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ORIGINAL PAPER

Thermal Polymerisation and Autoxidation of Technical Grade Linoleic Acid

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Abstract Oligomerisation of technical grade linoleic acid was studied over a broad temperature range. Effects of water and air were specifically addressed. The products were analysed by size-exclusion chromatography to give directly the concentrations of dimers and trimers. Oligomerisation of technical grade linoleic acid was seen to be dependent on temperature and the activation energy for monomer disappearance was 109 kJ/mol. A phenomenological kinetic model was proposed for the linoleic acid oligomerisation giving good model predictions. The presence of water inhibited the oligomerisation reaction. Extensive dimerisation and trimerisation occurred under a continuous air flow, whereas introduction of air pulses resulted in only a minor enhancement of trimerisation.

Keywords Polymerisation · Autoxidation · Linoleic acid

Introduction

Fatty acids and their derivatives have several industrial applications being used as detergents, paints, cosmetics, rubber impregnation agents, etc. [1]. In particular fatty acid oligomers serve as ingredients in paints and glues [2]. Polymerisation of fatty acids can be either thermal or catalytic [3]. Both homogeneous [4, 5] and heterogeneous catalysts [3, 6] can be applied. During linoleic acid oligomerisation Diels–Alder reaction involving conjugated linoleic acids also occur [7–9]. Additionally, cyclic dimers can be formed via a cation mechanism [7]. Oligomerisation of fatty acids can proceed at high temperatures (280 °C) under inert atmospheres [3]. There exist several publications describing thermal polymerisation of oils, namely polymerisation of anchovy and linseed oil in the temperature range of 260–280 °C [10] and polymerisation of canola oil [11]. Furthermore it is known, that during distillation of fatty acids at high temperatures, ca. 270 °C under high vacuum, anhydrides are also formed, and these are unstable and can in turn polymerise [12, 13].

Autoxidation of unsaturated fatty acids is also of importance, since the properties of fatty-acid-containing mixtures are changed during the reaction. Autoxidation is regarded mainly as harmful, since the properties of fatty acids can deteriorate [14]. Autoxidation of linoleic acid can occur at temperatures as low as 90 °C. Kinetics of the autoxidation of methyl eleostearate was reported in [15]. Furthermore, fatty acids autoxidise faster than their corresponding esters [14]. Typically autoxidation has been studied by differential scanning calorimetry giving the possibility of calculating the activation energies and rate constants. The kinetics of fatty acid autoxidation is complex, since reactions, including oxidation, decarboxylation and polymerisation can occur [14, 16].

Thermal oligomerisation of linoleic acid can occur for instance during distillation of fatty acids, thus the kinetics of this reaction and its temperature dependence are of importance from a practical viewpoint. Since in distillation it is an unwanted process, inhibition of oligomerisation by addition of water was also studied. Additionally, the quality of fatty acids can deteriorate due to autoxidation, therefore this reaction was also investigated in the present study.

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The aim of this work was to study kinetics of thermal oligomerisation of technical grade linoleic acid determining activation energies for the formation of dimers and trimers. A second aim was to investigate the kinetics of technical grade linoleic acid autoxidation at 280 °C in the presence of varying amounts of air in order to quantify the effect of air on the reaction rate and to elucidate the reaction mechanism.

Materials and Methods

The kinetic experiments were performed in an autoclave using technical grade linoleic acid (Fluka) as the reactant containing 65 wt% linoleic acid and 35 wt% oleic acid. In a typical experiment, 130 g of the above mentioned reactant mixture containing corresponding 0.463 mol was used under an inert atmosphere (either nitrogen, AGA, 99.999% or argon, AGA, 99.999%). In some cases synthetic air (AGA, 99.999%, below 3 ppm water) was introduced into the reactor in order to study autoxidation of the fatty acids.

Some experiments were performed in the temperature ramping mode as follows: the reaction mixture was heated to 260 °C, thereafter the temperature was increased by 10 °C and kept constant for 120 min and this procedure was repeated four more times up to 300 °C. Analogously to temperature ramping the amount of air was also added stepwise by using a coil of volume 5.0 ml corresponding to 0.0408 mmol of oxygen per pulse, when calculating its amount from the ideal gas law.

The polymerisation/autoxidation of linoleic acid was additionally performed in the presence of a continuous air flow (45 ml/min), which was started when the reaction temperature reached 280 °C.

The reaction products were analysed by a SEC-HPLC technique using three different columns connected in series: the first column was a Jordi precolumn, the second and the third were either two similar Jordigel DVB500A or TSK G300HHR columns. Two similar columns were applied in series in order to improve the separation. The detector was an LT-ELS (low temperature evaporative light-scattering detector, Sedex 85, Sedere LT-ELSD). The samples were calibrated with soybean oil. Soybean oil was used as a standard, since its retention time was close to the retention times of fatty acid monomers, dimers and trimers, i.e. the retention time of soybean oil was 15.40 min, whereas the retention times for monomer, dimer and trimer were 17.40, 16.23 and 15.40 min, respectively. In order to quantify the trimers, known amounts of soybean oil were added to the reaction mixture and its area was subtracted from the peak appearing at the retention time of 15.40 min. A detailed description of the analysis method is given in [3, 17]. In the sample preparation, the samples were filtered using a filter (0.2 µm membrane material made of polytetrafluoroethylene) before being injected into the SEC-HPLC apparatus in order to prevent high molecular compounds entering the column.

Results

Effect of Reaction Temperature

The initial reaction rate increased with an increase in the reaction temperature by 20 °C (Table 1, entry 1 and 2). The formation of dimers and trimers is strongly dependent on temperature as can be seen from Fig. 1. No trimers were present at 260 °C, whereas at 280 °C, trimer formation started after 110 min of reaction time, when the dimer yield was about 3.5% indicating the consecutive reaction mechanism for trimers. A more accurate identification of reaction products was only performed for the reaction mixture obtained by using a catalyst, H-MCM-41 [3]. The dimers were confirmed in their silylated esters by the GC-MS technique, whereas NMR analysis revealed the presence of unsaturated compounds, like cyclohexene and traces of aromatic compounds [3]. Thus it was concluded that both the Diels–Alder reaction and dehydrogenation occurred during catalytic oligomerisation of technical grade linoleic acid. The product mixture from thermal

Table 1 Kinetic data from the polymerisation/oxidation experiments of technical grade linoleic acid

Entry	Description	Temperature (°C)	P (bar)	Initial rate (mmol/min)	Y_{dimer} after 240 min (%)	Y_{trimer} after 240 min (%)
1	Thermal (N_2)	260	4	0.05	1[a]	0[a]
2	Thermal (Ar)	280	4–5	0.3	6.0 (4.3[a])	3.0 (2.5[a])
3	Temperature ramping (Ar)	260–300	5–6	–	4.1	2.0
4	Thermal + water	280	8–14	0.17	5.0[b]	1.6[b]
5	1 bar air and Ar	200	3–4	0.05	<1	<1
6	1 bar air and Ar	250	4–5	0.14	2.7	2.3
7	Addition of air pulses (Ar)	280	3–15	0.7	7.4	4.0
8	Continuous air flow and Ar	280	4	0.7	18	14

Y indicates yield

[a] 180 min

[b] 230 min

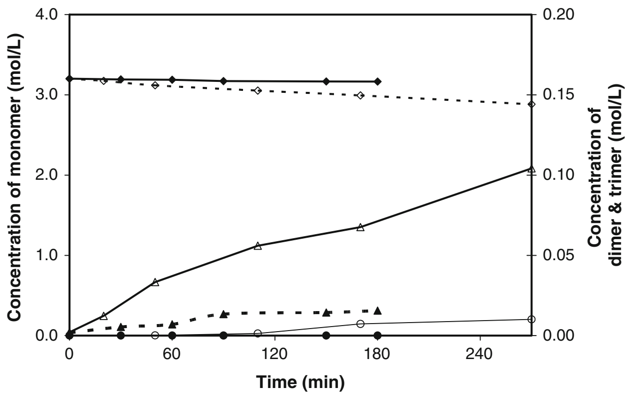


Fig. 1 Thermal oligomerisation of technical grade linoleic acid at 260 °C under nitrogen (*solid symbols*) and at 280 °C under argon (*open symbols*). Symbols: monomer (*squares*), dimer (*triangles*) and trimer (*circles*). Pressure 4 bar

oligomerisation of linoleic acid exhibited in SEC-analysis peaks with the same retention times indicating that the same reactions occurred in the current case.

The activation energy for the disappearance of technical grade linoleic acid was calculated from the experimental data achieved by using a temperature ramping approach (see the Materials and Methods section). The oligomerisation kinetics was determined by measuring the kinetics over a temperature range of 260–300 °C (Fig. 2) and the activation energy for monomer reaction was 109 kJ/mol. The dashed line in Fig. 2 displays the sum of the monomer, dimer and trimer concentrations indicating a slight decrease in the total concentration. This result shows that some high molecular weight products are also formed, which cannot be analysed by the SEC-method, since these were filtered away (see see the Materials and Methods section).

The modelling of the kinetic data from the temperature ramping experiment was performed by using a simplified reaction scheme for oligomerisation (Scheme 1) where reversibility of the reaction steps was proposed by Brat et al. [18]. The complete reaction scheme would imply isomerisation, hydrogenation, dehydrogenation as well as formation of intermediate products and higher oligomers. They were, however, not included due to the lack of precise analytical data not achievable by the SEC-HPLC method.

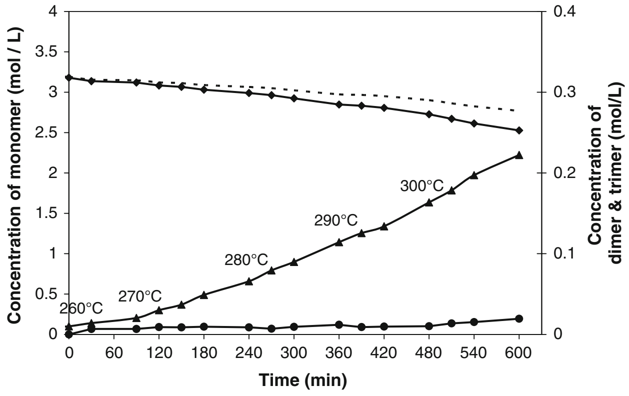
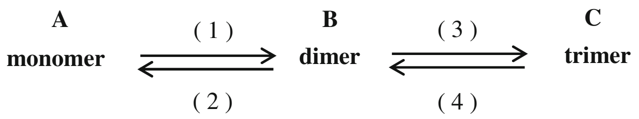


Fig. 2 Kinetics in the oligomerisation of technical grade linoleic acid using a temperature ramping technique. Symbols: monomer (*squares*), dimer (*triangles*) and trimer (*circles*). Atmosphere Ar, 5 bar. The *dashed line* is the sum of monomer, dimer and trimer concentrations



Scheme 1

The formation rates for A (monomer), B (dimer) and C (trimer) are described according to the simplified model

$$r_A = -r_1 + r_2 \quad (1)$$

$$r_B = r_1 - r_3 + r_4 - r_2 \quad (2)$$

$$r_C = r_3 - r_4 \quad (3)$$

The reaction rates for r_1, r_2, r_3 and r_4 according to formal kinetics are written as follows:

$$r_1 = k_1 c_A^2 \quad (4)$$

$$r_2 = k_2 c_B \quad (5)$$

$$r_3 = k_3 c_A c_B \quad (6)$$

$$r_4 = k_4 c_C \quad (7)$$

where k_1, k_2, k_3 and k_4 are kinetic constants.

The temperature dependence of the rate constants follows the Arrhenius equation:

$$k = \bar{k} e^{-\left(\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right)} \quad (8)$$

where $\bar{k}$ is defined as

$$\bar{k} = A e^{-\left(\frac{E_a}{R T_{\text{ref}}}\right)} \quad (9)$$

and T_{ref} is the reference temperature 553.15 K, A is the frequency factor and E_a is the activation energy. The mass balance for the batch reactor can be written as

$$\frac{\mathrm{d}c_i}{\mathrm{d}t} = r_i \quad (10)$$

where i is the concentration of either monomer (A), dimer (B) or trimer (C). The rate equations were combined with the mass balance and the modelling was performed by using software ModEst [19]. The numerical values of the parameters were estimated by the simplex-Levenberg–Marquardt method [20], in which the sum of the residual squares Q

$$Q = \sum_t \sum_i \left(c_{it} - c_{it,\text{exp}}\right)^2 \quad (11)$$

Table 2 Parameter values obtained from the thermal oligomerisation of technical grade linoleic acid using the temperature ramping technique

Reaction (*i*)	k_i	$E_{a,i}$ (kJ/mol)
1	0.000073 l/(mol min)	97
2	0.00256 1/(min)	22
3	0.0389 l/(mol min)	65
4	0.7431 1/(min)	95

The degree of explanation $R^2 = 99.99\%$. $T_{\text{ref}} = 280$ °C. The numbers of the reactions are given in Scheme 1

was minimised in Eq. (11). c_{it} is the estimated concentration for component i at time t and $c_{it,\text{exp}}$ is the experimental concentration for compound i at time t.

The kinetic parameters for the reactions (4)–(7) are presented in Table 2 and the model prediction is depicted in Fig. 3, indicating that the proposed model was able to describe the experimental data very well. The activation energy for reaction (1) was 97 kJ/mol being close to the value calculated from the kinetic data.

Effect of Water

The presence of water was proposed as inhibiting the oligomerisation of linoleic acid by reacting with fatty acid anhydrides [12] being intermediates for oligomerisation. In the reaction between anhydrides and water, free acids are formed. In order to investigate whether this would be the case in the present study the reaction was started by using the molar ratio of technical grade linoleic acid to water equal 2.2:1 when performing the experiment under argon at 280 °C (Table 1, entry 4, Fig. 4). As a result the reaction pressure increased even at the beginning of the experiment up to 14 bar due to the high vapour pressure of the water. The initial oligomerisation rate with the addition of water (Table 1, entry 4) was only 57% of the one obtained under dry conditions (compare with Table 1, entry 2) indicating that water inhibited the oligomerisation reaction. The effect of water was, however, relatively mild after prolonged reaction times. It should be pointed out here that due to the high vapour pressure of water, the major part of it could be, however, in the gas phase, thus reducing its effect in the liquid phase. The dimer and trimer concentrations after prolonged reaction times are thus most probably too low compared to the situation when all water would be in the liquid phase.

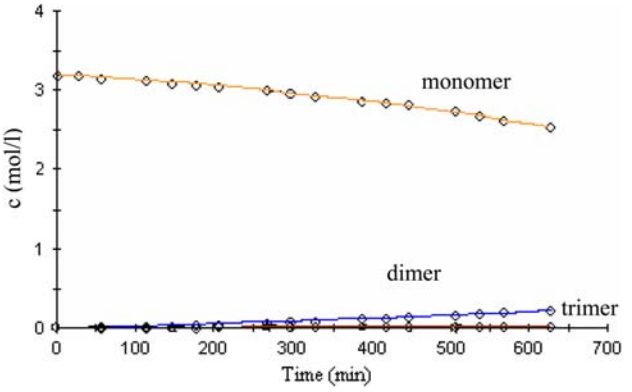


Fig. 3 The results from the kinetic model based on the temperature ramping experiment (Fig. 2). *Points* are experimental data, the *line* is the model prediction

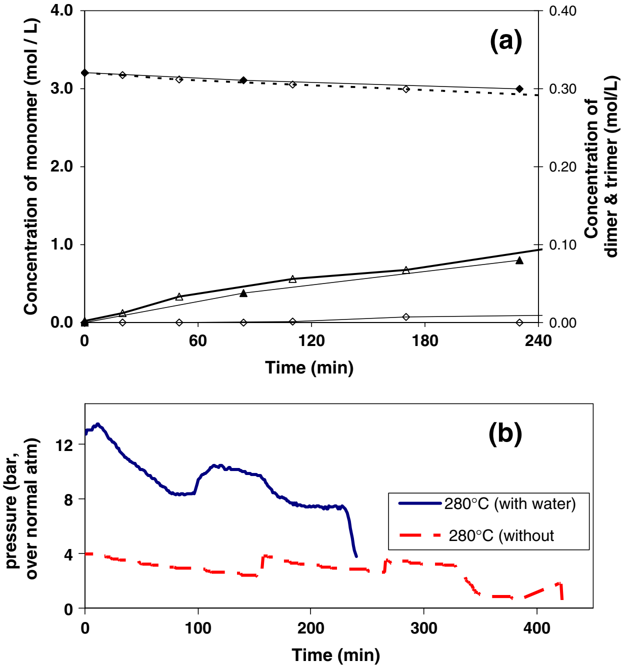


Fig. 4 **a** Thermal oligomerisation of linoleic acid at 280 °C with (*open symbols*) and without water addition (*solid symbols*) under 4 bar argon. Symbols: monomer (*squares*), dimer (*triangles*) and trimer (*circles*), **b** pressure profile during the thermal oligomerisation of technical grade linoleic acid with and without water

Effect of Air

The effect of dry air and increased temperature was studied at two different temperatures (200 and 250 °C). In addition, increasing amounts of air pulses were introduced to the reaction mixture. Furthermore continuous air bubbling during the course of the reaction was performed (Table 1, entries 5–8). The initial oligomerisation rate for the monomer in the presence of 1 bar air increased from 200 to 250 °C by a factor of 2.8 (Table 1, entries 5, 6) thus emphasising the importance of temperature on the oligomerisation rate. At the higher temperature of 250 °C, it can be seen that the concentration of monomer decreased faster within the first 60 min reaction time thereafter it declined with the rate being only 47% of the initial one. The dimer

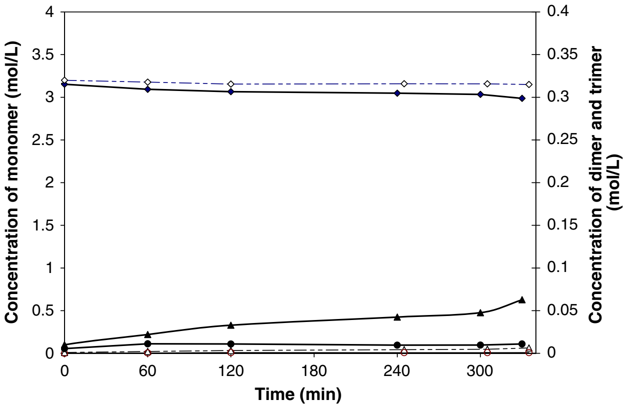


Fig. 5 Oligomerisation of technical grade linoleic acid at 200 °C (*open symbols*) and at 250 °C (*solid symbols*). Symbols: monomer (*squares*), dimer (*triangles*) and trimer (*circles*). Atmosphere 1 bar air, 3 bar argon

concentration increased continuously in the presence of air at 250 °C, while the trimer concentration remained relatively constant (Fig. 5). This result is in accordance with the literature since oxygen is known to react with a double bond in a molecule and thus not cross-link with other molecules [16]. The remaining double bonds can react with fatty acids and thus in the presence of oxygen, the polymer formed has poor mechanical properties [16].

In the second type of experiment, an increasing number of air pulses was added to the reaction mixture, and a slightly faster monomer reaction was observed than without air (Fig. 6a). The pressure and temperature profiles during the air pulse experiment are shown in Fig. 6b. The initial reaction rate in the presence of air pulses was 2.3 higher than in their absence suggesting that air has a catalyzing effect on the initial oligomerisation rate of linoleic acid (Table 1).

After 30 min of reaction time, the reaction rates, however, became about the same for linoleic acid oligomerisation with and without air (Fig. 6a), indicating that the cross-linking between different fatty acid chains is not very much enhanced in the presence of oxygen as stated above. The dimer concentration with air addition was 1.2-fold the value obtained without air addition after 270 min of reaction time (Fig. 6a). Furthermore the trimer concentrations with and without air were about the same after 180 min of reaction time (Fig. 6a).

The initial oligomerisation rate of linoleic acid in the presence of a continuous air feed was about the same as in the case where air was injected as a pulse into the reaction system (Table 1, entries 7, 8). The dimer formation was, however, more prominent, when air was fed continuously into the system compared to the air pulse experiment, i.e. after 360 min of reaction time 0.38 and 0.14 mol/l of dimers were formed in the former and in the case (Fig. 7). The same trend was observed for trimers and the corresponding concentrations were 0.1 and 0.02 mol/l. This result indicated that the continuous air bubbling through the reaction mixture was able to catalyse both dimerisation and trimerisation of linoleic acid during the course of the

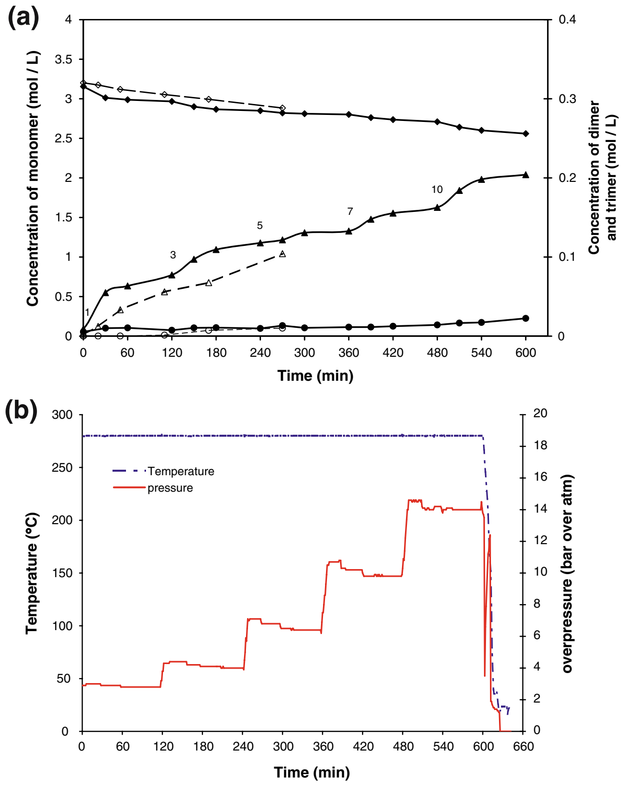


Fig. 6 **a** Oligomerisation of technical grade linoleic acid at 280 °C under argon with adding air pulses (*solid symbols*) and without air (*open symbols*). The pressure changed from 3 to 15 bar during the experiment. The number of air pulses is given in the picture. Symbols: monomer (*squares*), dimer (*triangles*) and trimer (*circles*), **b** temperature and pressure profiles during the experiment

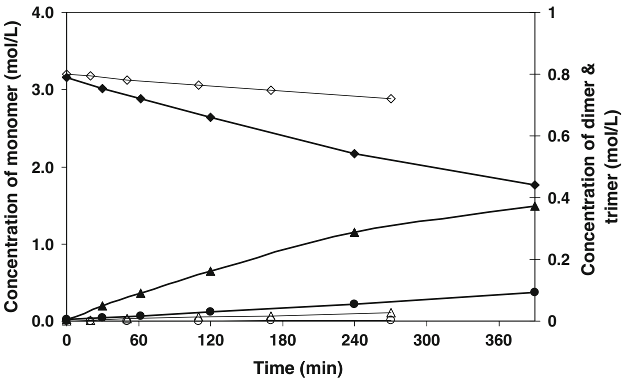


Fig. 7 Oligomerisation of technical grade linoleic acid under argon with a continuous air flow (*solid symbols*) and without air (*open symbols*) at 280 °C. The total pressure was 4 bar. Symbols: monomer (*squares*), dimer (*triangles*) and trimer (*circles*)

reaction. The colour of the reaction mixture changed in the presence of air from yellow to dark brown indicating formation of ketones, which was proposed in [21]. The exact chemical nature of the compounds remained beyond the scope of this study, since only monomer, dimer and trimer concentrations were determined. On the other hand size-exclusion chromatography facilitated the quantification of the above mentioned species thus being a much more informative method than calorimetry applied previously [14, 16]. The main conclusion from the oligomerisation of technical grade linoleic acid in the presence of air is that both dimerisation and trimerisation were strongly catalysed during the air bubbling through the reaction mixture.

Oligomerisation of technical grade linoleic acid was studied at different temperatures in aerobic and anaerobic conditions, as well as in the presence of water. The initial reaction rates were strongly dependent on the reaction temperature. Activation energies for monomer and dimer reactions were determined and the model based on formal kinetics was able to describe the experimental data. The presence of water retarded the oligomerisation of linoleic acid possibly due to its reaction with fatty acid anhydrides, which are intermediates for oligomerisation. Continuous air flow enhanced both dimerisation and trimerisation, whereas adding air in pulses did not promote trimer formation.

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