Supplementary Information

Effect of Isomerization and Copolymerization of Itaconic Anhydride During the Synthesis of Renewable Monomers Using Vegetable Oils

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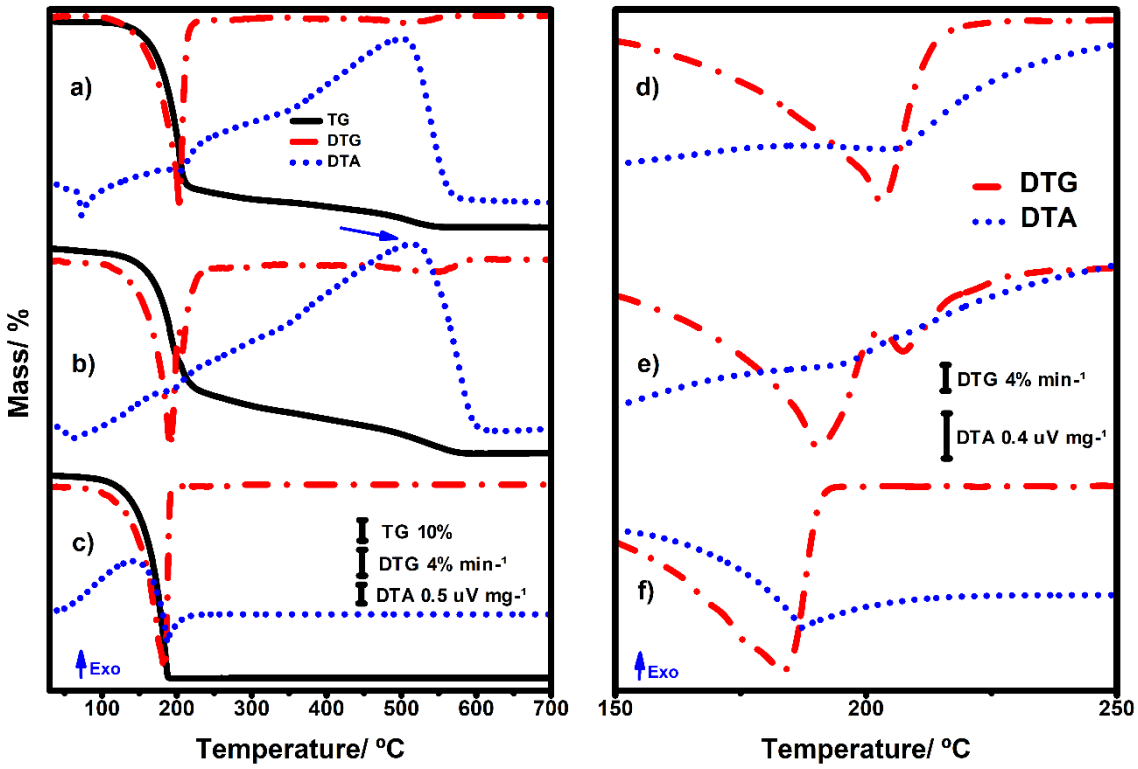

Figure S1. TG/DTG-DTA curves (in dry air atmosphere) of (a) ITA (itaconic anhydride), (b) sample obtained from ITA heating up 250 ºC, and (c) CTA (citraconic anhydride). Magnification of DTG and DTA curves between 150 and 250 ºC of (d) ITA, (e) sample obtained from ITA heating up 250 ºC, and (f) CTA.

Figure S1a shows the TG/DTG-DTA curves of ITA for comparison, while the curves of CTA are shown in Figure S1c. CTA is a liquid anhydride at room temperature, and as expected, it started to evaporate at room temperature finishing the process at 190 ºC (Δm = 99.57%, maximum evaporation rate (MER) = 40% min^{-1}). The endothermic peak associated to this mass loss appeared at 187 ºC. For the ITA sample heated to 250 ºC (Figure S1b), three consecutive steps of mass loss were observed in the TG curve. The first (30-92 ºC, Δm = 2.35%) and second step (92-231 ºC, Δm = 67.17%) could be attributed to the evaporation of residual CTA and ITA, as suggested by the endotherm event between 175 and 215 ºC (magnified in Figure S1e). Moreover, the endothermic peak in DTA curve related to the ITA melting was displaced to a lower temperature (T_p = 61 ºC) than observed for the pure ITA (T_p = 72 ºC, Figure 4a in the article). The sample heated to 250 ºC presented two peaks in its DTG curve between 100 and 230 ºC ($T_{MDR\ 1}$ = 190 ºC and MDR_1 = 28% min^{-1} and $T_{MDR\ 2}$ = 207 ºC and MDR = 12% min^{-1}), which can be better visualized in Figure S1e). The last step of mass loss occurred between 231 and 590 ºC (Δm = 30.37%) simultaneously with an exothermic peak at 514 ºC in the DTA curve (pointed by a blue arrow in Figure S1b). The changes in the TG/DTG curves (compared to the isolated anhydrides) indicated that the sample heated to 250 ºC presented the isolated anhydrides (ITA and CTA), but also a third product.

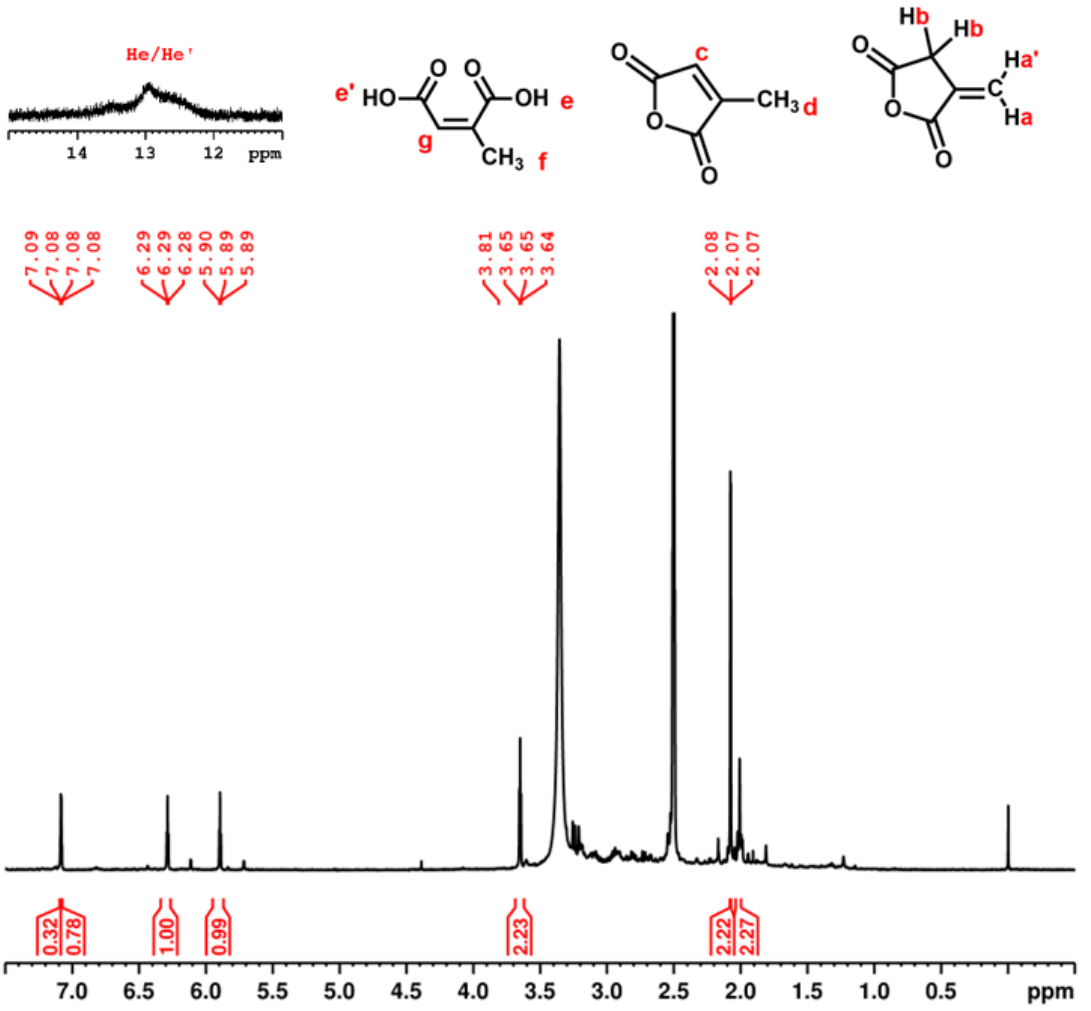

Figure S2. ^{1}H NMR (600 MHz, $(CD_3)_2SO$) of ITA (itaconic anhydride) (25 °C).

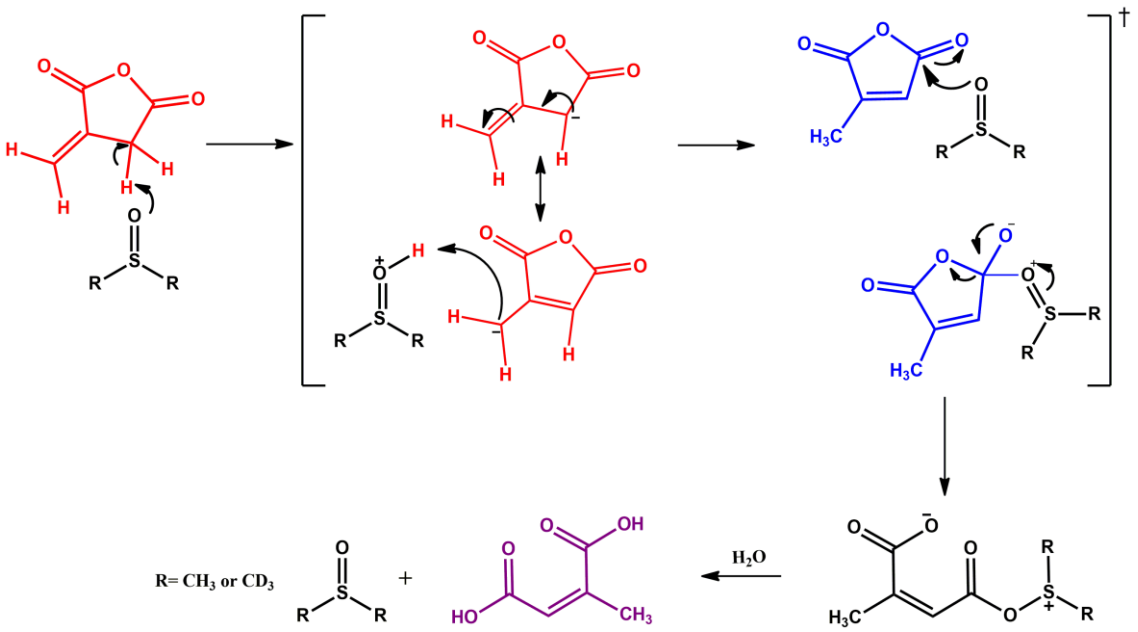

Figure S3. Reaction mechanism suggestion for isomerization of ITA (itaconic anhydride) in CTA (citraconic anhydride) and formation of citraconic acid in DMSO or $(CD_3)_2SO$.

Table S1. Temperature ranges (θ), experimental mass losses (Δm), maximum degradation rate (MDR), temperature of maximum degradation rates (T_{MDR}), and temperature of peak (T_p) observed for each step of mass loss in TG/DTG-DTA curves for ITA, CTA, and the precipitates obtained after the itaconization of grape seed oil by microwave irradiation at 120 °C (P120), 180 °C (P180), and 235 °C (P235)

Step of mass loss		ITA	CTA	P120	P180	P235
1st	Δm / %	79.69	99.57	3.69	17.37	5.66
	θ / °C	105-217	30-190	30-133	30-209	30-229
	T_p / °C	164 ↓	187 ↓	–	–	–
	T_{MDR} / ºC MDR / (% min^{-1})	203/ 28.8	184/ 40	–	117/ 2.1	–
2nd	Δm / %	19.79	–	58.79	43.09	94.18
	θ / °C	217-561	–	133-258	209-402	229-640
	T_p/ °C	501 ↑	–	164 ↓ 215 ↓	208 ↓ 360 ↑	503 ↑ 569 ↑
	T_{MDR}/ ºC MDR/ (% min^{-1})	–	–	213/16.2	333/ 3.1	564/ 4.0
3rd	Δm / %	–	–	37.60	38.76	–
	θ / °C	–	–	258-546	402-547	–
	T_p / °C	–	–	498 ↑	498 ↑	–
	T_{MDR} / ºC MDR / (% min^{-1})	–	–	500/3.1	493/ 5.8	–

↑exothermic peak; ↓: endothermic peak.

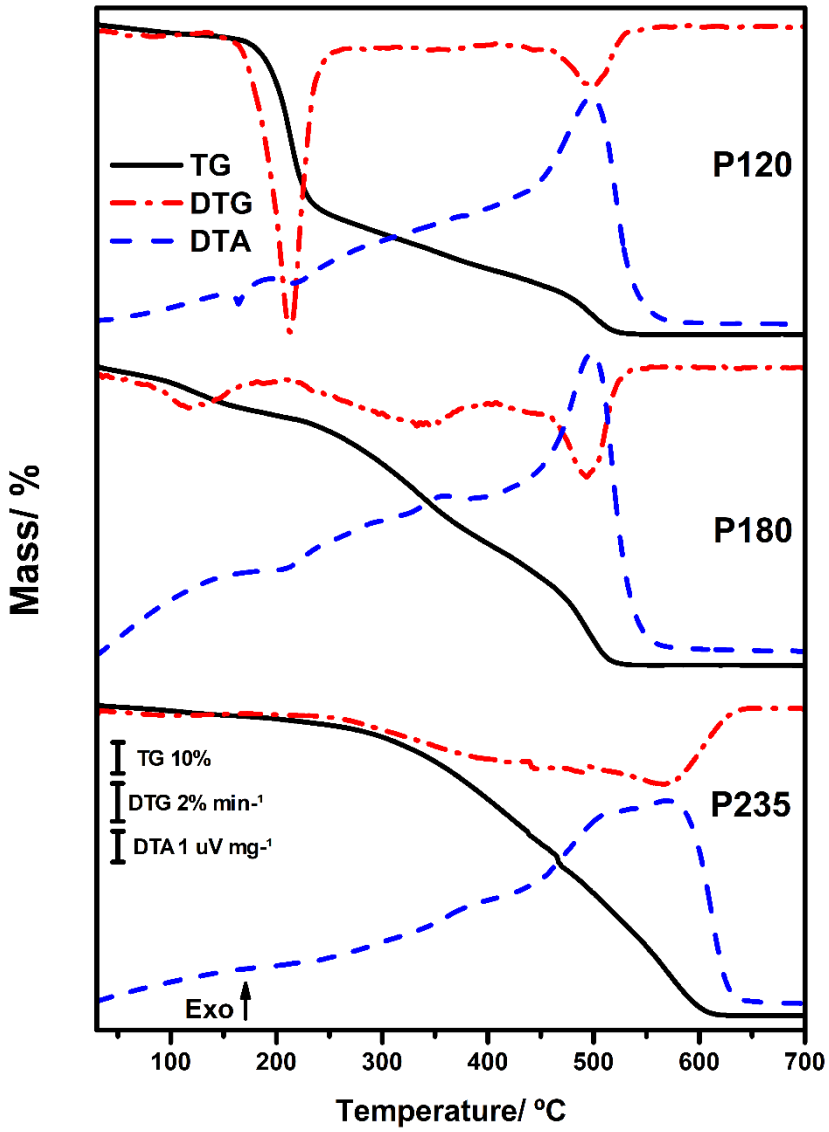

Figure S4. TG/DTG-DTA curves of purified precipitates obtained after the itaconization of grape seed oil by microwave irradiation at 120 °C (P120), 180 °C (P180), and 235 °C (P235).

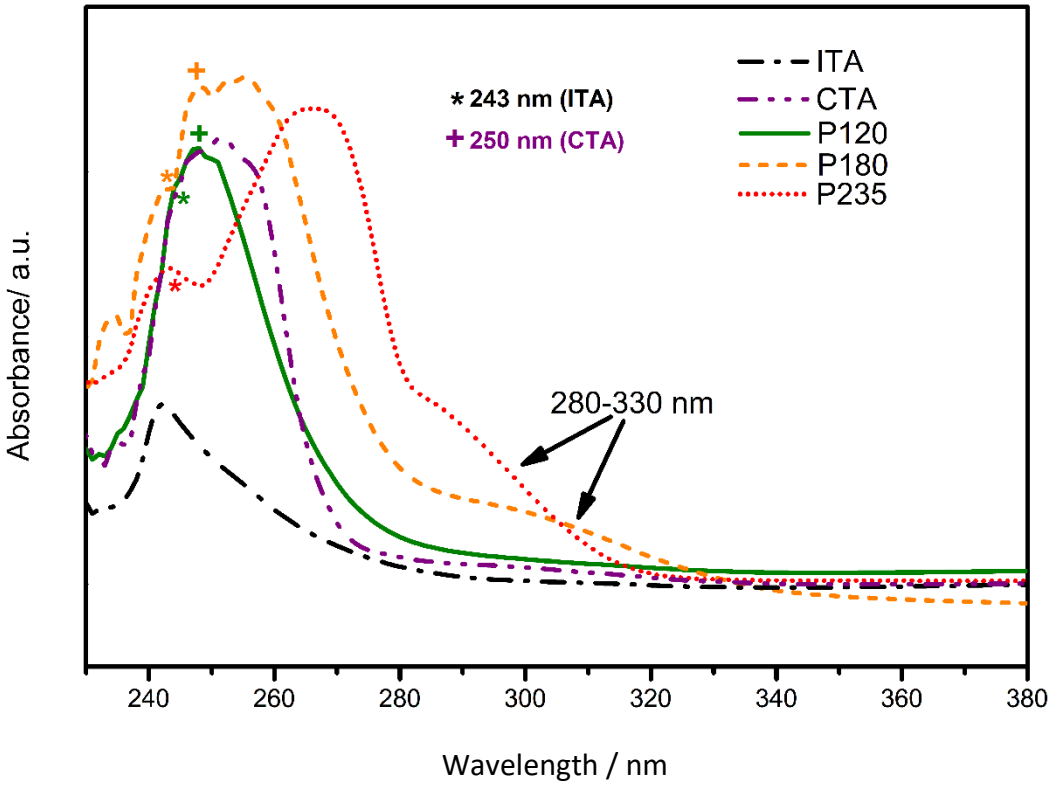

Figure S5. UV-Vis spectra of ITA (itaconic anhydride), CTA (citraconic anhydride) and precipitates obtained after the itaconization of grape seed oil by microwave irradiation at 120 °C (P120), 180 °C (P180), and 235 °C (P235).

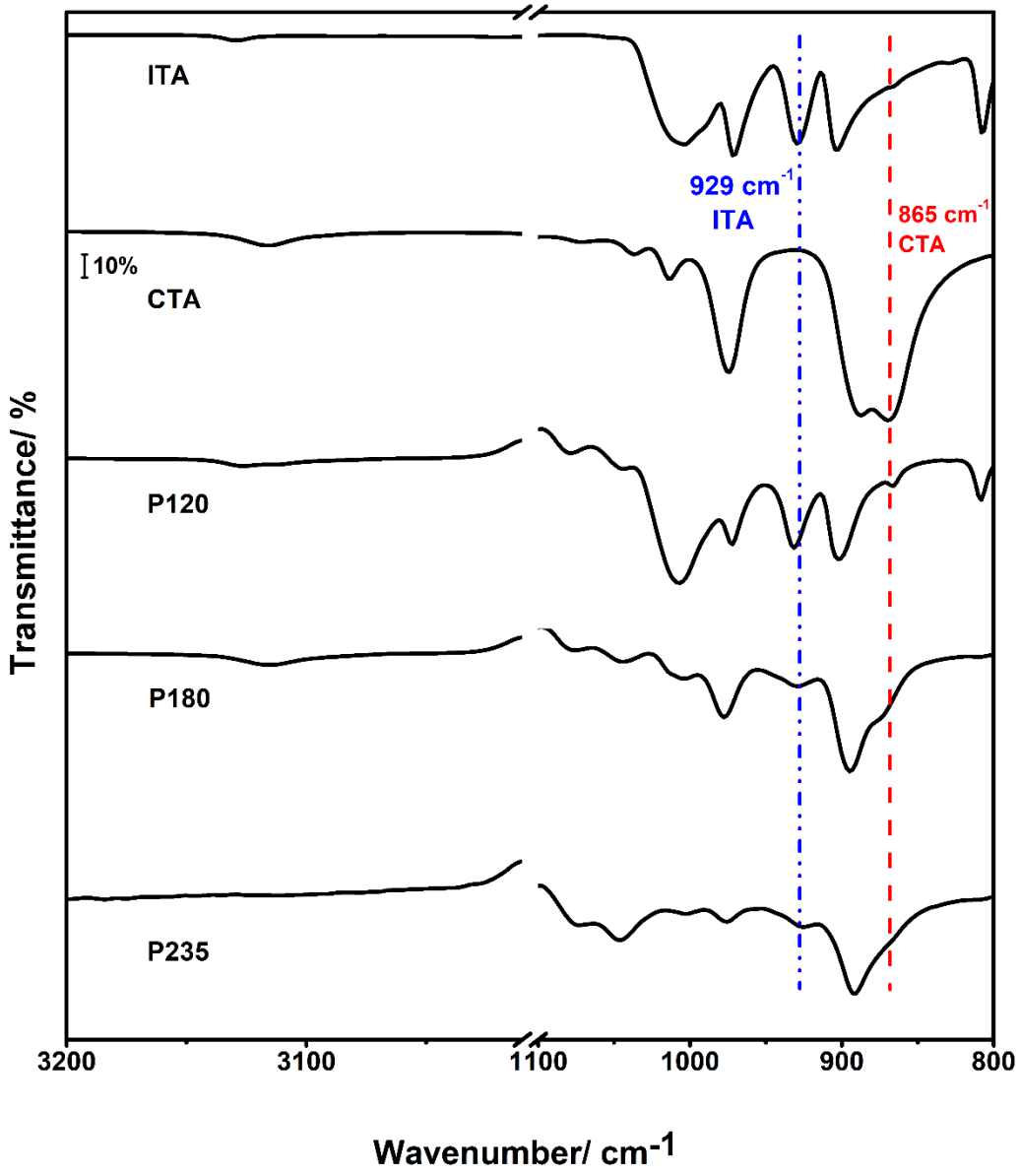

Figure S6. MIR spectra of ITA (itaconic anhydride), CTA (citraconic anhydride) and precipitates obtained after the itaconization of grape seed oil by microwave irradiation at 120 °C (P120), 180 °C (P180), and 235 °C (P235).

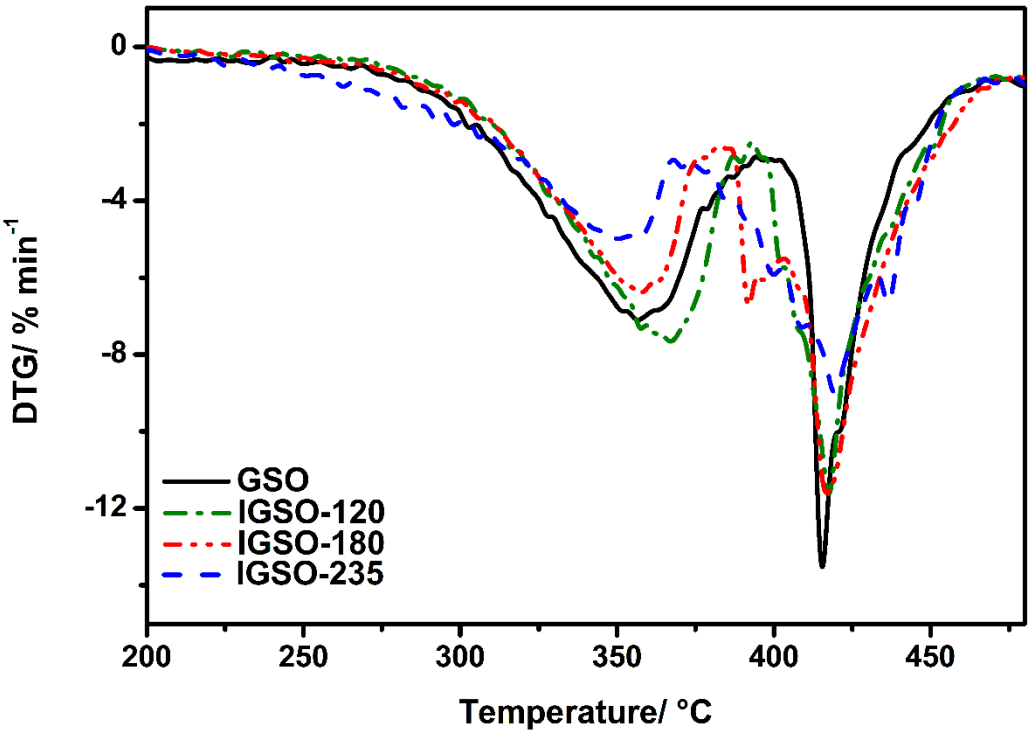

Figure S7. DTG curves obtained for GSO (grape seed oil) and the IGSO (itaconized grape seed oil) samples obtained at different temperatures: 120 ºC (IGSO-120), 180 ºC (IGSO-180), and 235 ºC (IGSO-235) under microwave irradiation.