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Production of a low molecular weight polymer from the cometathesis reaction of palm oil and cyclooctene

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Abstract

Cometathesis of cyclooctene (CO) with triolein (TO) and palm oil (PO) leads to the formation of a low molecular weight polymer. Various ratios of TO to CO and PO to CO were studied (8:1 – 1:8). With a ratio of 8:1 – 1:1 (TO or PO:CO) the cometathesis products are in the form of a liquid. However, when the amounts of CO were increased (1:2 – 1:8) the cometathesis products in the form of white solid were produced. The FTIR spectra of both liquid and solid products are similar but differ in terms of intensities only. The FTIR spectral pattern consists of a combination of bands due to TO and CO or PO and CO. These observations were supported by the presence of the C=O band at 1747 cm^{-1} from the TO or triglycerides (PO) or the ester group. Content of the *cis* and *trans* products in the cometathesis of TO and CO or PO and CO were also estimated from the intensities of the $=CH_{trans}$ (966 cm^{-1}) and $=CH_{cis}$ (725 cm^{-1}) bands in the FTIR spectra. Gel permeation chromatography (GPC) analysis of the solid products gave the weight average molecular weight, $\overline{M}_w$ ranging from 14000 up to 29000 and the number average molecular weight, $\overline{M}_n$ from 9000 to 17000. From the GPC data obtained solid products are proposed to be polymeric materials. Melting temperatures of the solid products were also obtained from the DTA analysis.

Keywords: Cometathesis; Cyclooctene; Triolein; Palm oil; Polymer

1. Introduction

Palm oil is made up predominantly of triglycerides which consist of a glycerol unit and three units of fatty acids which may be saturated or unsaturated. The combination of these glycerol and fatty acids will give between 125 to 1000 species of triglyceride molecules [1]. Table 1 shows the percentage composition of known triglycerides in palm oil. The composition of unsaturated triglycerides is about 92% compared to the saturated triglycerides. Unsaturated triglycerides of palm oil are promising and cheap feedstock for metathesis [2,3], and for this reason, the reaction has attracted much attention in the oleochemical industries [4,5]. Metathesis of unsaturated fatty acid esters or triglycerides can proceed either intra- or intermolecularly, and from the literature the intermolecular reaction proceeds predominantly [6,7]. In previous work by others [8–11], the cometathesis of unsaturated esters and cycloolefins gave polymeric products. In this paper, the synthesis and characterization of the product isolated from the cometathesis reactions of triolein (TO) with cy-

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Table 1
Percentage composition of known triglycerides in palm oil

Number of double bonds	Types of triglycerides [a]	Percentage
0	PMP, MPP, PPP, PPS, PSP	8.3
1	POP, PPO, POS, SPO, PSO	36.8
2	MOO, POO, OPO, PLP, PPL, SOO	35.8
3	POL, PLO, OPL, OOO, SLO, SOL	14.2
4	PLL, LPL, OOL, OLO	
5	LLO	5.0

[a] L = linoleic, M = myristic, O = oleic, P = palmitic, S = stearic.

clooctene (CO) and palm oil (PO) with cyclooctene will be discussed.

2. Experimental

2.1. Chemicals

WCl_6 (Fluka) was purified by vacuum sublimation and kept under nitrogen. Triolein and $(CH_3)_4$ Sn with 99% of purity were supplied by Merck. Toluene (Merck) and tetrahydrofuran (Merck) were dried over P_2O_5, distilled and degassed in vacuo. Palm oil was obtained locally with purity 98%.

2.2. Procedure

All reactions were carried out under an atmosphere of nitrogen. Triolein (8.0 g) and toluene (100 ml) were made oxygen free under vacuum. Cyclooctene (1.0 g) was added and stirred. The cocatalyst, $(CH_3)_4Sn$ (812 mg), was added followed by the catalyst, WCl_6 (0.90 g), and the mixture was left to stir at room temperature for 24 h. Tetrahydrofuran (10 ml) was added to quench the reaction and the mixture was then left to stand at room temperature for 1 h. The reaction mixture was filtered; the filtrate obtained was evaporated to dryness on a rotavap and redissolved in toluene followed by precipitation in acetone.

The above reaction was repeated using different weight ratios of triolein to cyclooctene and different weight ratios of palm oil to cyclooctene as shown in Table 2.

2.3. Analysis

Reaction products were identified by GC and GCMS using a capillary column containing 35% methyl and 65% phenyl silicone programmed for 20°C min^{-1} from 100 to 340°C and 1°C min^{-1} from 340 to 350°C for triglycerides analysis. FTIR spectra were recorded using a Perkin Elmer 1600. Molecular weight were determined by GPC using polystyrene standards. DTA data were determined from Perkin Elmer DTA-7.

3. Results and discussion

The ratio by mole of the catalyst, WCl_6, to co-catalyst during the reaction was always maintained at 1:2. Table 3 shows the physical nature of the products obtained from the cometathesis reaction using different weight ratios of triolein (TO) to cyclooctene (CO) and palm oil to cyclooctene (CO).

Table 2
Different weights of starting materials used in experiment

Ratio of TO:CO or PO:CO	8:1	6:1	4:1	3:1	2:1	1:1	1:2	1:3	1:4	1:6	1:8
TO (g) or PO (g)	8.0	6.0	4.0	3.0	2.0	1.0	1.0	1.0	1.0	1.0	1.0
CO (g)	1.0	1.0	1.0	1.0	1.0	1.0	2.0	3.0	4.0	6.0	8.0
WCl_6 (g)	0.9	0.7	0.5	0.4	0.3	0.2	0.3	0.4	0.5	0.7	0.9
$(CH_3)_4$ Sn (mg)	812	631	451	361	271	180	271	361	451	631	812

TO = triolein, CO = cyclooctene, PO = palm oil.

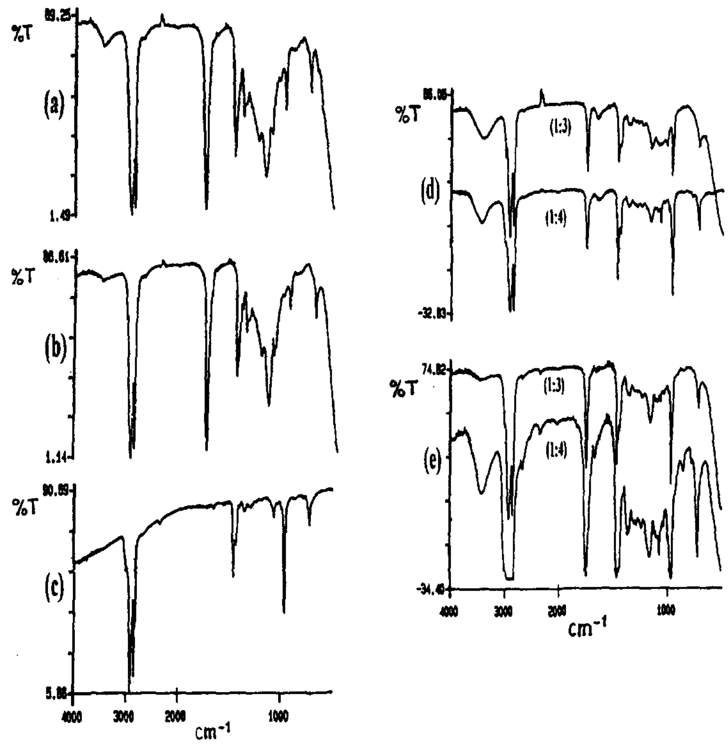


Fig. 1. FTIR Spectrum for metathesis of (a) triolein, (b) palm oil, (c) cyclooctene and cross metathesis of (d) triolein (TO) with cyclooctene (CO) and (e) palm oil (PO) with cyclooctene (CO).

Referring to Table 3, as the amounts of CO were increased, the physical state of the products also differed. Compounds **1–6** are in the form of liquid while compounds **7** and **8** are gels. The complete formation of polymeric materials in the form of white solid were observed in compounds **9–11**. These polymers are found to be slightly brittle and are completely soluble in toluene. The FTIR spectra of compounds **8–9** given in Fig. 1d and 1e are very similar but the intensities of the bands present are weaker in compound **8** (liquid) compared to those in com-

Table 3
Physical data of products from the cometathesis reaction of TO:CO and PO:CO

Compound	ratio of TO:CO or PO:CO	Physical state of product		Colour of product
		TO:CO	PO:CO	
1	8:1	ℓ	ℓ	light brown
2	6:1	ℓ	ℓ	light brown
3	4:1	ℓ	ℓ	light brown
4	3:1	ℓ	ℓ	light brown
5	2:1	ℓ	ℓ	light brown
6	1:1	ℓ	ℓ	light brown
7	1:2	g	g	yellow (y)
8	1:3	g(y)	S	white
9	1:4	S	S	white
10	1:6	S	S	white
11	1:8	S	S	white

ℓ = liquid; S = solid; g = gel.

Table 4
GPC data of compounds **6–11**

Compound (Ratio of TO/PO:CO)	Cometathesis of TO:CO $\overline{M}_w$	$\overline{M}_n$	PDI [a]	Cometathesis of PO:CO $\overline{M}_w$	$\overline{M}_n$	PDI
6 (1:1)	–	–	–	–	–	–
7 (1:2)	–	–	–	–	–	–
8 (1:3)	–	–	–	14243	12084	1.2
9 (1:4)	15167	9584	1.6	32673	22267	1.5
10 (1:6)	22074	14149	1.6	19475	12687	1.5
11 (1:8)	23258	15028	1.5	28532	17286	1.7

[a] PDI = polydispersity index.

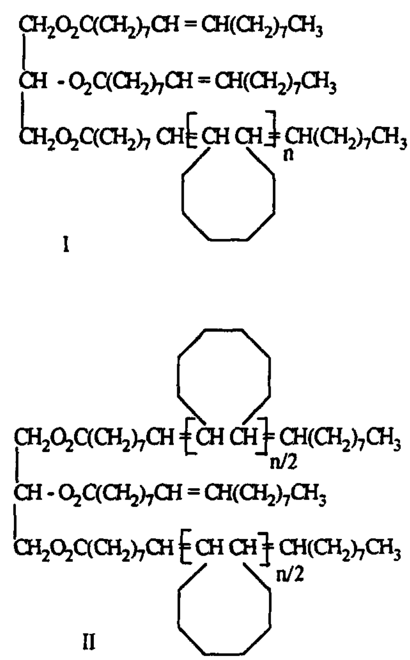
pound **9** (solid). A strong C=O band at 1747 cm^{-1} appeared indicating that the cometathesis products contain either modified TO or modified triglycerides from palm oil or ester group combined with the olefinic moiety. Similar patterns in the FTIR spectra for compound **10–11** (solid) were observed inferring that the products may be similar but differ in terms of chain lengths. The relative intensities of the $=CH_{trans}$ at 966 cm^{-1} is greater than the $=CH_{cis}$ band at 725 cm^{-1} from the FTIR spectra. From these observations we infer that the *trans* content is probably greater than the *cis* in the cometathesis product of both TO with CO and PO with CO. Results obtained from the FTIR data are compatible with previous work reported by other workers [9]. The liquid and solid products were then subjected to GPC studies, using a linear Ultrastyragel type column (7.8 × 300 mm) which is suitable for detecting polymers of fairly large molecular weights in the range from 2000 to 1000000. Results obtained from the GPC studies of compounds **6–11** are summarized in Table 4.

GPC studies showed that compounds **6–8** from the cometathesis of TO:CO and compounds **6** and **7** from the cometathesis of PO:CO may be low molecular weight polymers. However, their molecular weights could not be determined using the type of column above. Compounds **9–11** (TO:CO) and compounds **8–11** (PO:CO) are found to be polymeric materials with weight average molecular weights, $\overline{M}_w$, ranging from 14000 to 29000 and number average molecular weights, $\overline{M}_n$ ranging from 9000 to 17000. These data proved that compounds **9–11** for the cometathesis of TO and CO are similar but differ in terms of chain lengths. GPC studies for compounds **8–11** from the cometathesis of PO and CO gave similar results with slightly higher values of $\overline{M}_w$ and $\overline{M}_n$ (Table 4). These $\overline{M}_w$ and $\overline{M}_n$ values of the solid products were much lower than those of the polyoctanemer obtained from the reaction of ROMP cyclooctene ($\overline{M}_w$ = 130000 and $\overline{M}_n$ = 78000) [12,13].

The products from the cometathesis of monoester [14] with cyclooctene from previous work showed that ring opening and polymerization of the cyclooctene ring has taken place to a certain extent. With these findings, we proposed that a similar ring opening and some polymerization of the cyclooctene ring has taken place in compounds **9–11** (TO:CO) and compounds **8–11** (PO:CO).

Two structures have been proposed and these are shown in Fig. 2.

A structure with ring opening polymerization



I

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Fig. 2. Proposed structures of polymeric products from the cometathesis of triolein and cyclooctene (TO:CO).

Table 5
DTA data of solid products

Weight ratio	Cometathesis of TO:CO			Cometathesis of PO:CO			
(compound)	1:4 (**9**)	1:6 (**10**)	1:8 (**11**)	1:3 (**8**)	1:4 (**9**)	1:6 (**10**)	1:8 (**11**)
$T_{crystallisation}$ (°C) [a]	200	200		190	180	210	180
	280	275	430	405	405	430	405
		425					
$T_{melting}$ (°C) [a]	240	220		210	240	240	210
	290	270	475	470	470	470	465
	460	450					

[a] T = temperature.

occurring on all three fatty acid chains is highly unlikely due to steric constraints. Proposed structure of the cometathesis product of PO and CO are not shown here because there would be more than two possible structures depending on the type of triglycerides in the palm oil composition which are involved in the cometathesis reactions.

Thermal analysis of the solid products from the cometathesis reactions are given in Table 5. These data illustrate the thermal stability of the products. Compounds **9** and **10** (TO:CO) showed three stages of melting, indicating that the polymer may consist of some oligomers or other components. When the amount of CO was increased in compound **11** (for TO:CO; 1:8) a single melting temperature at 475°C was observed and similar to the melting temperature of the polyoctanemer (475°C). Similar results were obtained for compounds **8–11** in the cometathesis products of PO with CO.

4. Conclusion

The cometathesis reactions of triolein with cyclooctene and palm oil with cyclooctene yielded low molecular weight polymeric materials when the ratios of triolein or palm oil to cyclooctene are between 1:3 to 1:8. The molecular weights of the polymeric materials determined by GPC were found to be between 14000 to 29000. These values are less than the molecular weight of polyoctanemer obtained from the ROMP of cyclooctene.

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