Radiation Effects on Triglyceride

EIICHI FUKADA, Institute of Physical and Chemical Research, Bunkyo-ku, Tokyo
MITSUNOBU MASUZAWA, Oji Factory, Nippon Oils and Fats Co., Ltd., Oji, Tokyo

Abstract

High energy electron beam irradiations up to 900 mrads were given to tristearin and triolein. Differential thermal analysis and x-ray diffraction measurements revealed that the degree of crystallinity decreased with radiation dose after an initial small rise and that the unstable forms in crystal modification were increasingly stabilized. Measurements of intrinsic viscosity and gel fraction for solutions of tristearin and triolein showed that the gel formation took place at about 700 and 350 mrads, respectively. The number of unsaturated bonds determined by iodine absorption increased with radiation dose in tristearin but decreased in triolein.

Introduction

THERE HAVE BEEN some reports dealing with chemical reactions in fatty substances induced by high energy irradiation such as decoloration (1) and hydrogenation (2). The modification of physical properties of fats by means of high energy irradiation has not yet been fully investigated. The present paper reports some radiation effects on glyceryltristearate and glyceryltrioleate. The former is the ester compound of glycerol $CH_2(OH)CH(OH)CH_2(OH)$ and stearic acid $CH_3(CH_2)_{16}COOH$ with the molecular weight of 790 and is usually called tristearin. The latter is the ester compound of glycerol and oleic acid $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ with the molecular weight of 784 and is called triolein.

These substances were prepared in the laboratory from the natural Tsubaki oil. The acid components of triglyceride in this oil consist of oleic acid (80%), stearic acid (8%) and other fatty acids. The sample of tristearin was obtained by the complete hydrogenation of Tsubaki oil followed by repeated recrystallization in acetone solution. The iodine value for the sample was found to be almost zero, indicating that the content of the unsaturated acid was negligible. According to gas chromatography, the fraction of stearic acid in the total components of fatty acid was determined as 98%. The sample of triolein was fractionated from the acetone solution of Tsubaki oil by the repeated crystallization at low temperature. The analysis by gas chromatography showed that the oleic acid occupied 90% of fatty acid components.

An electron beam irradiation with an energy of 1.5 Mev from a Van de Graaff accelerator was given to the specimens in air up to a maximum radiation dose of 900 mrads.

About 5 g of the molten specimen was poured into a shallow circular glass vessel with a diameter of 5 cm. The thickness of the layer of the specimen was about 3 mm, which was within the penetration range of 1.5 Mev electron beam. The glass vessel was surrounded by dry ice to prevent the overheating of specimen. Though the temperature during irradiation has not been measured, it is very probable that the specimen under irradiation was in the molten state due to the high energy input per unit of time.

Results

The differential thermal analysis and x-ray diffraction measurements have been used in determining the change in physical properties of irradiated triglyceride. The measurements of intrinsic viscosity and solubility of solutions of the irradiated specimens were also carried out to investigate the chemical changes introduced in molecular structure.

Figure 1 represents typical results of the differential thermal analysis (DTA) for the irradiated tristearin. Prior to the measurement the test cap containing the specimen was heated from room temperature to about 80C with an approximate rate of 1C/min to melt the specimen; it was then immersed into the ice water for 1 to 2 hr in order to solidify the specimen completely. The specimen was gradually heated from 0C up to 90C with an approximate temperature rise of 1C/min. The curve designated as 0 mrad shows the result for an unirradiated specimen and has three peaks corresponding to α, β', and β crystalline modifications. As shown in the figure, the β peak, the most stable modification, disappears with a radiation dose of 8.6 mrads. Up to a dose of about 50 mrads, the β' peak decreases and the α peak increases with irradiation. At 70 mrads only the α peak is observed. Above 100 mrads a new peak which is unspecified yet but labelled α' appears at a lower temperature and with the increase of radiation dose the α peak decreases and the α' peak slightly increases. The areas of the peaks in DTA

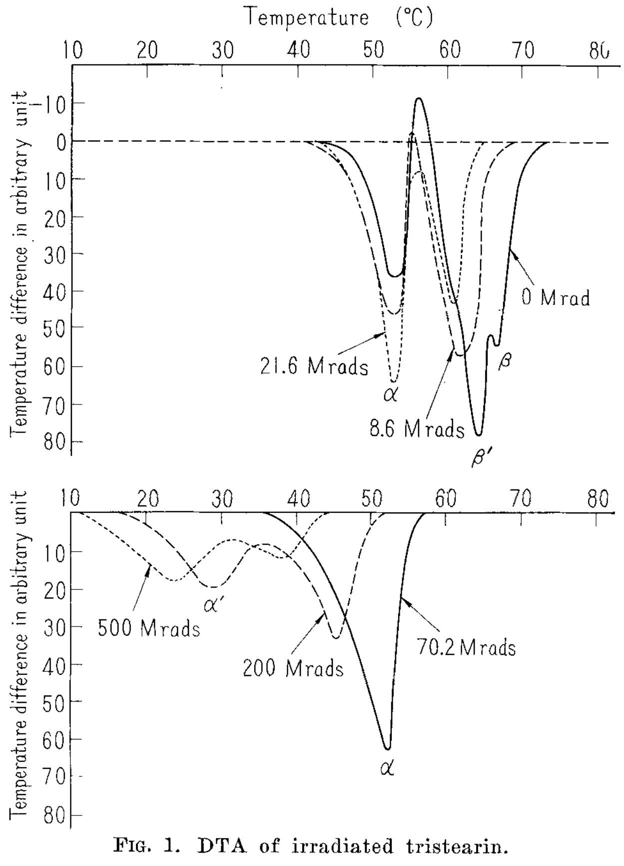

FIG. 1. DTA of irradiated tristearin.

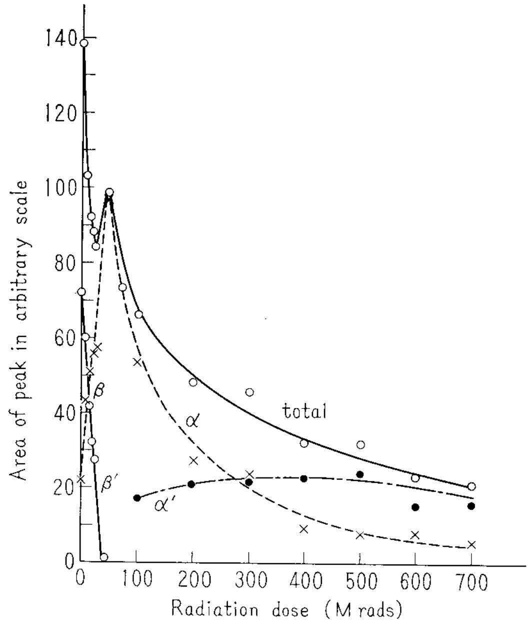

FIG. 2. Change of area for each peak of DTA.

correspond to the heat of fusion for each type of crystalline state and these are plotted in Figure 2 against the radiation dose. The curve designated total represents the relative change of the degree of crystallinity with the radiation dose.

The melting temperatures for each crystal modification were determined by the rising points in the DTA curve and these are plotted in Figure 3. The rising point is defined as the point where the curve first departs from the base line. The apparent melting temperature as determined by a microscopic observation during heating is also plotted in the figure. It is seen that the melting temperature of each type of crystal modification decreases with the radiation dose. The total heat of fusion calculated from the DTA curve is plotted against radiation dose in Figure 4. The gradual decrease in heat of fusion suggests that the degree of crystallinity decreases with radiation dose.

Figure 5 illustrates some examples of x-ray diffraction patterns in irradiated tristearin measured at room temperature. The curve for 21.6 mrads represents the diffraction mainly of α modification at $2\theta = 21.4°$ with slight peaks corresponding to β at $2\theta = 19.4°$ and β' at $2\theta = 27.0°$. The larger amounts of β and β' modifications found in the DTA curve seem to be due to a recrystallization above the melting temperature of the α state. The curve for 200 mrads shows an α peak and a large peak at $2\theta = 4.8°$; this latter peak appears above 100 mrads and is thought to be due to the α' state. The curve of 700 mrads shows a pattern of almost amorphous character with a small α peak. The degree of crystallinity determined from the area of the x-ray diffraction patterns is plotted against radiation dose in Figure 6. The degree of crystallinity for the unirradiated specimen seems to be too small. This may be due to the ambiguity in the correction for the back ground scattering. However, the relative change of degree of crystallinity with the radiation dose would be significant. The degree of crystallinity attains a maximum at about 70 mrads and then decreases gradually with irradiation, which is quite similar to the results shown in Figure 4.

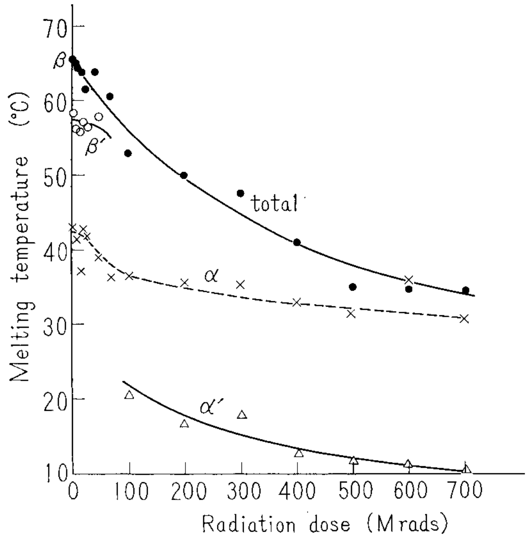

FIG. 3. Change of melting point derived by DTA.

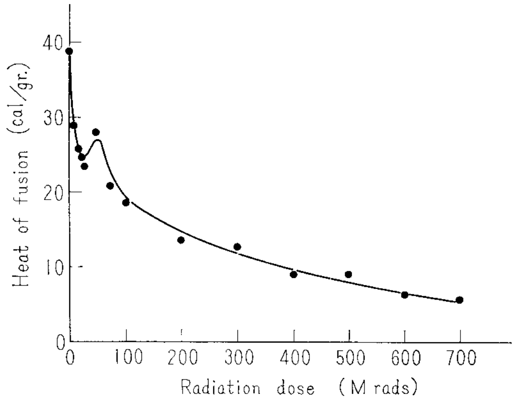

FIG. 4. Relation between heat of fusion and radiation dose for irradiated tristearin.

The intrinsic viscosity of chloroform solutions of irradiated tristearin was measured after filtration of the solution and the gel fraction of the irradiated specimens was also determined. The results are shown

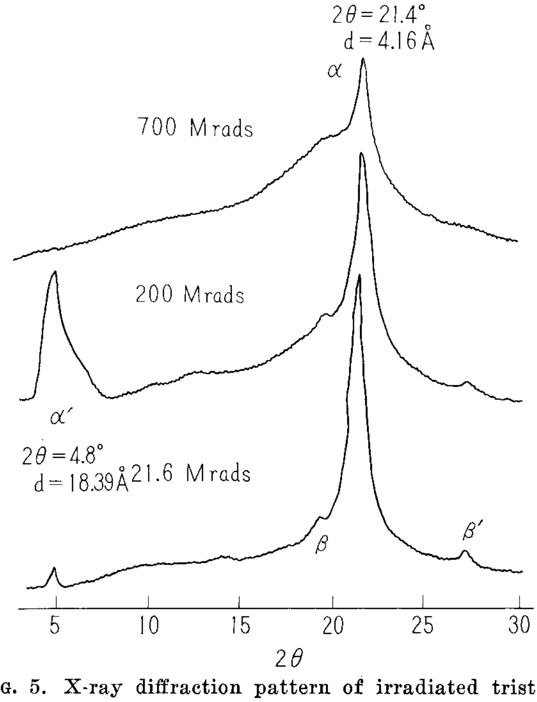

FIG. 5. X-ray diffraction pattern of irradiated tristearin.

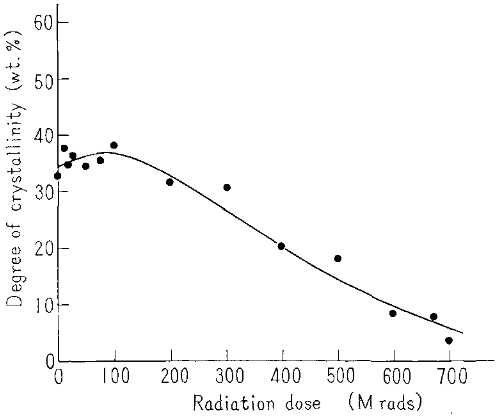

FIG. 6. Relation between degree of cyrstallinity and radiation dose for irradiated tristearin.

in Figure 7. The intrinsic viscosity initially decreases with radiation dose, reaches a minimum at about 70 mrads and then gradually increases until the sharp rise at 700 mrads. The gel fraction also becomes observable at that dose and increases further with radiation dose. It is obvious that cross-links are introduced between tristearin molecules due to irradiation and that the molecular weight increases gradually until a molecular network is formed at 700 mrads. However, the decrease of intrinsic viscosity up to 70 mrads shows that a scission in molecules also takes place during the initial stage.

This change of molecular weight should correspond to the change of degree of crystallinity described above. It has been seen in Figure 3 that the melting temperature for the β', α and α' modifications gradually decreases with irradiation. When the scission takes place in one hydrocarbon branch of triglyceride the resulting molecule would be a mixed triglyceride molecule which has two stearyl branches and one branch shorter than the stearyl. It is known that the melting temperature for such mixed triglycerides is lower than that of the original triglyceride (3).

Unirradiated tristearin contains a fairly large amount of molecules existing in an amorphous state. If the orientation and rearrangement of such molecules are facilitated by the scission of some branches, the crystallization will be promoted and the degree of crystallinity will increase, although the melting temperature of the crystal is decreased because of the alteration of the molecules into the mixed tristearin state. At the same time cross-links are introduced between molecules both in the crystalline and amorphous regions which prohibit the regular alignment of molecules and distort the crystal structure. As a result, there is a gradual decrease in the degree of crystallinity with a further increase of radiation dose. Under these circumstances it is quite reasonable that the stable form β quickly disappears and only the unstable α form is observed.

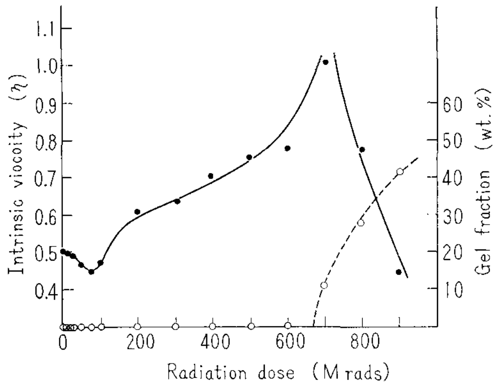

FIG. 7. Changes of intrinsic viscosity and gel fraction for irradiated tristearin.

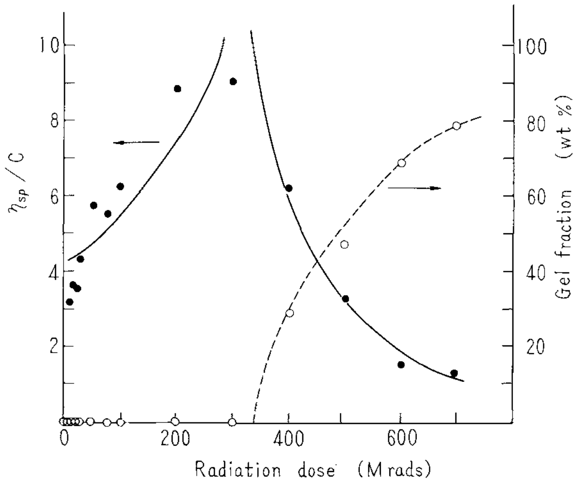

FIG. 8. Changes of instrinsic viscosity and gel fraction for irradiated triolein.

The intrinsic viscosity and gel fraction of triolein irradiated up to 700 mrads were measured and are illustrated in Figure 8. The sharp rise of intrinsic viscosity and the incipient gel formation were observed at the radiation dose of about 350 mrads which is half of the gel dosage for tristearin. The initial decrease of intrinic viscosity was not observed in this case. The change of the density of unsaturated bonds was also estimated by the iodine absorption method for irradiated tristearin and triolein. The results are shown in Figure 9. The number of unsaturated bonds increases gradually with irradiation for tristearin, while it decreases steadily with irradiation for triolein. Therefore it is very probable that the unsaturated bond in triolein act as the crosslinking points and result in the decrease of gelation dose as described above. Measurements of the infrared absorption spectrum in irradiated tristearin also showed the gradual increase in absorption of transvinylene unsaturation as well as carboxyl group with the increase of radiation dose.

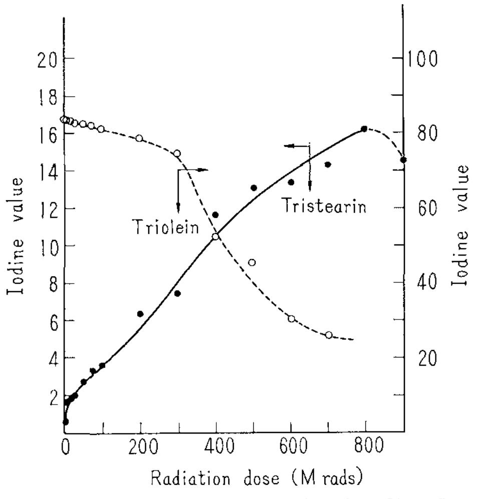

FIG. 9. Change of iodine value for irradiated tristearin and triolein.

Discussion

From the experimental results described above, it can be concluded that the radiation produces scission and cross-link reactions in molecules of triglyceride. The former is more significant for a radiation dose of less than about 70 mrads in the case of tristearin; the latter becomes predominant for a radiation dose of more than 100 mrads. A three-dimensional network of molecules is thus formed due to the cross-linkage and produces the gel fraction in solution. Similar behavior is generally observed in many kinds of high polymeric substances (4).

In general the relation between sol fraction S and radiation dose R is given by both theoretical and experimental investigations as follows (4):

$$S + \sqrt{S} = \frac{\dot{r}}{\dot{q}} + \frac{1}{\dot{q}\,U_n\,R} \qquad [1]$$

where $\dot{q}$ and $\dot{r}$ are the probabilities of cross-linkage and scission with unit radiation dose per atom in the backbone chain of the molecule, respectively; U_n is the number of atoms in the backbone molecular chain summing up three branches. If this relation holds, $S + \sqrt{S}$ is linear with $1/R$; $\dot{q}$ is derived from the slope of the straight line, and the intercept of the line with the vertical axis gives $\dot{r}$.

An estimation of $\dot{q}$ and $\dot{r}$ for tristearin was tentatively obtained by means of this equation, giving $\dot{q} = 0.17 \times 10^{-10}$ rad^{-1} and $\dot{r} = 0.05 \times 10^{-10}$ rad^{-1}. The value of U_n was assumed to be 60, including 3 oxygen atoms and 57 carbon atoms in the backbone of the molecule.

In the study of radiation effect on polymers such as polyethylene, U_n is usually defined as the number of monomers in the macromolecule. Therefore U_n is the half of the number of carbon atoms in the backbone of the molecule. The probabilities of cross-link and scission with unit radiation dose per monomer unit are now defined as $\dot{q}$ and $\dot{r}$, respectively. It has been determined for branched polyethylene that $\dot{q} = 0.8 \times 10^{-10}$ rad^{-1} and $\dot{r} = 0.2 \times 10^{-10}$ rad^{-1} approximately (4). In order to compare the values of $\dot{q}$ and $\dot{r}$ obtained for tristearin with these values for polyethylene, the value of U_n has to be halved, which results in $\dot{q} = 0.3 \times 10^{-10}$ rad^{-1} and $\dot{r} = 0.1 \times 10^{-10}$ rad^{-1} for tristearin. It seems likely that the efficiency of radiation reaction in tristearin is approximately half of that in polyethylene.

The data on the solubility of triolein does not fit well in equation 1, probably because the unsaturation of molecules acts preferentially in the network formation and involves a different mechanism to that considered in equation 1.

The precise mechanism involved in cross-link and scission reactions in triglyceride is not yet understood. Since triglyceride is a branched molecule, cross-links can be introduced into the same molecule through the reaction between two branched chains. Such intramolecular cross-links will not affect the gel formation even though they distort the orientation of molecules in crystalline regions. Much work still has to be done to fully understand the radiation effects on triglyceride.

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