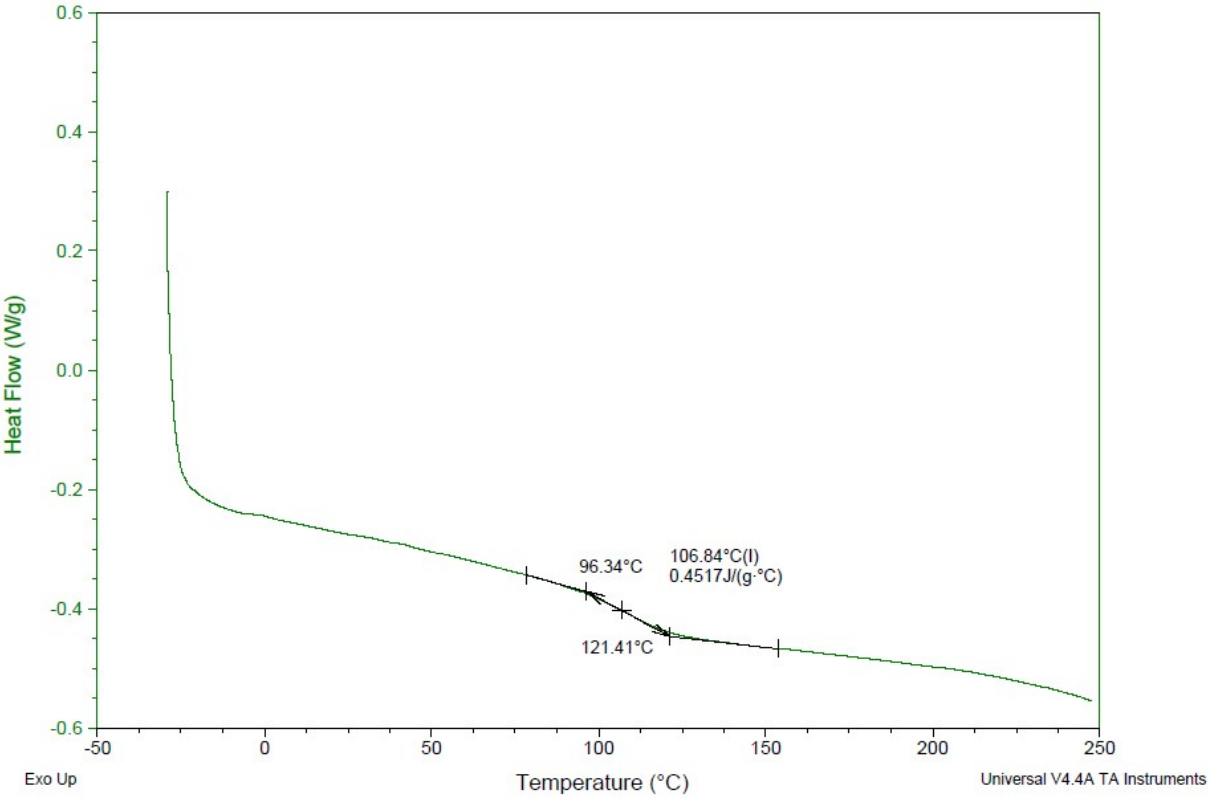


Figure S 17 : DSC thermogram of PIMA 75100 g/mol

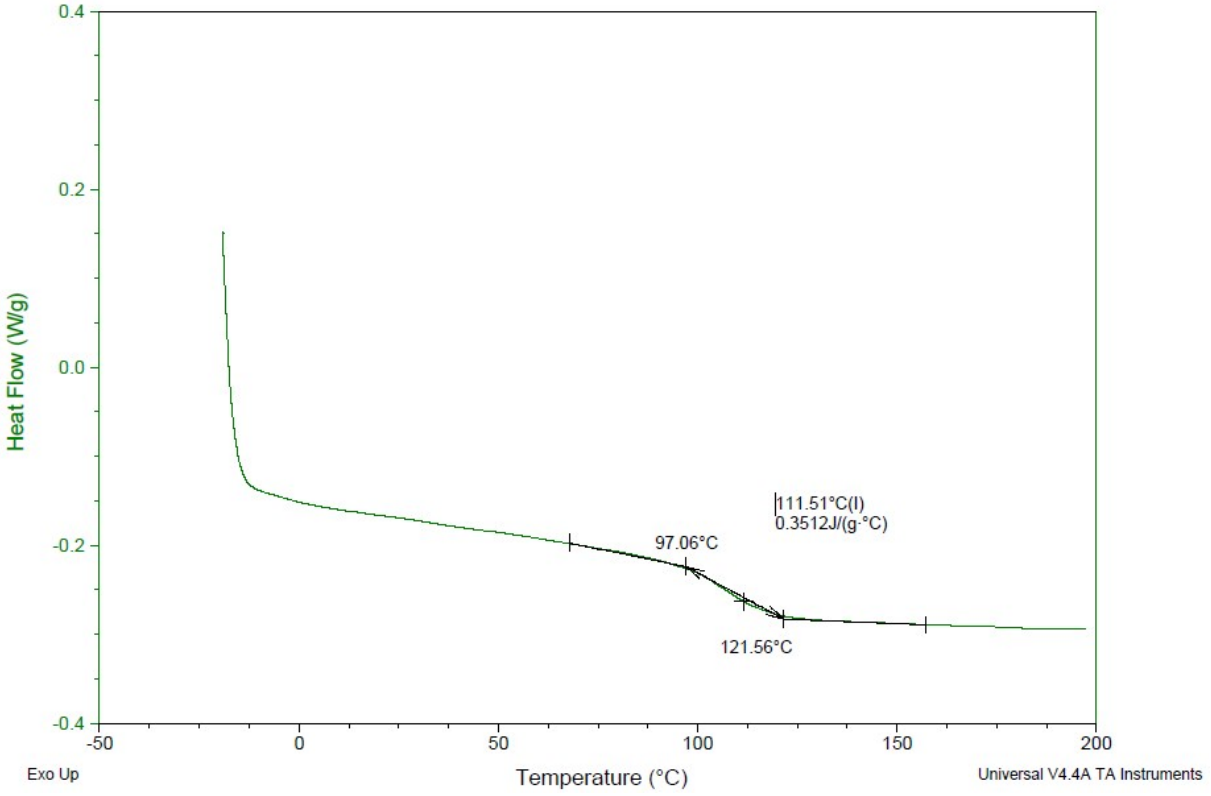


Figure S 18 : DSC thermogram of PIMA 78600 g/mol

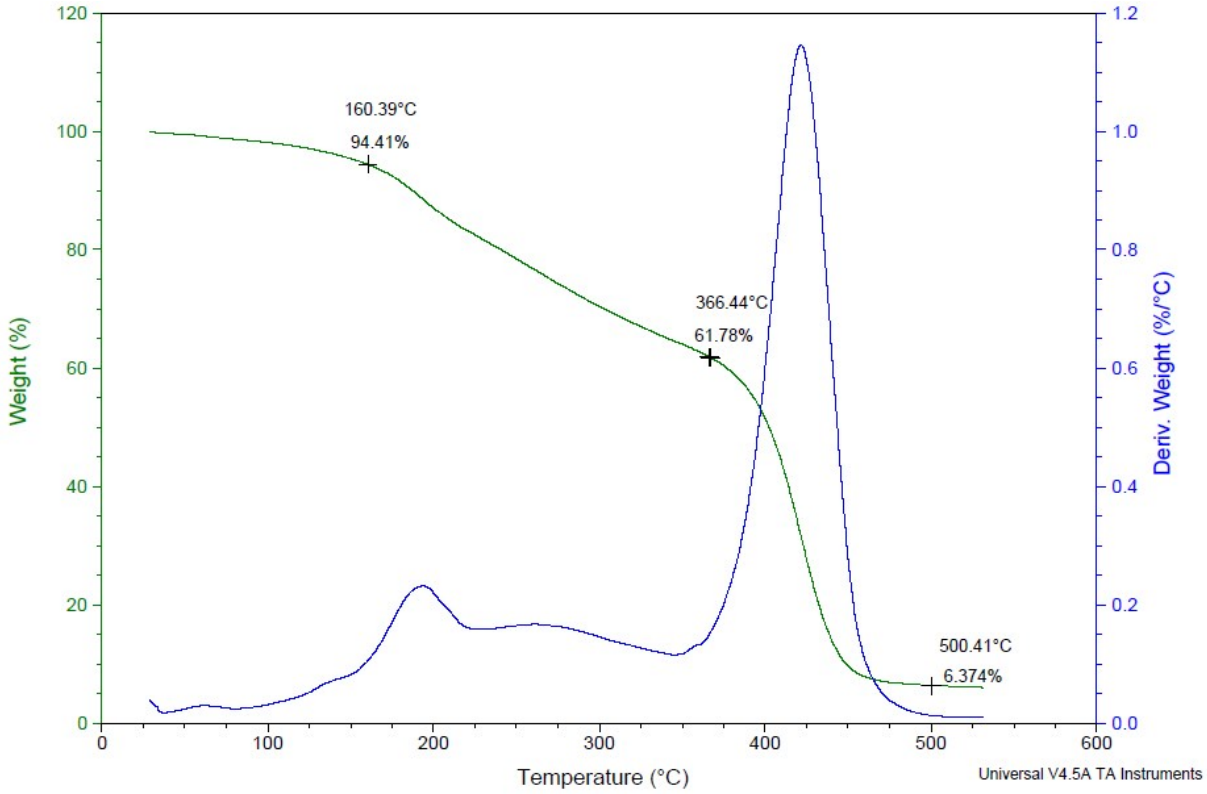


Figure S 19 : TGA thermogram of PIMA.

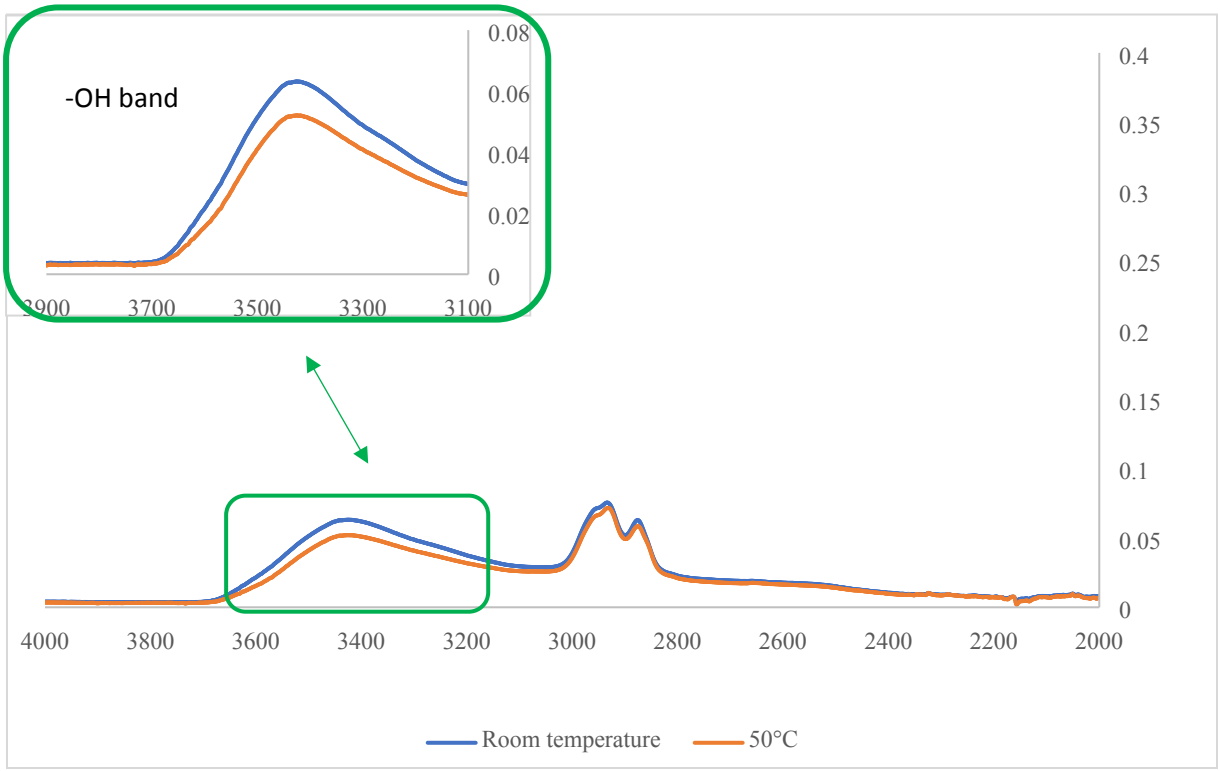


Figure S 20 : FTIR analysis of PIMA in function of temperature.

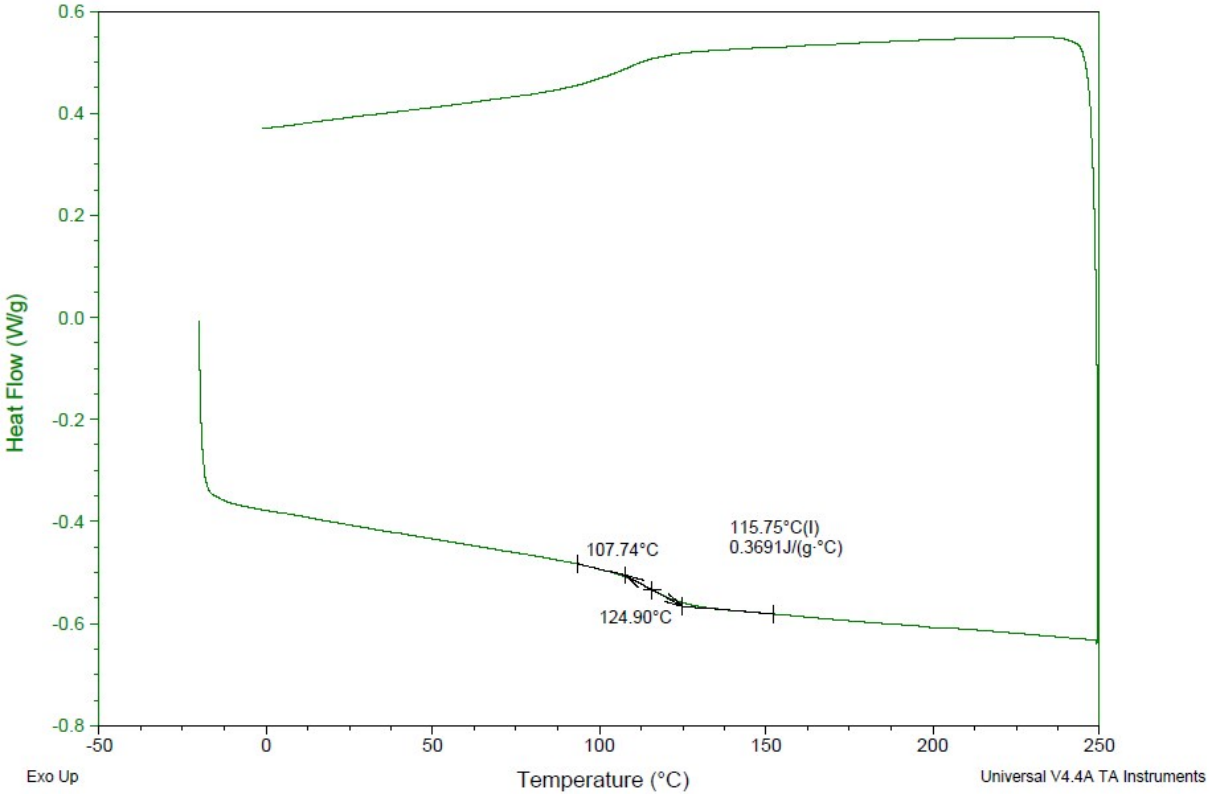


Figure S 21 : DSC thermogram of PIMA thermoset (10% crosslinker)

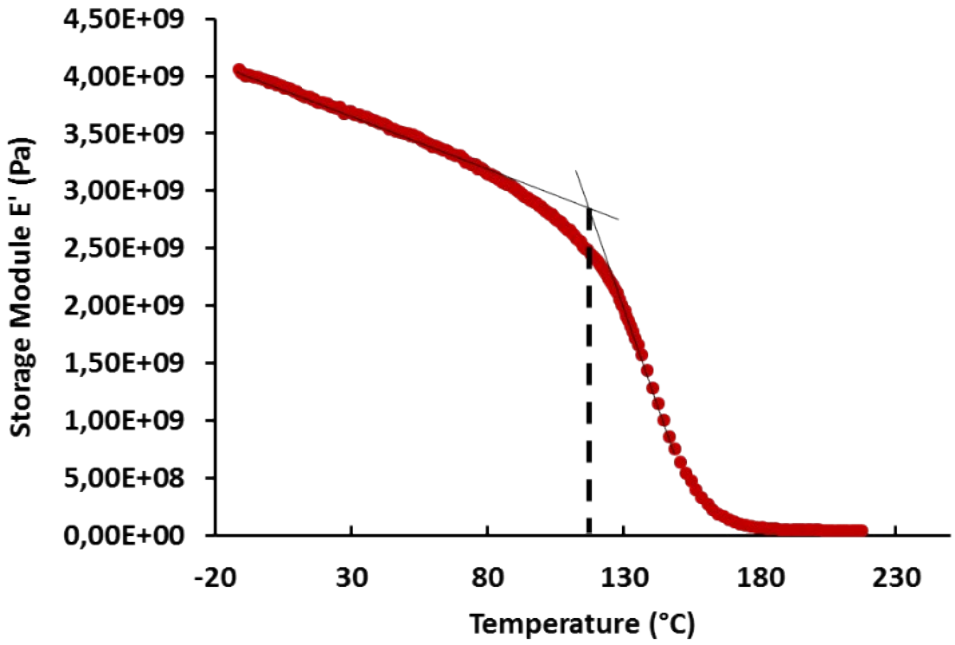


Figure S 22 : DMA analysis of PIMA thermoset (10% crosslinker)

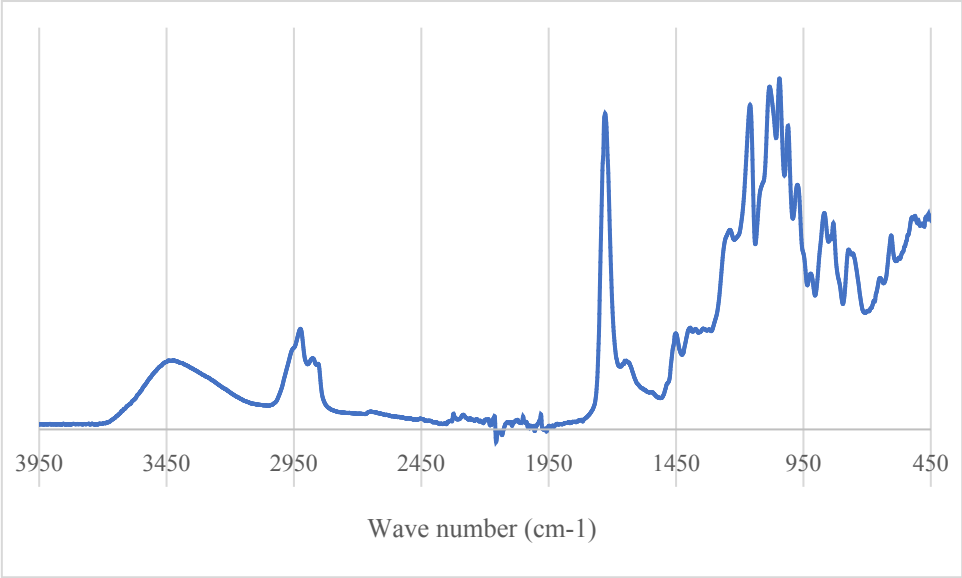


Figure S 23 : FTIR analysis of PIMA thermoset (10% crosslinker)

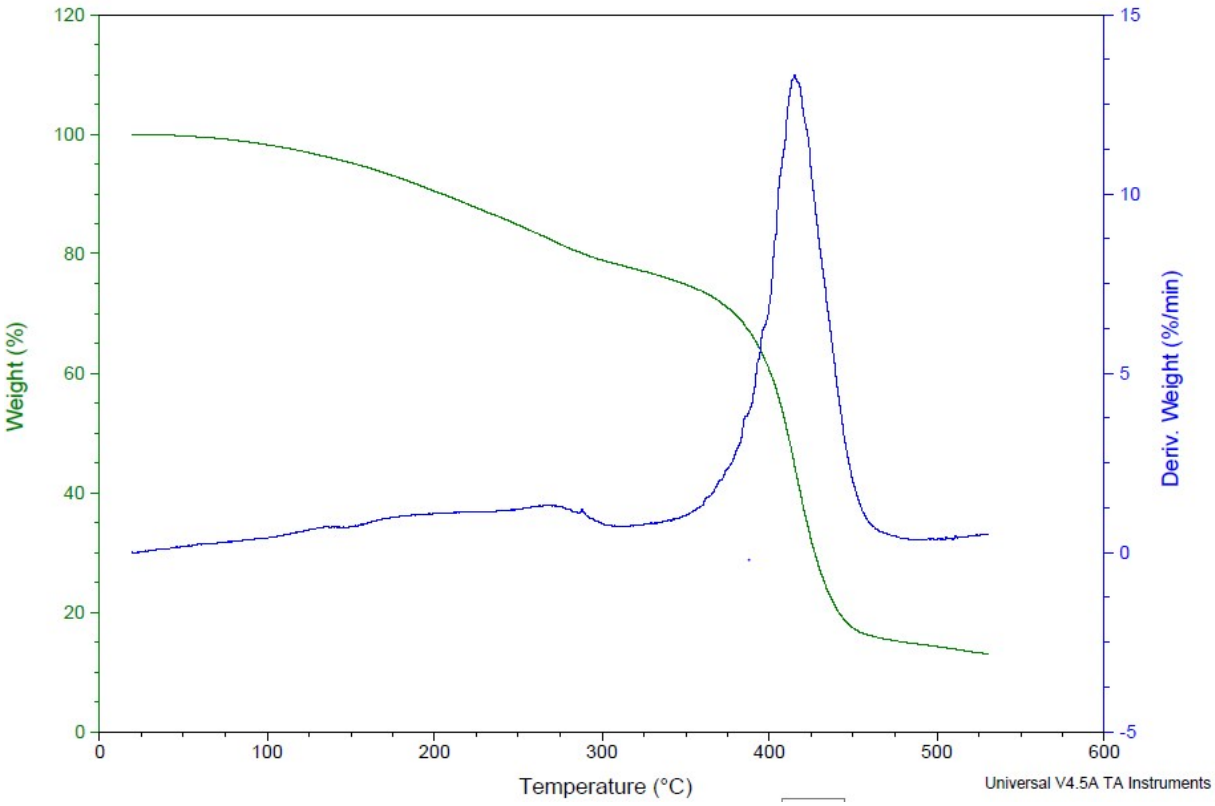


Figure S 24 : TGA thermogram of PIMA thermoset (10% crosslinker)