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Order of Authors:	Maria del Carmen Aguilar Castro, Plastics Engineering
	Mariamne Dehonor Gomez, Ph.D.
	Manuel Gutierrez Nava, Ph.D.
	Jose Manuel Rojas Garcia, Ph.D.
	Luis Edmundo Lugo Uribe, Ph.D.
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Please provide the principal investigator's name and affiliation. (Principal investigator MUST be listed as a co-author on the submission; please DO NOT list all other co-authors in this section.)	Luis Edmundo Lugo Uribe CIATEQ A.C.

Bio-based polyester, obtained from bi-functional monomers through metathesis of fatty acids, as precursor to synthesize polyurethanes

Carmen Aguilar-Castro[1], Mariamne Dehonor Gomez[1], Manuel Gutierrez Nava[1], Jose Manuel Rojas García[1] and Luis Edmundo Lugo Uribe [1]

[1] CIATEQ Centro de Tecnología Avanzada, Circuito de la Industria Pte Lte 11 Mza 3 No 11, Parque Industrial Ex Hacienda Doña Rosa, Lerma Edo. de México, 52004, México

ABSTRACT

Bio-based unsaturated aliphatic polyesters and polyurethanes were obtained from fatty acid monomers with double functionality synthesized through cross metathesis of oleic acid and oleic alcohol. Chemical structure and thermal behavior of the monomers and polymers were analyzed by several physical-chemical testing, and oscillatory rheometry and optical microscopy were used to determine their rheological properties, and to observe the crystal formation of the obtained polyesters, respectively.

It has been found that the polyesterification reaction depends on reaction temperature and to a lesser degree on both the reaction time and catalyst addition. Melt temperature and enthalpy of the obtained bio-based polymers pointed out that the monomer chain length has an effect in both crystallinity and thermal transitions of the polymers as can be explained by the group contribution analysis showing excellent correlation.

INTRODUCTION

The search for alternative feedstock for the production of polymers is increasingly of interest, given the reduction that each year exists in fossil resources. Bio-based monomers, obtained from

plant biomass, are one of the main alternatives that have been studied to make new kinds of polymers with similar or improved properties compared to current fossil-based polymers. [1-4]

Fatty acid derivatives have been considered one of the most promising source of chemicals to synthesize polymers, because of the presence of functional groups in their chemical structure that can be used as polymerization centers, such as carboxylic acid, hydroxyl group or unsaturation[5]. Therefore, polyurethanes and polyester could be made by using the step growth polymerization process.

It has been reported in the literature, the development of novel polyurethanes (PU's) from fatty acid derivatives through different research approaches. One first approach considers the synthesis of fatty acid-based diisocyanates to be reacted with bio-based polyols to yield plant-derived polyurethanes with different properties [6-8]. Other approaches consider chemical processes, such as (1) acyclic triene metathesis (ATMET) polymerization to produce some shape memory polyurethanes[9], (2) enzymatic route to produce soybean oil-based shape-memory PU's[10], (3) combination of different diols derived from different vegetable oil and poly(ε-caprolactone) diol to yield hyperbranched shape-memory PU[11] and (4) one-step synthesis to produce epoxidized rapeseed oil-based PU network[12].

On the other hand, polyesters derived from fatty acids have been developed taking advantage of the natural carboxylic acid that is present in their chemical structure, but recent developments have considered other processes. For examples, (1) fatty acid cross self-metathesis has been used to produce fatty alcohols and amines, which can be used to synthesize either polyesters and

polyamides[13] or thermoplastic poly(ester-amide)[14] and (2) biochemically synthesized fatty acid derivatives can produce renewable polyesters and polyamides[15].

Cross metathesis has been one of the most important chemical routes that has been used to obtain new molecules from renewable resources, particularly vegetable oil or biomass derivative compounds [16-24]. In this study, monomers with double functionality obtained from olefinic cross metathesis of fatty acid derivatives were used to synthesize fully and partially bio-based linear unsaturated polyesters and polyurethanes. Reaction parameters such as temperature, time, catalyst addition and concentration, were evaluated to establish their impact on glass transition temperature, melt temperature and rheological properties. The effect of monomer length size was observed in their thermal properties by using a group contribution approach.

EXPERIMENTAL

Materials

Second generation Grubbs catalyst, oleic acid (99 % purity), oleic alcohol (85 % purity), N,N-diethylhydroxymethylamine (≥ 98 % purity), cis-2-butene-1,4-diol (97 % purity), adipic acid (99 % purity), 4,4'-methylene-bis(phenyl isocyanate) (MDI 98 % purity), p-toluene sulfonic acid monohydrate (p-TSA 98.8 % purity), 1,5,7-Triazobicyclo [4,4,0] dec-5-ene (TBD purity 98 %), hexane (95% purity) and ethyl acetate (99.8 % purity) were purchased from Sigma-Aldrich and used as received.

Synthesis of 1,18-octadec-9-enedioic acid

Synthesis of 1,18-octadec-9-enedioic acid was made according to Ngo and coworkers [20, 21]. For the reaction, 100 mL (0.315 mol) of oleic acid and 0.122 g (1.437×10^{-4} moles) of Grubbs second-generation catalyst (previously dissolved in 5 ml of dichloromethane) were mixed in a 250 mL Schlenk flask. The mixture was held for 48 hours at 50 °C, under a nitrogen atmosphere and constant stirring, after which the reaction was quenched with 4 ml of N,N-diethylhydroxymethylamine (DEHA). The product was purified in a hexane / ethyl acetate mixture (60/20 v: v) for 48 hours, to ensure complete removal of impurities. Finally, it was filtered using a Büchner funnel and dried in a laboratory oven at 40 °C for 4 hours and ==was purified through crystallization and column chromatography using a mixture of hexane/ethyl acetate.==. The reaction between the fatty acids and the second-generation Grubbs catalyst is shown in FIGURE 1.

Synthesis of 1,18-octadec-9-enediol

Synthesis of 1, 18-octadec-9-enediol was made by following the study of Riepl and co-workers[13], but changing reaction conditions and catalyst ratio to improve the reaction yield. The synthesis was carried out by mixing 100 mL (0.316 mol) oleic alcohol and 0.144 g (1.696×10^{-4} moles) of second-generation Grubbs catalyst (previously dissolved in 5 mL of dichloromethane). The mixture was held for 48 hours at 50 °C, under nitrogen atmosphere and constant stirring, after which the reaction time was quenched with 4 mL of DEHA. The product was purified in 100 mL of hexane for 48 hours, filtered with Büchner funnel and dried in a laboratory oven at 40 °C for 4 hours.

Synthesis of bio-based polyester

Bio-based polyesters were synthesized by mixing 1,18-octadec-9-enediol and 1,18-octadec-9-enedioic acid with a molar ratio OH/COOH of 1, as is shown in FIGURE 2, in a 50 mL Schlenk flask with magnetic stirring that previously was set at the given reaction temperature. The Schlenk was purged with nitrogen and vacuum several times. Vacuum pressure was maintained during the reaction time. For cis-2-butene-1,4-diol experiments, it was verified that at this conditions there were not losing of cis-2-butene-1,4-diol from the reaction media. Magnetic stirring was used at the first stages of the reaction (oligomerization), but a high conversion, the viscosity is too high to assure stirring and the reaction continues as a bulk polymerization. At the end of the reaction, bio-based polyester was then recovered and finally washed to remove any remaining monomer. Experimental conditions, as catalyst type, monomer/ catalyst ratio, reaction temperature and reaction time, were studied at several levels to study their effect in the synthesis of bio-based polyester.
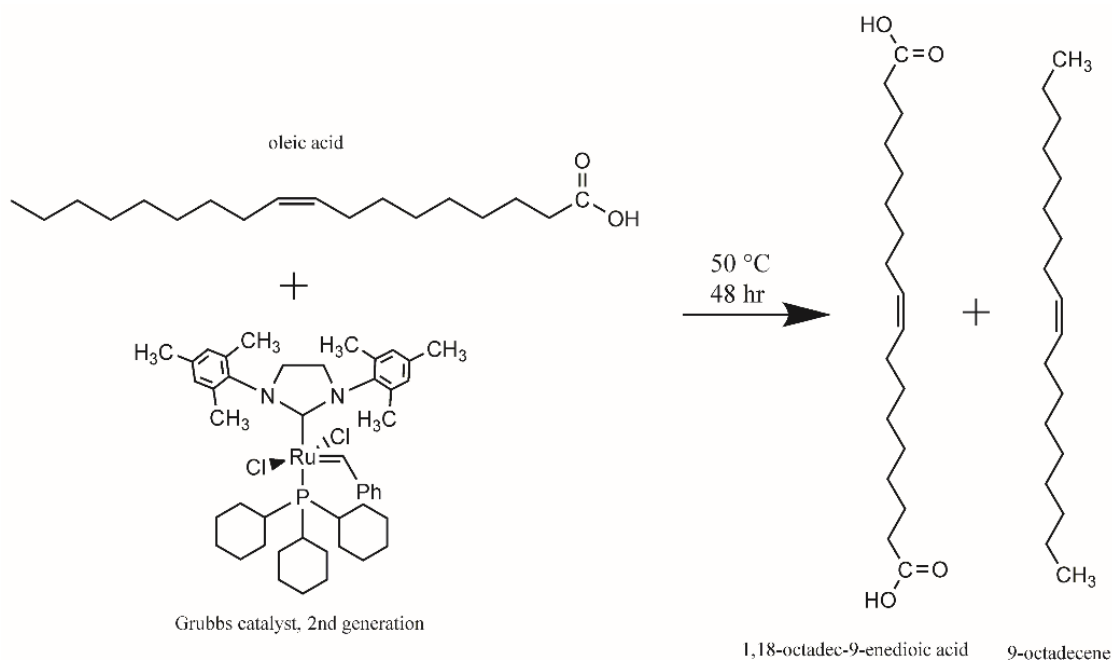
FIGURE 1 Metathesis reaction of oleic acid using a second-generation Grubbs catalyst

Synthesis of bio-based polyurethane

Partial bio-based polyurethanes were synthesized by mixing bio-based polyester obtained from the reaction between 1,18-octadec-9-enediol and 1,18-octadec-9-enedioic acid and an aromatic diisocyanate (MDI) in a 50 mL Schlenk flask with magnetic stirring that previously was set at 70 °C. The reaction system was purged with nitrogen and vacuum several times, and vacuum pressure was held for 2 hours as residence time. Then, temperature was risen at 120 °C for additional 2 hours. At the end of the reaction, bio-based polyurethane was recovered and washed to remove any remaining monomer.
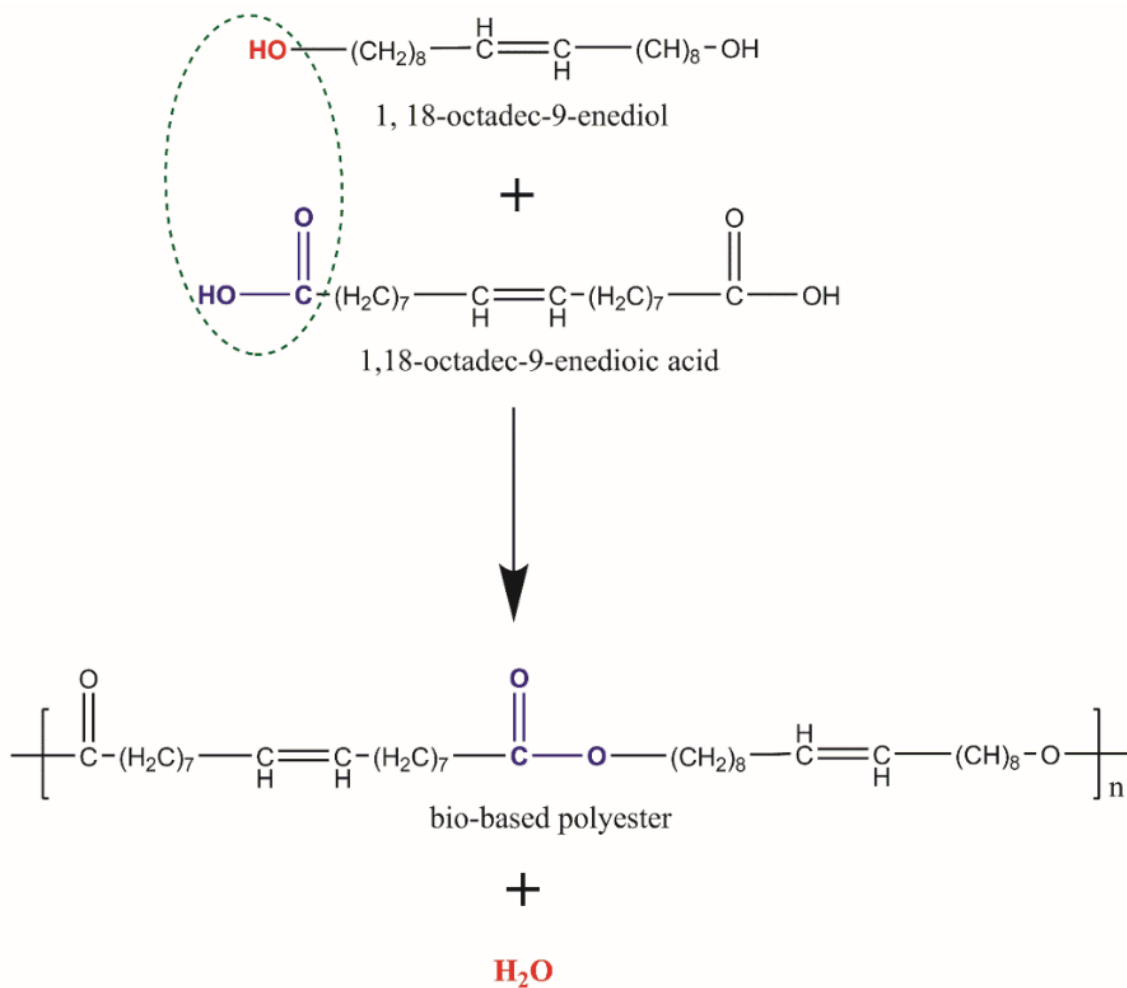
FIGURE 2 Reaction scheme for synthesis of bio-based polyester

Characterization of bio-based monomers and polymers

Bio-based monomers obtained from cross metathesis of fatty acid derivatives were characterized by Attenuated Total Reflectance – Fourier transformed infrared spectroscopy (ATR-FTIR), differential scanning calorimetry (DSC), and proton nuclear magnetic resonance (^{1}H-NMR), whereas bio-based polyesters and polyurethanes were characterized by ATR-FTIR, DSC, oscillatory rheometry and optical microscopy.

ATR-FTIR analysis was made by using a spectrometer Cary 4500a with spherical diamond crystal in 650-4000 cm^{-1} range. Thermal transitions were obtained using a TA-Instrument Q2000 instrument. Samples were placed on a hermetic aluminum pan and were analyzed under an inert atmosphere. All cycles were performed at a heating rate of 5 °C/min and a temperature range from 20 °C to 200 °C for monomers and from -90 °C to 200 °C for polymers. ^{1}H-NMR was performed using a Brüker Avance-III 500 (500 MHz, CD$_3$OH-d$_4$, δ) spectrometer.

The rheological analysis was performed in a TA-Instruments AR 2000 rheometer by using a 25 mm-parallel plate geometry for both temperature and frequency sweeps. Temperature sweep experiment was performed from 20 to 120 °C at a heating rate of 3 °C/min, 1.25 % strain and 1 Hz frequency. Frequency sweep experiment was made from 0.01 to 100 Hz at several temperatures applying 1.25 % strain.

Optical microscopy was made by using a vertical microscope Zeiss Axio Imager A2m (objective CE Plan-Neofluar 20x/0.5 M27) with a heating plate (Lincam). Bio-based polyesters were subjected to heating up to 70 °C with a heating rate of 20 °C/min and after that were cooled up to 30 °C with a cooling rate of 5 °C/min.

RESULTS AND DISCUSSION

Bio-based monomers

Cross self-metathesis of oleic acid and oleic alcohol was carried out by using a second-generation Grubbs catalyst, which has tolerance to carboxylic acid and hydroxyl functional groups. Reactions conditions were optimized to improve conversion compared to prior studies [20, 25].

We have found that conversion to 1,18-octadec-9-enedioic acid is a function of the chosen oleic compound because the oleic acid have yielded 48.5 % (23.8 g produced) whereas oleic alcohol yielded 35.0 % (16.12 g produced). These conversion data are in agreement with previous works for oleic acid[20] and oleic alcohol [13] when the amount of catalyst is 0.1 mol%. In this work, instead of using the half of catalyst of previous studies (0.05 mol%), a higher amount of bi-functional monomer produced per gram of catalyst were obtained.

Evidences that metathesis reaction occurs in the oleic compound are: (i) the shift of the carbonyl band from 1685 cm^{-1} to 1712 cm^{-1}, (ii) the emerging band at 960 cm^{-1} attributed to the -trans units presented in the di-acid and diol, and (iii) the disappearance of the band at 730 cm^{-1} attributed to -cis units from oleic acid and alcohol derived from fatty acids. A -trans selectivity had been reported by Grubbs research group for this kind of catalysts when cross-metathesis reaction is carried out with olefins[26]. Details of the spectra can be found in the supporting information file.

On the other hand, thermal analysis through DSC was carried out to determine crystallization and melt temperatures and enthalpies of the telechelic molecules. DSC plots can be consulted in supporting information. The acid functional telechelic monomer shows a melting temperature of

96.8 °C with an enthalpy of 204.0 J/g and a crystallization temperature of 80.6 °C with an enthalpy of 180.6 J/g; whereas the diol functional telechelic monomer shows a melting temperature of 52.0 °C with an enthalpy of 56.6 J/g and crystallization temperature of 49.0 °C with an enthalpy of 52.8 J/g. Therefore, both telechelic monomers show higher melting and crystallization temperatures than the mono-functional monomer. The difference can be explained because the hydrogen bond of either the acid group or the alcohol group now interacts on both sides of the telechelic monomer rather than on a single side for the case of the mono-functional monomer. Then, the dual interaction of the hydrogen bond form a crystal structure, and more energy is required to unlink this new structure. The differences in thermal behavior between the acid telechelic monomer and the alcohol telechelic monomer can also be explained by the interactions of the hydrogen bond since the carboxylic acid has stronger interactions compared to those of alcohol, as seen in the obtained DSC results.

^{1}H NMR was used to confirm bi-functional molecules formation. The ratio between areas of the chemical shift of α and η protons points out monofunctional (ratio=1.0) or bi-functional molecule (ratio=2.0). Oleic alcohol has two α protons with a chemical shift at 3.5 ppm and two η protons with a chemical shift at 5.4 ppm having an area ratio α/η for this molecule of 1. For the bi-functional alcohol, the number of α protons is four, and the area ratio α/η must be 2. The ratio α/η was calculated for oleic alcohol metathesis product obtaining a value of 1.9, establishing a bi-functional oleic diol. Regarding 1,18-octadec-9-enedioic acid, α protons have a chemical shift at 2.27 ppm; with a ratio of areas α/η of 1.8. The difference of both area ratios respect to the theoretical value of 2.0 is attributed to presence of remaining monofunctional monomer, as can be confirmed by the chemical shift at 0.9 ppm assigned to $-CH_3$ protons.

Table 1 Experimental conditions for total and partially bio-based polyesters

Mon/ Cat [b]	Cat.	Diol [c]	Di-acid [d]	Reaction time [hr]	Temp. [°C]	Conv. [e] [%]	Melt [f] Temp. [°C]	Melt [f] Enthalpy [J/g]	Cryst. [f] Temp. [°C]	Cryst. [g] Percent [%]	$[\eta^*]$ [h] @ 1 Hz, 80°C [Pa.s]
60	p-TSA	Oleic	Oleic	6	160	90.55	50.53	98.73	39.14	49.1	5959
60	p-TSA	Oleic	Oleic	6	160	88.17	49.40	78.42	37.84	43.8	9737
120	p-TSA	Oleic	Oleic	6	160	82.89	44.98	70.49	32.23	41.2	31710
60	p-TSA	Oleic	Oleic	12	160	91.55	47.44	76.22	33.27	45.5	20840
-	-	Oleic	Oleic	6	160	78.35	30.93	33.71	15.12	39.0	22270
60	p-TSA	cis-butene	Oleic	6	160	78.04	33.50	58.01	23.77	49.5	3057
-	-	cis-butene	Oleic	6	160	74.40	12.88	36.43	4.91	47.2	2744
60	TBD	Oleic	Oleic	24	140	70.82	44.71	64.24	26.30	35.2	46380
-	-	Oleic	Oleic	6	190	94.03	47.25	95.27	33.41	46.8	22
-	-	Oleic	Adipic	6	190	95.98	47.78	92.03	34.77	51.8	8

[a] Reaction condition: Monomers = 2.5×10^{-3} mol; OH/COOH = 1 (molar ratio) [b] Molar Ratio; [c] Oleic diol refers to 1,18-octadec-9-enediol; [d] Oleic di-acid refers to 1,18-octadec-9-enedioic acid; [e] Conversion was calculated from fraction of insoluble mass in CH_2Cl_2 with respect to original monomers mass; [f] Obtained by DSC analysis; [g] Obtained from enthalpies calculated using group contribution method [h] Obtained from $[\eta^*]$ vs frequency [Hz] curves generated by oscillatory rheometry [i] Run 1 was made without vacuum pressure; Run 2 to Run 10 were made with vacuum pressure

Table 1 shows the experimental conditions for the esterifications reactions. It was studied the effect of use or not catalyst and the catalyst type, monomer/catalyst ratio, reaction time and temperature. All reactions were performed with an acid/alcohol ratio of 1:1 using vacuum pressure to remove sub-product (water) from the reaction medium, with exception of Run 1 where reaction was made at atmospheric pressure. Table 1 shows results of esterification reaction conversion, melt and crystallization temperatures and melt enthalpy obtained from DSC analysis; and dynamic viscosity (η^*) obtained from oscillatory rheometry.

For polyester polymerization, the reaction conversion is between 70 to 95 %, and it is a function of temperature, reaction time, presence of the catalyst and type of monomer. It was not possible to get reaction conversions above 95 % because of the effect of high viscosity in the reaction medium.

Effect of reaction temperature. Experiments without addition of catalyst, run 5 (160 °C) vs. run 9 (190 °C) show different conversion of 16 % among them because at 160 °C the conversion is 78 %, while at 190 °C the conversion is 94 %. Then, we can elucidate that higher reaction temperature promotes higher reaction conversion, as expected in an esterification process.

Effect of addition of catalyst p-TSA. As expected, the use of a catalyst p-TSA in experiment Run 2 vs. Run 5 (without catalyst) increases 10 % the reaction conversion, as can be seen in Table 1.

Effect of type of alcohol. In Table 1, it can be observed that conversion obtained with butenediol is lower than that with oleic diol. Therefore, the type of diol has an effect on conversion when a catalyst p-TSA is used. <mark>It means that the decrease in the reaction conversion is not so related to the length of the monomer chain but rather to the double bond in the butenediol, which should affect the hydroxyl reactivity.</mark>

<mark>Effect of type of acid. Adipic acid experiment (Run 10) shows no difference in reaction conversion with respect to oleic di-acid experiment (Run **9**).</mark>

Esterification reaction was confirmed using Attenuated Total Reflection Infrared Spectroscopy (ATR-FTIR) through observing the disappearance of the signals corresponding to acid and hydroxyl functional groups and the emerging of characteristic ester group signals. ATR-FTIR spectra comparison corresponding to bio-based polyester formed from the reaction between 1,18-octadec-9-enedioic acid and 1,18-octadec-9-enediol, as well as the spectra of the monomers, are shown in FIGURE 3 (a). Ester group formation can be confirmed by the presence of the 1725 cm^{-1} and 1170 cm^{-1} bands in the polyester spectra, corresponding to C=O and C-O stretching

vibrations respectively, as well as by the disappearance of –OH group at 3250 cm^{-1} band of the diol spectra and acid carbonyl at 1680 cm^{-1} of the di-acid spectra. Similar results were reported by Vilela and Meier for the synthesis of plant-oil polyester obtained from C26 monomers[30]. FIGURE 3 (b) shows the ATR spectra comparison of polyesters formed by cis-2-butene-1,4-diol / 1,18-octadec-9-enedioic acid with or without catalyst p-TSA and by 1,18-octadec-9-enedioic acid / 1,18-octadec-9-enediol formed without catalyst, whereas FIGURE 3 (d) shows the spectra comparison between polyester formed by 1,18-octadec-9-enedioic acid / 1,18-octadec-9-enediol and by adipic acid / 1,18-octadec-9-enediol.

Experiments where short chain monomers (cis-2-butene-1,4-diol and adipic acid) were used show two peaks in the carbonyl band between 1650 and 1800 cm^{-1}, one corresponding to acid group and other to ester group. Besides, typical behavior of organic acid spectra is observed at 2500 – 3500 cm^{-1} region, suggesting a large concentration of acid functional groups in these samples. This behavior can be attributed to a difference in reactivity of the smaller monomers 1,4-butenediol or adipic acid with respect to oleic monomers that could be yield polyester with acid end-functionality.

Bio-based polyesters obtained by some of the short chain monomers (1,4-butenediol or adipic acid) exhibited acid functionality in their ATR-FTIR spectra, as can be seen in FIGURE 3 (b and d). This behavior could be due to differences in functional group reactivity associated with chain length generating preferably acid end-chain functionality. On the other hand, both catalyst use or type and conversion do not show an effect over acid functionality in the polyester, as can be observed in FIGURE 3 (b and c) and also in Table 1.

Thermograms of differential scanning calorimetry (DSC) of fatty acid monomers and a synthesized polyester (Run 1) obtained from them are shown in FIGURE 4. Bio-based polyester shows a well-defined melting peak at around 50 °C, similar to 1,18 octadec-9-enediol but the polyester peak is sharper and larger, whereas 1,18 octadec-9-enedioic acid shows a sharp peak at 97 °C. These DSC thermograms allow confirming high conversion from oleic monomers to polyester, since there are not any crystallization and melting peak that can be attributed to oleic diacid.

DSC thermograms comparison of bio-based polyester obtained under different conditions is shown in FIGURE 5. Diol chain length effect on melting behavior of polyester can be observed in these thermograms. Polyesters prepared with 1,4-butenediol/oleic diacid (T_m=33.5 °C, ΔH_m=58 J/g) have a lower melting temperature and enthalpy compared with polyester prepared from oleic diol / oleic diacid (T_m=49.4 °C, ΔH_m=78.4 J/g) under similar conditions. Results reported by other authors show a dependence of the melting temperatures with the chain length of monomer as was observed for linear aliphatic polyester obtained from erucic acid derivatives with melting temperature of 104 °C for a PE 26,26 and 74 °C for a PE 4,26 [30] or other bio-based saturated polyester, such as PE 23,23 (T_m = 99 °C)[31] or PE 20,20 (T_m = 103 °C)[32]. This behavior, along with our results, suggests that unsaturated linear polyester presents a lower melting temperature than that of saturated polyesters. This can be attributed to molecular bend caused by double bonds presents in the unsaturated linear polyester, reducing the interactions between aliphatic moieties of the polymer, and therefore reducing the temperature where these interactions are dissociated. When adipic acid is used as a monomer, a higher melting temperature (T_m = 47.8 °C) is obtained (FIGURE 5 (c)) compared to polyester produced from 1,4-

enediol (T_m = 12.9 °C), confirming that a saturated polyester presents a higher melting temperature. Anzenberger and coworkers synthesized oligomers of unsaturated aliphatic esters that contained from 1 to 5 monomeric units of oleyl oleate. They found that increasing the number of monomeric units caused an increment in melting temperature, starting at 25°C for a dimer and tending to reach a limit value of 50 °C [33]. Therefore, the obtained data for the bio-based polyesters in this work agree to the Anzenberger's results.
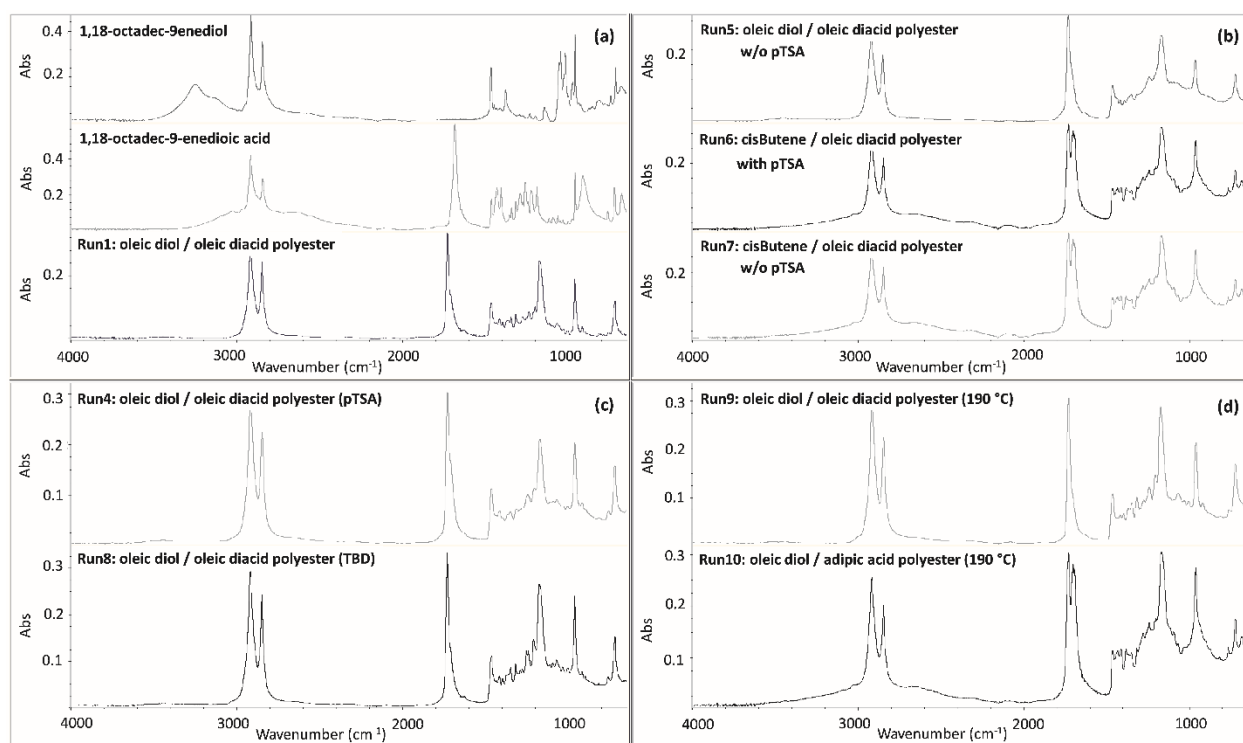
FIGURE 3 ATR spectra comparison corresponding to (a) Run1 bio-based polyester prepared from 1,18 octadec-9-enediol and 1,18-octadec-9-enedioic acid; (b) Run 5 bio-based polyester prepared from oleic diol and oleic diacid; Run 6 partially bio-based polyester prepared from cis-2-butene-1,4-diol and oleic diacid using p-TSA catalyst and Run 7 partially bio-based polyester prepared from cis-2-butene-1,4-diol and oleic diacid without catalyst (c) Run 4 bio-based polyester obtained with p-TSA catalyst; Run 8 bio-based polyester obtained with TBD catalyst (d) Run 9 bio-based polyester from oleic diacid and oleic diol; Run 10 bio-based polyester from adipic acid and oleic diol

Catalyst usage during polyesterification has an effect on melting and crystallization temperatures and enthalpy of the polymer, as can be observed in FIGURE 5 (a) and Table 1. Polyesters obtained using catalyst show a sharper melting peak at a higher temperature compared to polyester

obtained without catalyst addition. Furthermore, it can be observed that reaction time or catalyst/monomer ratio does not have a significant effect on thermal properties.
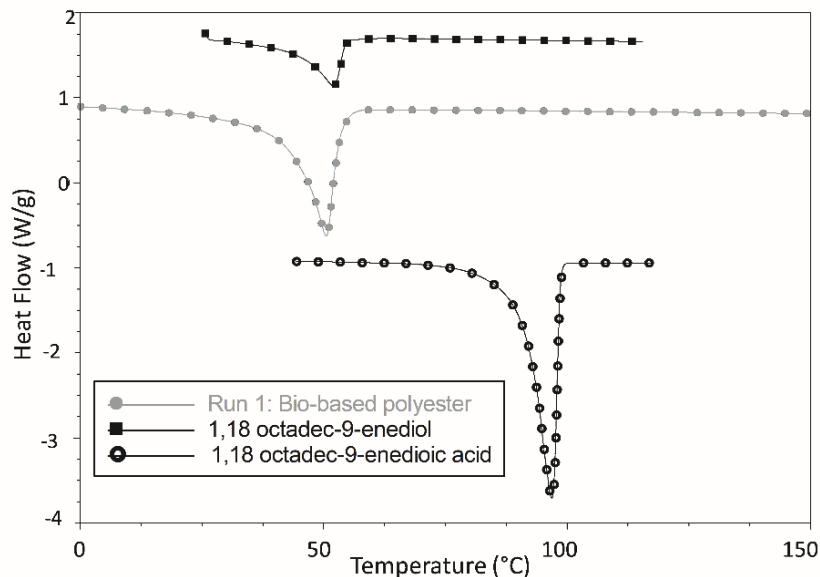
FIGURE 4 DSC heating thermograms corresponding to 1,18-octadec-9-enediol, 1,18-octadec-9-enedioic acid and the bio-based polyester using both.

In order to determine crystallization percentage, theoretical enthalpy was estimated using Group contribution addition method described by Van Krevelen[34]. Polyester synthesized from 1,18-octadec-9-enedioic acid and 1,18-octadec-9-enediol has a melting enthalpy estimated by group contribution of 201.1 J/g, the polyester synthesized from 1,18-octadec-9-enedioic acid and cis-2-butene-1,4-diol has a value of 157.7 J/g and the polyester synthesized from adipic acid and 1,18-octadec-9enediol has a melt enthalpy of 185.1 J/g. This estimation suggests that monomer with shorter chain length or double bond in its structure reduces the melting enthalpy. From these values, crystallization percentage was calculated for all the experiments and are presented in Table 1. Crystallization percentage was between 35 to 52 %, which are typical values for semi-crystalline polymers as HDPE, PP, PET or PBT.

Optical microscope in polarization mode, coupled to a heating plate, was used to observe crystallization process of bio-based polyester. FIGURE 6 presents the evolution of crystallization process during cooling observed by polarized optical microscopy for oleic/oleic polyester (Run 9: pictures a to d) and for adipic/oleic polyester (Run 10: pictures e to h). Both polymers show similar crystallization process forming spherulite regions, which confirm the semi-crystalline nature of the polyesters. Nucleation process starts at around 42 °C, whereas at 36 °C can be observed a high concentration of crystalline regions.
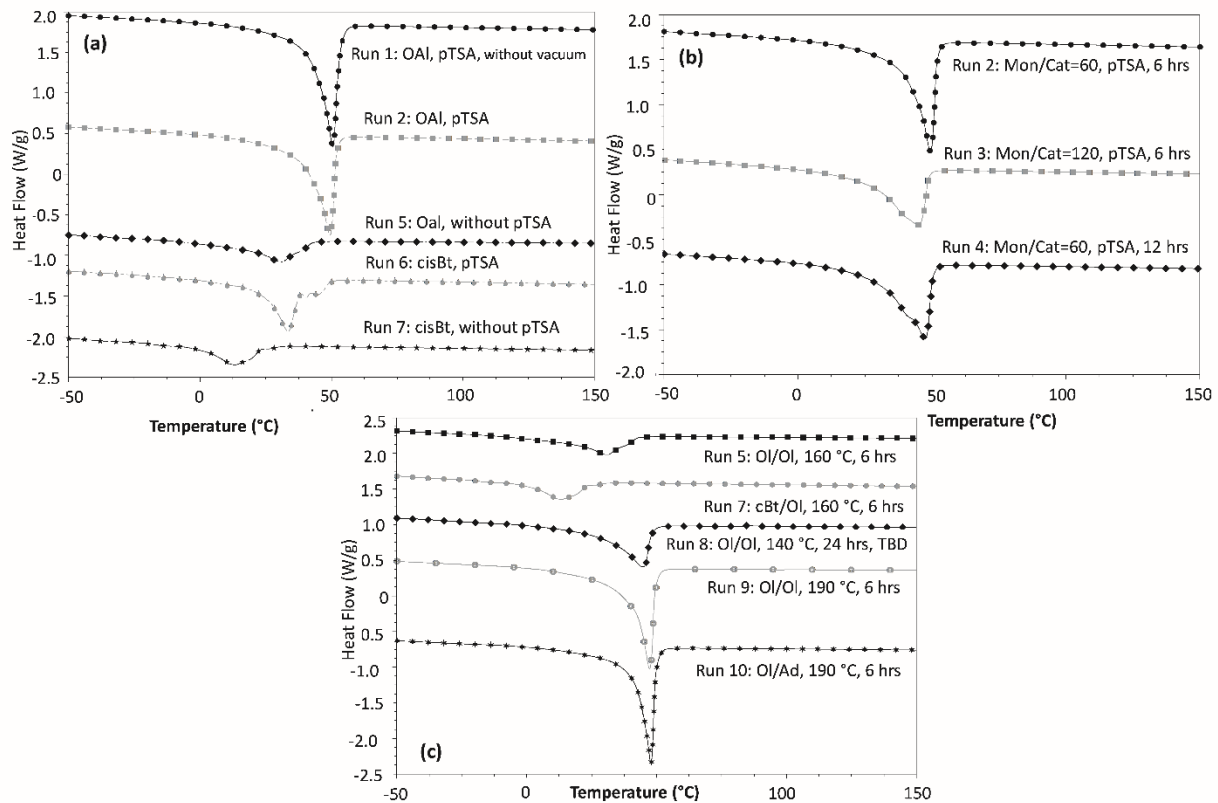
FIGURE 5 DSC heating thermograms corresponding to (a) total and partially bio-based polyester obtained with or without pTSA catalyst; (b) bio-based polyester obtained with different monomer/catalyst ratio and reaction time and (c) total and partially bio-based polyester obtained at different temperature and bio-based polyesterobtained with TBD catalyst at 140 °C and 24 hours
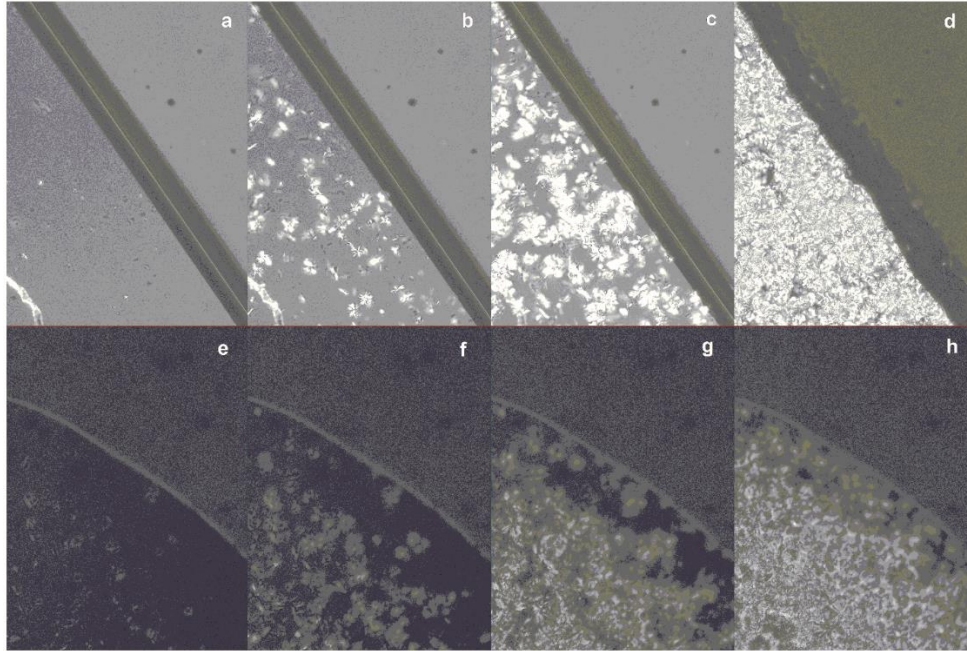
FIGURE 6 Optical microscopy pictures of bio-based polyester obtained with heating plate and polarization corresponding to bio-based polyester (Run 9) obtained from 1,18-octadec-9-enedioic acid and 1,18-octadec-9-enediol @ 190 °C during cooling at: a) 45 °C, b) 42 °C, c) 39 °C, d) 36 °C and partially bio-based polyester (Run 10) obtained from adipic acid and 1,18-octadec-9 enediol @ 190 °C during cooling at e) 45 °C, f) 42 °C, g) 39 °C, h) 36 °C.
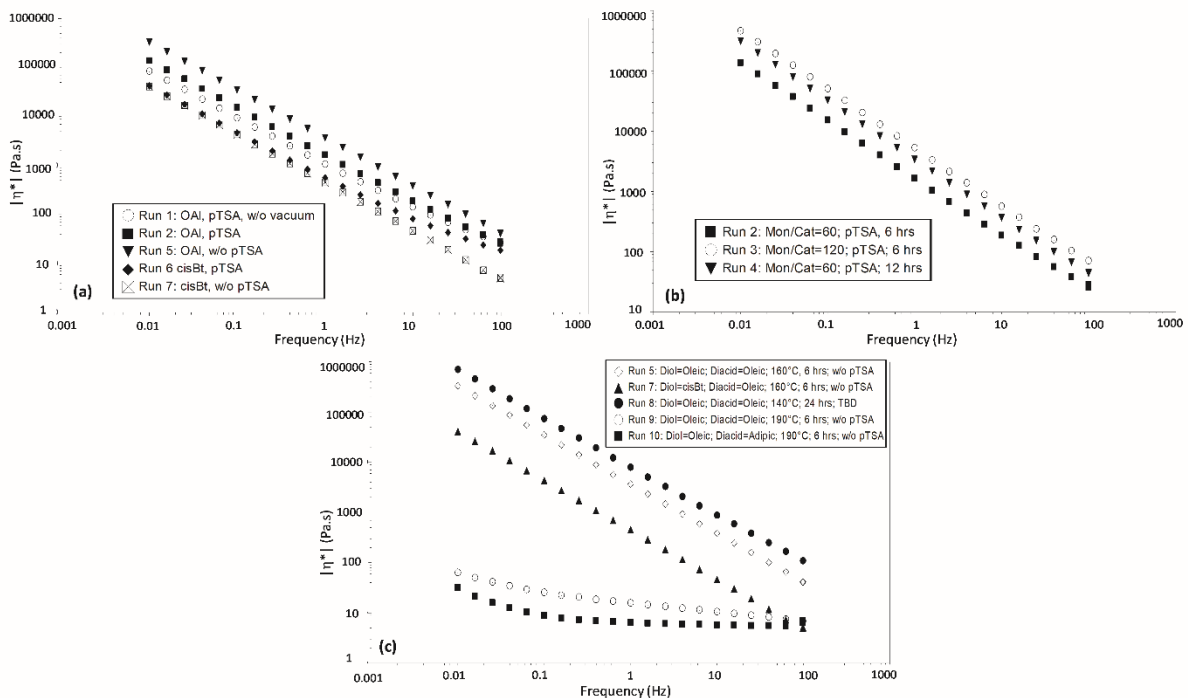
FIGURE 7 Dynamic viscosity η^* as a function of frequency obtained from oscillatory rheometry at 80 °C corresponding to (a) total and partially bio-based polyester obtained with or without pTSA catalyst; (b) bio-based polyester obtained with different monomer/catalyst ratio and reaction time and (c) total and partially bio-based polyester obtained at different temperature and bio-based polyester obtained with TBD catalyst at 140 °C and 24 hours

The rheological analysis was carried out on the samples in the molten state in order to estimate differences in molecular weight through dynamic viscosity curves obtained at 80 °C (FIGURE 7). It can be observed that polyester prepared with 1,4-butenediol or adipic acid have lower dynamic viscosity compared to polyester obtained from oleic diol or diacid under similar conditions.

Besides, vacuum pressure helps to get a higher viscosity, suggesting a higher molecular weight, as can be observed comparing curves of Run 1 and Run 2. Catalyst addition and concentration is shown in FIGURE 7 (a and b), respectively. The amount of catalyst has a positive effect on dynamic viscosity since it yields a higher polymerization degree. Reaction time has an effect on dynamic viscosity; a change from 6 to 12 hours produces a significant increment in viscosity. Increase of reaction temperature, as can be observed for Run 5 and Run 9 in FIGURE 7 (c), cause a significant reduction in dynamic viscosity, suggesting that the molecular weight of polyesters obtained at 190 °C is much lower compared than that of polyesters obtained at 160 °C. Actually, the best result of all experiments was obtained in Run 8 with the lowest reaction temperature (140 °C), as can be seen in FIGURE 7 (c). This result can be explained by the selectivity of the catalysts. TBD catalyst promotes trans-esterification reactions [15, 35, 36] whereas pTSA has been used as esterification catalyst [37, 38]. This difference in selectivity could have an effect on polymerization degree.

On the other hand, FIGURE 8 presents rheological curves of dynamic viscosity as a function of temperature. In these curves is evident that higher dynamic viscosities (and therefore higher molecular weight) can be obtained at lower reaction temperatures, under vacuum pressure and preferably adding a higher level of catalyst. These curves show that most of the synthesized

polyesters are rheologically stables as a function of temperature, it means, there are no changes

in rheological properties when the temperature is increased, with exception of Run 9 and Run 10,
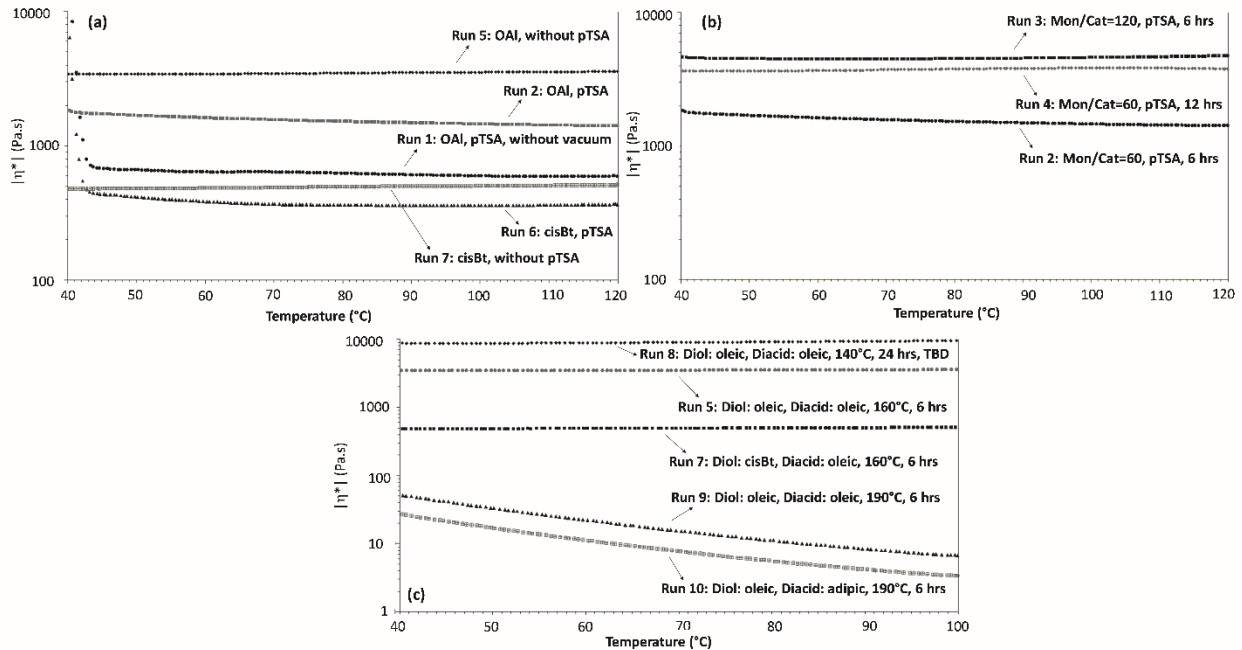
which were prepared at 190 °C.

FIGURE 8 Dynamic viscosity η^* as a function of temperature obtained from oscillatory rheometry at 1 Hz and 1.25 % of strain corresponding to (a) total and partially bio-based polyester obtained with or without pTSA catalyst; (b) bio-based polyester obtained with different monomer/catalyst ratio and reaction time and (c) total and partially bio-based polyester obtained at different temperature and bio-based polyester obtained with TBD catalyst at 140 °C and 24 hours

An attempt was made to prepare master curves for bio-based polyester, but all samples have

shown rheological complex behavior. So, when plotting the phase angle δ as a function of the

complex module G* for the obtained curves at different temperatures, it was found that they did

not overlap or has regions where there are not overlapping, pointing out that it is not possible to

predict the temperature dependence by applying the WLF or Arrhenius model, and therefore, not allowing to apply the time-temperature superposition principle.

Bio-based polyurethanes

Bio-based polyurethanes have been developed for a long time from vegetable oil derivatives since it has taken advantage of the presence of functional groups that are necessary for their synthesis in the structure of the triglycerides of the oil that allows the production of bio-based polyols or even bio-diisocyanates [5, 39-41]. Polyurethanes are very versatile materials because flexible or high-rigidity materials can be obtained depending on the structure of the selected polyol or diisocyanate monomers. In this work, it has been synthesized partially bio-based polyurethane using polyester obtained from reaction between 1,18-octadec-9- enedioic acid and 1,18-octadec-9-enediol (bio-based oleic polyester diol) and MDI (PU-1) and a reference petrochemical polyurethane prepared from MDI and cis-2-butene-1,4-diol (PU-2). The monomeric units of both polyurethanes are shown in FIGURE 9.

PU-1 bio-based polyurethane

PU-2
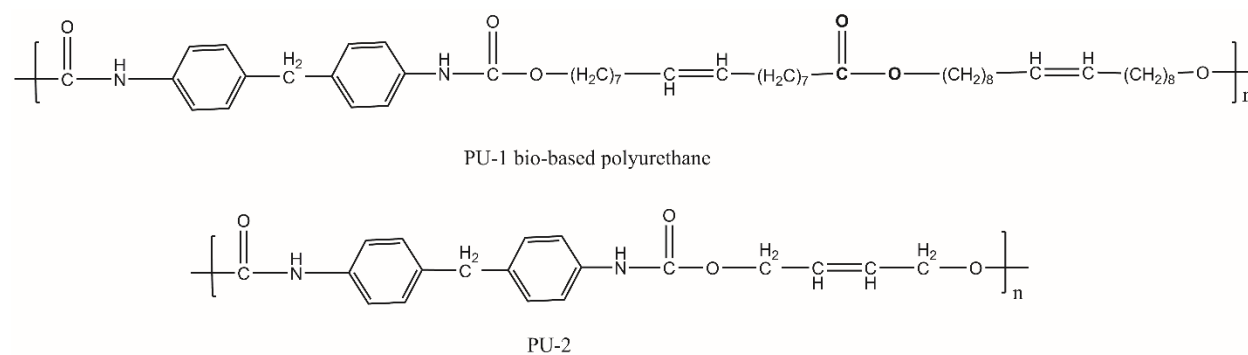
FIGURE 9 Monomeric units of bio-based PU (PU-1) and petrochemical PU (PU-2)

ATR-FTIR spectra comparison of monomers and resulting bio-based and petrochemical polyurethane is shown in FIGURE 10. Urethane functional group formation is confirmed by –C=O

stretching band at 1699 cm^{-1}, N-H flexion at 1519 cm^{-1} and N-C-O stretching band at 1213 cm^{-1}.

On the other hand, isocyanate N=C=O band at 2270 cm^{-1} that is present in the MDI spectrum disappear in both polyurethane spectra. Diol –OH band at 3250 cm^{-1} that is shown in cis-2-butene-1,4-diol spectrum disappear and instead can be observed the N-H stretching band at 3309 cm^{-1} corresponding to polyurethane. Unlike the polyurethane synthesized from butenediol, the ATR-FTIR spectrum of the polyurethane obtained from the oleic diol has the -CH$_2$ stretching bands between 2850 and 2930 cm^{-1}, which are visible due to the greater amount of CH$_2$ groups of the oleic monomer. Other difference that can be observed between both PU spectra is that partially bio-based PU presents a band at 965 cm^{-1} corresponding to -trans double bond asymmetric flexion that was generated from metathesis reaction as was exposed before.

DSC and oscillatory rheometry data of the samples of partially bio-based and petrochemical polyurethane are shown in Table 2. Glass transition temperature (T$_g$) data show that PU-1, synthesized from MDI and bio-based oleic polyester diol, has a T$_g$ at around 58 °C, whereas the PU-2, obtained from MDI and cis-2-butene-1,4-diol has a Tg at around 86 °C (FIGURE 11). This can be explained by the chain length of the oleic unit, along with the double bond that gives more mobility to the polymer chain. Through group contribution method, it was estimated a theoretical value for partially bio-based polyurethane, resulting in a value of 53 °C, which is in good agreement with experimental results (58 °C). In contrast, group contribution T$_g$ estimation for MDI/butenediol polyurethane was 131 °C, having a significant difference to the experimental value of 86 °C. This difference should be explained by a low conversion in the polymerization process; then, the remaining butenediol monomer acts as a plasticizer decreasing the Tg value.
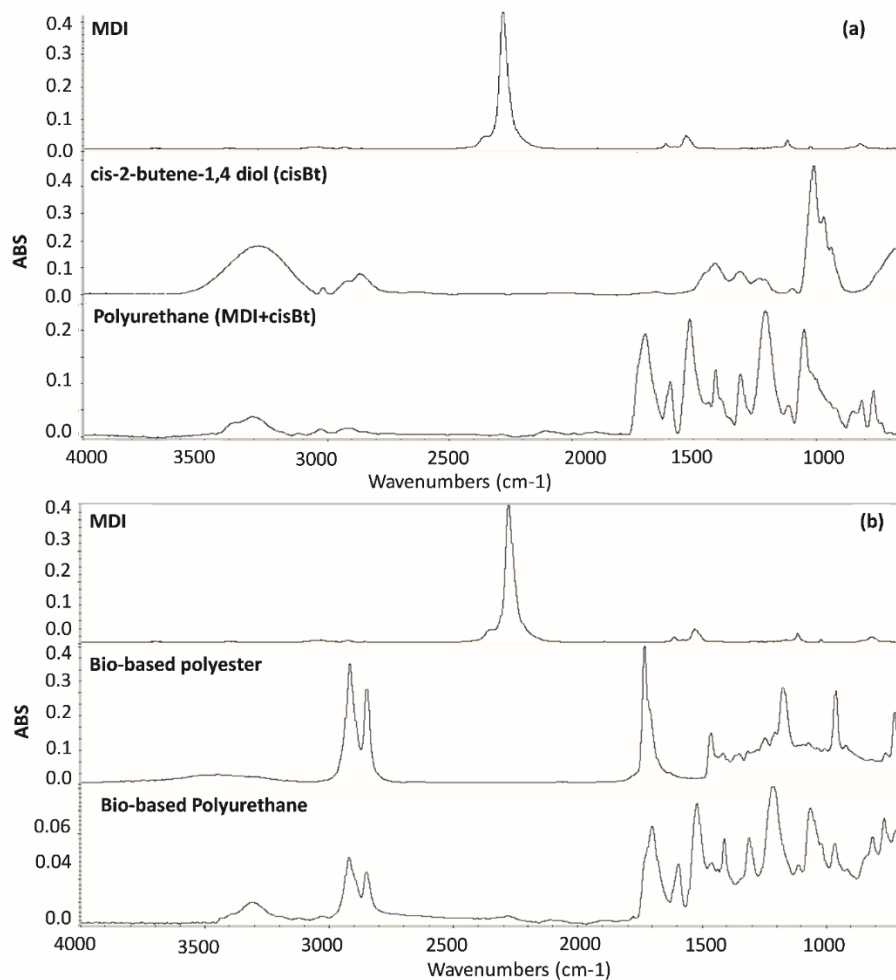
FIGURE 10 ATR spectra comparison corresponding to (a) PU-2 polyurethane prepared from MDI and 2-cis-butene-1,4-diol; (b) PU-1 partially bio-based polyurethane prepared from MDI and bio-based oleic polyester diol

Table 2 Experimental conditions for polyurethane synthesis

Run [a]	Diol	Diisocyanate [b]	-NCO/-OH [c]	T_g [d] [°C]	$[\eta^*]$ [e] @ 1 Hz, 90°C [MPa.s]	G'/G'' crossover [f] [°C]
PU-1	Bio-based oleic polyester diol	MDI	1	58.1	1.15	54.5
PU-2	Cis-2-butene-1,4-diol	MDI	1	86.4	0.29	35.0

[a] Reaction condition: Monomers = 14.8x10^{-3} mol; Reaction time: 2 hours at 70 °C, followed by 5 hours at 120 °C [b] MDI = methylene diphenyl diisocyanate; [c] Molar ratio [d] Obtained by DSC analysis; [e] Obtained from [η*] vs Temperature [°C] curves generated by oscillatory rheometry; [f] Obtained by DSC analysis; [g] Obtained from G' and G'' vs Temperature [°C] curves generated by oscillatory rheometry
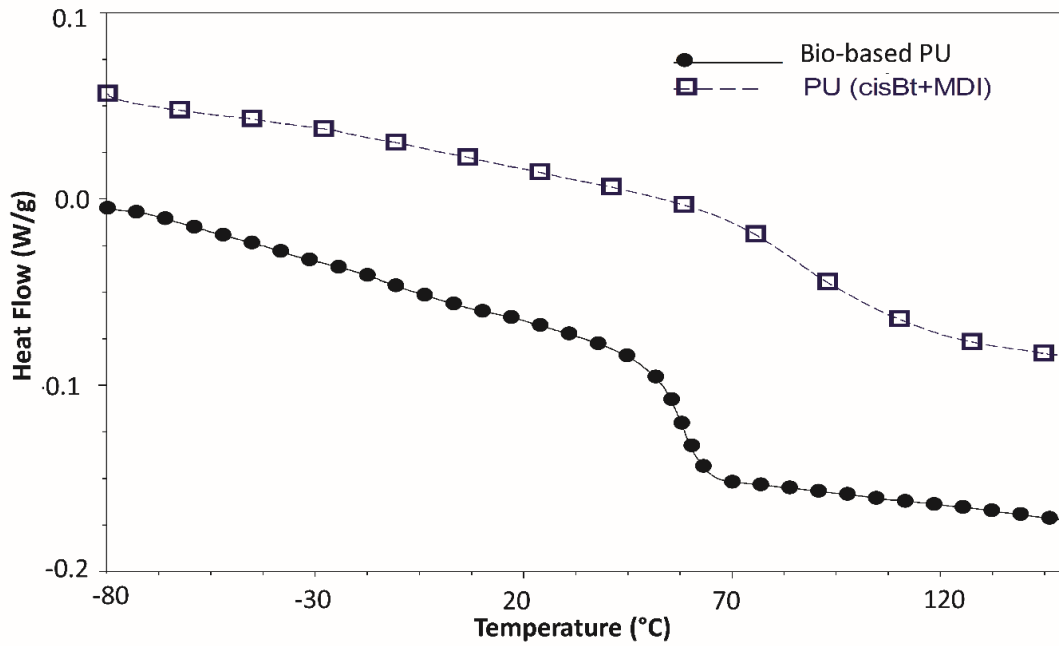
FIGURE 11 DSC thermograms of partially bio-based polyurethane synthesized from MDI and oleic polyester diol and petrochemical polyurethane obtained from MDI and cis-2-butene-1,4-diol

Rheological curves obtained during the curing process of the samples PU-1 and PU-2 are shown in FIGURE 12. Dynamic viscosity [η^*] vs. Temperature curves present a typical behavior for curing process, starting at very low viscosity values, but increasing it when the curing process takes place until a plateau is reached. In the case of partially bio-based polyurethane, [η^*] curve was started at 50 °C due to melting temperature of oleic diol. Dynamic viscosity plateau was higher for the partially bio-based polyurethane compared to the petrochemical polyurethane. This behavior should be explained by the differences in the molecular structure of the polyurethane due to the higher length of the diol.
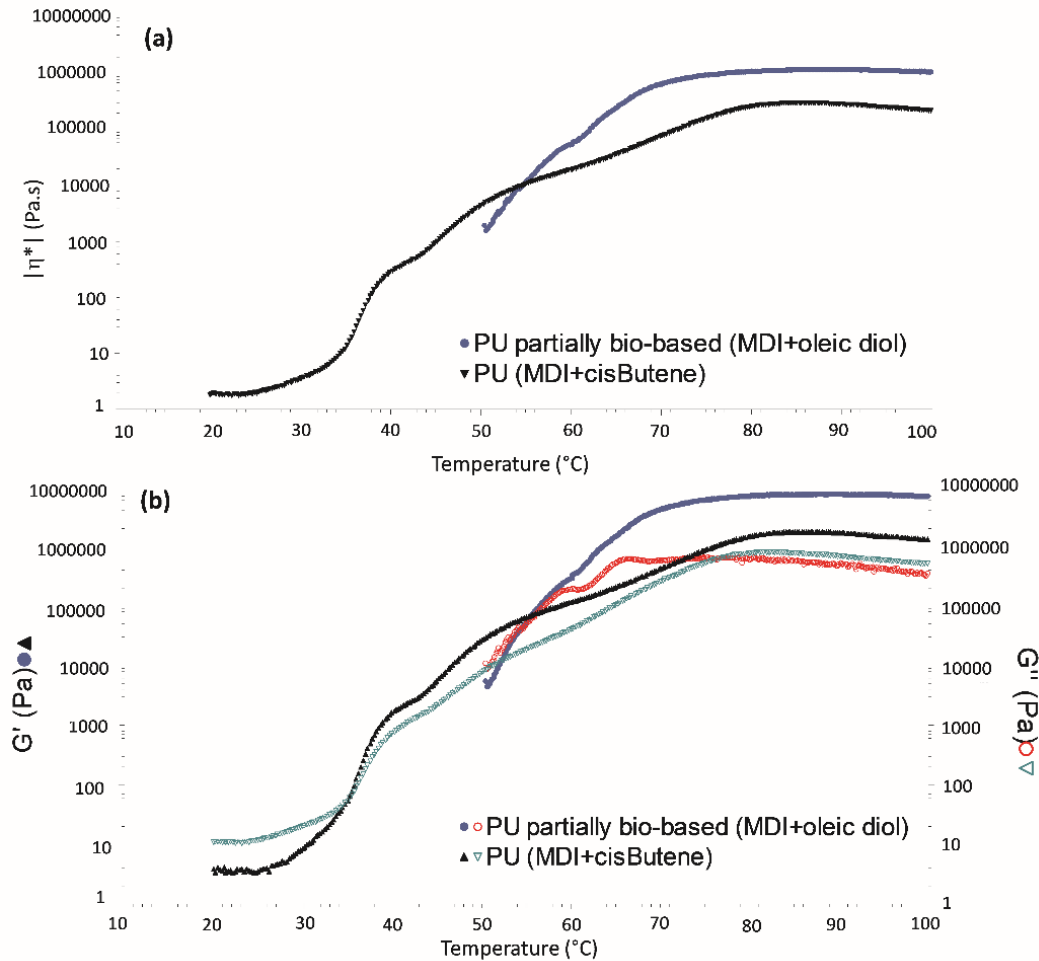
99

FIGURE 12 Rheological curves carried out during curing process corresponding to partially bio-based polyurethane obtained from MDI/1,18-octadec-9-enediol (PU-1) and petrochemical polyurethane from MDI/cis-2-butene-1,4-diol (PU-2): a) dynamic viscosity [η] versus temperature, b) G' and G'' versus temperature*

On the other hand, G' and G'' curves obtained during PU curing can be used to estimate the gel point temperature that occurs before the curing of the polymer. The gelification point is determined as the crossover of the G' and G" curves, it means when the material reach a thermodynamic equilibrium, and this point is considered as the beginning of the transition of the material from viscous to elastic behavior. The polyurethane obtained from MDI/2-cis-butene-1,4-diol (PU-2) shows a gel point at 35.0 °C, whereas PU synthesized from MDI/bio-based oleic polyester diol (PU-1) has a gel point at 54.5 °C. This last observation can be due to that melting

point of the oleic diol is above 50 °C and only when the monomer is in the melting state the polymerization reaction take place. Although PU-2 curing start at a lower temperature, its G' plateau is reached above 80 °C, whereas sample PU-1 reaches the plateau from 65 °C, and considering that gel point occurs at 54.5 °C, this means that reaction with the oleic monomer is faster than that with the butenediol monomer. As it was observed by dynamic viscosity, storage module G' plateau of PU-1 is higher than G' plateau of PU-2, this behavior is attributed to a longer chain of oleic diol that can produce larger polyurethane chain that could increase entanglements in the polymer.

CONCLUSIONS

Cross metathesis reaction was used to convert fatty acid derivatives in bio-based telechelic monomers, where their end-functionality was validated because the α/η molar ratio calculated from ^{1}H NMR data, is close to 2.0, and their melting and crystallization temperatures have shown some differences attributed to either acid or hydroxyl functionality. Both type of end-functional monomers exhibited a -trans isomerism in the double bond, as seen in the ATR-FTIR results, caused by transposition during metathesis reaction.

The telechelic monomers obtained were polymerized by step growth reaction to produce bio-based polyester and polyurethanes. Under comparable reaction conditions, the polymerization kinetics depend on the reaction temperature and to a lesser degree on both the reaction time and catalyst addition. Their melt temperature and enthalpy results pointed out that the monomer chain length has an effect in both crystallinity and thermal transition of the polymers. Group contribution analysis showed excellent correlation to explain this behavior.

Rheological analysis has been useful to follow the polymerization degree under some reaction conditions and monomer differences. It was found that polymers obtained with oleic monomers can get higher viscosity and viscoelastic modules compared to short chain monomers.

ACKNOWLEDGEMENTS

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GRAPHICAL ABSTRACT

Figure 1

oleic acid

+

Grubbs catalyst, 2nd generation

50 °C
48 hr

1,18-octadec-9-enedioic acid   9-octadecene

Figure 2

1, 18-octadec-9-enediol

+

1,18-octadec-9-enedioic acid

bio-based polyester
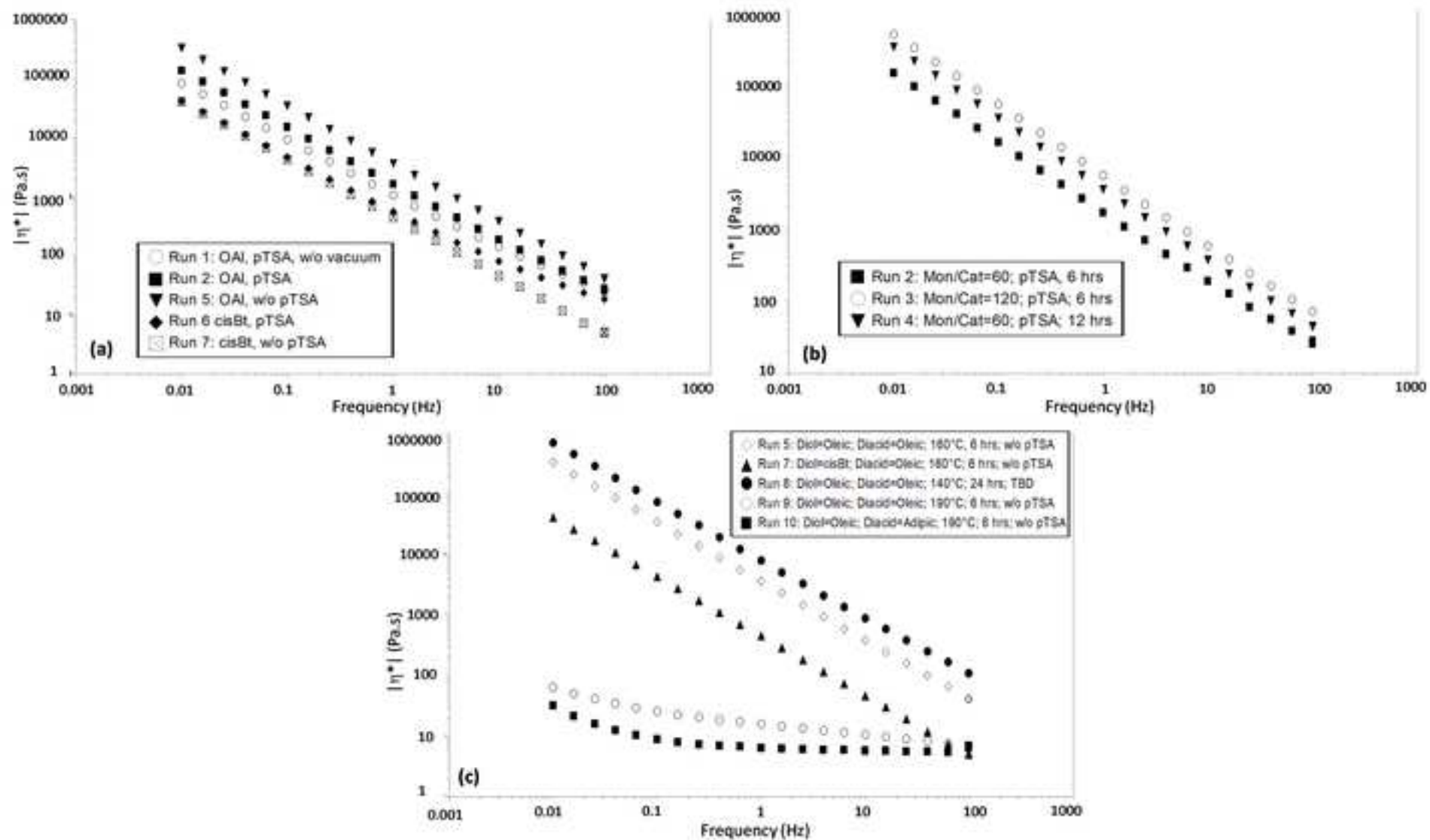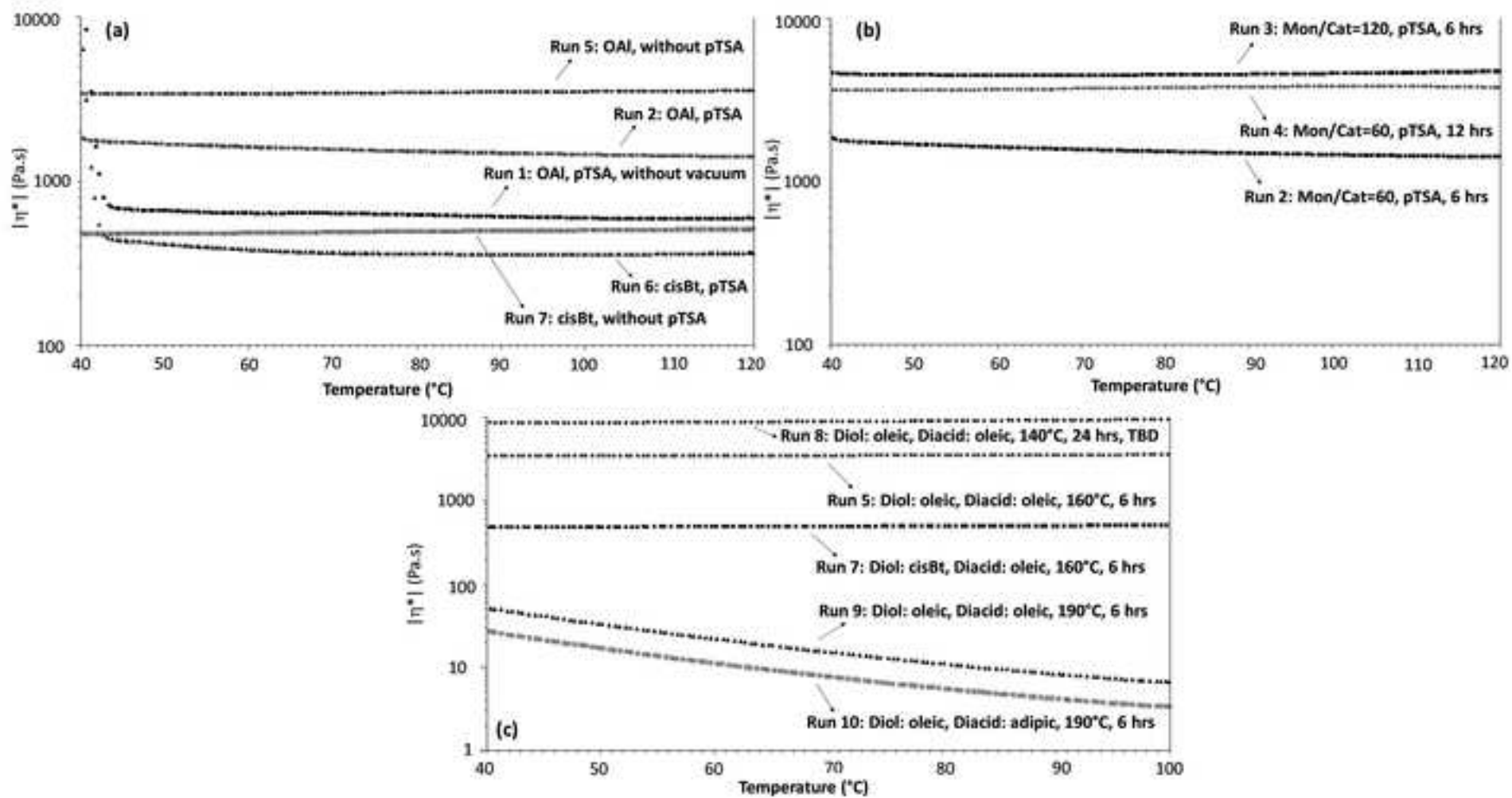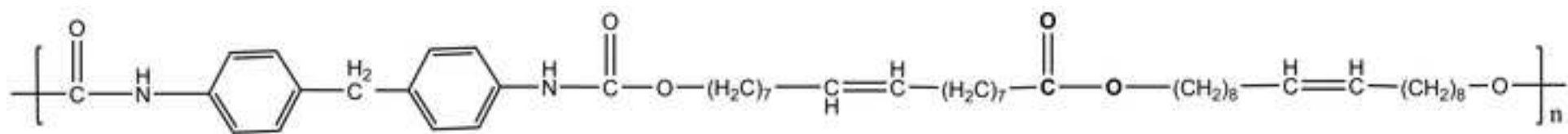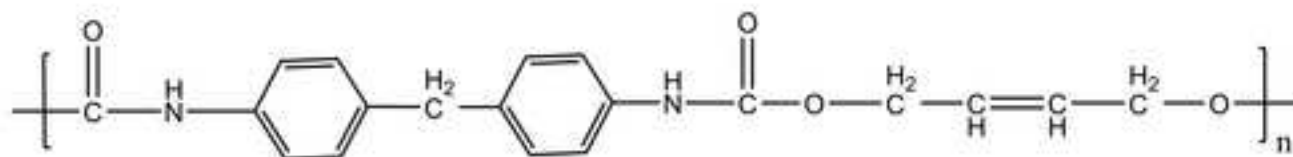
+

H₂O
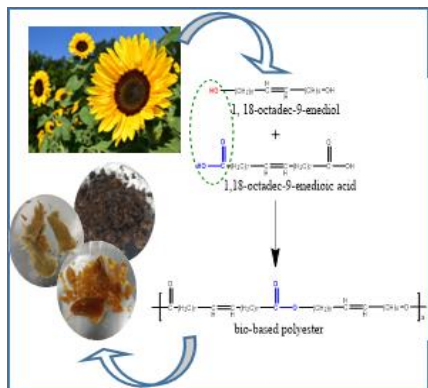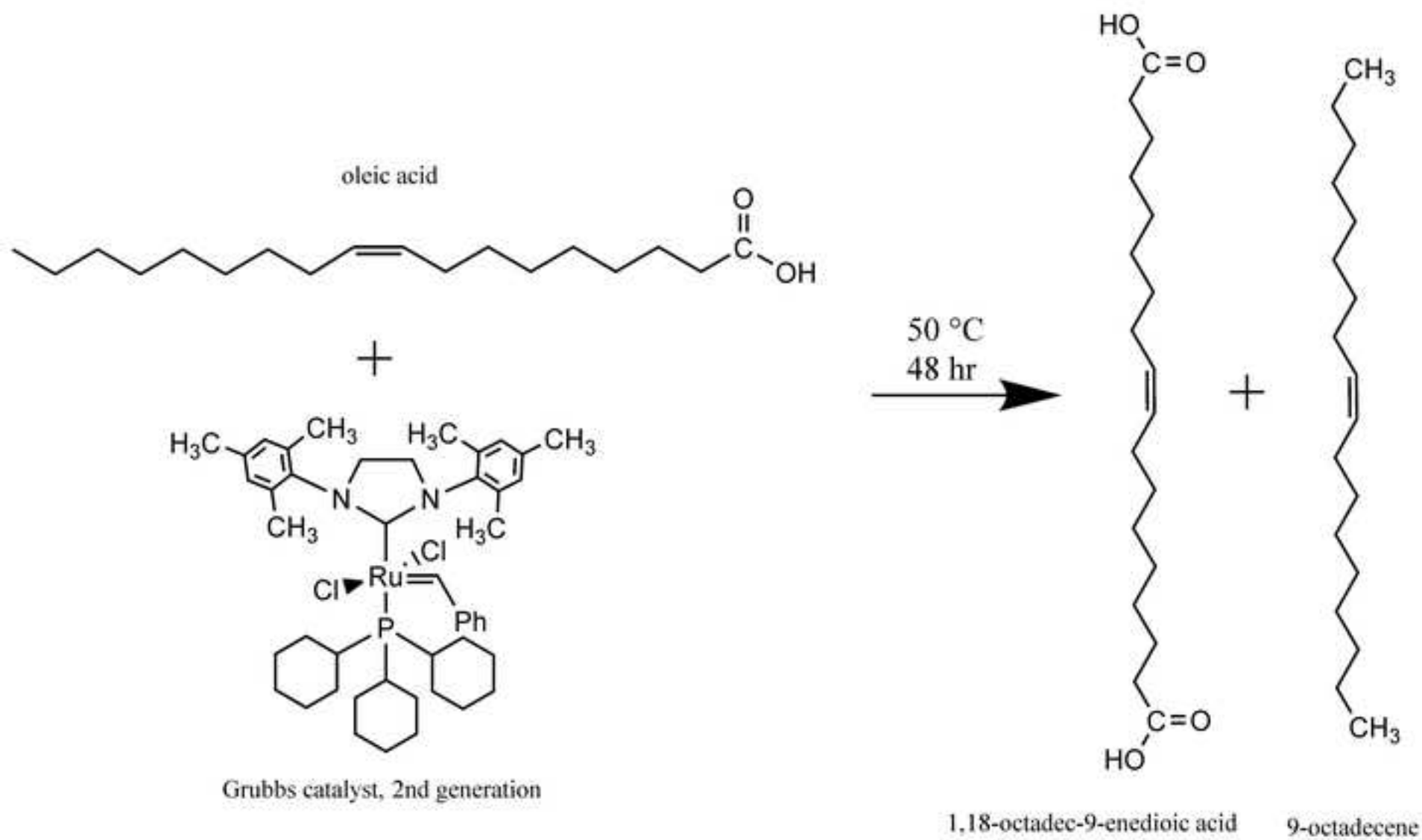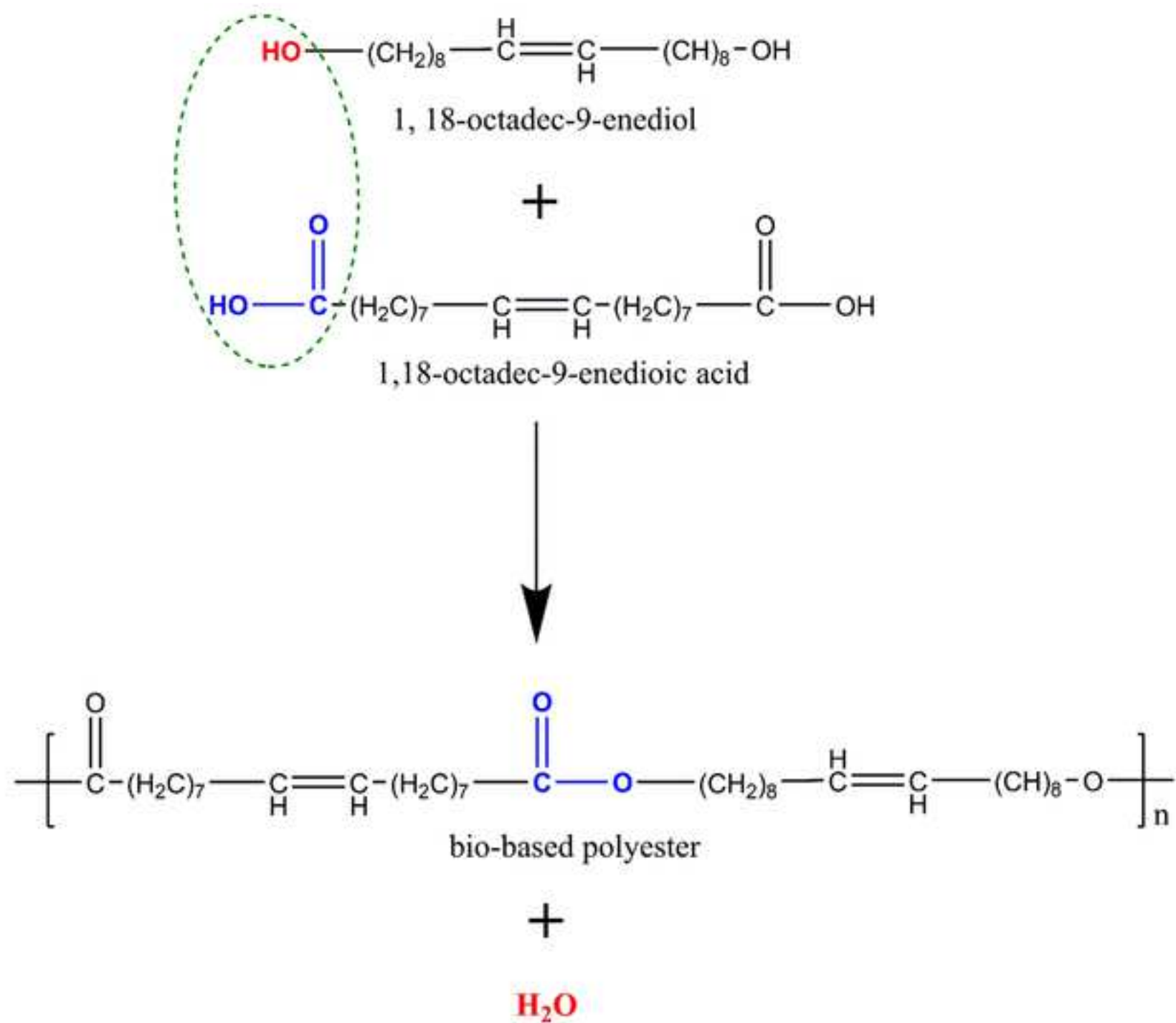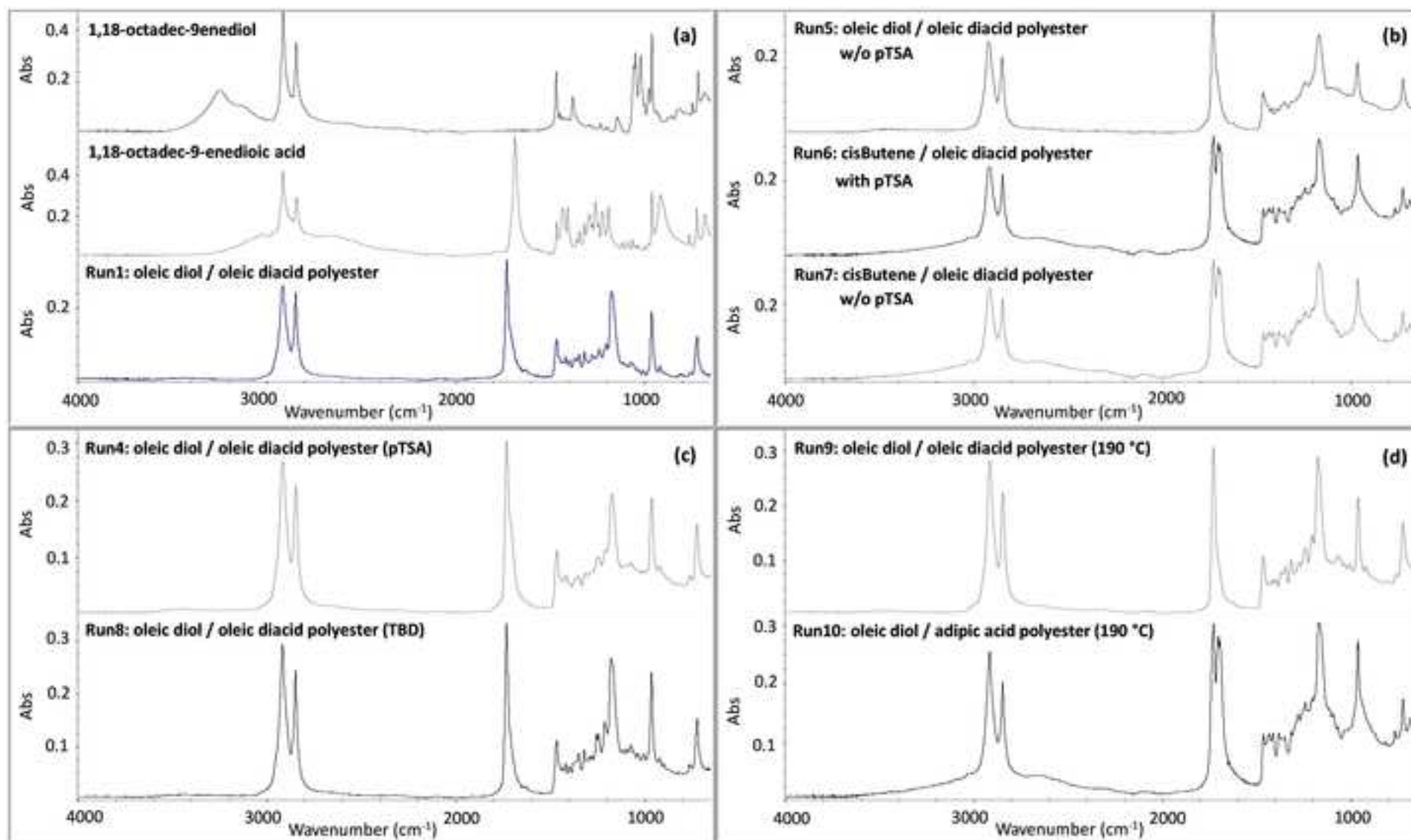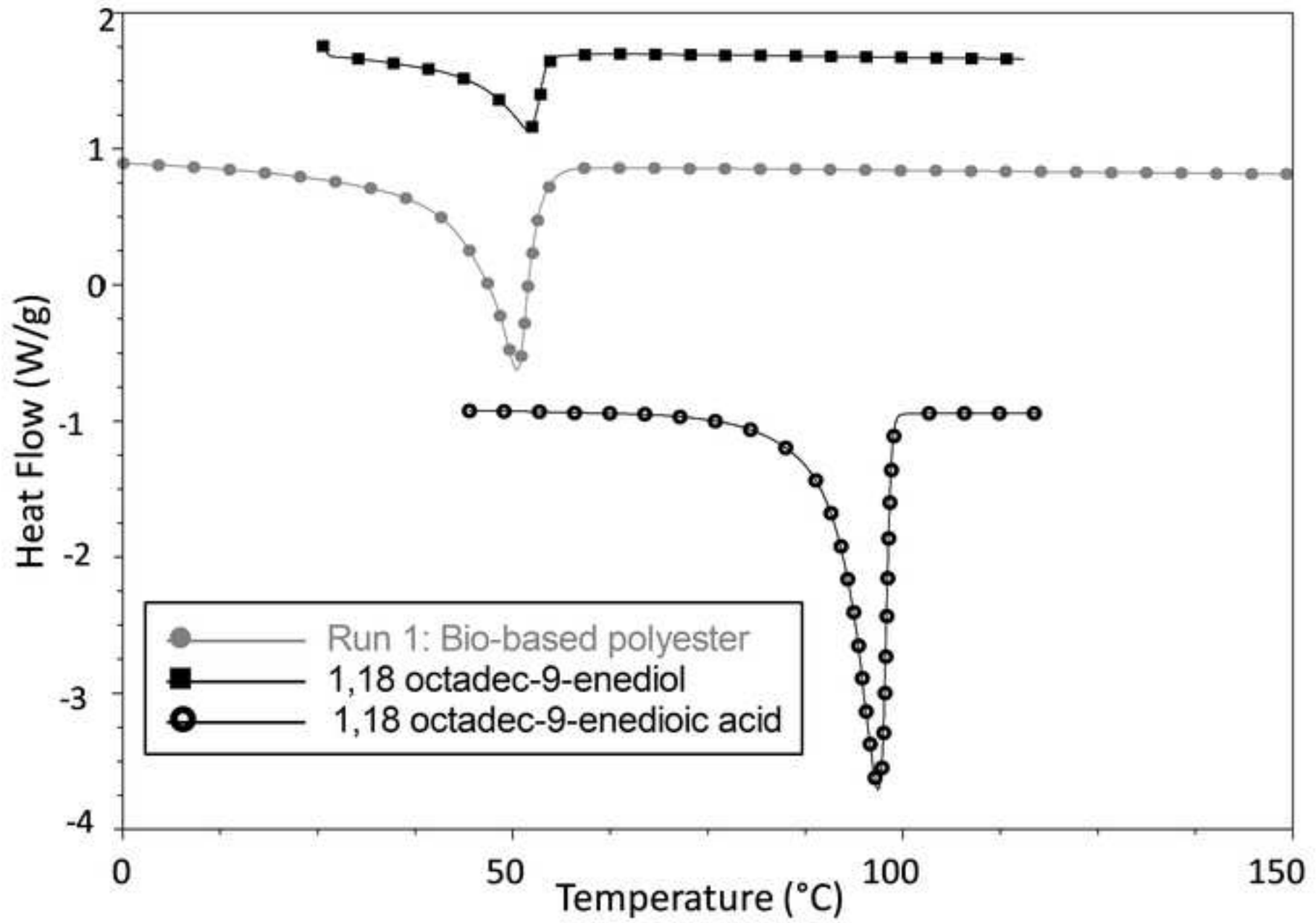
Figure 3

Figure 4

Figure 5
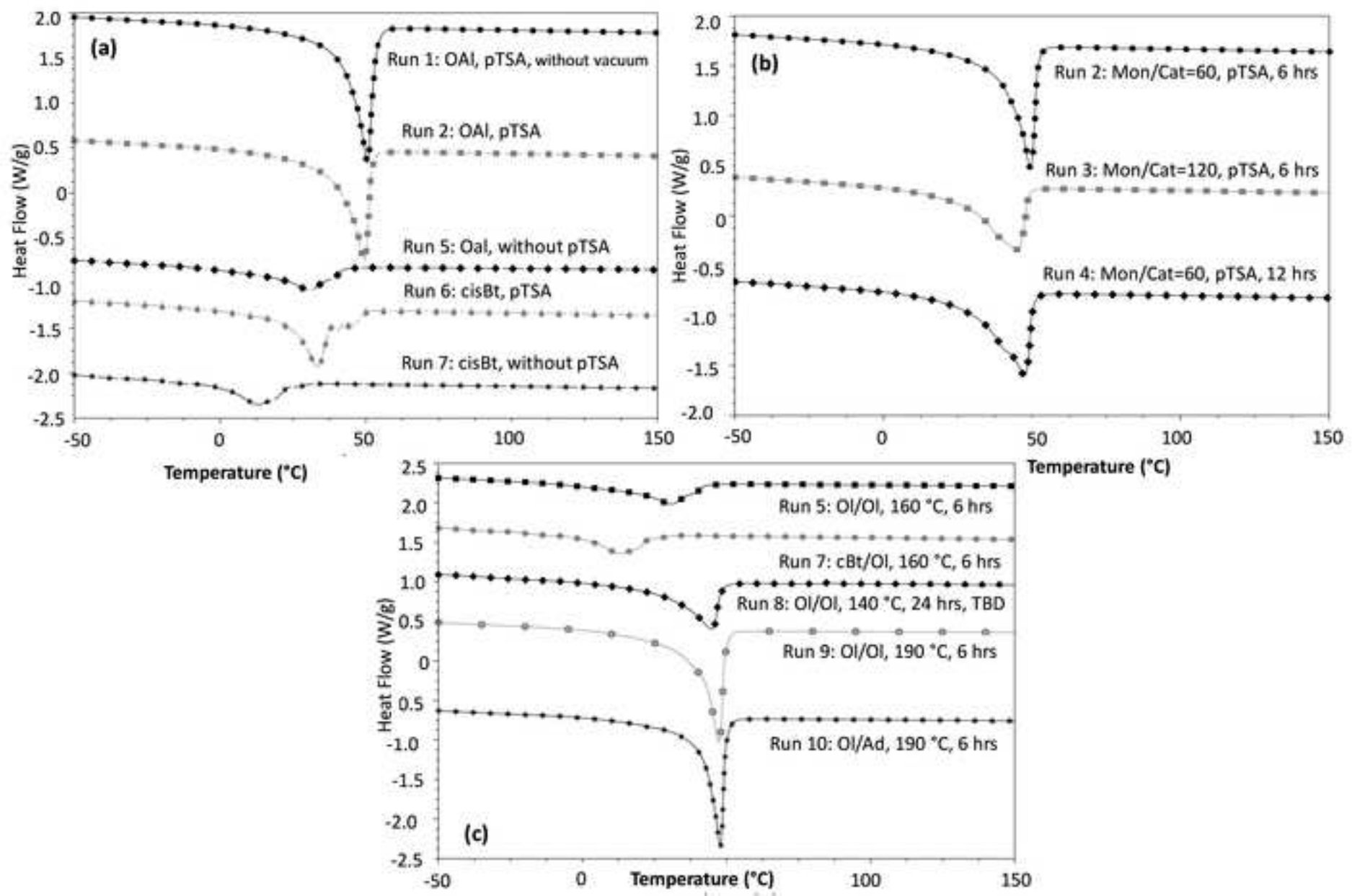
Figure 7

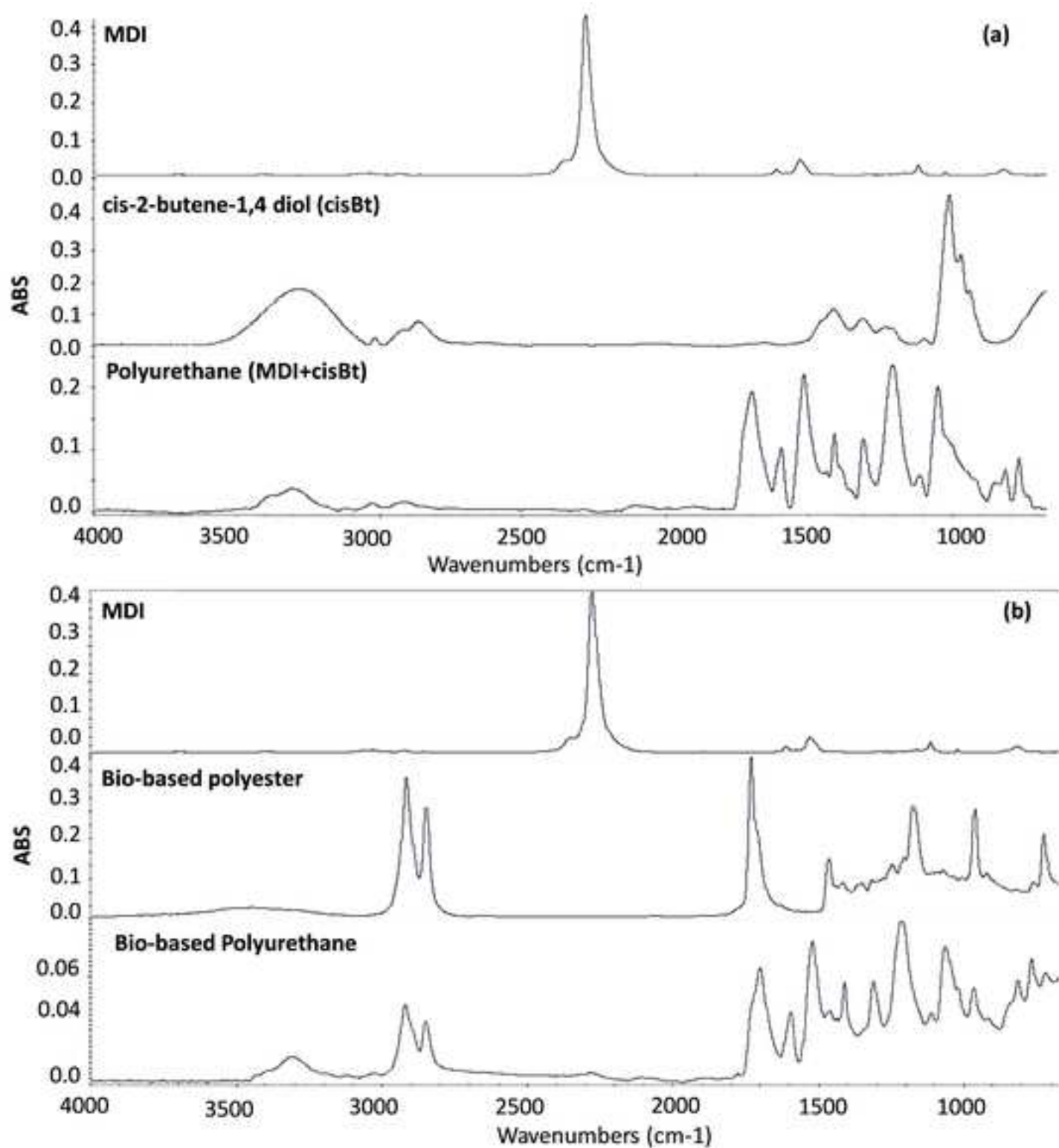Figure 8

Figure 9

PU-1 bio-based polyurethane

PU-2

Figure 10

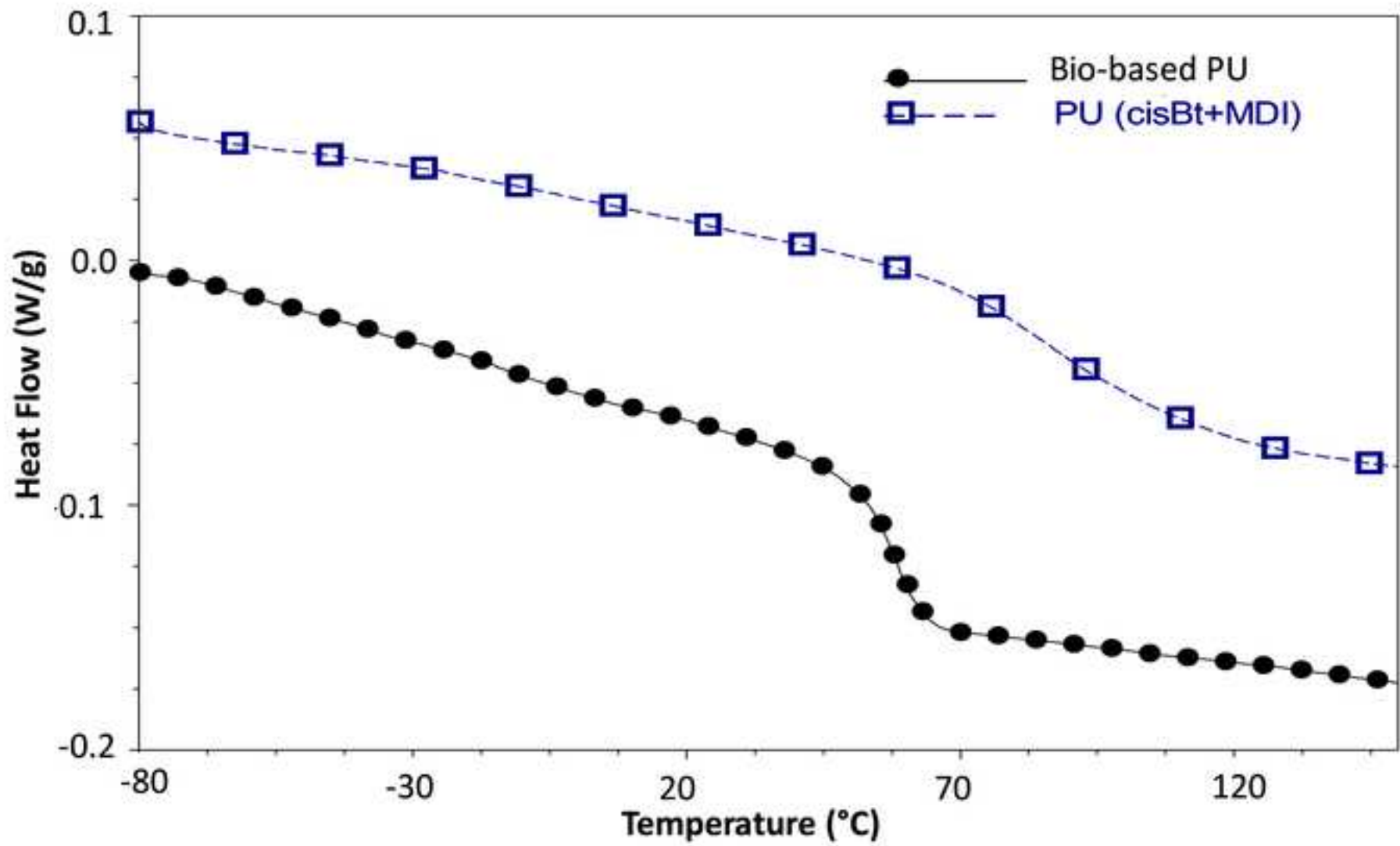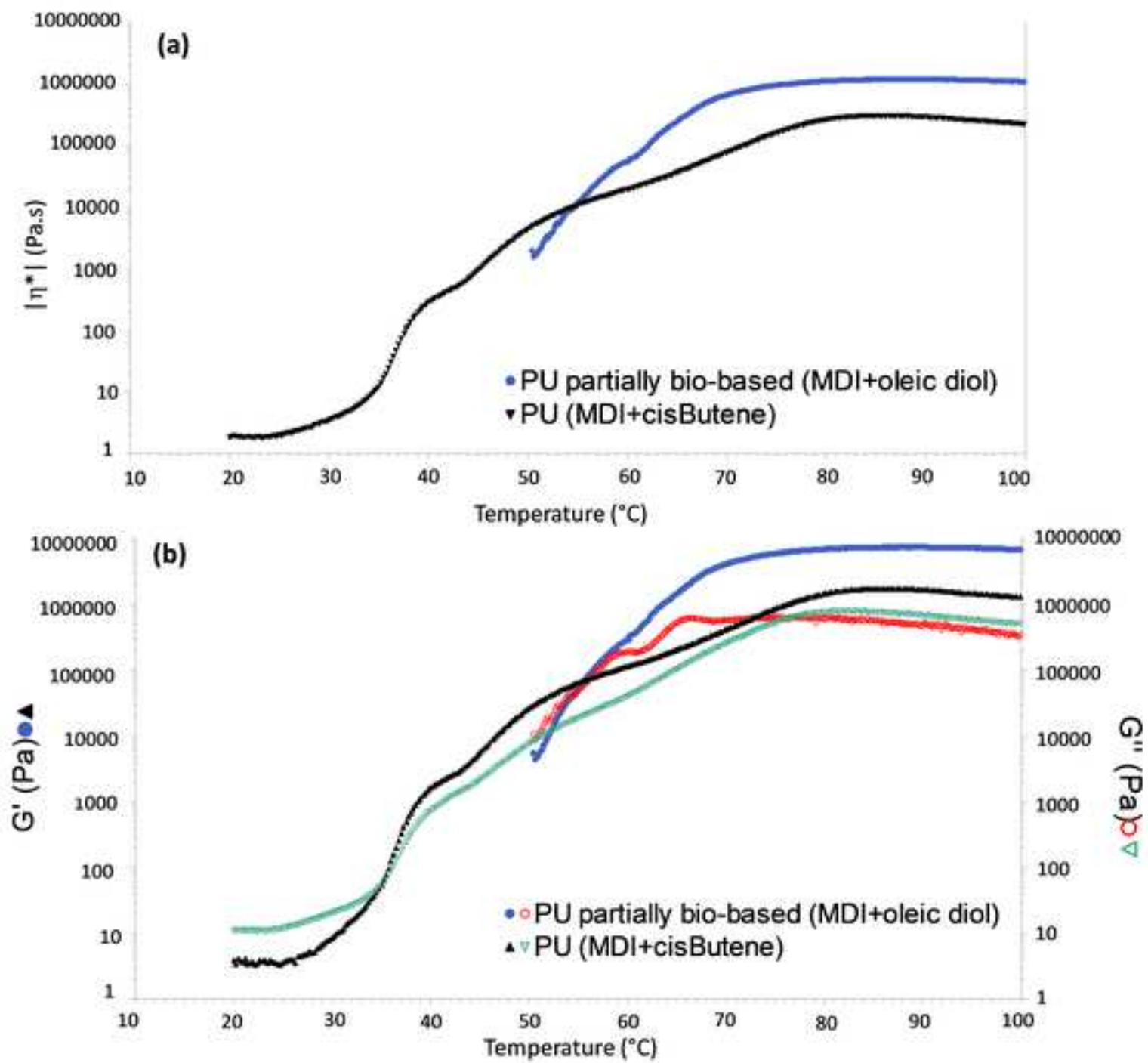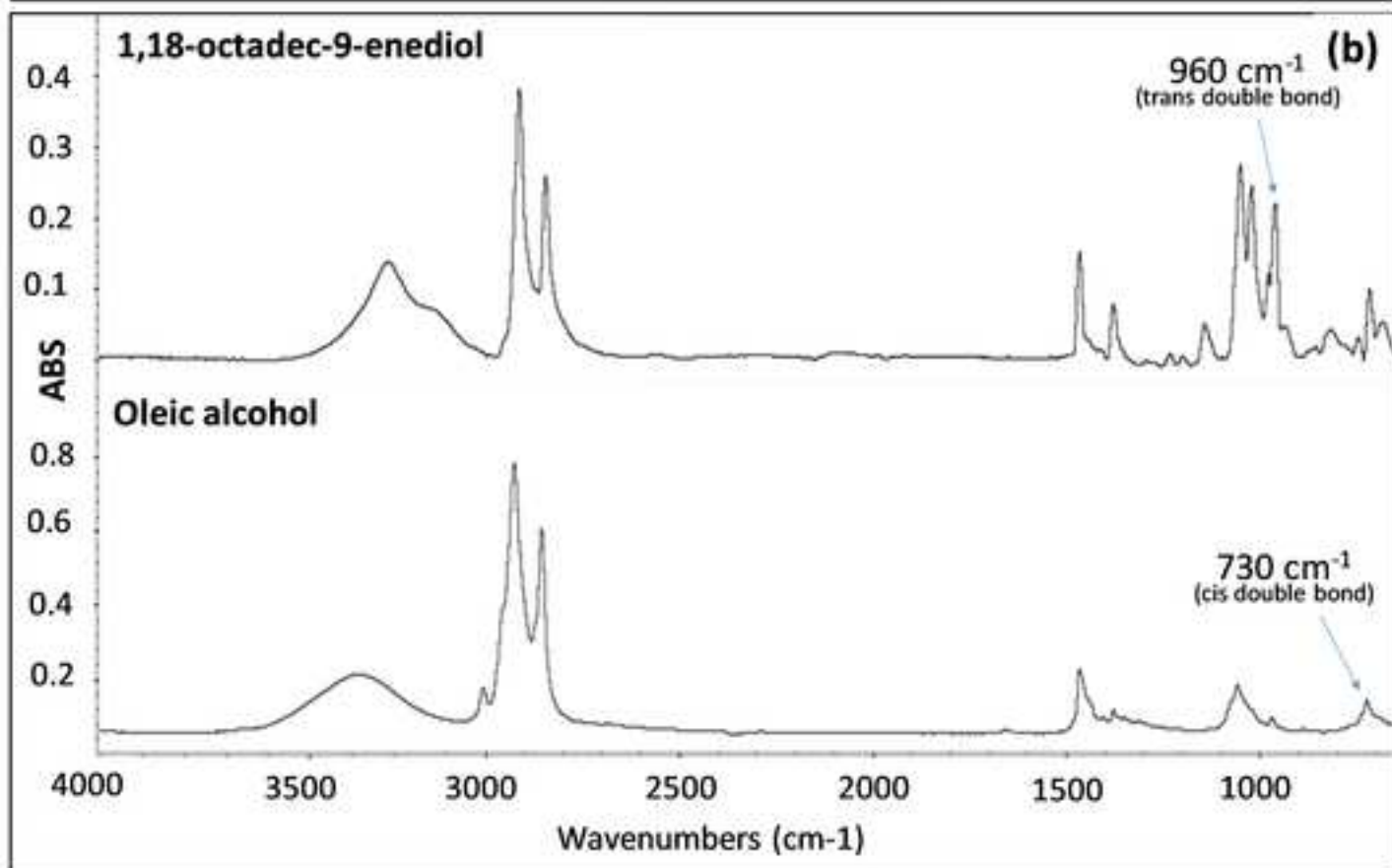Figure 11

Figure 12
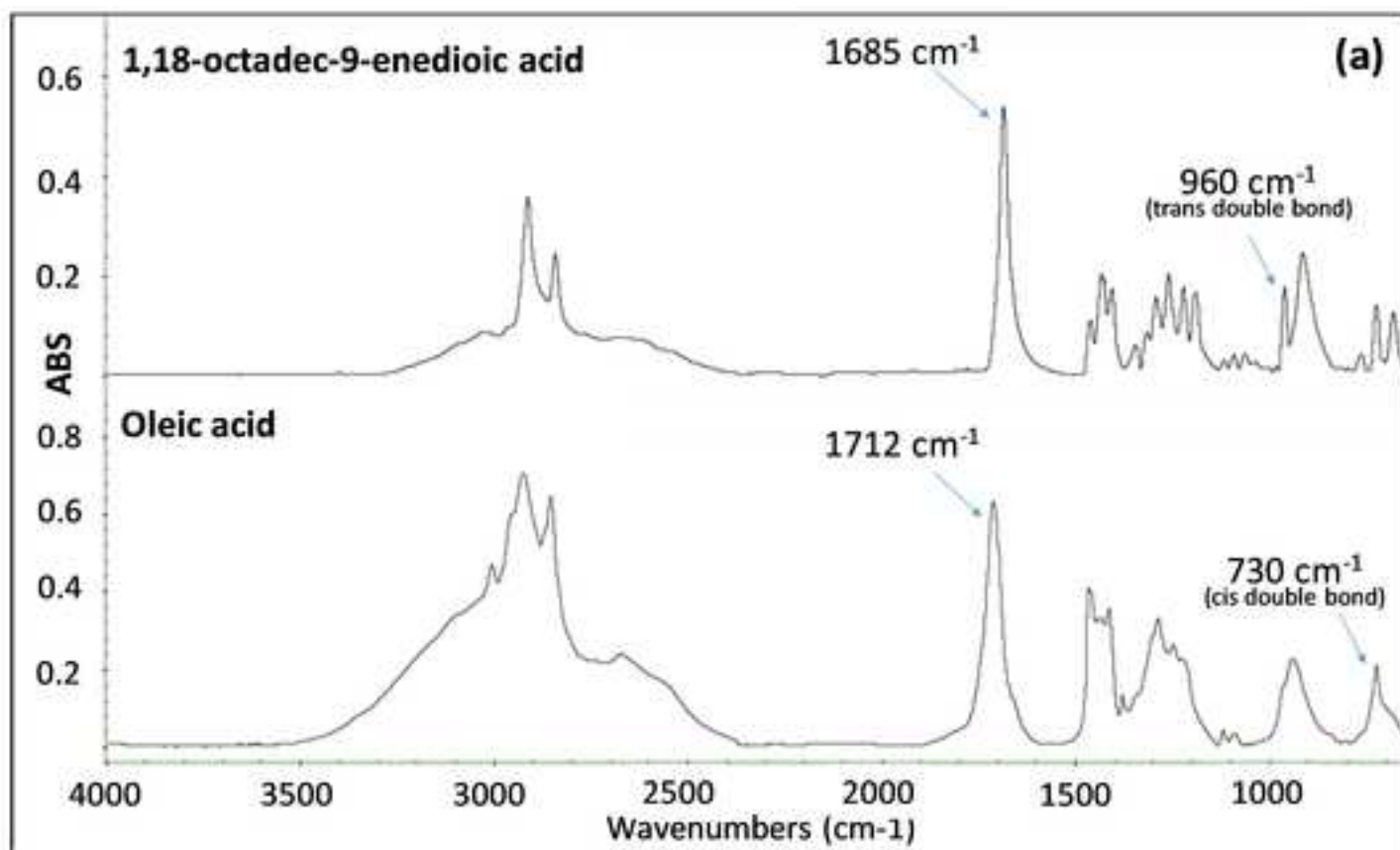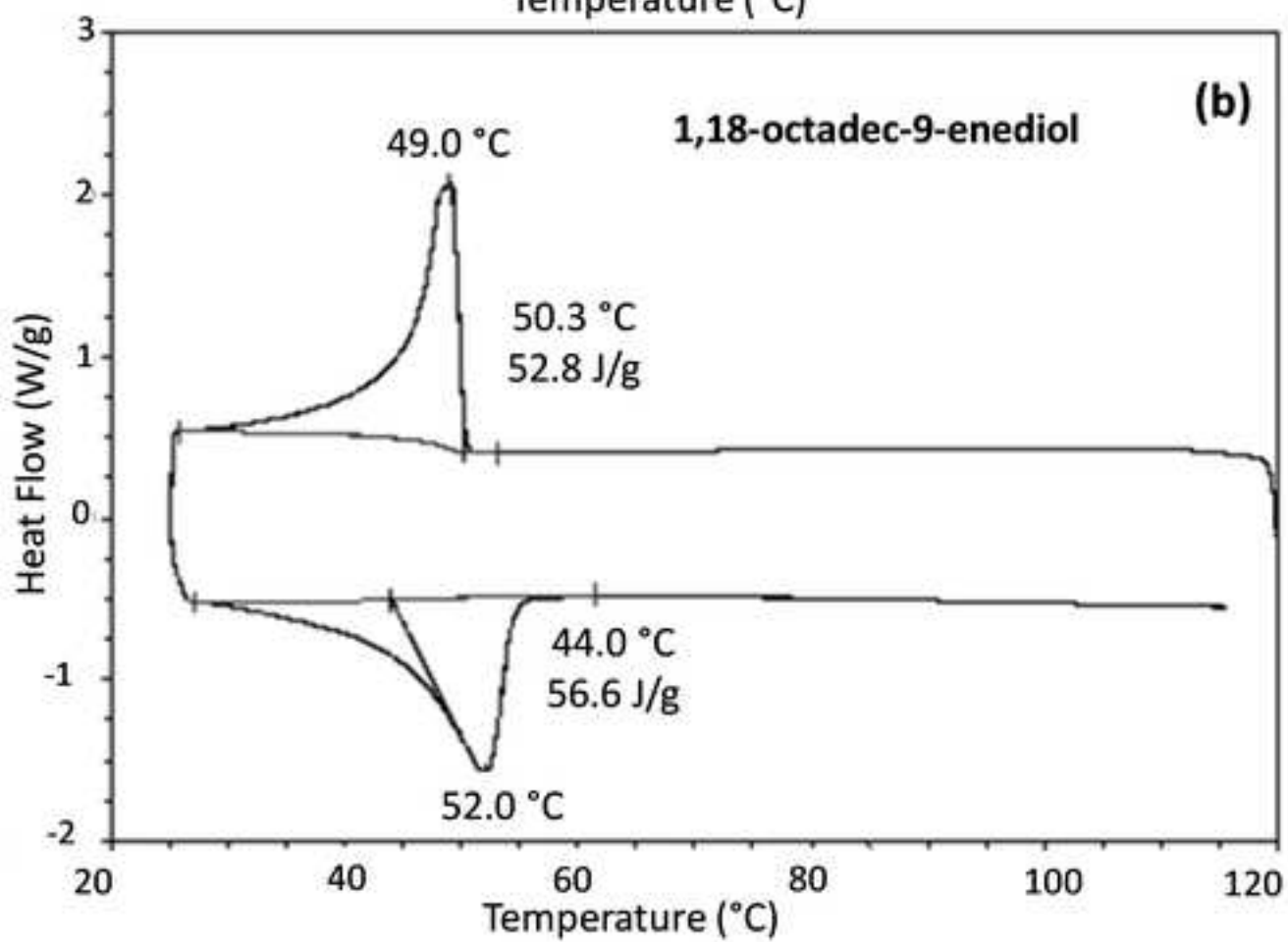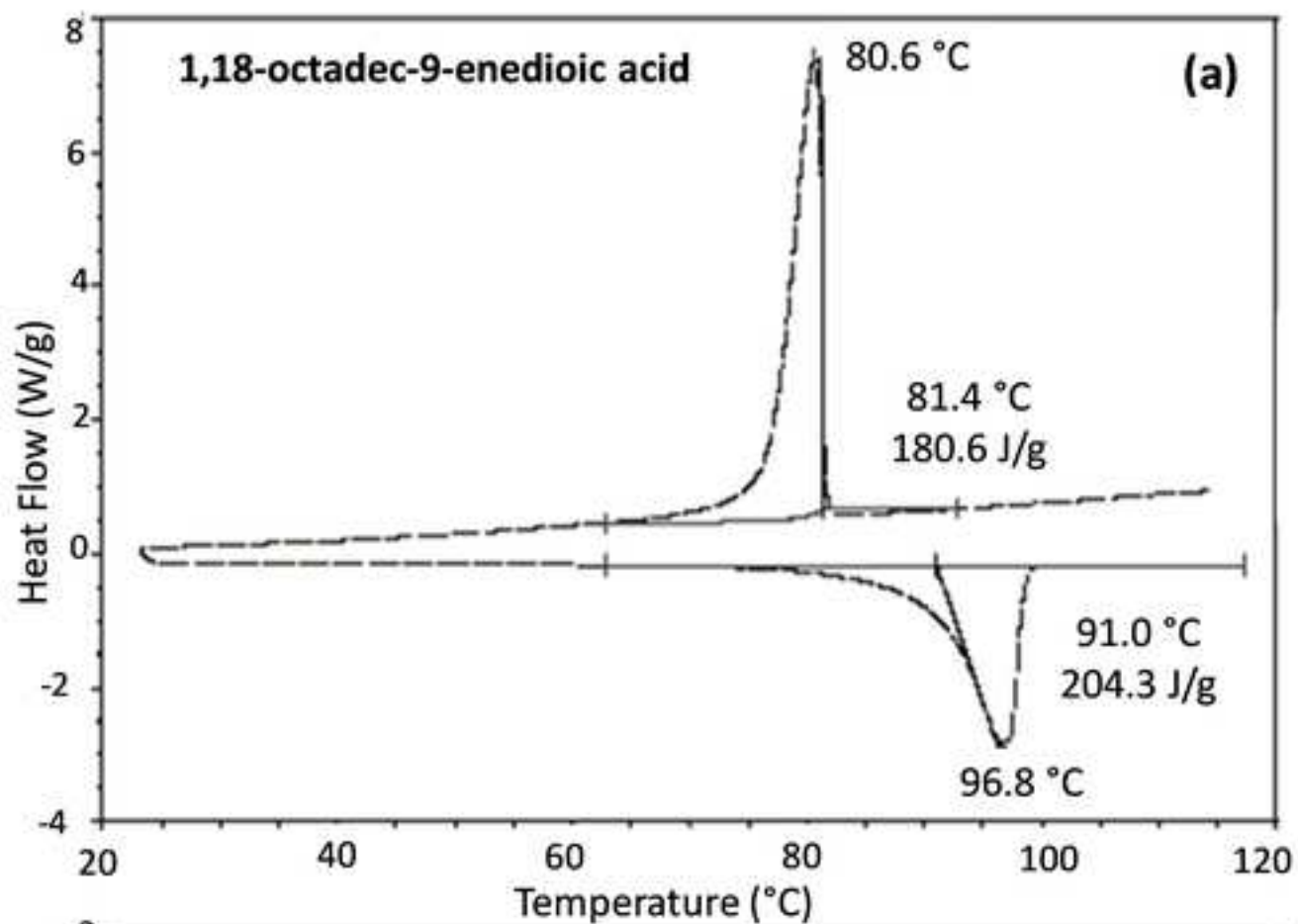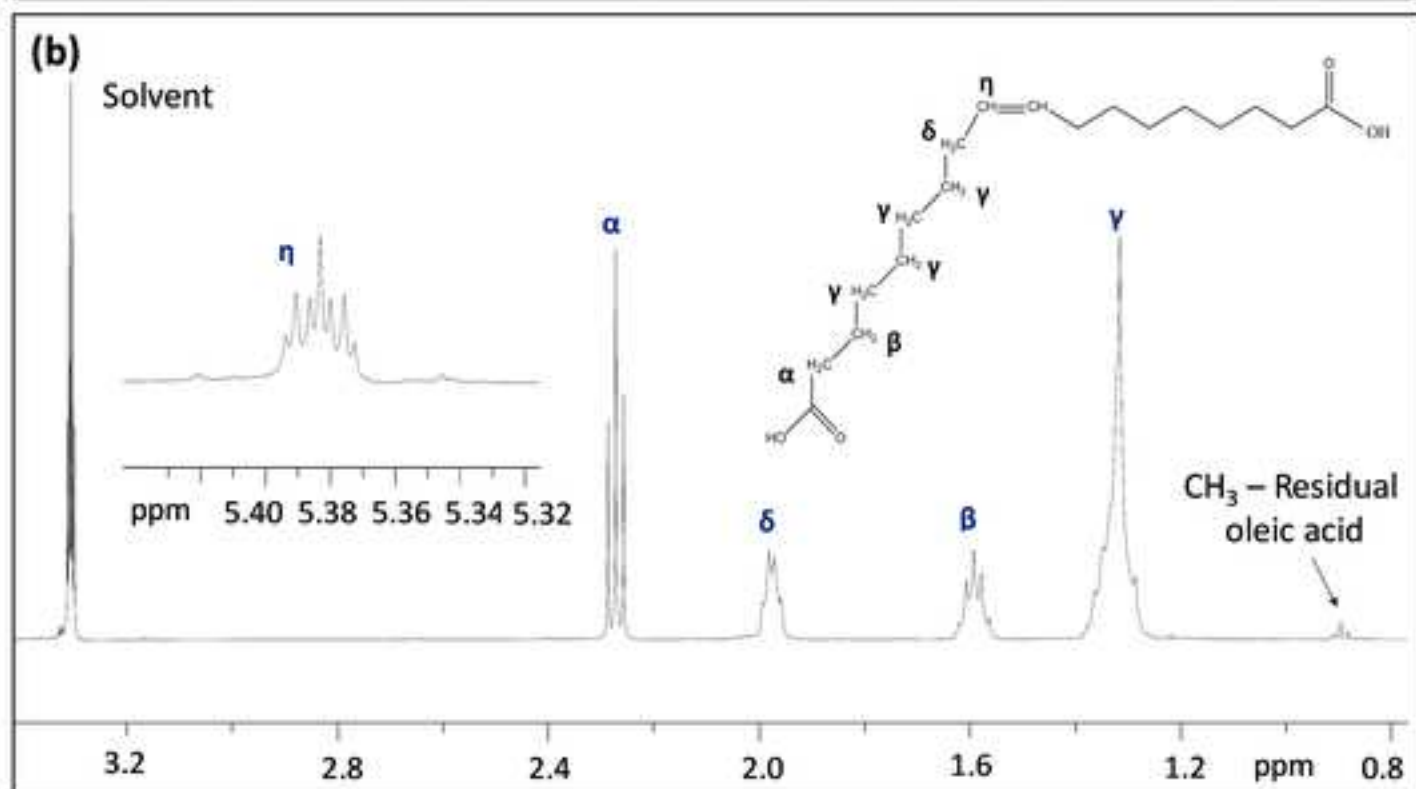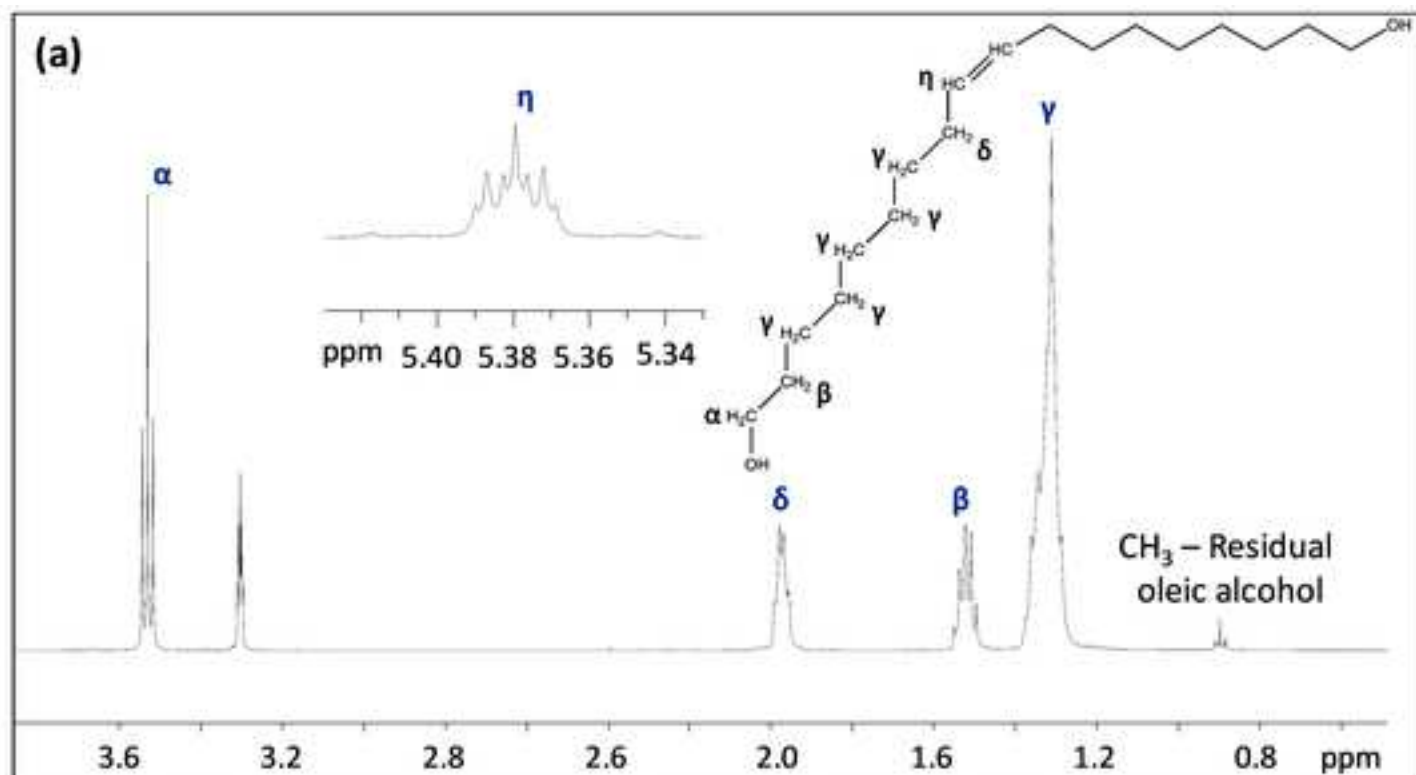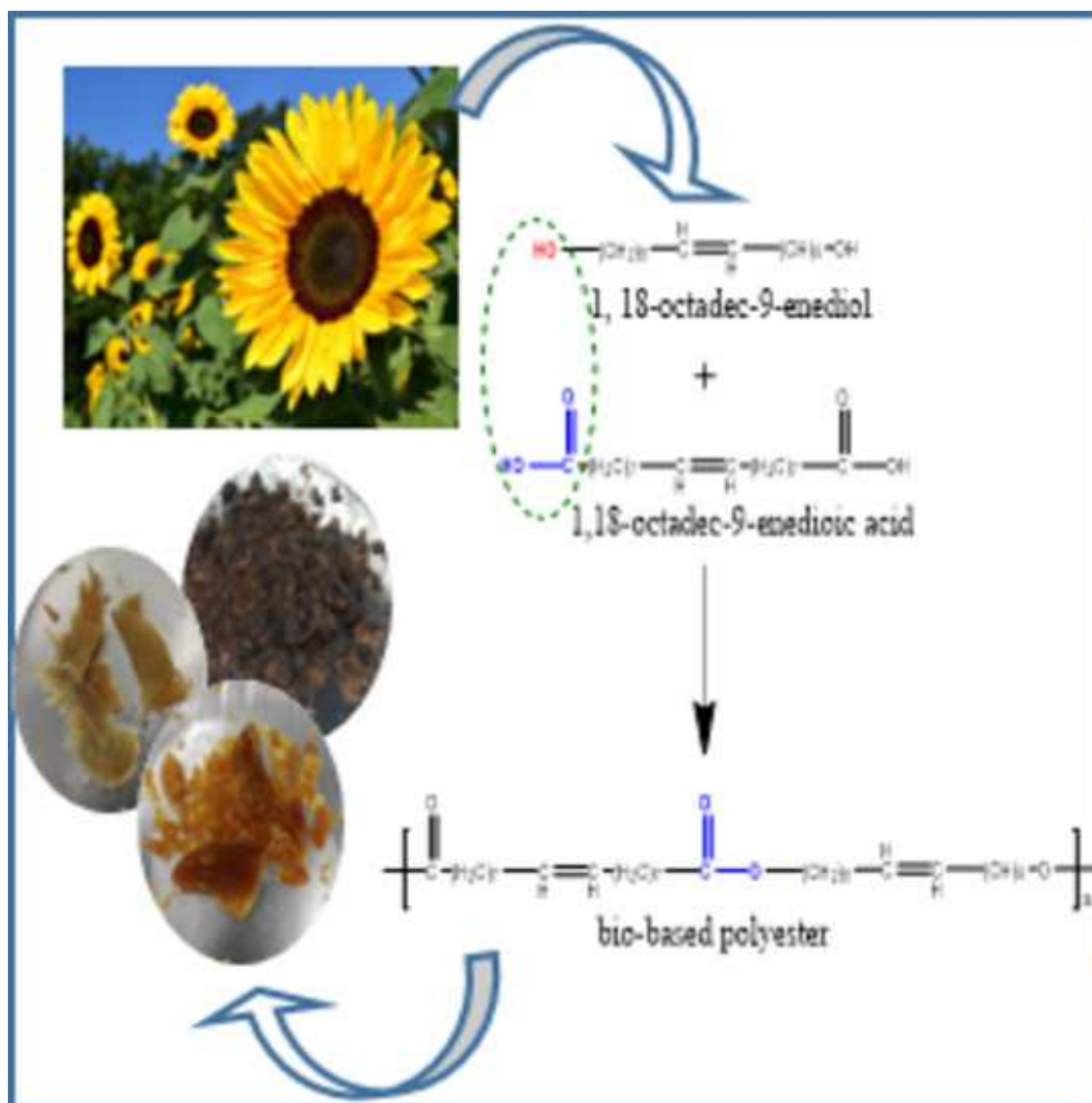
(a) DSC thermogram of 1,18-octadec-9-enedioic acid showing peaks at 80.6 °C, 81.4 °C (180.6 J/g), 91.0 °C (204.3 J/g), and 96.8 °C.

(b) DSC thermogram of 1,18-octadec-9-enediol showing peaks at 49.0 °C, 50.3 °C (52.8 J/g), 44.0 °C (56.6 J/g), and 52.0 °C.

1, 18-octadec-9-enediol

+

1,18-octadec-9-enedioic acid

bio-based polyester

Bio-based polyester, obtained from bi-functional monomers through metathesis of fatty acids, as precursor to synthesize polyurethanes

Carmen Aguilar-Castro[1], Mariamne Dehonor Gomez[1], Manuel Gutierrez Nava[1], Jose Manuel Rojas García[1] and Luis Edmundo Lugo Uribe [1]

[1] CIATEQ Centro de Tecnología Avanzada, Circuito de la Industria Pte Lte 11 Mza 3 No 11, Parque Industrial Ex Hacienda Doña Rosa, Lerma Edo. de México, 52004, México

Correspondence to: Luis E. Lugo Uribe (E-mail: *luis.lugo@ciateq.mx*)

Supporting Information

S.I 1 (a) shows a comparison of the spectra corresponding to oleic acid and 1,18-octedec-9-enedioic acid, whereas S.I 1 (b) shows the spectra of oleic alcohol and 1,18-octacec-9-enediol.
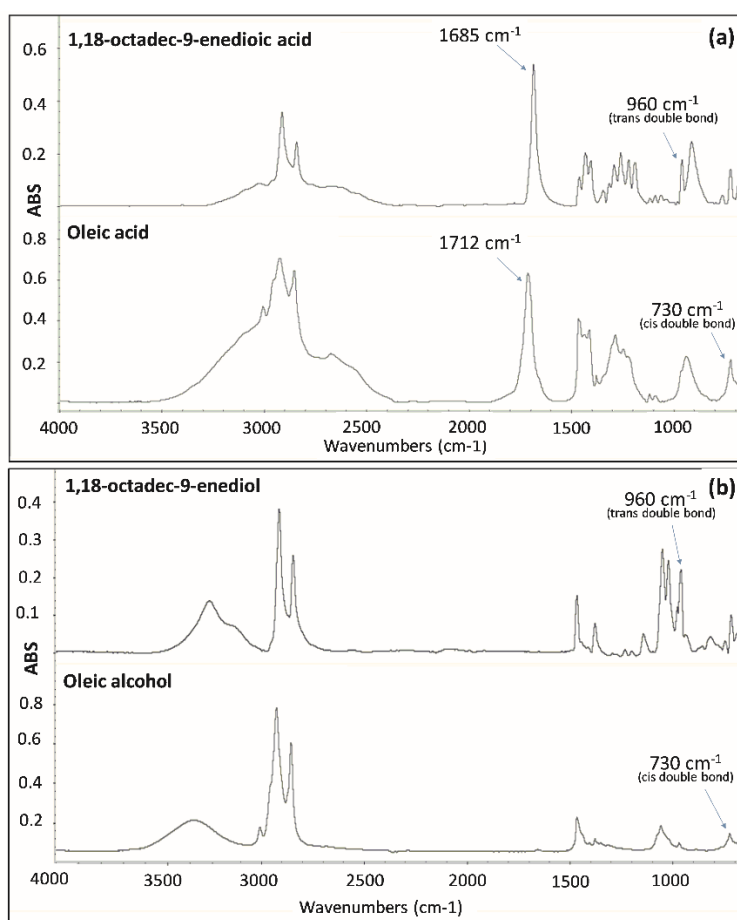

S.I 1 ATR spectra for (a) oleic acid and 1,18-octadec-9-enedioic acid and (b) oleic alcohol and 1,18-octadec-9-enediol

S.I 2 shows the thermogram corresponding to (a) 1,18-octadec-9-enedioic acid and (b) 1,18-octadec-9-enediol. Peak with exothermic direction (up) relates to crystallization process, whereas peak with endothermic direction (down) relates to melting process.
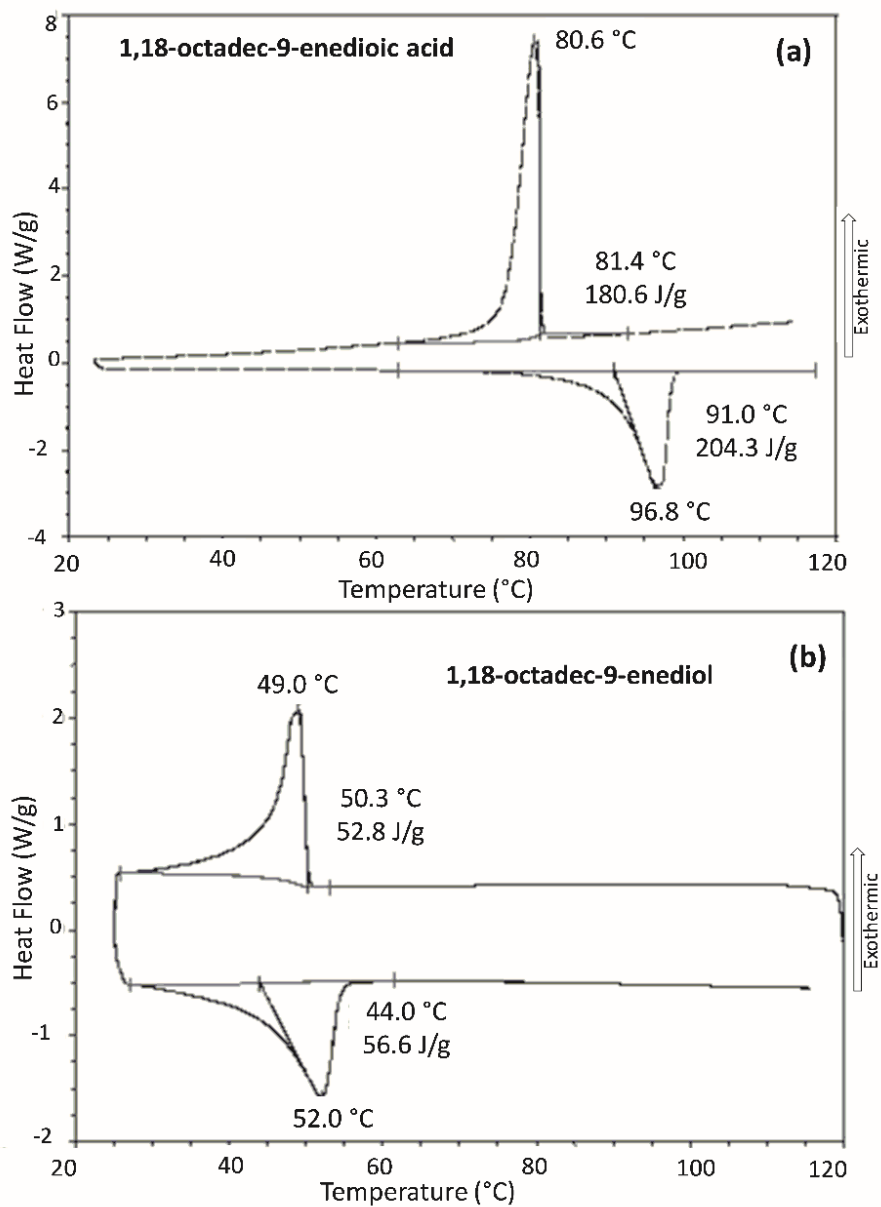
S.I 2 Thermal behavior plots by DSC for (a) 1, 18-octadec-9-endioic acid and (b) 1, 18-octadec-9-enediol

S.I 3 shows the proton spectra of 1,18-octadec-9-enediol (a) and 1,18-octadec-9-enedioic acid (b).
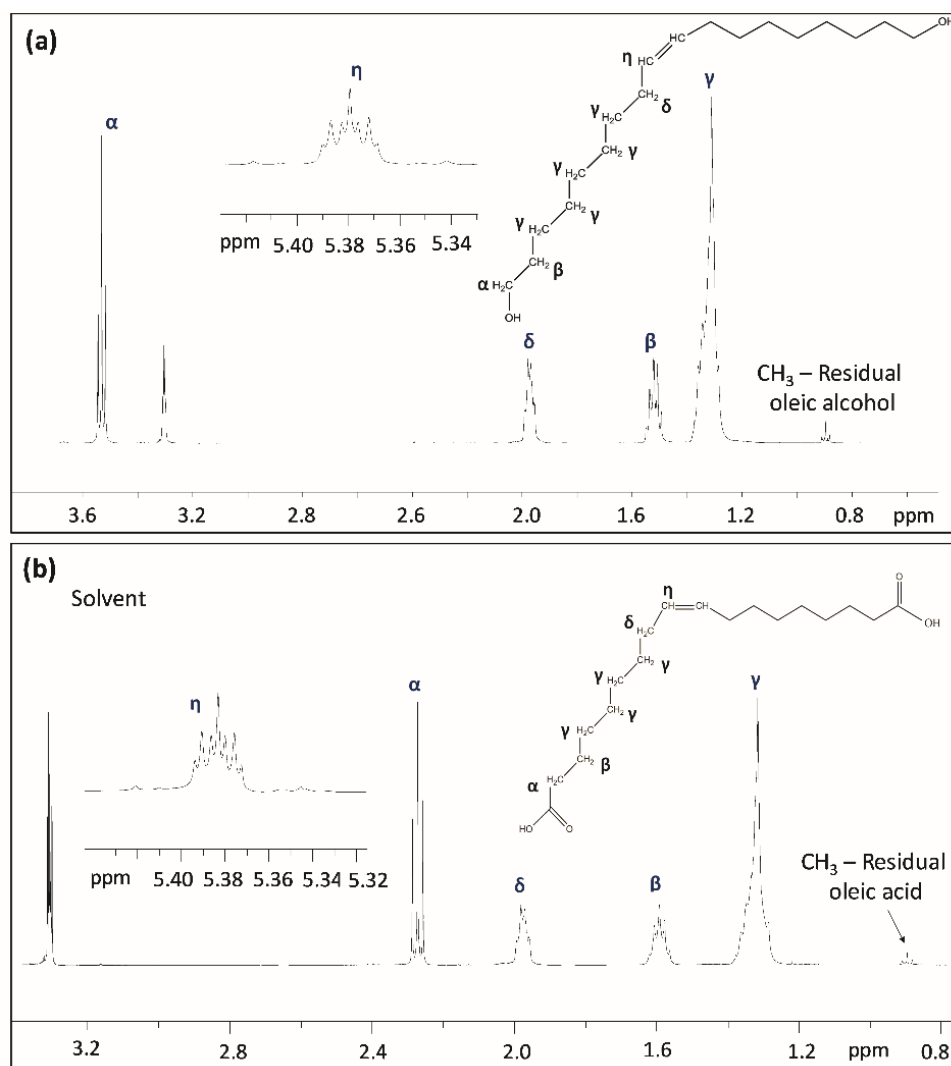
S.I 3 NMR ^1H spectra of (a) 1,18-octadec-9-enediol and (b) 1,18-octadec-9-enedioic acid