

Preparation and application of radiation curable trimethylolpropane trioleate-based epoxy acrylate

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ABSTRACT

Trimethylolpropane (TMP) trioleate is part of branched neopentyl polyols used as environmental-friendly biolubricant. This project is developed to diversify the use of TMP trioleate. A new type of vegetable oil-based UV-curable oligomers from TMP trioleate has been synthesized and used in the coating formulation. The trimethylolpropane (TMP) trioleate was epoxidised and further reacted with acrylic acid to make acrylated TMP trioleate. The acrylation reaction was monitored throughout the reaction by dwindling acid value and oxirane oxygen content. The obtained acrylated TMP trioleate was characterized by FTIR and NMR spectroscopy to ensure there was a ring-opening reaction and the degree of acrylation obtained was 50.21%. The acrylated molecule is able to participate in free-radical polymerization reactions to form high molecular weight polymers. The acrylated TMP trioleate was applied for UV free radical polymerization with monomer, trimethylolpropane triacrylate (TMPTA) and photoinitiator Irgacure 184 in various ratios. The acrylated TMP trioleate blends with TMPTA resulted in radiation cured coating with good crosslink density as indicated by the gel content, thermal and mechanical properties from glass transition temperature, T_g and Konig Pendulum hardness. These biobased UV-curable oligomers have potential uses in applications such as composites, adhesives, and surface coating.

Scheme

Part 1

- Epoxidation
- in-situ* performic acid, hydrogen peroxide, washed with brine and dried

Part 2

- Acrylation
- Ring-opening reaction with acrylic acid and chromium-based catalyst

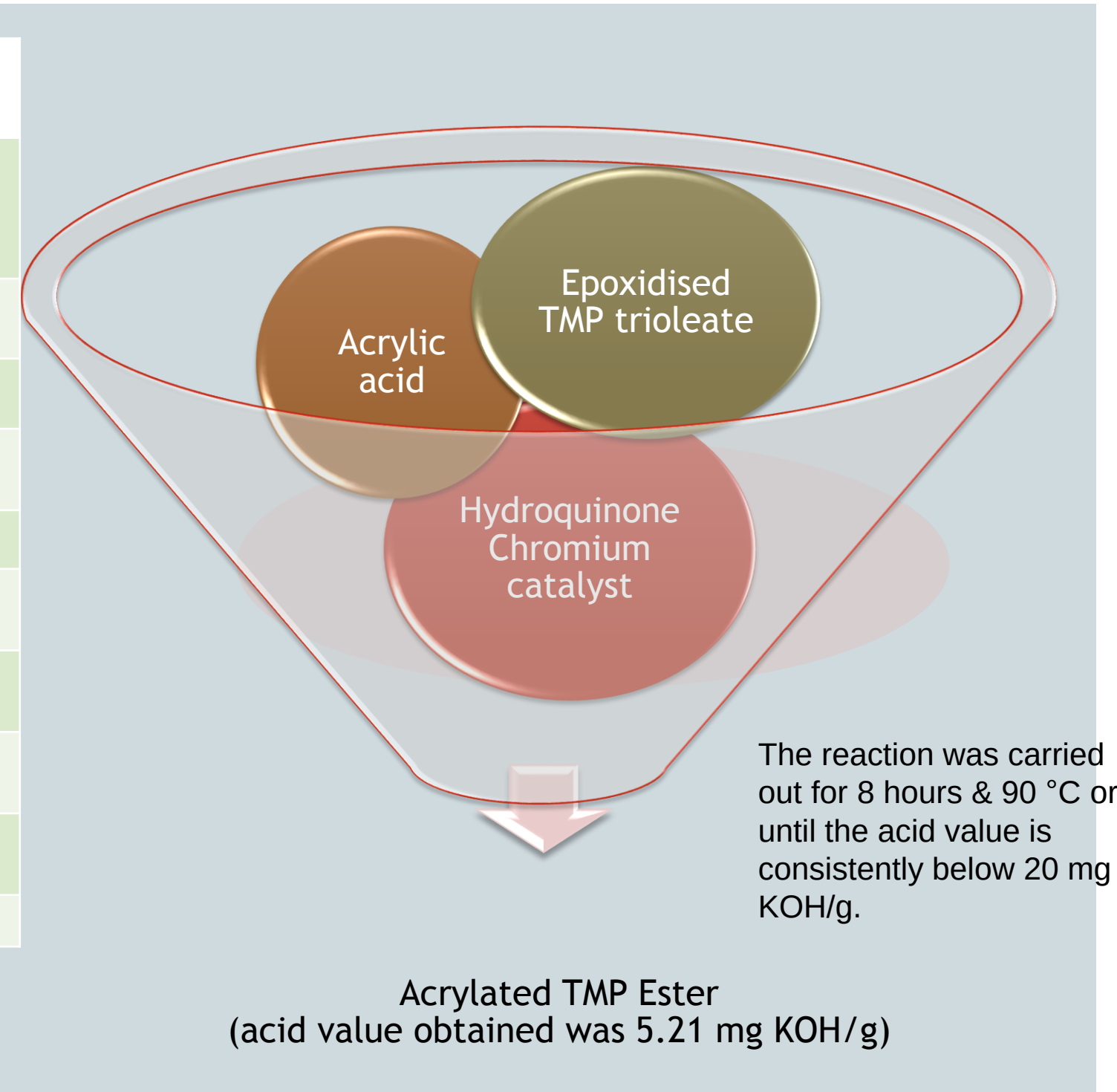
Part 3

- UV beam curing
- Application in surface coating with monomer and photoinitiator

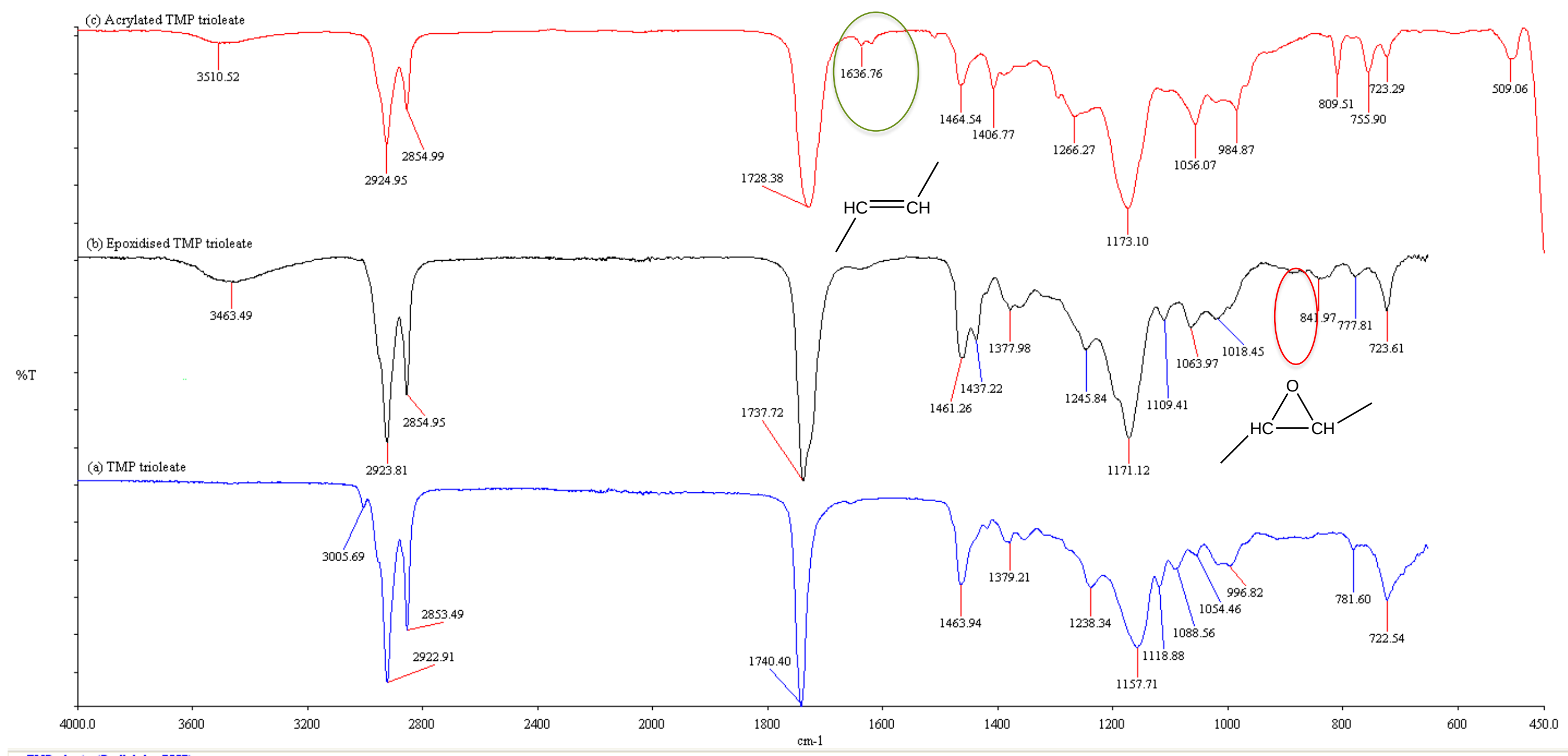
Part 1: Properties of epoxidised TMP trioleate

	TMP trioleate	Epoxidised TMP trioleate
Molar ratios of unsaturated ester/formic peroxide	-	1:1:2.5
Appearance	Pale yellow liquid	Clear liquid
Density (g/cm ³)	0.937	0.962
Viscosity at 25 °C (mPa.s)	103.3 ± 2.9	535.0 ± 0.1
Moisture (%)	0.01	0.25
Acid value (mg KOH/g)	0.23 ± 0.03	1.48 ± 0.1
Iodine value (g I ₂ /100g)	85.65 ± 1.73	2.91 ± 1.5
Oxirane oxygen content (%)	0.01	4.33 ± 0.03
No. of epoxide per molecule	-	2.56
Degree of epoxidation, DOE (%)	-	89.5

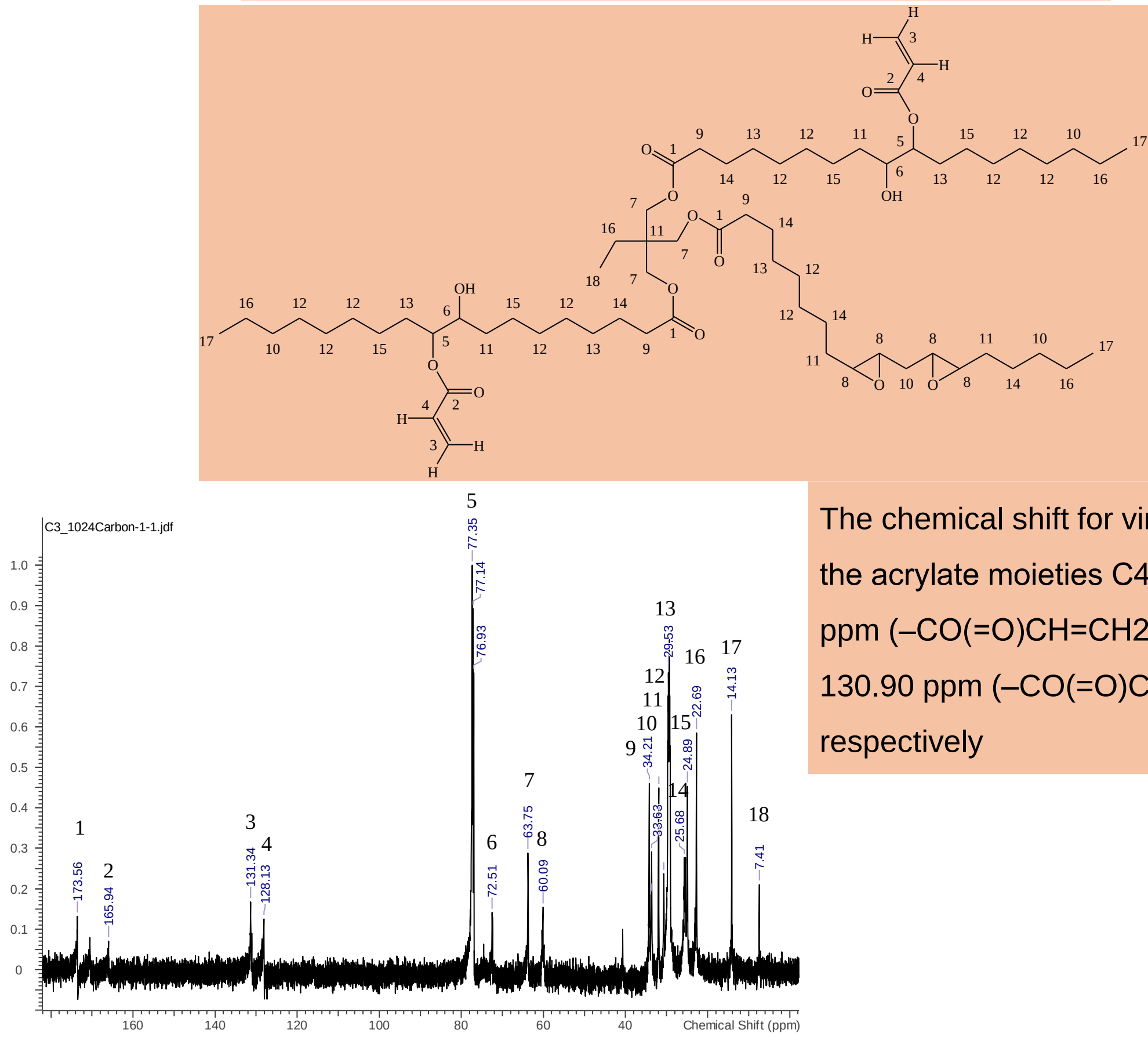
Part 2: Acrylation process



FTIR spectra of (a)TMP trioleate, (b)epoxidised TMP trioleate, (c)acrylated TMP trioleate.

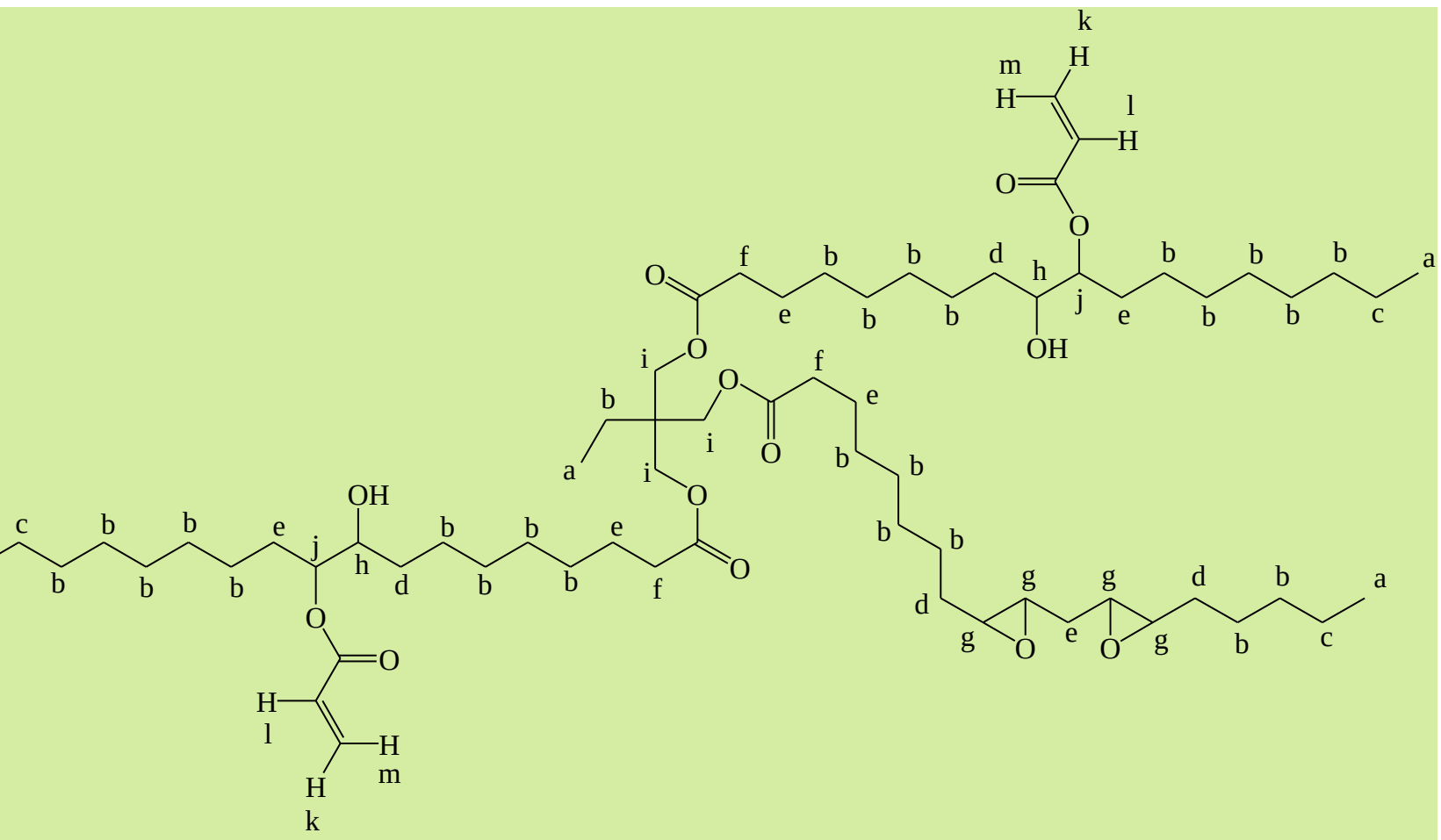
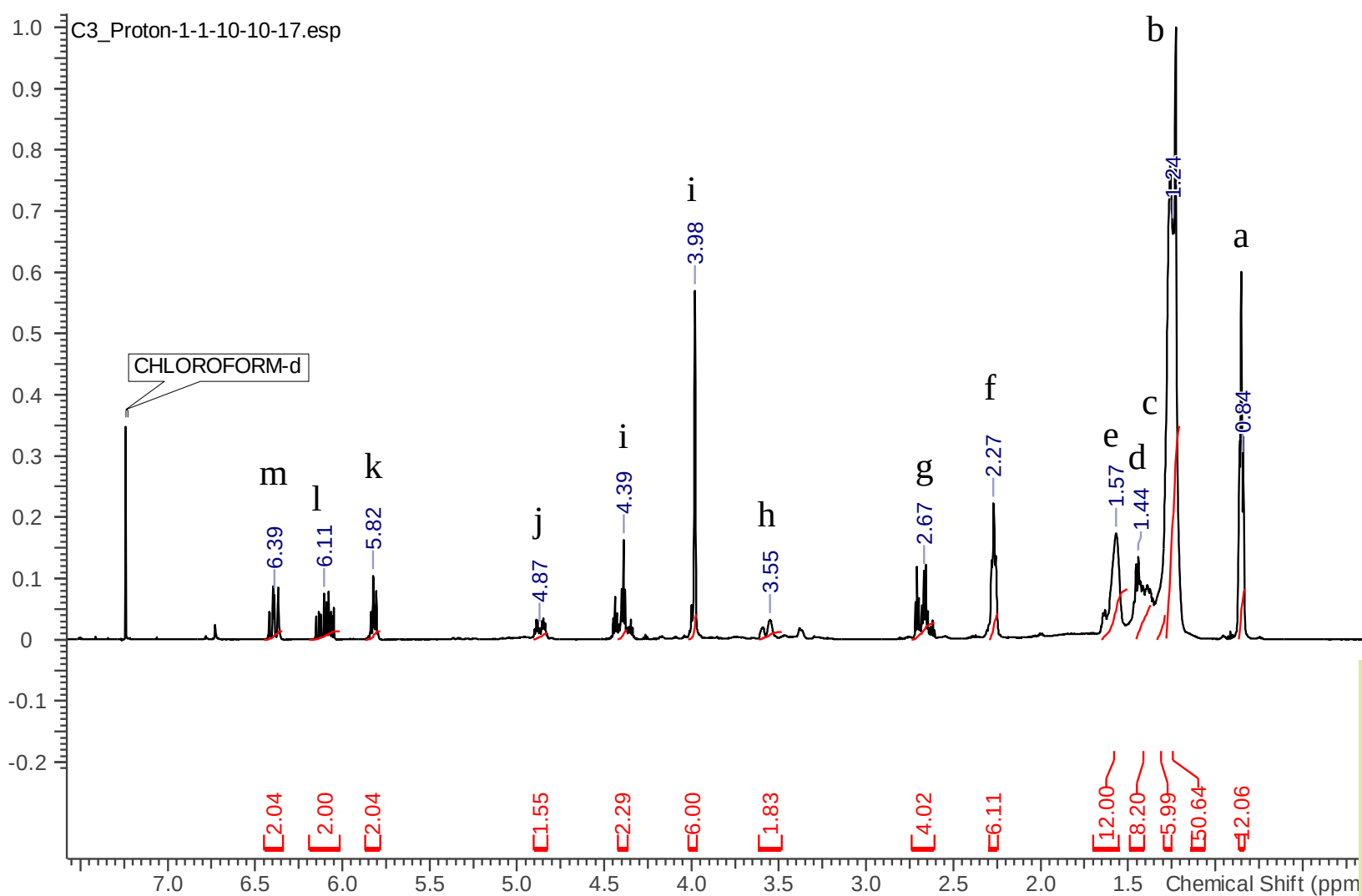


¹³C-NMR spectrum of acrylated TMP trioleate



The chemical shift for vinyl group in the acrylate moieties C4, δ 127.74 ppm (–CO(=O)CH=CH2) and C3, δ 130.90 ppm (–CO(=O)CH=CH2) respectively

¹H-NMR spectrum of acrylated TMP trioleate



$$DOE = \frac{\text{number of epoxide groups}}{\text{number of starting double bonds}} \times 100$$

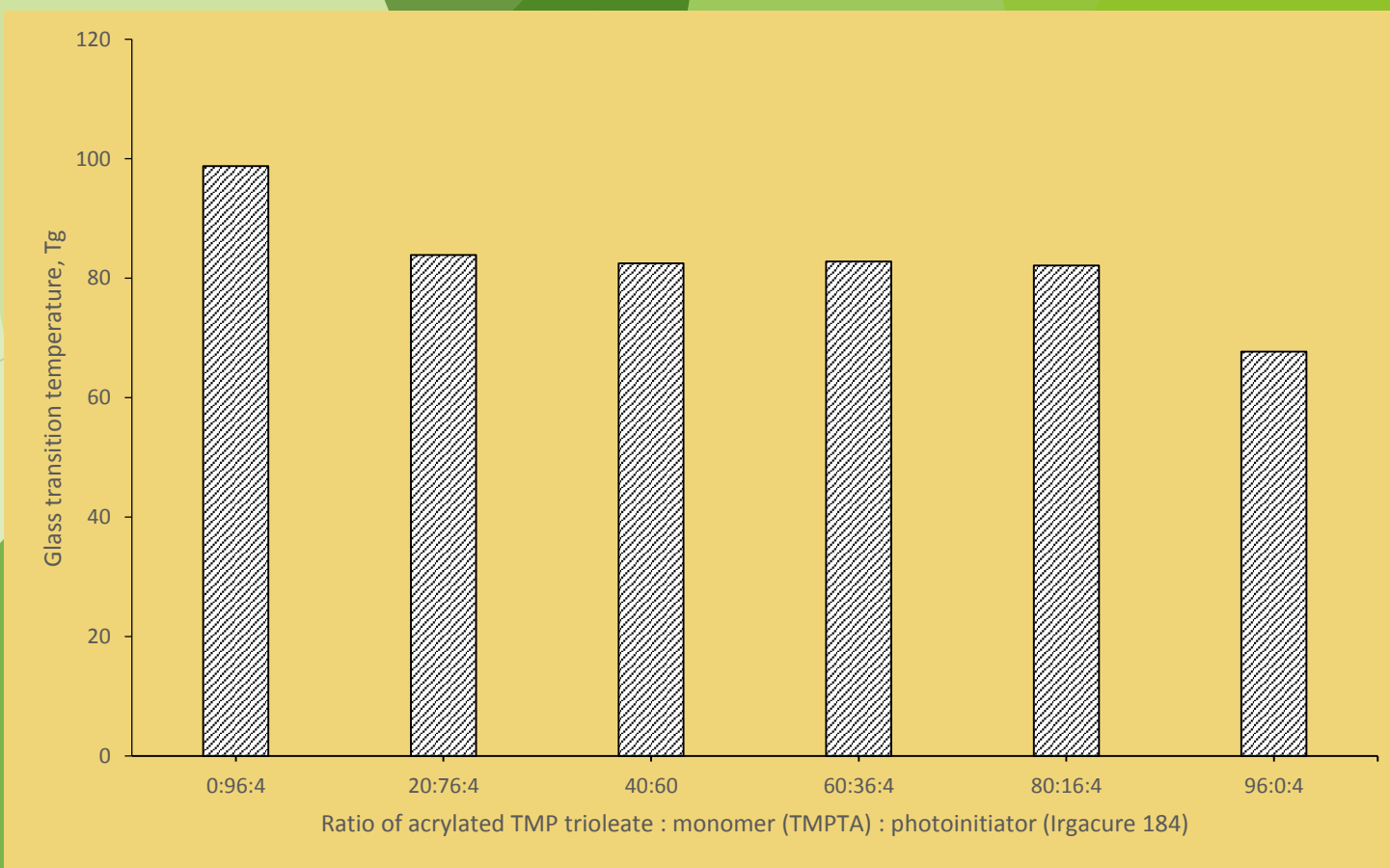
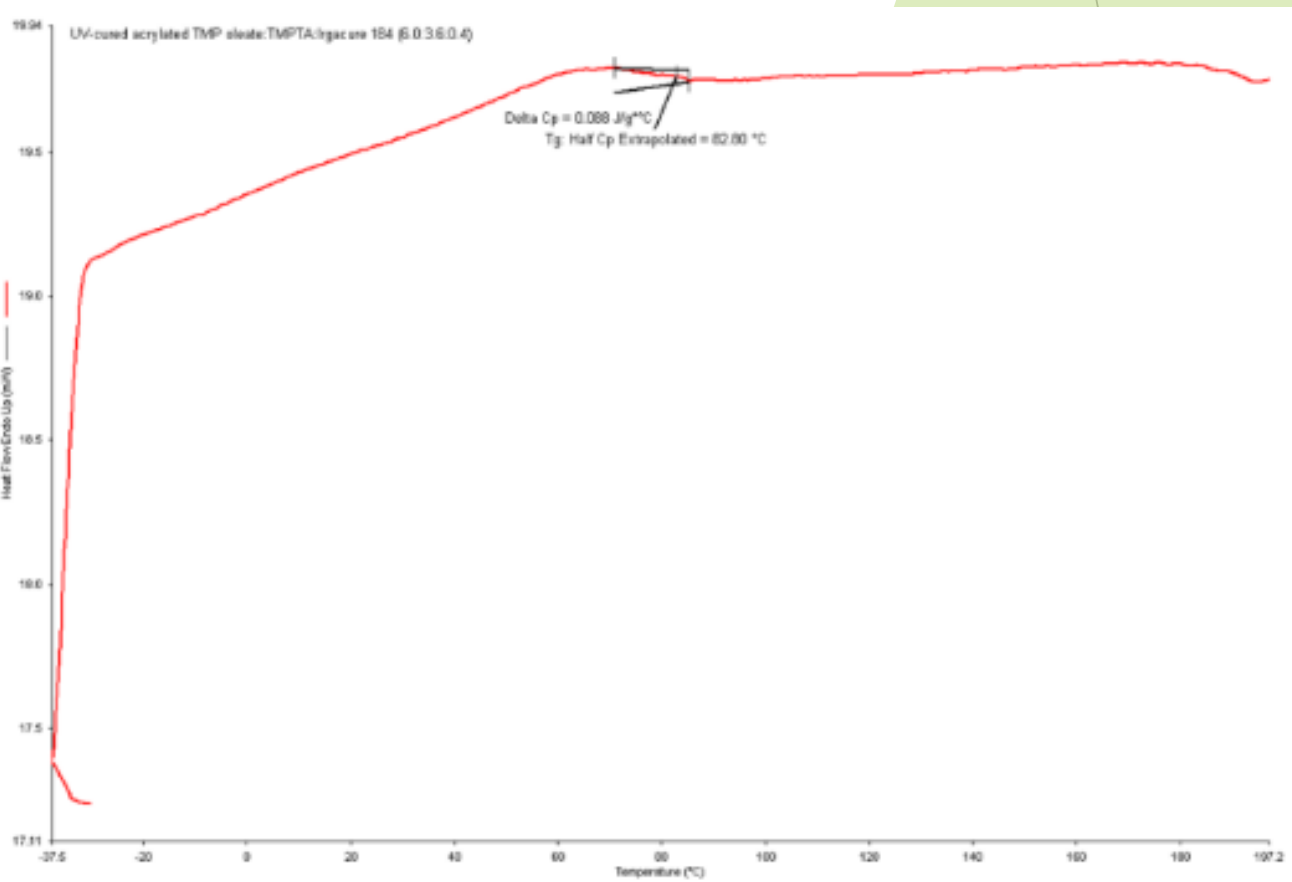
The integrated peaks at δ = 5.27 - 5.38 ppm for the fatty acids unsaturation.
The integrated peaks at δ = 2.83 - 3.11 ppm for the epoxy group.
The degree of epoxidation = 85.5%

Part 3: Formulation of UV curable formula



For the films made from blended systems, an increase in T_g was observed as the degree of acrylation was increased which is attributed to the higher functionality and crosslink density from the diluent TMPTA. The recorded T_g of cured acrylated TMP trioleate with 4% of photoinitiator Irgacure 184 is 67.73 °C while the cured blended version of acrylated TMO trioleate with TMPTA has a consistent T_g between 83.89-82.13 °C. As anticipated, the T_g for vegetable-based acrylates is generally lower as given from the preceding examples. The long-chain carbon backbone in fatty acids confers flexibility as it allows for mobility of the acrylate groups during heating. (Fertier *et al.*, 2013; Childers *et al.*, 2014; Ding and Matharu, 2014; Ma *et al.*, 2014).

Glass transition temperature, T_g of the UV-cured acrylated TMP ester with TMPTA.



Conclusion

- Palm oil-based acrylated TMP ester has been synthesized and characterized. The acrylated TMP ester is able to participate as oligomer in free-radical polymerization reactions to form high molecular weight polymer.

References

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