

divided into the proportions as percentages of each of the individual components. For crude palm oil it is interesting to compare the observed distribution with what might be expected in a random distribution assuming each component had the same fatty acid composition as the crude palm oil.

	FFA		MG		DG		
	P	O	P	O	PP	PO	OO
Observed	49	51	31	69	12	53	35
Random	46	54	49	51	21	50	29

The free fatty acids do have the approximately random distribution that would be expected by random hydrolysis of the triglycerides. In contrast, the mono- and diglycerides have a distribution which is different from random.

As previously noted, detergent fractionation concentrates FFA and diglyceride in the olein and monoglyceride in the stearin. The results given in Figure 3 also show that the proportion of P and O and of PP, PO and OO change, with the more unsaturated partial glycerides, like the triglycerides, concentrating in the olein.

On bleaching, FFA increases slightly, monoglycerides are reduced and diglycerides are unchanged.

After steam refining and deodorization FFA is reduced almost to zero. For palm stearin, the proportions of P and O seem to have altered, but since P (mainly palmitic acid) would be expected to be more volatile, this may be due to experimental error at these very low levels. Monoglycerides also are substantially reduced, with O (mainly monoolein) being the only detectable monoglyceride. Total diglycerides show no significant change, but the proportions of PP, PO and OO do change in the direction of increased random distribution. This is expected at the high temperatures used in the steam refining. However, it also should be noted that

the total amount of P in the diglycerides increases, suggesting that there also may be some interchange of fatty acids between di- and triglycerides or free fatty acids. Percentage of P (mainly palmitic acid) in total diglycerides before and after steam refining:

	Before	After
Olein	37.5	41.5
Oil	38	39.5
Stearin	45	50.5

ACKNOWLEDGMENTS

We thank L.P. Lee for most of the experimental work and Ms. P.K. Oh for help with sample collection and analysis.

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[Received July 21, 1984]

Studies on Kinetics of Catalytic Isomerization of Methyl Linoleate

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ABSTRACT

Kinetics of isomerization of methyl linoleate are studied on ruthenium (5%) on carbon in the temperature range 200-270°C with different solvents. Some equilibrium experiments also are carried out with rhodium and ruthenium catalysts. The reactions taking place are isomerization, hydrogenation and polymerization. The activities and the selectivities are dependent on the nature of the solvent used. Highly protic solvents like methanol or isopropyl alcohol exhibited very high activity and selectivity for hydrogenation, whereas aprotic solvents like hexane or cyclohexane showed very high selectivities for isomerization reaction. The reaction kinetics were found to be further complicated by polymer formation at low solvent concentrations. The effects of temperature, solvent concentration, catalyst quantity and time of reaction also were investigated.

INTRODUCTION

Isomerization of vegetable oils to conjugated oils is an important reaction which finds applications essentially for making alkyd resins. A number of papers have appeared in

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the past which describe processes using homogenous metal complexes and heterogeneous catalysts (1-8). Supported noble metals like palladium, rhodium and ruthenium are well known hydrogenation catalysts (8,10), but their performance for isomerization has been studied very little. Their activity for isomerization is to be expected from the fact that they have vacant d-orbitals which can interact with π bonds of fatty acids as well as activating an adjacent C-H bond, a necessary step for double bond migration. Furthermore, it is likely that the most predominant pathway for the hydrogenation of a dieneic fatty acid could be via conjugation (10). In a recently published French paper (6) and patent (7), results on isomerization of sunflower oil and methyl linoleate on rhodium and ruthenium catalysts were presented. Most of the experiments were carried out up to equilibrium using pure oils or traces of protic solvents. No detailed kinetic data is reported for this system so far.

In the present study, we have investigated detailed kinetics of the network of reactions starting with methyl linoleate as the reactant. We report results of the effects of parameters such as nature of solvent, temperature, catalyst quantity on the kinetic behavior and the product profile.

KINETICS OF METHYL LINOLEATE ISOMERIZATION

EXPERIMENTAL PROCEDURE

Materials

Ruthenium (5%) on carbon was supplied by Fluka (Switzerland). The surface area was around 1100 m²/g. Rhodium (5%) on carbon was supplied by Strem Chemicals (U.S.A.), and had a surface area of 1050 m²/g. Methyl linoleate of 78% purity was supplied by Acme Chemicals (Bombay, India). The impurities were methyl oleate (15%) and methyl palmitate (7%), which were added to serve as an internal standard for GC analysis. All solvents used were of A.R. grade (BDH, India).

Reaction Procedure

Measured amounts of methyl linoleate and a solvent are mixed and placed in a high pressure autoclave (Autoclave Engineers, Erie, Pennsylvania, USA). A known amount of catalyst is then charged into the autoclave. The air above the reaction mixture is purged with nitrogen and the autoclave pressurized up to 100 torr of nitrogen. The temperature of the autoclave is raised slowly to the reaction temperature while the contents are stirred at 700 rpm. For the kinetic experiments, small amounts of sample are withdrawn from the autoclave from time to time through a sampling valve. Methyl linoleate, its conjugated isomers and the hydrogenated products are analyzed by GC using a column of 10% EGSS-X coated on chromosorb WHP 80/100, with temperature programming. The peaks were identified by injecting authentic samples. Polymer content is measured by using methyl palmitate as the internal standard. The increase in concentration of methyl palmitate after the reaction could easily be correlated to the polymer content. It is assumed that methyl palmitate is not affected during the reaction.

RESULTS AND DISCUSSION

Rhodium on Carbon

All the reactions on rhodium catalysts were carried out for a specified duration of time (4 hr). On ruthenium catalysts kinetic data also was collected. Table I reports the activity and selectivity data on rhodium catalyst, obtained at the end of 3 hr, while Table II reports those on ruthenium

TABLE I

Activity and Selectivity Data on Rh/C for Isomerization of Methyl Linoleate

Solvent	^a Total conversion (%)	^b Conjugation (%)	^c Hydrogenation (%)	S _C	S _H
1. Hexane	53.1	37.37	15.54	0.70	0.30
2. Cyclohexane	40.2	34.12	5.7	0.85	0.15
3. Isopropyl alcohol	78.65	4.29	73.29	0.05	0.95

Conditions: Temperature: 230 C

Solvent: 150 c.c.

Catalyst: 250 mg

Methyl linoleate: 2.5 c.c.

Pressure of N₂: 100 psi

Reaction time: 4 hr

$$\text{Selectivity for conjugation } S_C = \frac{\% \text{ conjugation}}{\text{total conversion}}$$

$$\text{Selectivity for hydrogenation } S_H = \frac{\% \text{ hydrogenation}}{\text{total conversion}}$$

^aAll percentages refer to weight percentages.

^bIncludes all geometric isomers.

^cIncludes both methyl oleate and methyl stearate.

TABLE II

Activity and Selectivity Data on Ru/C for Isomerization of Methyl Linoleate

Solvent	Total conversion (%)	Conjugation (%)	Hydrogenation (%)	S _C	S _H
1. Hexane	34.82	30.64	3.46	0.88	0.12
2. Cyclohexane	42.61	31.38	9.14	0.74	0.26
3. Tertiary butyl-alcohol	45.4	35.26	10.11	0.78	0.22
4. Isopropyl alcohol	99.83	2.2	96.44	0.22	0.98

Conditions: Temperature: 250 C

Solvent: 150 c.c.

Methyl linoleate: 2.5 c.c.

Catalyst: 250 mg

N₂ pressure: 100 psi

Reaction time: 4 hr

S_C and S_H are defined in the same way as in Table I.

catalyst. It is clear that solvent has a definite influence on the total conversion as well as on the selectivity for conjugation and hydrogenation. On rhodium catalyst, when a highly protic solvent (IPA) is used, conversion is very high (78.6%), but the hydrogenated products predominate, resulting in very poor selectivity for conjugation reaction (0.05). As one considers less protic solvents like hexane and cyclohexane, total conversions fall (53.1% and 40.2%, respectively) but there is considerable enhancement of selectivity for conjugation. The selectivities for conjugation are 0.70 and 0.85 for hexane and cyclohexane solvents, respectively. The remaining product is essentially methyl oleate. The same trend also is observed on ruthenium catalysts (Table II).

The above results could be rationalized as follows: Hydrogenation activity is caused essentially by the hydrogen derived from solvent. Then the scheme (11) shown in Figures 1a and 1b could explain the changes in activity and selectivity.

In Figure 1a, initially a hydrogen atom adds to methyl linoleate to give a metal-alkyl intermediate. When a good concentration of surface M-H species (M for metal) exists on the catalyst (as for IPA as solvent), a second hydrogen atom adds, leading to hydrogenated products. On the other hand, if the concentration of M-H species is low on the catalyst (as in the case of cyclohexane solvent), hydrogen abstraction by the metal takes place from an adjacent carbon atom, as shown in Figure 1b. This leads to double bond migration. In essence, the ease of availability of hydrogen from the solvent system influences the concentration of M-H species on the catalyst. This, in turn, affects the activity and selectivity pattern observed. In order to further investigate the reaction pathway, kinetic experiments were carried out on ruthenium on carbon; the results are reported below.

Ruthenium on Carbon

On this catalyst, experiments were carried out at very high concentrations of solvent (methyl linoleate:solvent, 1:30) as well as very low concentrations of solvent (methyl linoleate:solvent, 1:1 to 10). A high concentration of solvent was used to avoid complications due to polymer formation. Mixtures of cyclohexane and isopropyl alcohol (IPA) were used, and the temperature of reaction was varied between 200 C and 270 C. Cyclohexane and IPA were chosen because it would be of interest to study the effect of a mixture of a highly protic solvent and an almost non-protic solvent.

Figure 2 shows a typical kinetic plot for the above sol-

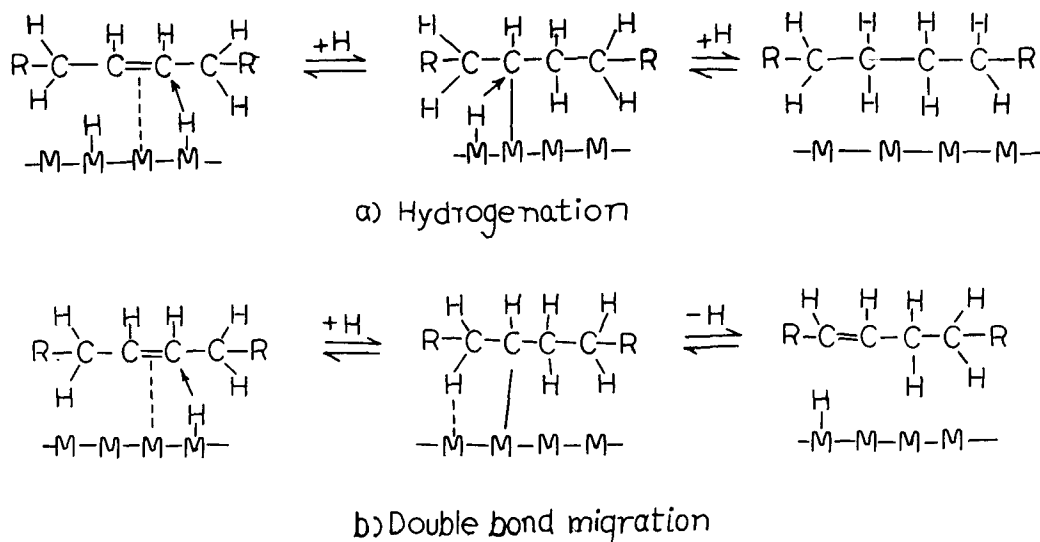


FIG. 1a. Scheme for hydrogenation. FIG. 1b. Scheme for double bond migration.

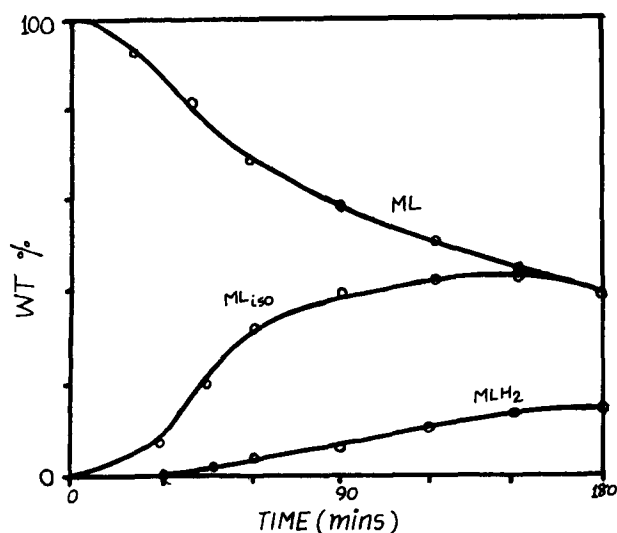


FIG. 2. Kinetic experiment at 240 C (ML:solvent = 1.30, ML:catalyst = 1:0.1). (Solvent-IPA/cyclohexane = 50/100 ml).

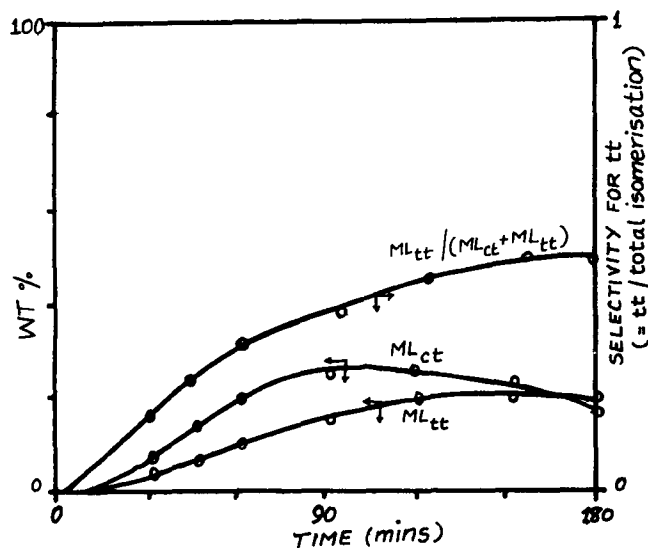
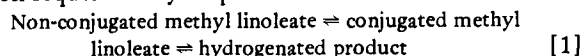


FIG. 3. Kinetics of isomer distribution and selectivity (conditions same as Fig. 2).

vent system. In all the figures ML denotes non-conjugated methyl linoleate, MLH_2 is hydrogenated methyl linoleate, ML_{iso} refers to conjugated methyl linoleate, $\text{ML}(c-t + c-c)$ and $\text{ML}(t-t)$ refer to the *cis-cis*+*cis-trans* and *trans-trans* isomers of conjugated methyl linoleate, respectively, and ML poly refers to polymerized methyl linoleate. The plot in Figure 2 is characteristic of a consecutive reaction, wherein the concentration of an intermediate product (in this case conjugated methyl linoleate) increases with time, reaches a peak and then slightly decreases. Typically, the final hydrogenated product starts building up later in comparison to conjugated methyl linoleate. Thus, the following reaction sequence may be postulated:



Such a scheme was suggested earlier in the case of hydrogenation of vegetable oils with palladium and copper chromite catalysts (8,10).

Our kinetic data proves this point unequivocally. In fact, in a paper dealing with mathematical modelling of the kinetics, we have been able to confirm the above scheme without any uncertainty (12).

Isomer Distribution

Figure 3 shows the distribution of isomers of the conjugated methyl linoleate and the variation of selectivity for *trans-trans* and (*cis-trans*+*cis-cis*) isomer with time. It is interesting to note that selectivity for *trans-trans* isomer increases with time while that for (*cis-trans*+*cis-cis*) decreases. This is to be expected, because *trans-trans* isomer is thermodynamically more stable than *cis-cis* or *cis-trans* isomer and as the system approaches equilibrium with time, thermodynamic selectivity should prevail at the end of the run.

Effect of Temperature

Figure 4 shows the effect of temperature on total conversion, conjugation, isomer selectivity and hydrogenation. The following points may be noted from the figure:

1. As the temperature is increased, selectivity for *trans-trans* isomer increases while that for (*cis-trans*+*cis-cis*) decreases. This is probably because non-selective thermal reactions also could contribute to products to some extent.

2. With a temperature increase, the total methyl linoleate converted increases, most of the contribution coming from hydrogenation. In fact, as one goes from 240 C to 270 C, hydrogenation jumps from 14% to 60% while isomerization drops slightly from 44% to 40%.

KINETICS OF METHYL LINOLEATE ISOMERIZATION

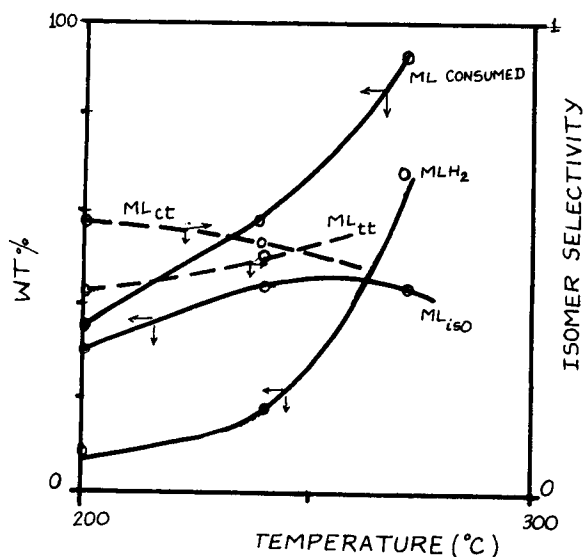


FIG. 4. Effect of temperature on reaction (conditions same as for Fig. 2; values refer to maximum obtained during the run).

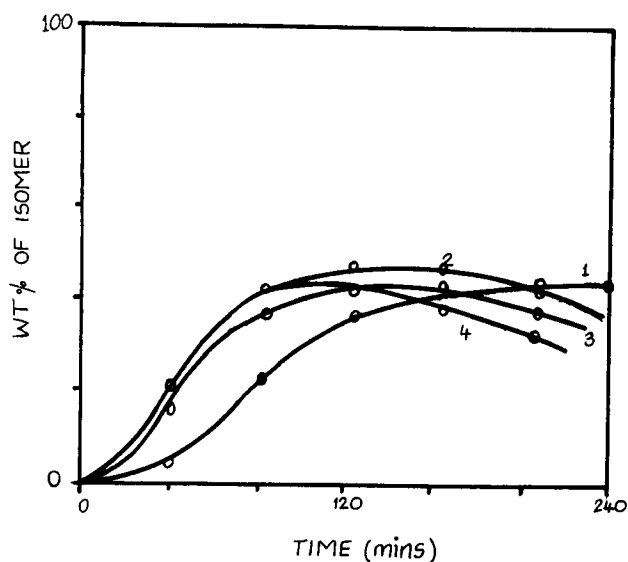


FIG. 5. Effect of solvent composition on isomerization (IPA:cyclohexane, curve 1 = 0/150 ml; 2 = 10/140; 3 = 50/100; 4 = 150/0).

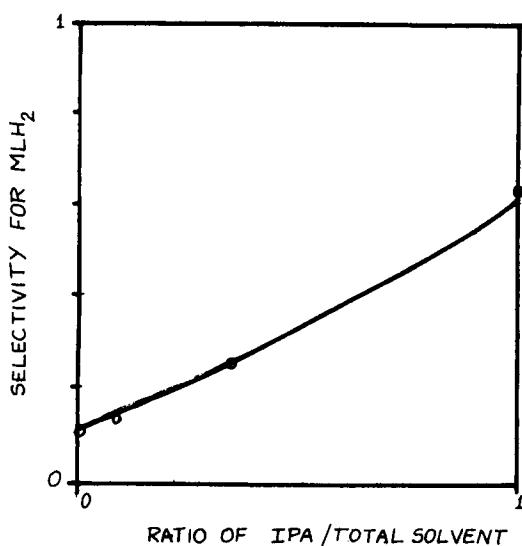


FIG. 6. Effect of solvent composition on selectivity for hydrogenation (conditions same as for Fig. 2; selectivity refers to values at the end of 3 hr).

Effect of Solvent Composition

It is clear that as IPA is added to cyclohexane, the time at which maximum conjugation occurs shifts to the left in Figure 5. In general, the overall rate of conversion of methyl linoleate increases as IPA is added to cyclohexane. The effect of IPA is seen at as low a volume as 10 ml of IPA out of a total solvent volume of 150 ml.

Figure 6 shows that selectivity for hydrogenation increases with increase in concentration of IPA in the solvent mixture. These observations can be rationalized on the basis of the fact that IPA, even at low concentrations, supplies enough hydrogen to the catalyst (leading to M-H species), which drives the reaction to right (equation 1) faster than in the case of pure cyclohexane. However, it is noteworthy that the maximum percentage of conjugation is more or less constant ($43 \pm 2\%$) in all cases (Fig. 5). This could be an indication that in all cases conjugation reaction is taking place by the same mechanism, namely, hydrogen addition followed by elimination as explained before. Thus, it is very clear that the nature of the solvent has a definite influence on the reaction, and subtle variations of activity and selectivity for conjugation or hydrogenation can be effected by varying solvent composition, time of reaction or temperature.

Results at Low Concentration of Solvents

Figure 7 shows a typical kinetic plot at low solvent concentrations (solute:solvent, 1:1). Under these conditions, the catalyst is active even at low catalyst loadings (1 wt % with respect of methyl linoleate). However, in addition to isomerization and hydrogenation, polymerization of methyl linoleate also takes place. Hydrogenated product starts accumulating a little later compared to isomerized product and the polymer. This seems to indicate that even the non-conjugated methyl linoleate contributes directly to polymer, whereas hydrogenation seems to proceed essentially via conjugated methyl linoleate. Mathematical modelling of the kinetic network is being published elsewhere and has thrown further light on the reaction pathway (12).

The polymerization activity is found to be very sensitive to the following parameters: (i) temperature of reaction; (ii) solvent concentration; (iii) amount of catalyst, and (iv) time of reaction, each of which is considered in turn below.

Effect of Temperature

Figure 8 shows the effect of temperature on polymerization.

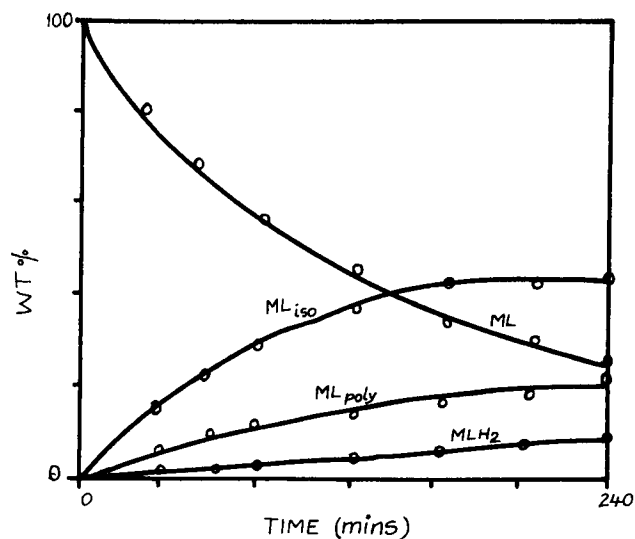


FIG. 7. Kinetic experiment at 200 C (ML:solvent = 1:1, ML:catalyst = 1:0.01).

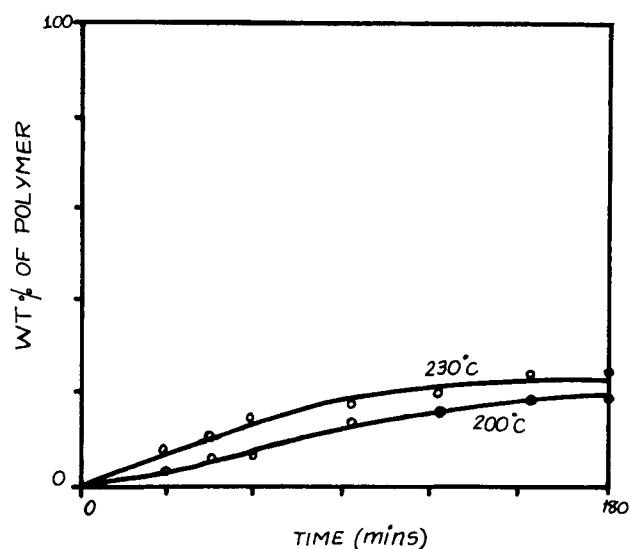


FIG. 8. Effect of temperature on polymerization.

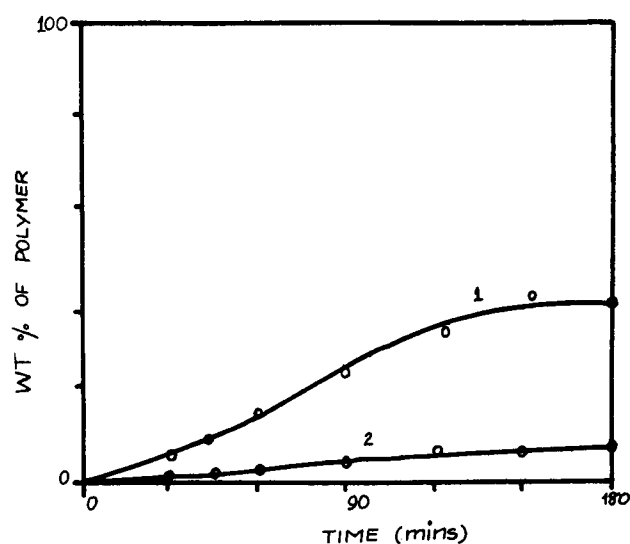


FIG. 10. Effect of catalyst quantity on polymerization at 200 C (ML: catalyst, curve 1 = 1:0.025; 2 = 1:0.0125).

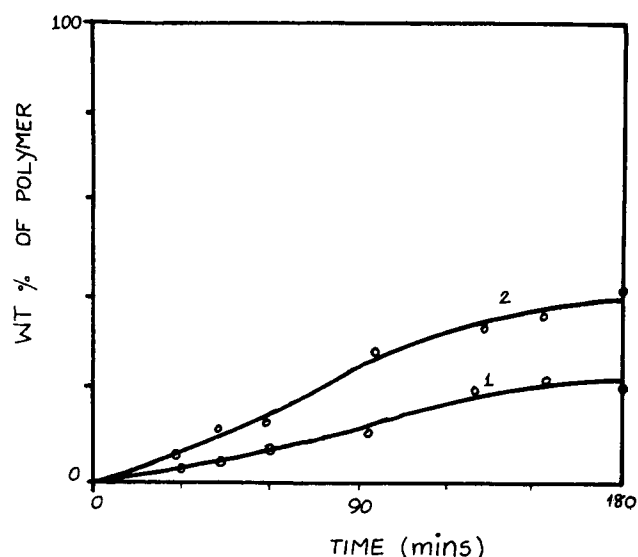


FIG. 9. Effect of solvent quantity on polymerization at 200 C (ML: cyclohexane, curve 1 = 1:2.5; 2 = 1:1).

At higher temperatures, more polymer is formed. Clearly, thermal polymerization (by Diels-Alder reaction) becomes important at higher temperatures.

Effect of Solvent Concentration

At low solvent concentrations, polymer formation is greater in comparison to experiments at high solvent concentrations (Fig. 9). Obviously, at low solvent concentrations methyl

linoleate molecules have lower mean free path relative to high solvent concentrations which would facilitate isomerization by the Diels-Alder reaction.

Effect of Catalyst Quantity

Figure 10 shows the effect of catalyst quantity on polymer formed. The larger the quantity of catalyst, the more the polymer formed. This seems to indicate that polymerization on the slightly basic carbon support also could contribute to polymer formed.

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[Received July 21, 1984]