

**SYNTHESIS AND POLYMERIZATION OF PLANT OIL
MONOGLYCERIDE MALEATES**

by

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ABSTRACT

In this study, rigid thermoset polymers were synthesized from radical copolymerization of the soybean oil monoglyceride maleates with styrene. In the first part of the study, soybean oil monoglycerides (SOMG) were obtained from the reaction of soybean oil with glycerol at 220-240⁰C. An optimization of the glycerolysis reaction was achieved through the use of a large amount of excess glycerol and with a rapid cooling process at the end of the reaction to maximize the monoglyceride yield. In the following step, soybean oil monoglycerides (SOMG) were reacted with maleic anhydride at temperatures around 100⁰C to produce the SOMG maleate half esters. Different catalysts and different reaction conditions were examined to increase the maleate half ester's yields. The reactions were followed by IR and ¹H-NMR and the products were characterized by mass spectrometry. In the final step, the radical initiated copolymerization of the SOMG maleates with styrene produced rigid, thermoset polymers. The SOMG maleates were found to be effective emulsifying agents, thus the emulsion copolymerization of the SOMG maleates with styrene was also carried out successfully without the addition of an emulsifier. The obtained polymers were characterized by IR and ¹H-NMR, the cross linked network structure of the copolymers was examined with the swelling behaviour in different solvents. The resulting copolymers of SOMG maleates with styrene are suitable for fiber reinforcement and can be used as a liquid molding resin with the right fiber reinforcement.

ÖZET

Bu çalışmada, soya yağı monogliserid maleatlarının stiren ile kopolimerizasyonu sonucu katı, termoset polimerler sentez edilmiştir. Çalışmanın ilk bölümünde, soya yağının gliserol ile 220-240°C sıcaklıklarındaki reaksiyonu sonucu soya yağı monogliseridleri (SOMG) elde edilmiştir. Monogliserid verimini arttırmak üzere, gliseroliz reaksiyonu çok miktarda gliserol fazlası kullanılması ve reaksiyon sonucu ürününün hızlı bir biçimde soğutulması ile optimize edilmiştir. Soya yağı monogliseridleri, bir ileriki adımda, maleat yarı esterlerini oluşturmak üzere 100°C de maleik anhidrit ile reaksiyona sokulmuşlardır. Bu aşamada, maleat yarı esterlerinin verimlerini arttırmak üzere, farklı reaksiyon koşulları ve farklı katalistler test edilmiştir. Reaksiyonlar, IR ve ¹H-NMR spektroskopi yöntemleri ile takip edilmiş, ürünlerin karakterizasyonunda kütle spektroskopi yöntemi de kullanılmıştır. Son aşamada ise, SOMG maleatlarının stiren ile radikal kopolimerizasyonu, katı termoset polimerler vermiştir. SOMG maleatlarının etkili emulsifiye edici özellikleri görülerek, stiren ile emülsiyon kopolimerizasyonu başka bir emulsifiye edici katılmadan başarı ile gerçekleştirilmiştir. Elde edilen polimerler, IR ve ¹H-NMR ile karakterize edilmiş, ve kopolimerlerin ağ yapısı değişik çözücülerdeki şişme davranışları ile test edilmiştir. SOMG maleatlarının stiren ile kopolimerleri, elyaf takviyesine uygun olup, doğru elyaf takviyesi ile sıvı döküm reçinesi olarak kullanılabilirler.

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LIST OF ABBREVIATIONS

g	:	gram
DMSO	:	dimethyl sulfoxide
MEKP	:	methyl ethyl ketone hydroperoxide
SOMG	:	soybean oil monoglyceride
MA	:	maleic anhydride
Mg	:	monoglyceride
Dg	:	diglyceride

1. INTRODUCTION

1.1. Glyceride Oils

1.1.1. Structure and Uses

Glyceride oils of either vegetable or animal origin are the glyceryl esters of fatty acids, so called triacylglycerides. The structure of a triacylglyceride is shown in Figure 1.1.

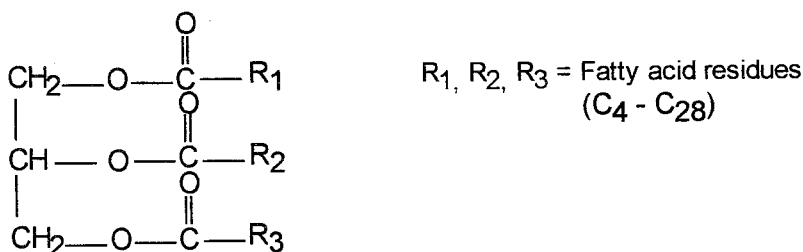


FIGURE 1.1. Structure of a triacylglyceride.

The groups R_1 , R_2 and R_3 are usually long chain alkyl groups which may either be completely saturated or may contain one or more double bonds. Such long chain carboxylic acids are called fatty acids and usually different fatty acids are present in natural oils. Most natural fatty acids have unbranched chains and because they are synthesized from two carbon units, they have an even number of carbon atoms. Fatty acids differ in both the type and amount of carbon carbon unsaturation present and these structural features influence subsequent chemical reactions. Most naturally occurring fatty acids contain two or three double bonds. The oils that these come from are called polyunsaturated oils. The first double bond of an unsaturated fatty acid commonly occurs between C_9 and C_{10} , the remaining double bonds tend to begin with C_{12} and C_{15} . These double bonds are therefore non-conjugated. The non-conjugated system of double bonds

occurs in the cis geometrical isomer in most natural oils such as linseed, soybean and safflower oils. Triple bonds rarely occur in fatty acids [1].

In this research project, soybean oil which is a polyunsaturated oil has been used. Soybean oil obtained from the seeds of the legume *Soja max*, is the highest volume vegetable oil produced in the world. The crude oil is obtained by pressing or solvent extraction methods. The main uses of the oil after refining, bleaching and deodorization and partial hydrogenation are in the manufacture of margarine and shortenings. The unhydrogenated oil is also used in blends with other oils, but its tendency to revert when exposed to air or high temperatures limits its use. Soybean oil is also used extensively in the manufacture of drying oil products. The free fatty acid content of good crude soybean oil, like that of many other vegetable oils, is slightly in excess of 0.5 %. The average iodine number of soybean oil which is a measure of unsaturation is in the 125-130 range. Assuming an average molecular weight of 871.5, this number corresponds to 4.47 carbon carbon double bonds per triglyceride. Other average characteristics are as follows: saponification number, 192; refractive index at 25°C, 1.470- 1.476; density at 25°C, 0.917-0.921 [2].

The molar fatty acid composition obtained by hydrolysis of soybean oil is given in Table 1.1.[1]. A symbolical structure of the oil therefore that shows the three unsaturated fatty acids namely; oleic, linoleic and linolenic acids present in the oil is shown in Figure 1.2.

TABLE 1.1. Fatty acid composition obtained by hydrolysis of soybean oil

FATTY ACIDS				Fatty acids mol %
C _{No}	Name	Formula	Unsaturation	
C ₁₄	Myristic (tetradecanoic acid)	C ₁₄ H ₂₈ O ₂	—	1 - 2
C ₁₆	Palmitic (Hexadecanoic acid)	C ₁₆ H ₃₂ O ₂	—	6 - 10
C ₁₈	Stearic (Octadecanoic acid)	C ₁₈ H ₃₆ O ₂	—	2 - 4
	Oleic (cis-9-Octadecenoic acid)	C ₁₈ H ₃₄ O ₂	1	20 - 30
	Linoleic (cis-9,cis-12-Octadecadienoic acid)	C ₁₈ H ₃₂ O ₂	2	50 - 58
	Linolenic (cis-9,cis-12,cis-15-Octadecatrienoic acid)	C ₁₈ H ₃₀ O ₂	3	5 - 10

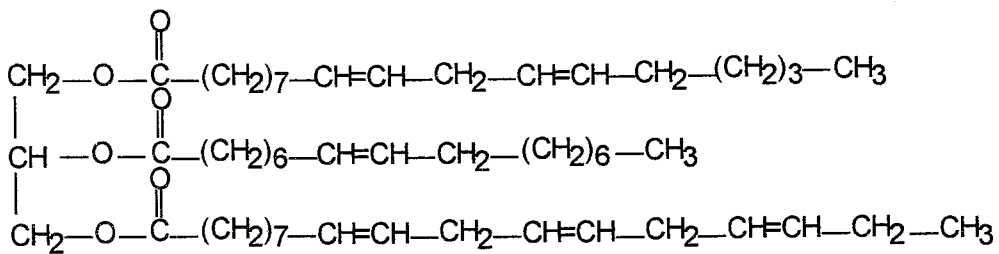


FIGURE 1.2. A representative structure of soybean oil.

1.1.2. Polymerization of Glyceride Oils

Polymerization of triacylglycerides result in the formation of dimers, trimers and sometimes of oligomers via autoxidation, by heat or by adding free radical initiators. However, the polymerization of triacylglycerides to high molecular weight polymers through their double bonds has not been observed yet.

Autoxidation is an important process occurring between unsaturated oils and atmospheric oxygen. The primary autoxidation products of unsaturated oils are allylic hydroperoxides. The double bonds remain but may have changed position and configuration from their original form. The change of an oil film from a viscous sticky liquid to a dry hard film via autoxidation involves the decomposition of the hydroperoxides and other oxygenated products. Associated with the decomposition reactions is the formation of dimers and oligomers of the triacylglyceride with a cross-linked structure

The union of two fatty acids in a Diels Alder reaction requires the presence of conjugated double bonds in one of the fatty acid radicals. Thus in the case of non-conjugated oils, it is necessary to postulate a preliminary isomerization to yield double bonds in a conjugated position [2].

Dimerization of fatty acids or their derivatives can also be carried out by using a free radical initiator; generally di-tert-butyl peroxide. The dimer acids differ from those derived from thermal polymerization in that they have an open chain structure and contain unsaturation equivalent to the original fatty acid. Treatment of methyl stearate at 130°C with di-tert-butyl peroxide results in dimerization, via the carbon atom α - to the ester group and the formation of tert-butanol as shown in Figure 1.5.

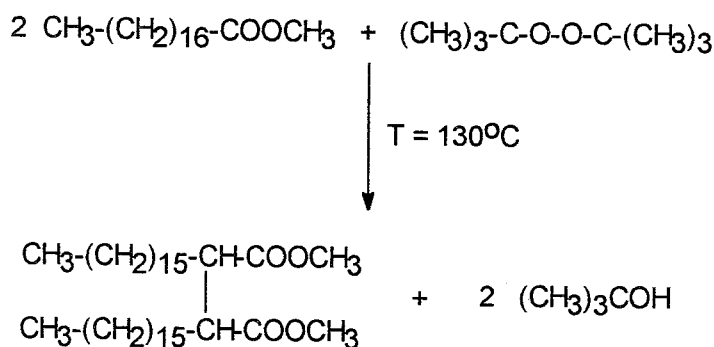


FIGURE 1.5. Dimerization of methyl α -eleostearate in presence of di-tert-butyl peroxide at 130°C.

In the case of oleates, linoleates, and linolenates on the other hand, the peroxide attack is predominantly at the methylene group α to the unsaturated portion of the molecule, since these are much more susceptible to radical reactions than the methylene α to the carboxyl group. Therefore the coupling takes place through the resonating radicals formed at the allylic positions [4].

1.2. Alkyd Resins

Alkyd resins represent a class of polymers that are used extensively in surface coating formulations because of their low cost and versatility. The term alkyd resin is often used in a restrictive manner to describe a fatty acid modified polyester. The principal alkyd components are therefore polyol, polybasic acid and fatty acid or the oil. Alkyds with relatively high fatty acid contents are called long oil alkyds; if the oil percent is relatively low, then the alkyd is designated as short oil alkyd. Glycerol is the workhorse polyol component of alkyd resins closely followed by pentaerythritol. Other polyols used in alkyd resin formulations include sorbitol, diethylene glycol and neopentyl glycol. The most important polybasic acid for alkyd resins is the phthalic acid which is used in the form of its anhydride. Maleic anhydride and fumaric acid are also used with amounts of one to ten per cent of the total phthalic anhydride content.

Fatty acid modified polyesters are prepared by a number of processes and each has commercial or technical considerations to recommend it. The two most common procedures are the fatty acid and the alcoholysis or the monoglyceride processes.

1.2.1. Fatty Acid Process

The fatty acid process in its simplest form involves the simultaneous condensation of the polyol, dibasic acid and fatty acid usually at temperatures of 200-240⁰C. This method allows greater freedom in formulation because any polyhydric alcohol or blend can be used. In the most common procedure the entire charge of fatty acids, polyol and dibasic acids is heated and maintained at temperatures of 200-240⁰C until the desired alkyd specifications are obtained [5]. Figure 1. 6. shows the idealized structure of an alkyd obtained from fatty acid process in which the resin components are the glycerol, phthalic anhydride and the monobasic fatty acid [4].

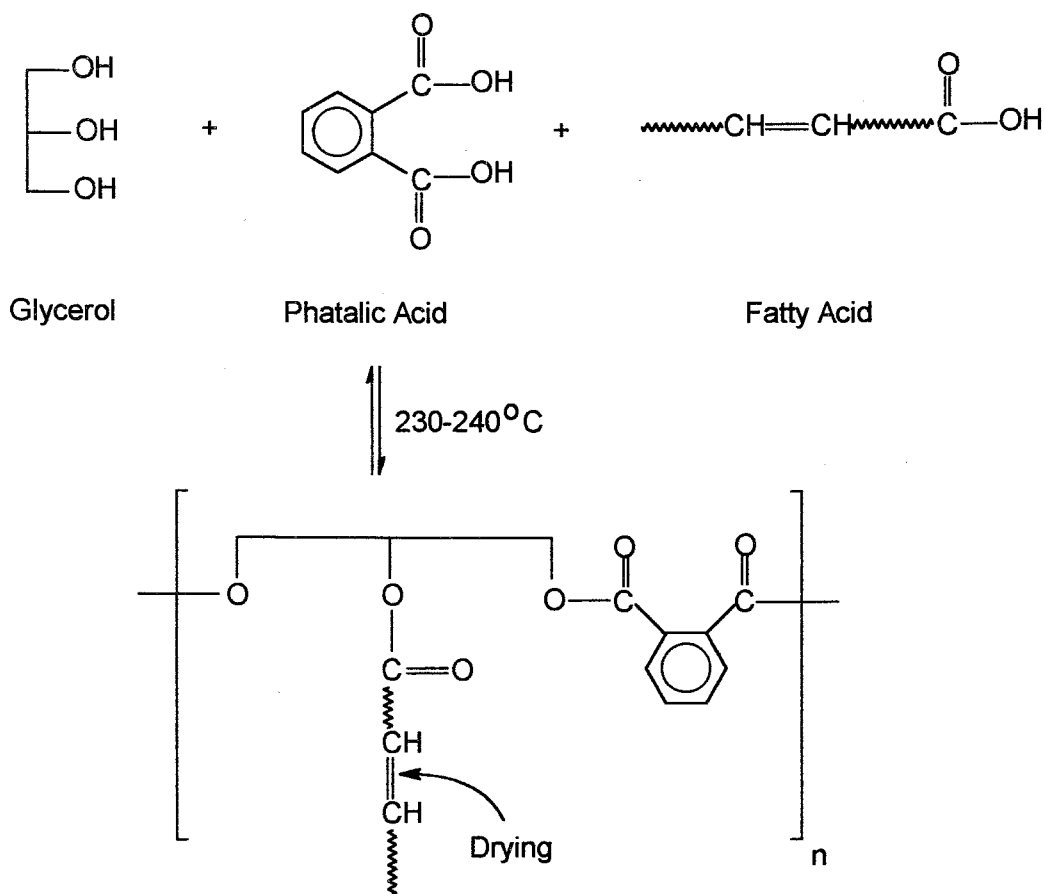


FIGURE 1. 6. Idealized structure of an alkyd obtained from fatty acid process. Alkyd resin components : glycerol, phthalic anhydride, fatty acid.

1.2.2. Alcoholysis or Monoglyceride Process

Because the source of monobasic acid is most often a naturally occurring glyceride oil and glycerol often forms at least a part of the polyol component of an alkyd, a mixture of an oil, a polyol and a dibasic acid or anhydride seems a reasonable starting point to produce alkyds. However if such a mixture is heated together, the polyol reacts solely with the dibasic component, and a useless heterogeneous mixture is obtained. The polyester is insoluble in the oil phase and rapidly forms an unmodified polyester which gels at a low degree of reaction. This incompatibility is overcome by first allowing the triglyceride oil to react with glycerol or other polyol in presence of a catalyst at temperatures of 225-250°C. When glycerol is used, the glycerolysis reaction can be represented in an idealized

manner with the first chemical equation shown in Figure 1.7. After the monoglyceride formation, when a dibasic acid such as phthalic is added, a homogenous resin results [4].

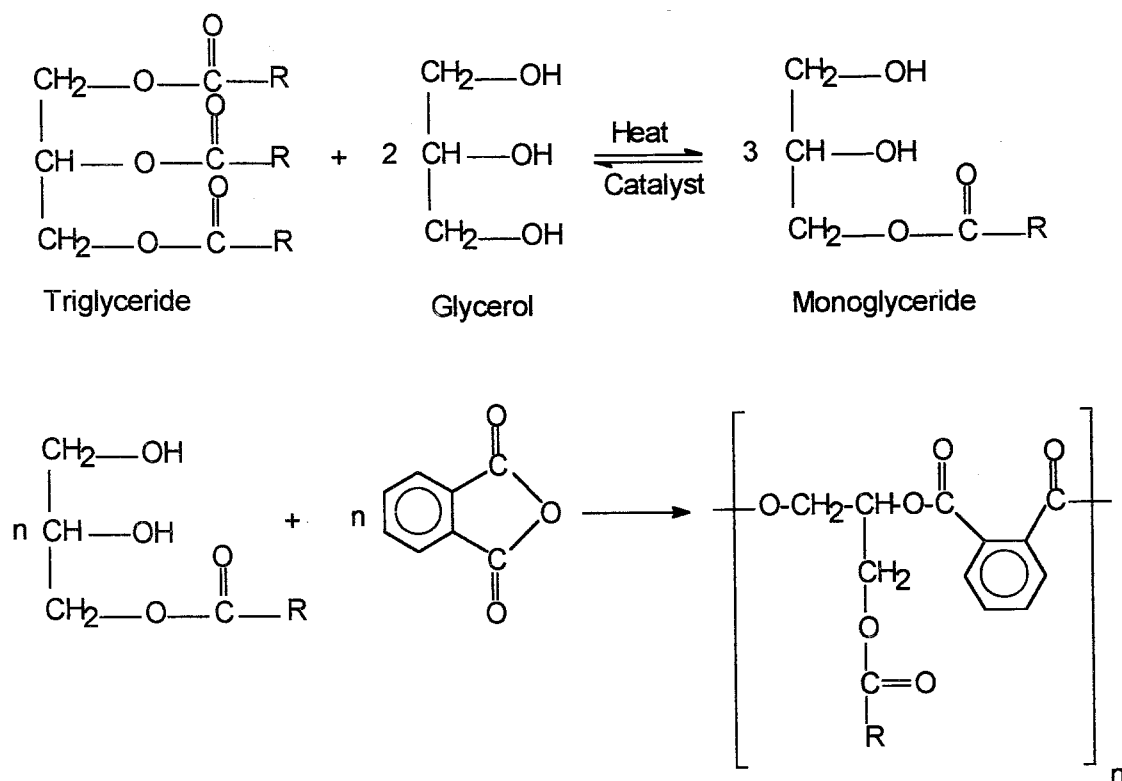


FIGURE 1.7. Idealized structure of an alkyd obtained from the alcholysis process.

Alkyd resin components: glycerol, phthalic anhydride, fatty acid.

Since, the first step of our synthesis involves the glycerolysis of soybean oil, a summary of the general characteristics of this complicated reaction will be given in the following section.

1.2.2.a. General Charecteristics of Fat and Oil Glycerolysis.

“With the possible exception of catalytic hydrogenation, few if any reactions in the realm of oleochemistry are as complex as fat glycerolysis. To compound the confusion associated with this reaction, the chemical literature abounds with examples of inconsistencies and half truths pertaining to it.” [6].

Actually the reaction used to represent the glycerolysis reaction in Figure 1.7. is a simplification. In reality, alcoholysis with glycerol results in an equilibrium consisting of mainly the different isomers of monoglycerides as well as the diglycerides and some unchanged triglyceride and free glycerol. These possible reaction products are shown in Figure 1.8. [4].

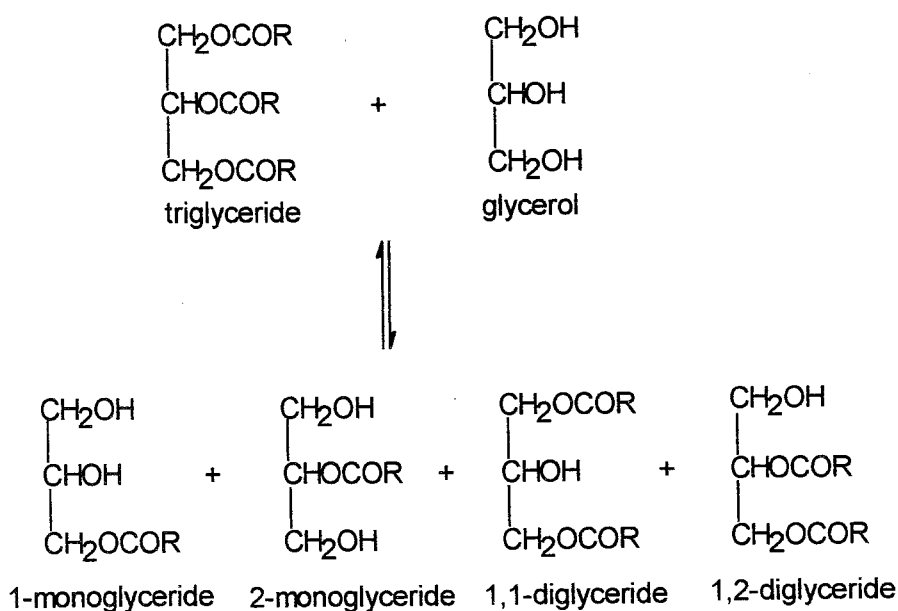


FIGURE 1.8. The possible reaction products resulting from glycerolysis of a triglyceride.

The 2-monoglyceride occurs in every reaction, at every temperature but generally in the range of 5-8 % at low temperatures to up to about 30 % at the very highest temperatures, of the total monoglyceride formed. There seems to be a temperature dependent equilibrium between 1- and 2- monoglycerides, and as a consequence of this temperature dependent equilibrium, the 2- isomer interchanges and thus decreases during cooling of reaction mixtures, with the corresponding increase of the 1-monoglyceride. It has been proposed by Bradner and Berkmeier that the preference for primary hydroxyl acylation, as represented by appropriate equation constants is about 2.3 at 200°C, and at room temperature, from six to ten, so that there is a shift of the equilibrium from 2- to 1-groups on cooling and that at room temperature the equilibrium is only slowly attained the

solid state. It has also been claimed that the intermolecular rearrangement of the acyl groups is largely arrested by cooling with solid monoglycerides [7].

The reaction is reversible when it is carried out homogenously or nearly homogenously as under conditions of superemulsification and is subject to Law of Mass Action. As a direct consequence of this, it is obvious that the use of excess glycerol over the two moles required results in the displacement of equilibrium to the right and thus higher total monoglycerides. Large percentages of glycerol may be used if it can be made soluble by employing a large amount of soap forming catalyst or if the reaction is conducted in a higher boiling solvent in which glycerol and glycerides are mutually soluble [2].

The main difficulty in achieving practical success in fat glycerolysis is in establishing a sufficient degree of homogeneity or mutual solubility, of the hydrophilic glycerol in the initial hydrophobic triglyceride fat or in subsequent fat like phases. Glycerol, at room temperature, is only soluble in common fats to the extent of 4%. This is less than the theoretical two moles required to react overall, and, thus no possibility exists for the use of excess glycerol to force the reaction to completion at room temperature. Consequently elevated temperatures must be used to increase the solubility of glycerol in the fat phases and today this temperature range is about 220-260°C.

At the end of glycerolysis reactions at high temperatures, as the reaction product is cooled, the solubility of excess glycerol in monoglyceride rich medium decreases and some of the excess glycerol separates as a lower layer. As the glycerol separates from the product the reaction reverses itself. To prevent this reversion, either catalyst neutralization is carried out in order to take the advantage of substantially lower rate of reaction both forward and backward of the uncatalyzed system or the reaction product is rapidly cooled to a temperature at which the reversion velocity is nil.

Glycerolysis reactions are catalyzed, preferably by alkaline catalysts like NaOH, KOH, $\text{Ca}(\text{OH})_2$ or with CaO even SrO or the sodium salts of lower aliphatic alcohols such as methanol, ethanol, tert-butanol. Alkaline catalysts are believed to function as emulsifiers; since alkalies generate small quantities of soap from free fatty acids present in all fats. Invariably emulsification of the media aids reactivity as the two otherwise immiscible or insoluble reactants are brought into more intimate contact with one another. Therefore the action of all catalysts could be attributed at least in part to that of emulsification [6].

Agitation throughout the reaction is necessary to throw the heavy glycerol layer up, into the lighter triglyceride layer especially in the initial part of the reaction. The use of inert gas such as nitrogen prevents oxidation and prevents the discoloration of the product, it also intensifies the effect of agitation. Generally the cycle times of glycerolysis reactions are in the neighborhood of four hours.

1.2.2.b. Patented Glycerolysis Processing.

The existing patented technology for both batch and continuous glycerolysis processing is summarized in a review paper by Norman O. V. Sontag [6]. Conventional batch type fat glycerolysis generally involve (a) optimal use of heat and agitation to maximize the solubility of glycerol in the fatty phases; (b) use of excess glycerol over the theoretical two moles required and removal of excess at the end of the glycerolysis reaction; (c) use of an emulsifier catalyst system; (d) catalyst neutralization, although not exclusively in all the known processes after completion of glycerolysis and before glycerol excess removal and cooling.

One obvious way to create an environment in which the Law of Mass Action can operate satisfactorily is to dissolve both glycerol and fat in a mutual solvent. Therefore a number of solvent fat glycerolyses have been reported or patented. By interesterification of one part by weight of hydrogenated soybean oil with one part of glycerol, in pyridine, 78 % monoglycerides, calculated on a monoglyceride basis has been obtained. Yields of monoglyceride up to 90 % by catalytic glycerolysis of natural fats in pyridine solution has

also been reported [8]. Phenol, cresols and, 1,4 dioxane are the other solvents used for fat glycerolysis. Solvents offer prospects of high yields at relatively low temperatures, but disadvantages in their handling, toxicity, noxious odors and the need to remove them completely from products are the reasons for the limited effort that has been directed to solvent glycerolysis [6].

It has been appreciated for over forty years that sodium salt of fatty acids, is an excellent emulsifier for fat glycerolyses in that it permits the use of higher effective glycerol concentrations in a state where more intimate contact and reactivity of glycerol and fat or partial fat are vastly promoted. Edeler and Richardson in two U.S. patents assigned to Protector and Gamble Company [9], [10] showed that with 1.4-2 % commercial soap based on glycerol, coco nut oil charge, monoglyceride yields could be nearly 97 %. A typical coco nut oil glycerolysis at 250⁰C without additon of soap on the other hand afforded only 68 % yield monoglycerides.

It has also been reported that under conditions of superemulsified media achieved through sonic energy, monoglyceride yields could nearly be about 95 % for hydrogenated cottonseed oil glycerolysis at 255⁰C. And still another patent work suggests a monoglyceride of 91 % with CO₂ catalyzed pressure glycerolysis of castor oil. The patent claims that “aqueous CO₂” is the catalyst implying that water is included in the charge [6].

Apart from the conventional batch type fat glycerolysis reactions, several investigations have been made for the enzymatic glycerolysis of triacylglycerides using lipase enzymes as a catalyst. High yields of monoglycerides from 60 to 90 % by weight could be obtained at ambient temperatures for several kinds of fats and oils, under a variety of conditions [11-13]

1.2.3. Modifications of Alkyd Resins

The wide spectrum of properties of alkyd resins is broadened by modification with a wide variety of reactive chemicals and other polymeric materials. Some of these reactive materials are urea, melamine and phenol formaldehyde resins, vinyl and epoxy resins, polyisocyanates and polyamides. Therefore the literature abounds with examples of different alkyd resin preparations involving modifications with one of these reactive chemicals [14,15].

The unsaturation in the fatty acid groups of the alkyds may allow interactions with some reactive vinyl monomers such as acrylonitrile. Vinyl or acrylic modified alkyds can be prepared by blending of the two polymer entities; intended copolymerization involving the unsaturation of the fatty acids; or chemical combination of the polymers by other functional groups, usually with an ester linkage between the component polymers. The most widely used method is the reaction in solution of a vinyl monomer with an alkyd resin containing centers of unsaturation, in presence of a peroxide initiator. The materials derived are not true copolymers and homogeneity of product is no criterium of copolymerization. Vinylated or acrylated alkyds are mixtures of drying oil modified alkyd, low molecular weight vinyl or acrylic polymer and some graft copolymer, which probably functions as a solubilizing agent [5]. In a representative patent work, Everard and Spoor prepared aliphatic hydrocarbon soluble styrenated alkyd resins by copolymerizing tall oil alkyd with styrene in presence of a chain transfer agent and a radical initiator such as di-tert-butyl peroxide at temperatures above 155°C. The resulting product was suitable for use in quick drying decorator paints, one-coat industrial paints, and printing inks [16].

1.3. Maleic anhydride

Maleic anhydride is one of the primary components of both unsaturated polyesters and alkyd resins. The structure of maleic anhydride is shown in Figure 1.9.

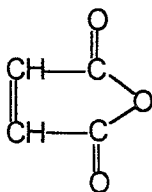


FIGURE 1.9. The structure of maleic anhydride.

The unsaturated linkage in maleic anhydride is activated due to conjugation with carbonyl groups. As a result, maleic anhydride not only undergoes reactions that are typical of an olefin, but it enters into reactions such as nucleophilic addition. The electrophilic character of the double bond produced by conjugation plays a significant role in a number of reactions of maleic anhydride, including Diels-Alder and photo reactions. Thus in addition to its internal anhydride function, maleic anhydride possesses an activity at the double bond and this property separates it from other anhydrides such as phthalic, succinic, etc.

1.3.1. Reactions of Olefinic Function

Maleic anhydride undergoes various reactions through the reactive double bond, including addition of amines, alcohols, sulfuric compounds and halogens and also different types of Michael and Diels Alder reactions.

The primary reaction of maleic anhydride with alcohols is esterification. However, under the influence of a strong base such as sodium alkoxide, esters of maleic anhydride, can add the elements of alcohol across the double bond in a Micheal Reaction as shown in Figure 1.10.

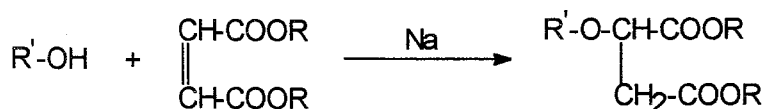


FIGURE 1.10. Addition of alchols to esters of maleic anhydride through the double bond.

Ethanol reportedly gave a sixty per cent yield of the adduct ($\text{R}^1 = \text{Et}$). Methanol and iso-butyl alcohol were also reported to react. The reaction product of maleic anhydride with methanol probably the mono-methyl maleate, on treatment with two equivalents of sodium in excess of methanol also gave 19 % of the acid ($\text{R}^1 = \text{Me}$) isolated as its salt [17]. Similarly, the addition of sodium salts of n-decyl and n-dodecyl alchols on diethyl maleate has also been reported [18].

1.3.2. Reactions of Anhydride Function

1.3.2.a. Hydrolysis.

Maleic anhydride like most other anhydrides, can be hydrolized to the corresponding acid. Simple dissolution of maleic anhydride suffices for the purpose. The reaction is shown in Figure 1.10.

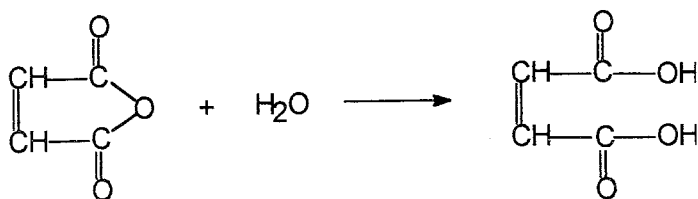


FIGURE 1.11. Hydrolysis of maleic anhydride.

The reaction is exothermic as expected. Controlled hydrolysis produces the cis (Z) acid. By prolonged warming the maleic acid can be converted to fumaric acid which is trans (E) acid as shown in Figure 1. 12. This phenomenon is common among all the ring opened products from the anhydride.

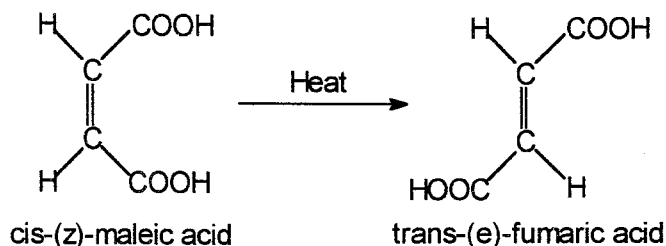


FIGURE 1.12. The isomerization of the cis- (Z) maleic acid to trans – (E) acid by heat.

1.3.2.b. Esterification

Maleic anhydride, being a cyclic anhydride, can give rise to two ester derivatives upon reaction with an alcohol as shown in Figure 1.13.

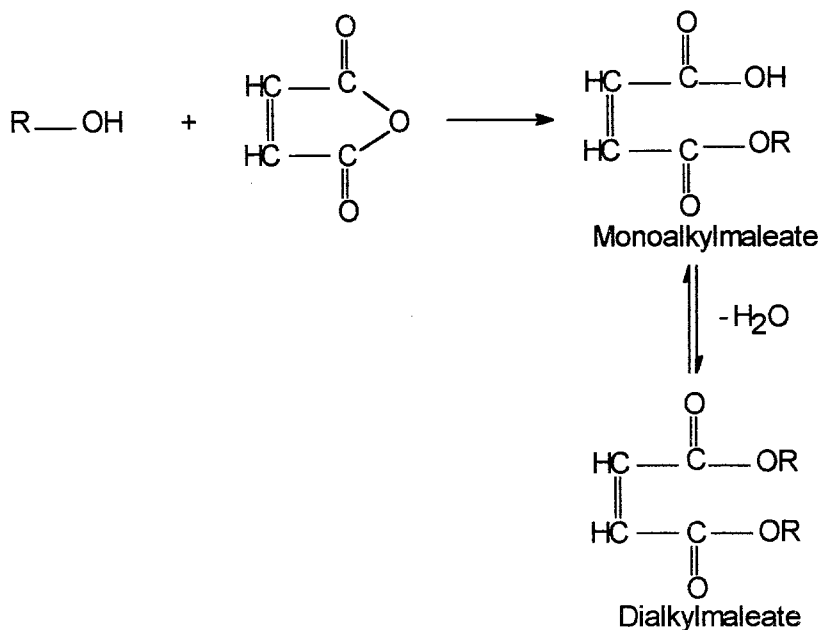


FIGURE 1.13. Esterification of maleic anhydride with alcohols to form mono- and di-alkyl maleates.

It has been reported that maleic anhydride reacts almost instantaneously with a number of primary alcohols, such as methyl, ethyl or propyl alcohol even at room temperature to form mono-alkyl maleates and that the secondary alcohol such as iso-propyl alcohol does not react at all [19]. However in more recent studies, this claim has been discarded. J. Grobelny, in an NMR study of the unsaturated polyesters prepared from maleic anhydride and 1,2-propylene glycol has reported the formation of the mono-maleate half esters from both primary and secondary hydroxyls of the alcohol [20]. In any case, the reaction between maleic anhydride and lower primary alcohols is nearly complete at room temperature. However half ester formation with long chain alcohols such as do-decyl, tri-decyl, and hepta-decyl alcohols is not as rapid as expected and an optimum temperature for each conversion has been reported. Mono ester formation is a key reaction involving maleic anhydride and a number of its polymeric derivatives. This is an efficient reaction, since in many cases, attainment of homogeneity may give quantitative yield. Mono-esters made from maleic anhydride and polyhydroxy alcohols, e.g., pentaerythritol, sorbitol, di-pentaerythritol and tri-pentaerythritol, have been claimed to be useful as detergent builders [21].

The mono-ester formation is a relatively easy step and is irreversible. The di-ester formation is not as easy as, the mono-ester now has all the attributes of a carboxylic acid and hence the second step of esterification is an equilibrium process. Since this forward reaction is slow, a catalyst is usually employed. This allows attainment of equilibrium in a reasonable amount of time. Removal of the product of reaction, in this case water by azeotropic agents has been employed as well [17].

1.3.3. Maleic anhydride in Condensation Polymers

When considering the use of maleic anhydride in condensation polymers, it is automatic to think of unsaturated polyesters. Unsaturated polyesters are based on macro molecules with a polyester backbone in which an unsaturated acid or combination of a saturated with an unsaturated acid are condensed with a glycol. Commercial unsaturated

polyester resin formulations consist essentially of a linear resin, a cross-linking monomer, and inhibitors to retard cross-linking until the resin is used by the fabricator. The simplest member of polyester series, ethylene maleate or ethylene fumurate is prepared as shown in Figure 1.14. Saturated dibasic acids are commonly employed with the unsaturated acid to modify the degree of unsaturation and thereby the reactivity of the resulting polyester [17].

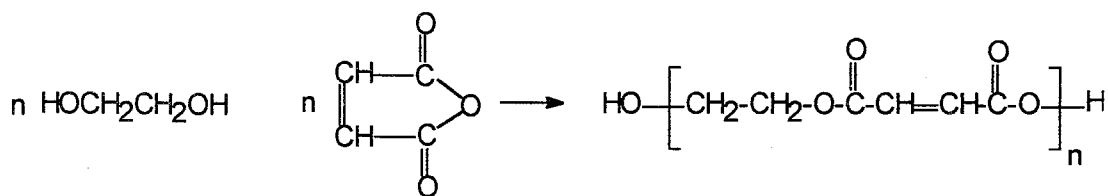


FIGURE 1.14. Ethylene glycol – Maleic anhydride Unsaturated Polyester.

The first quantitative data for the preparation of maleate polyesters with glycerol was published by Keinle and Petke [22]. It has been claimed that the reaction is complicated by intraesterification reactions and the occurrence of addition polymerization along with interesterification. It has also been reported that the total water evolved in the glyceryl maleate reaction is smaller than that resulting from the corresponding glycerol succinate reaction; but that the average molecular weights of the two resins at the corresponding stages are equal and this fact has been suggested as the evidence in the favor of the formation of addition polymerization.

The commercial resins are typically solutions of the unsaturated polyester polymers dissolved in unsaturated coreactant liquid monomers such as styrene. Free radical catalysts initiate cross-linking reactions involving the unsaturated polyester polymer and the unsaturated coreactant monomer, rapidly transforming the low viscosity resin into a rigid thermoset plastic state, having a three dimensional polymer network. A simple representation of this cross-linked structure is shown in Figure 1.15. for the ethylene maleate polyester.

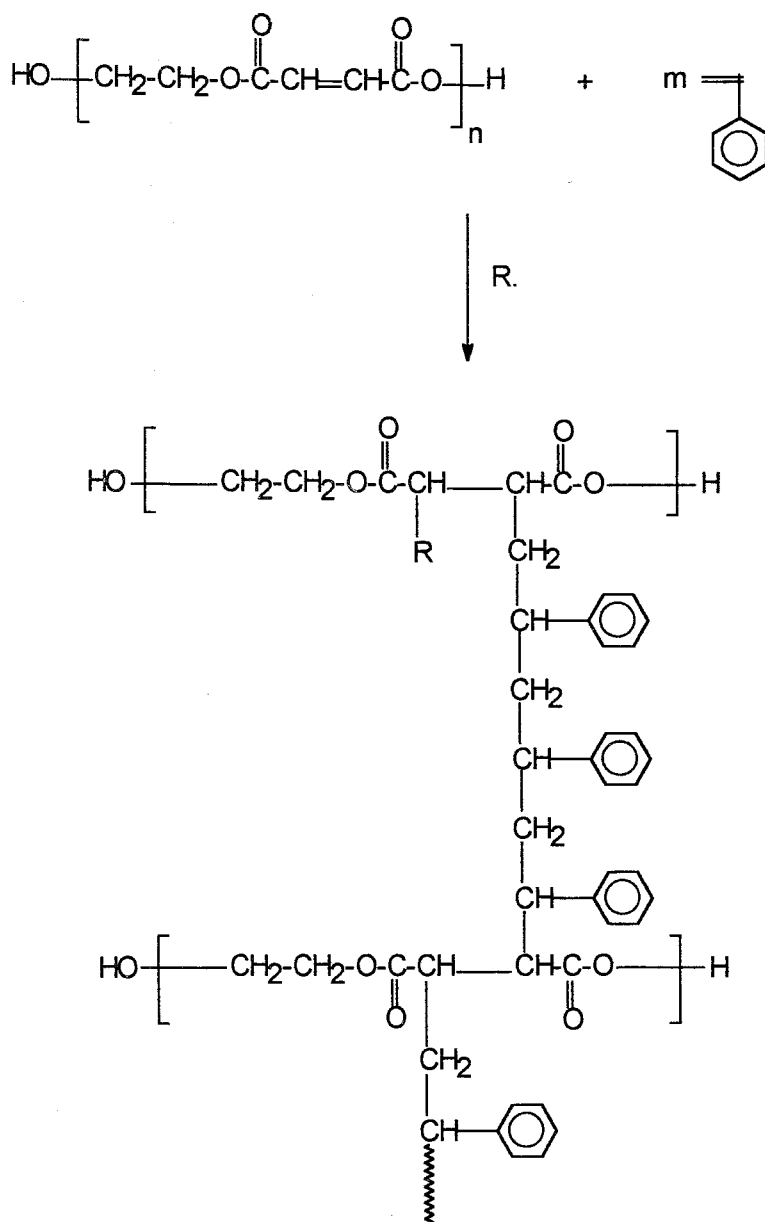


FIGURE 1.15. A simple representation of the cross-linked structure of the ethylene maleate polyester with styrene.

Polyester products are used in many markets of commercial significance, ranging from automotive to construction and electrical applications. The success of the unsaturated polyester resins in fabricated composites has been observed in conjunction with glass fiber or other types of reinforcing material. Petrochemicals supply most functional derivatives used for manufacture of polyester resins. Lower glycols are derived almost exclusively by

the oxidation of ethylene or propylene. Aromatic dibasic acids are produced by the oxidation of xylenes and maleic anhydride by the oxidation of benzene.

The synthesis of a new liquid molding resin that may match the wide spectrum of properties and performance versatility of unsaturated polyesters which is produced either totally or partially from the renewable sources would be very useful both in terms of cost and environment.

1.3.4. Maleate – Fumarate Isomerization

Maleic anhydride or fumaric acid confers the fundamental unsaturation to the polyester which provides the reactivity with coreactant monomers such as styrene. Maleic anhydride exists in a planar configuration of low conformational energy and the conversion into maleate diesters and oligomers during the initial polyesterification reaction increases the strain energy across the double bond because of steric hindrance. At lower reaction temperatures, i.e., 160°C , the maleate esters remain in this condition, but as the reaction temperature exceeds 180°C , they effectively relieve the strain by transforming to more planar trans-fumarate isomer which reduces steric congestion as shown in Figure 1.16. [5].

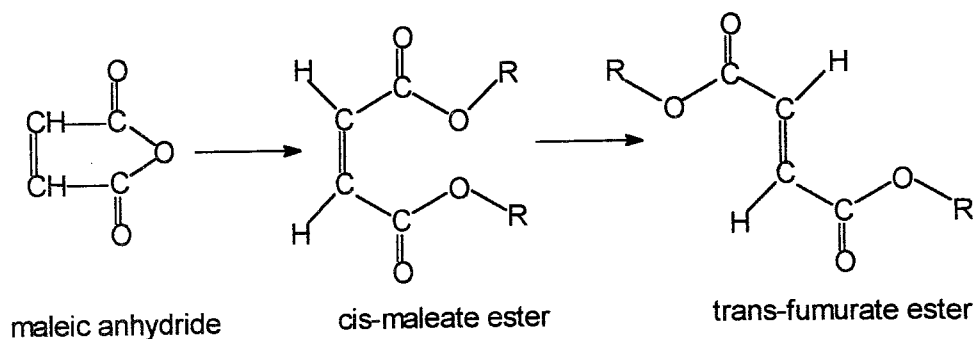


FIGURE 1.16. Cis-maleate trans-fumarate isomerization.

The presence of fumarate unsaturation sites on the polyester chain plays a key role in determining the physical and chemical properties of the final cross-linked polyesters owing to a higher reactivity of the trans isomer in copolymerization with vinyl monomers. The extent of maleate-fumarate transformation was reported to depend on the nature of the diols, presence of aromatic acids, concentration of catalyst, degree of polymerization as well as on the reaction temperature and time [20].

2. STATEMENT OF THE PROBLEM

Research in petrochemistry since 1945 has provided an extensive range of raw materials for polyester resin synthesis. Polyester products are widely used in automotive, construction and electrical applications in conjunction with glass fiber or other types of reinforcing material. The synthesis of new polymers from renewable resources such as plant or animal oil that matches the unique properties of the unsaturated polyesters would be very valuable with regard to diminishing petroleum resources and increasing petroleum prices. The polymerization of oils however, is only achieved with some appropriate modifications on the glyceride molecule and the polymers obtained are always low modulus polymers that are widely used in surface coatings as in the case of varnishes and alkyd resins. So the synthesis of a rigid, high modulus polymer from soybean oil which is the highest volume vegetable oil produced in the world would offer great advantages over the unsaturated polyesters due to its lower cost and for being much more environmentally friendly.

In this research project, the ester functional group of the triacylglyceride will firstly be hydrolyzed by a well known process; glycerolysis to give mono- and diglycerides which will then be maleinized to give a modified oil capable of undergoing radical polymerization. The glycerolysis and maleinization steps are summarized in Figure 2.1. The radical initiated homopolymerization of the maleates and their copolymerization with styrene is shown in Figure 2.2.

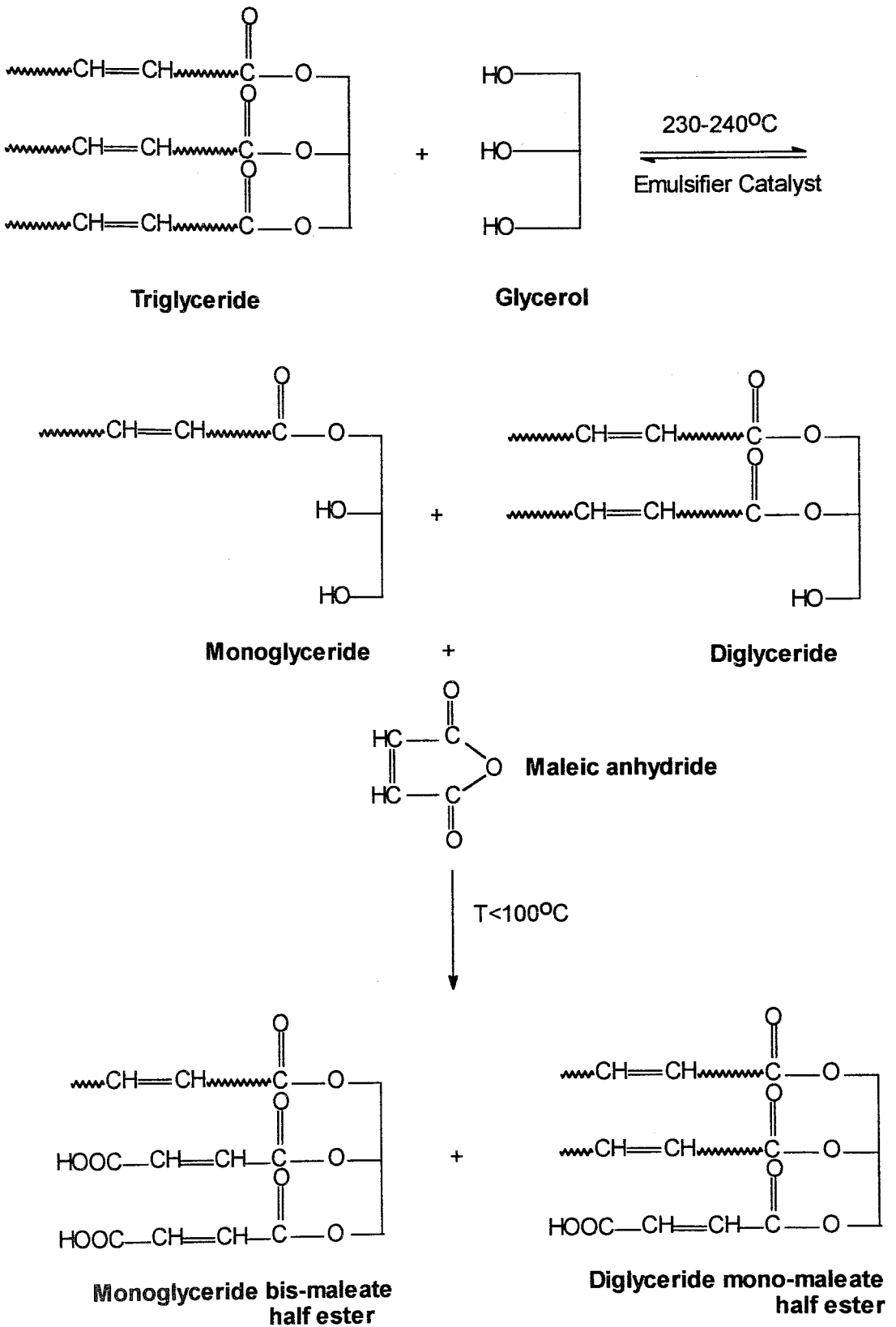
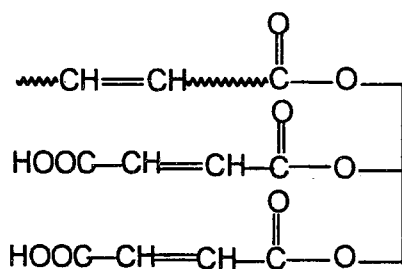


FIGURE 2.1. Synthesis of Soybean oil Monoglyceride Maleates.



Monoglyceride bis-maleate half ester

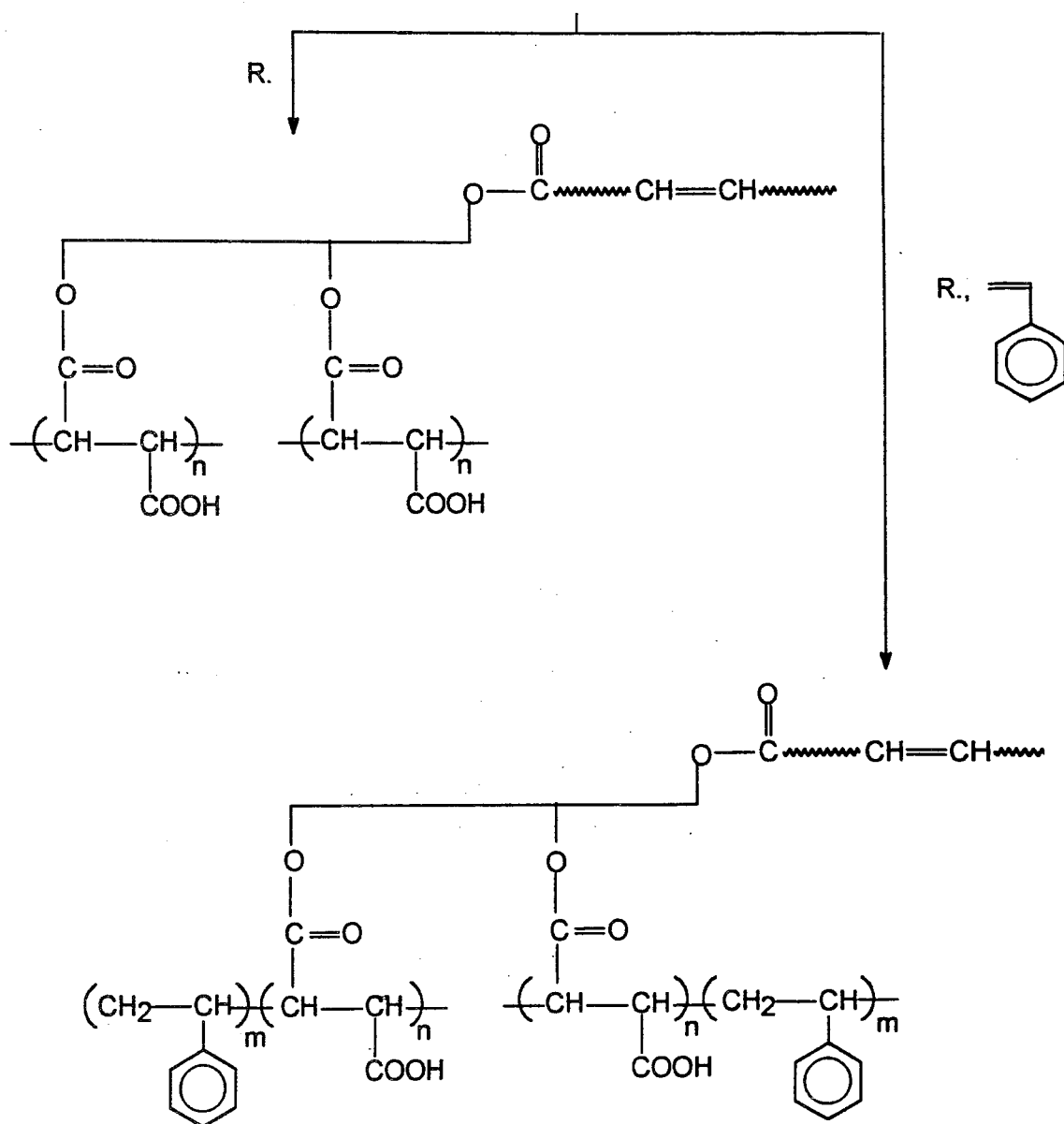


FIGURE 2.2. Radical initiated homo- and styrene co-polymerization of soybean oil monoglyceride maleates.

The first step of the synthesis involves the glycerolysis of the triglyceride oil at 230-240°C in presence of an emulsifier catalyst to give a mixture of products at equilibrium that consists of mainly the mono- and diglycerides as well as some unreacted triglyceride and free glycerol. In this research, we aim to maximize monoglycerides and minimize triglycerides in the product. In the second step, the addition of maleic anhydride to the mixture of glycerides at 80-100°C with either an acid or base catalyst will produce the corresponding maleate half esters without a by product. It should be noted here that, the excess glycerol in the glycerolysis product will also be maleinized to yield the corresponding mono-, bis-, and tris- maleate half esters although not depicted in Figure 2.1. Finally, at the third step, the radical initiated homopolymerization of the maleate half ester groups and their copolymerization with styrene should produce the born cross-linked polymers whose structures are depicted in Figure 2.2. assuming that the monoglyceride bis-maleate half ester is the only repeating unit. The diglyceride and glycerol maleate half esters will also polymerize and take their place in the polymer network structure.

The ultimate aim of this research project is to produce a high molecular weight unsaturated monomer that is soluble in an unsaturated co-reactant monomer such as styrene; forming a liquid molding resin that is capable of cross-linking in presence of free radical initiators without a by product and therefore transforming the low viscosity resin into a rigid thermoset in the mold. The resulting material should be a high modulus rigid polymer that is suitable for fiber reinforcement.

Different catalysts and different reaction conditions will be examined to improve the reaction yields. The structural analysis of the products will be done with ¹H-NMR, IR and Mass Spectroscopy. The industrial usefulness of the polymers obtained will also be examined.

3. RESULTS AND DISCUSSION

3.1. Glycerolysis of Soybean Oil

Glycerolysis of oils are well known reactions mainly used in production of alkyd resins as was described in Section 1.2.2. The glycerolysis reaction involves the transesterification of the triglyceride with glycerol in presence of a catalyst at temperatures of 220-260°C. The glycerolysis reaction can be represented in an idealized manner with the chemical equation shown in Figure 3.1.

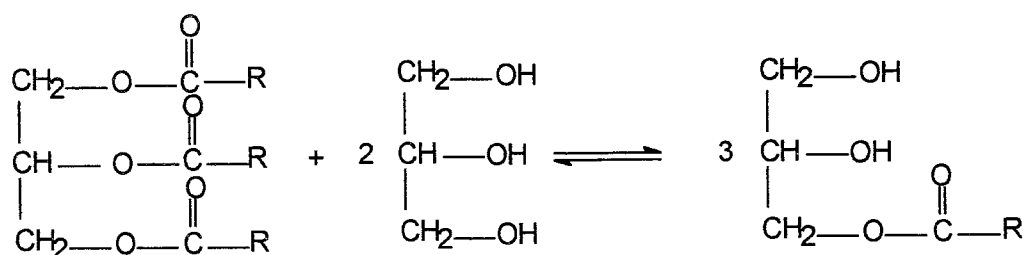


FIGURE 3.1. Glycerolysis of triglyceride.

The equation shown in Figure 3.1., however is only a simplification. In reality, the reaction results in an equilibrium that consists of mainly the monoglycerides as well as the diglycerides and some unchanged triglycerides and unreacted glycerol. The glycerolysis reaction is a reversible reaction, therefore the use of excess glycerol over the two moles theoretically required results in the displacement of the equilibrium to right, giving a higher concentration of monoglycerides. The amount of excess glycerol that might be used, however, is limited by the miscibility of the glycerol in the reaction mixture at the reaction temperature. Large percentages of excess glycerol may only be used if a surfactant is used to emulsify the glycerol in the oil, or if the reaction is conducted in a high boiling solvent in which glycerol and glycerides are all soluble.

In our work, we used 137 % excess glycerol. Glycerol was first heated to about 220-230°C under N_2 atmosphere and kept at this temperature for two hours to distill a trace amount of the water present in the glycerol. Otherwise, water may cause the hydrolysis of the triglyceride to fatty acids. Soybean oil was then added to the previously heated glycerol in five portions, at one hour intervals, in order to create a larger amount of excess glycerol in each addition. To permit the use of such an amount of excess glycerol, we performed our reaction with 1 % commercial soap, as an emulsifier catalyst, based on soybean oil charge. Edeler and Richardson, in the same manner, in two US Patents assigned to Procter and Gamble Company [9,10] showed that with 1.4 to 2.0 % commercial soap based on coco-nut oil glycerol charge, monoglyceride yields could be nearly 97 %.

We discovered that, if at the end of five hours at 230-240°C, the SOMG reaction product is rapidly cooled to room temperature in about five minutes some of the excess glycerol separates as a lower layer. The separated glycerol forms about 48 % of the excess glycerol in the SOMG product. This rapid cooling process is an important part of the procedure because at the end of glycerolysis reactions at high temperatures, as the reaction product is left for cooling, the solubility of excess glycerol in the SOMG product decreases so that some of the excess glycerol separates as a lower layer. As glycerol concentration in the SOMG product decreases, the reaction may revert itself to regenerate the di- and triglycerides. To prevent this reversion, either catalyst neutralization is carried out in order to take the advantage of the lower rate of both forward and backward reaction or the crude reaction product is cooled to a temperature at which the reaction rate is essentially nill. We did not prefer catalyst neutralization since neutralization of the soap may result in the formation of some by products which are to be left in the product one of which is water as described in two US Patents assigned to Best Foods Inc. [23,24]. In US Patent, 2.197.340 glycerol and H_2SO_4 are added to the monoglyceride product that contains the glycerides and the soap to form free fatty acid and Na_2SO_4 . The free fatty acids then esterify the glycerol to produce additional mono- and diglycerides with water. We therefore performed only the rapid cooling of the product to room temperature so that the rate of reaction was so much lowered that essentially no reversion could take place. Rapid cooling is also a suitable procedure for the large scale synthesis of soybean oil based resins.

We believe that, by creating a medium of such an excess glycerol that may go into intimate contact with the triglyceride oil, and with the aid of a sufficient amount of soap catalyst and lastly by preventing the reverse reaction with a rapid cooling process, we maximized the monoglyceride yield and minimized the amount of unreacted triglyceride oil. In fact, when the crude reaction mixture was extracted with pentane, no unreacted triglyceride could be extracted. This proves that there is no unreacted triglyceride left in our reaction mixture. Minimizing the amount of unreacted triglyceride oil is essential since, in the maleinization of the SOMG product, the triglyceride oil with no free hydroxyls in its structure will give no reaction with maleic anhydride and thus will not polymerize in the final step. The unreacted triglyceride oil in a considerable amount in the SOMG product, therefore may deteriorate the final mechanical properties of the resulting polymers by acting as a plastifying agent.

After the separation of excess glycerol, IR and ^1H -NMR analysis were performed on the crude reaction mixture which showed the characteristic peaks of both the alcohol and the oil. In the IR spectrum of the SOMG product given in Figure 3.2., the broad band at 3384 cm^{-1} belongs to O-H stretching vibrations of the alcohol groups and the sharp peak at 1738 cm^{-1} is a characteristic peak for the C=O stretching vibration of the ester groups. The characteristic signals in the ^1H -NMR spectrum of soybean oil is given in Table 3.1. The ^1H -NMR spectrum of the SOMG product given in Figure 3.3. differs from that of soybean oil with an additional signal at 3.7 ppm that is characteristic for (CH-OH or $\text{CH}_2\text{-OH}$) and also a peak that changes its chemical shift between 3.5 and 4.5 ppm that belongs to OH protons of either the alcohol groups or the trace amount of water present in the product. We observed that this peak disappears upon D_2O exchange as shown in Figure 3.4.

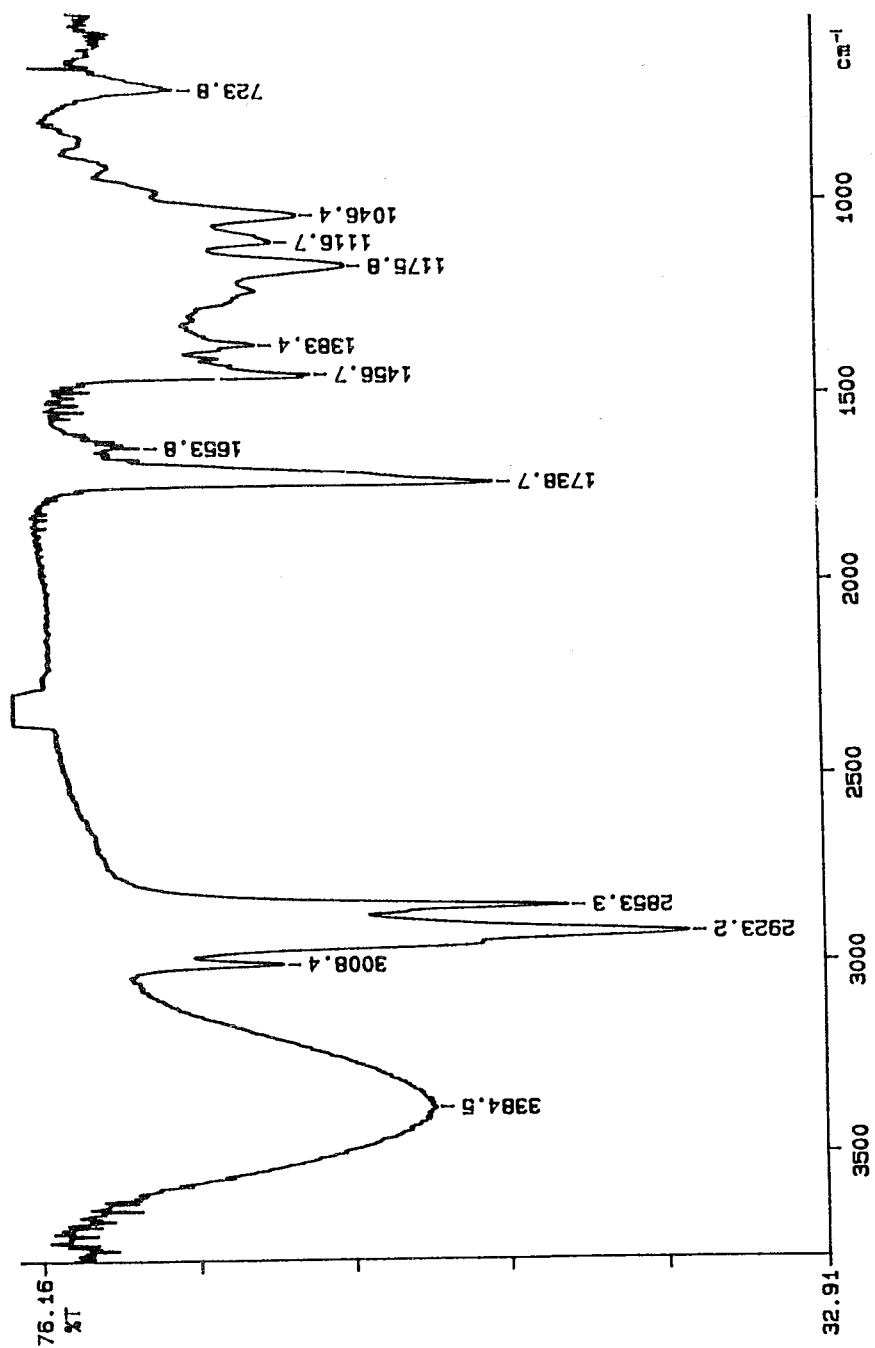


FIGURE 3.2. IR spectrum of SOMG.

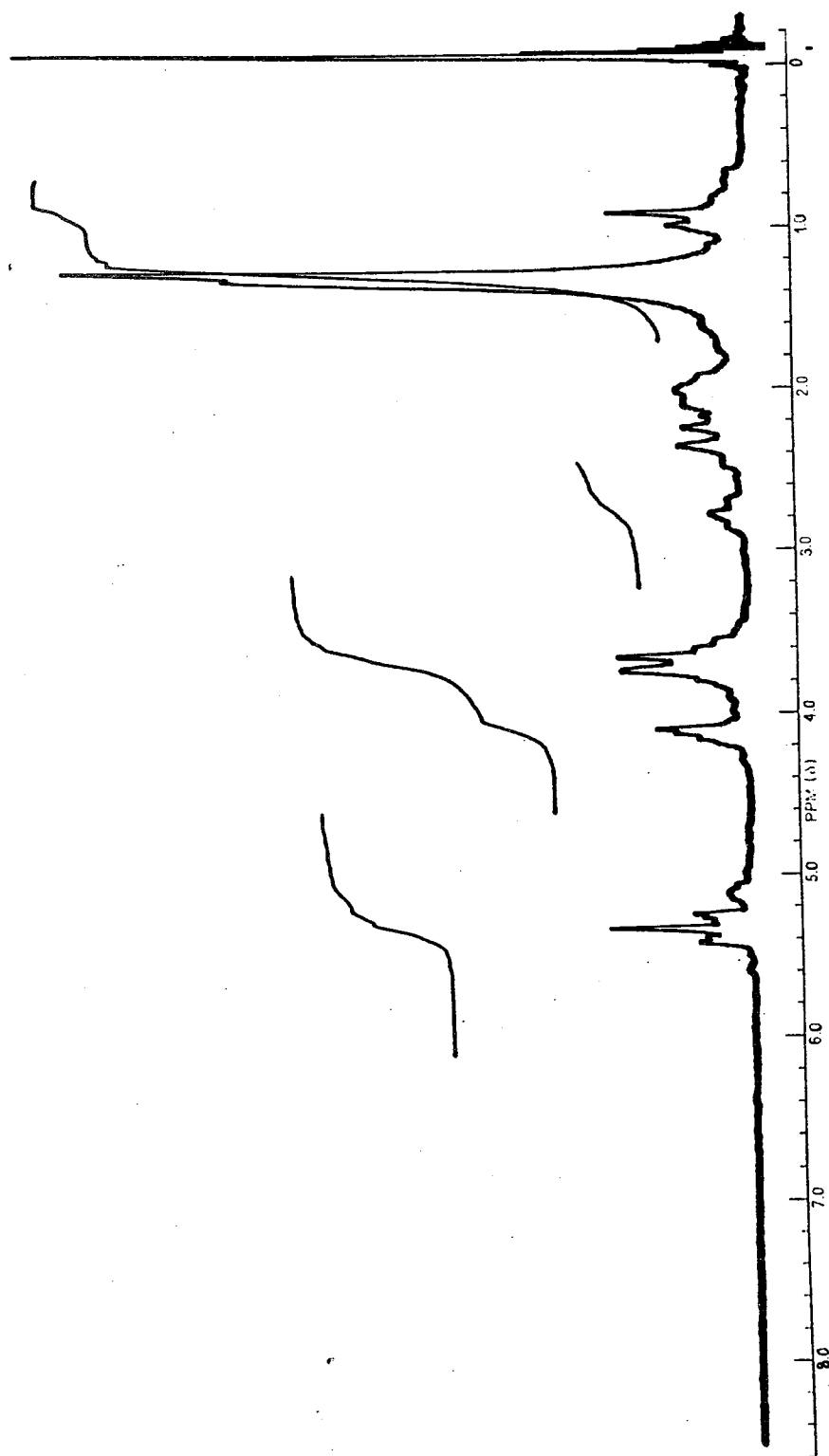


FIGURE 3.3. ^1H -NMR spectrum of SOMG (CDCl_3).

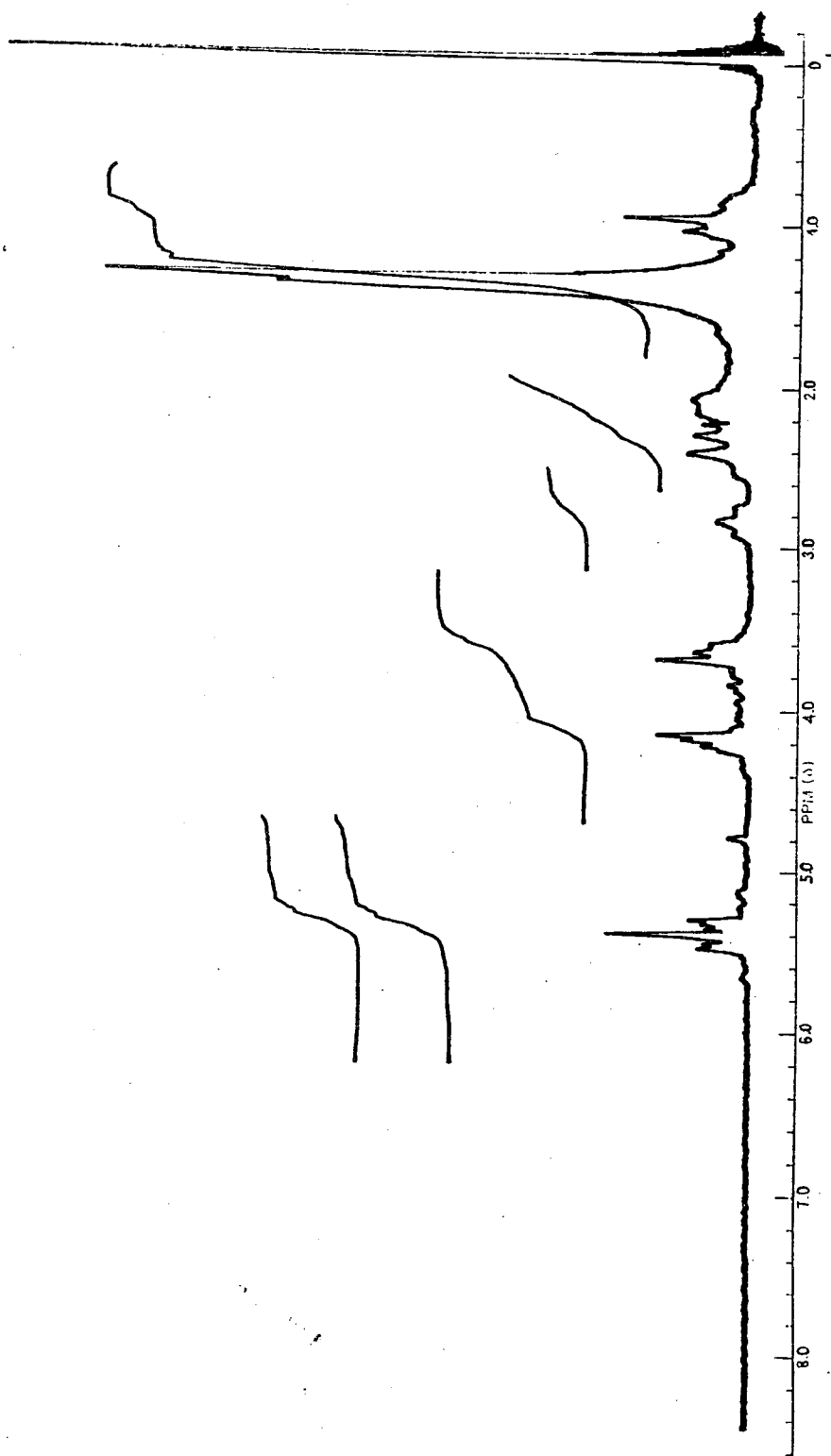




FIGURE 3.4. ^1H -NMR spectrum of SOMG ($\text{CDCl}_3 + \text{D}_2\text{O}$).

TABLE 3.1. Chemical shifts for different types of hydrogen nuclei in soybean oil triglycerides.

Type of Protons	Chemical Shift (ppm)
-CH ₃ (terminal)	0.9
-CH ₂ -	1.3
-CH ₂ -CH=CH-	2.0
-CH ₂ -(C=O)-O-	2.3
-CH=CH-CH ₂ -CH=CH-	2.8
-CH ₂ -O-(C=O)- 	4.2
-CH-O-(C=O)- 	5.1
-CH=CH-	5.3

Apart from the soap emulsified glycerolysis of soybean oil, the base (Ca(OH)₂) catalyzed glycerolysis of soybean oil was also carried out to perform the further maleinization reactions at different SOMG:MA weight ratios for mass analysis. The IR and ¹H-NMR data of this product showed the same characteristic peaks of the soap emulsified glycolysis product. In the Mass Spectrum of this SOMG product, shown in Figure 3.5., the peak at 355 corresponds to monoglyceride whereas the peak at 337 that is even more intense than the 355 peak corresponds to the dehydrated monoglyceride. The peak at 617 belongs to diglycerides whereas the peak at 599 belongs to dehydrated diglyceride. The signal for the triglyceride may either be matched with 860 or 906 peak assuming a molecular weight of 871.5 for soybean oil. Molecular weight of soybean oil was calculated by using the average fatty acid mole composition; 11 % palmitic acid, 4 % stearic acid, 25 % oleic acid, 51 % linoleic acid, and 9 % linolenic acid. Thus $MW_{\text{soybean oil}} = [((255 \times 0.11) + (283 \times 0.04) + (281 \times 0.25) + (279 \times 0.51) + (277 \times 0.09)) \times 3] + 41 = 871.52$. The peak at 729, however can not be matched with any possible reaction product of SOMG

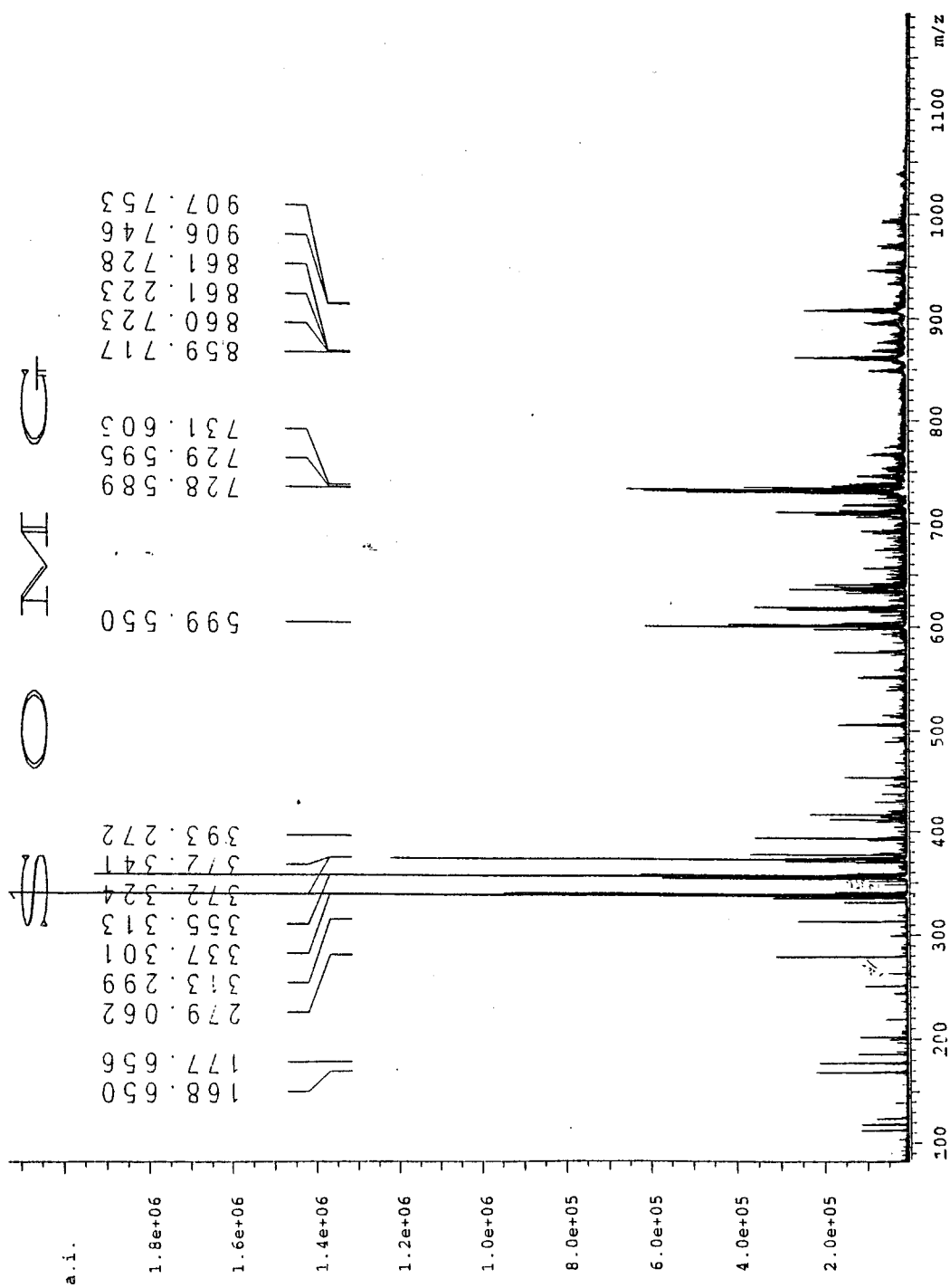


FIGURE 3.5. Mass spectrum of SOMG.

3.2. Maleinization of SOMG

The reaction of an alcohol with maleic anhydride in presence of either an acid or base catalyst can give rise to two different ester derivatives, one of which is monoalkylmaleate that results from an addition type of reaction, the other is dialkylmaleate that results from a condensation reaction between the alcohol and the anhydride. The structures of the mono- and dialkylmaleates are shown in Figure 3.6.

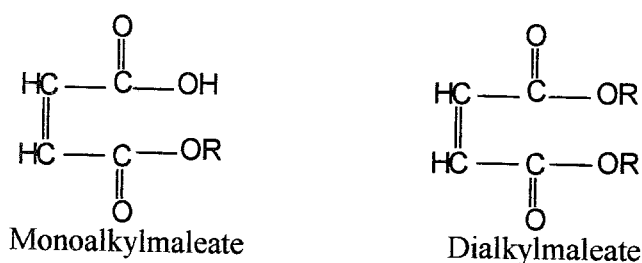


FIGURE 3.6. The structures of mono- and dialkylmaleates.

The reaction between lower primary alcohols and maleic anhydride to form monoalkylmaleates takes place very quickly at low temperatures whereas it has been reported that half ester formation with long chain alcohols such as dodecyl and heptadecyl alcohols is not as rapid as expected and necessitates an optimum temperature for each conversion [17]. In our work the maleinization of the SOMG product was performed under various conditions in which the SOMG : MA weight ratio, temperature and catalyst were the changing parameters to maximize the maleate half ester's yield. The related reactions' conditions and $^1\text{H-NMR}$ data are given in Table 3.2. Assuming that the number of fatty acid vinylic protons stays constant throughout the reaction, the ratio of the number of maleate vinylic protons to the number of fatty acid vinylic protons that is symbolized as N_m/N_{fa} in Table 3.2. gives a good comparison of the different reactions in terms of maleate yields.

TABLE 3.2. The conditions of the SOMG + MA reactions carried out and the ratio of the number of maleate and fumurate vilyic protons to the number of fatty acid vinylic protons according to ^1H -NMR data. [N_m = no of maleate vinylic protons; N_f = no of fumurate vinylic protons; N_{fa} = no of fatty acid vinylic protons].

Run No	SOMG : MA (Weight Ratio)	Catalyst	T ($^{\circ}\text{C}$)	Duration (Time spent out after MA addition)	$\frac{N_m}{N_{fa}}$	$\frac{N_f}{N_{fa}}$
1	2.34 : 1	NaOH	80-100	10minutes	0.370	—
				5 hours	0.388	—
2	1.76 : 1	NaOH	80-100	1 hour	0.357	—
				6 hours	0.588	—
3	1.50 : 1	NaOH	80-100	15 minutes	0.625	—
				6.5 hours	0.625	—
4	1.19 : 1	NaOH	80-100	50 minutes	0.500	—
				12.5 hours	0.300	0.150
5	1.50 : 1	H_2SO_4	50-70	2 hours	0.317	—
6	1.50 : 1	p-toluene sulfonic acid	50-60	15 minutes	0.322	—
				6 hours	0.330	—
7	1.50 : 1	N,N-dimethyl aniline	60-75	1 hour	0.550	—
				6.5 hours	0.660	—
8	1.50 : 1	2- methyl imidazole	80-100	3.5 hours	0.650	—
				5.5 hours	0.600	—
9*	1.50 : 1	2-methyl imidazole	80-100	35 minutes	0.800	—
				5 hours	0.853	—
10*	1.50 : 1	2-methyl imidazole	60-70	4 hours	0.705	—
11*	1.50 : 1 (MA added in in 3 portions)	2-methyl imidazole	80-90	15 minutes	0.580	—
				1.5 hours	0.730	—
				4 hours	0.821	0.143

TABLE 3.2. Continued.

Run No	SOMG : MA (Weight Ratio)	Catalyst	T (°C)	Duration (Time spent out after MA addition)	$\frac{N_m}{N_{fa}}$	$\frac{N_f}{N_{fa}}$
12*	1.50 : 1 (SOMG dried)	2- methyl imidazole	80-90	30 minutes	0.77	—
				4 hours	0.842	0.053
13	1.50 : 1	Heat	180-200	10 minutes	0.216	0.810
14*	1.00 : 2	2-methyl imidazole	90-100	3 hours	0.625	0.083
				5.5 hours	0.630	0.083

* Refers to reactions carried out in presence of trace amount of hydroquinone

Maximizing the monoglyceride yield in the glycerolysis step, and the monoglyceride bismaleate yield in the maleinization step are essential for us, since only by increasing the maleate half ester's yield, can we increase the amount of polymerizable groups and reach a higher cross-linking density that will result in a more rigid, tough polymer.

We carried out the maleinization reactions with different SOMG : MA weight ratios, since we do not know the exact amount of the mono- and diglycerides in the SOMG product. We can only predict the total number of moles of hydroxyls in our product since we know the amount of glycerol separated from the SOMG product at the end of glycerolysis reaction. It should be clear from the stoichiometry of the reaction that the total number of hydroxyl groups present in the final product is independent of the position of the equilibrium. Hydroxyl equivalents of all glycerolysis reaction products should be the same regardless of their equilibrium position and should be equal to three times the number of glycerol used. And, based on this assumption, only in the SOMG : MA = 1.19 : 1 weight ratio, maleic anhydride is in the right amount to maleinize all the hydroxyls present in the SOMG product.

A quick examination of the first four reactions in Table 3.2. shows that, the highest maleate half ester yield may only be obtained when the SOMG is in excess. The increase in maleic anhydride feed ratio increases the maleate half ester yield only when the SOMG is in excess. Thus, in (Reaction Run no: 4), the increase in maleic anhydride feed ratio does not increase the product half ester yield, instead decreases the yield, since SOMG is no more in excess in this weight ratio. This is contrary to the report by F. Siegel and K. Moran who claim that in the monoesterification of primary alcohols with the dibasic acid anhydrides, the amount of excess alcohol is of no importance, since in their work a 1:1 mole ratio of alcohol to anhydride gives the same result as that of 2:1 or 4:1 [19].

With regard to results of the first four reactions mentioned above, we decided that the best SOMG : MA weight ratio is 1.5 : 1, since this ratio gives the highest maleate half ester yield. We used different catalysts in our reactions including NaOH, N,N dimethyl aniline, 2-methyl imidazole as base catalysts and H₂SO₄ and p- toluene sulfonic acid as acid catalysts. 2-methyl imidazole was the best among the base catalysts used, the reaction with a weight ratio of SOMG : MA = 1.5 : 1 was completed in five hours at 80-100°C. N,N dimethyl aniline showed poor catalytic effect and the product obtained from reaction catalyzed by N,N dimethyl aniline gave dark green colored polymers since aromatic amines may form blue complexes with cobalt ion which is used later as an accelerator in the polymerization step.

In the best procedure for the reaction, SOMG was heated to about 60°C, maleic anhydride was then added and as it melted, 2-methyl imidazole was added to the homogenous mixture. The reaction was then followed with both IR and ¹H-NMR. In the IR, the 1779, 1849 cm⁻¹ peaks that belong to (C=O) asymmetric and symmetric stretching vibrations respectively and the 696 cm⁻¹ peak that belongs to olefinic (C-H) bending vibrations are characteristic for maleic anhydride. Throughout the reaction, these peaks decrease in intensity and finally disappear showing that maleic anhydride is consumed as shown in Figure 3.7. The formation of the broad acid band between 2500-3600 cm⁻¹ and the increase in the intensity of the peak at 1643 cm⁻¹ showing the (C=C) double bond stretching vibrations are the signs for the formation of maleate half esters. In the ¹H-NMR,

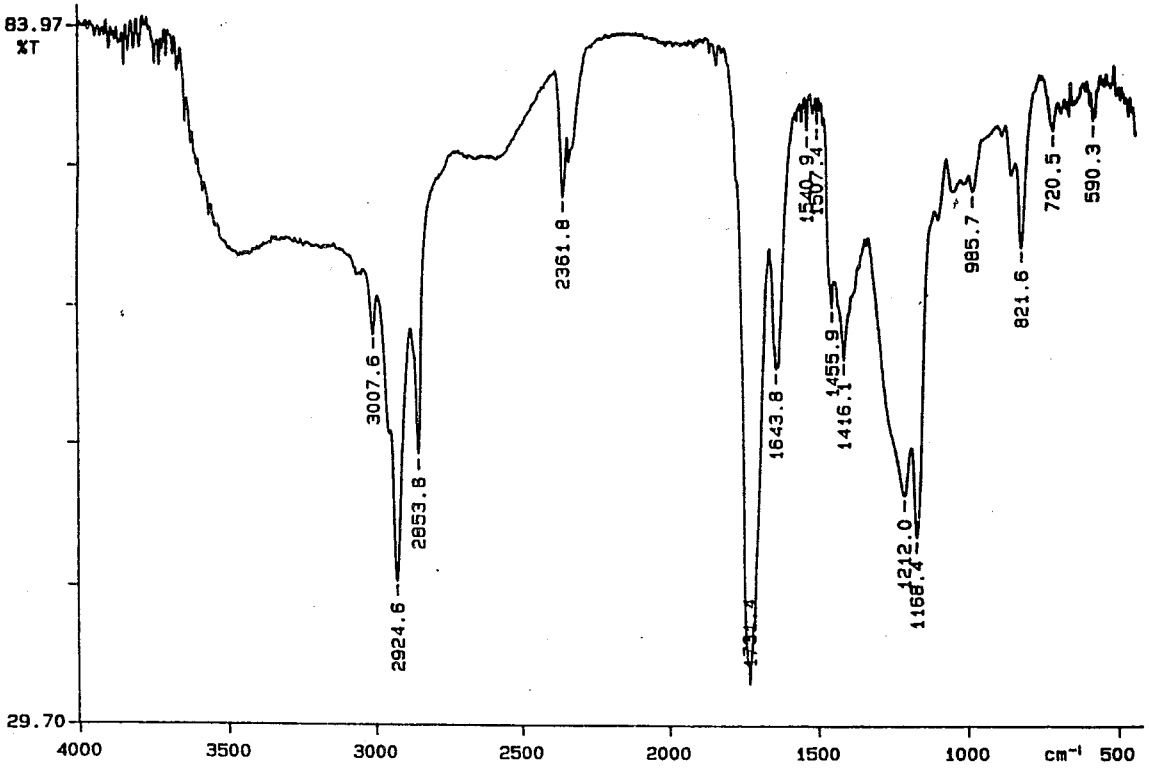


FIGURE 3.7 (a). IR spectrum of SOMG/MA ; beginning of reaction.

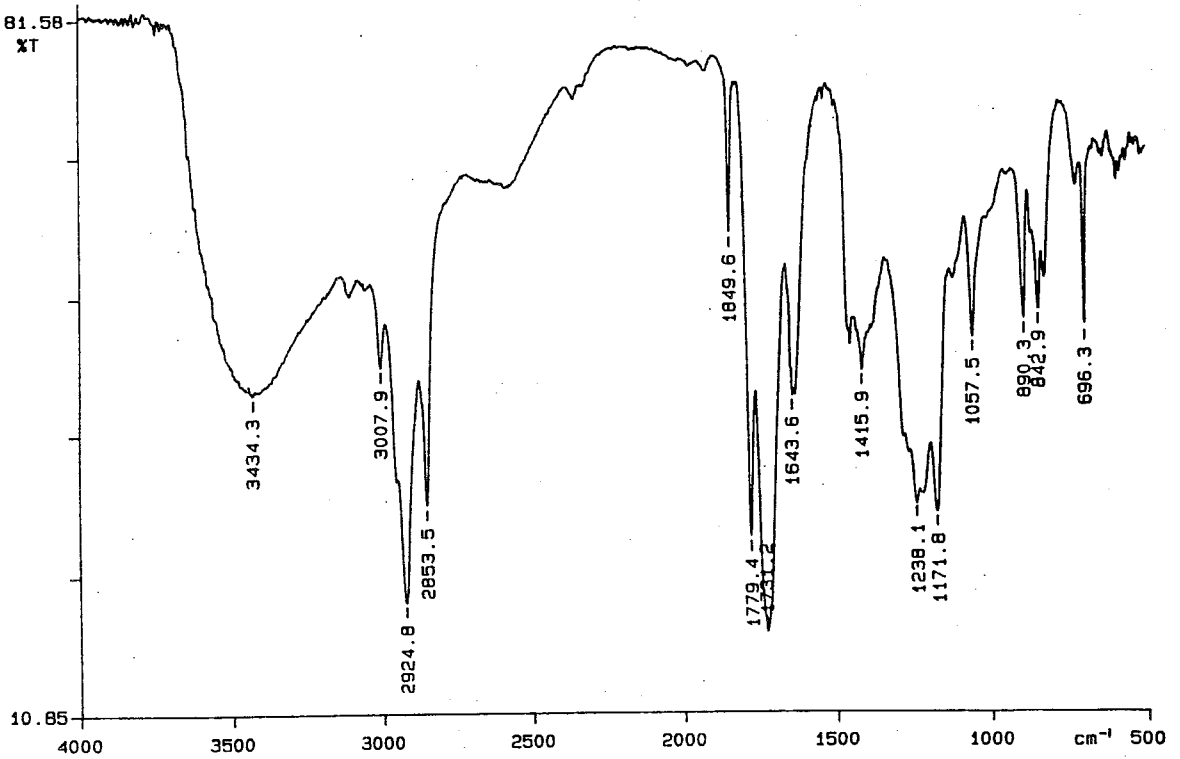


FIGURE 3.7 (b). IR spectrum of SOMG/MA ; end of reaction.

maleic anhydride is characterized with a sharp peak at 7.1 ppm. As the reaction proceeds, this peak decreases in intensity and the formation of the maleate half esters is proven by the appearance of the peak at 6.35 ppm that belongs to the maleate vinylic protons. Higher temperatures and longer reaction times may also result in the formation of trace amounts of fumurate half esters produced by cis to trans isomerization of the maleate double bond whose chemical shift appears around 6.9 ppm. These assignments are in well agreement with J.Grobelney [20] who suggests the same chemical shift values for the corresponding maleate and fumurate halfesters obtained from reactions of excess amounts of maleic anhydride with various diols including 1,2-propylene glycol. The ^1H -NMR spectrum of the reaction product at the end of five and half hours at 80- 100 $^{\circ}\text{C}$ is given in Figure 3.8. Apart from the appearance of the 6.3 ppm peak that belongs to maleate vinylic protons, the disappearance of the 3.7 ppm peak that is characteristic for the (CH-OH , $\text{CH}_2\text{-OH}$) and the appearance of the acid protons' signal at 8.95 ppm are the additional clues for the formation of the SOMG maleate halfesters.

Assuming that the number of fatty acid vinylic protons stays constant throughout the reaction, the ratio of the number of the maleic anhydride vinylic protons to the number of fatty acid vinylic protons at the beginning of the reaction should be equal to that of maleate and fumurate vinylic protons at the end of reaction. However, we found out that this ratio at the end of our reactions was smaller than the expected value which means that the reactive double bonds of the maleate half esters are consumed by some side reactions. In an attempt to prevent any radical side reaction that takes place, the reaction, (Run no:8 Table 3.2.) was repeated under the same conditions with the addition of a trace amount of hydroquinone; a known free radical inhibitor (Run no:9 Table 3.2). A considerable increase in the maleate half ester ratio was thus observed from 0.6 to 0.8 as can be seen in Table 3.2. The ^1H -NMR spectrum of this reaction product at the end of five and half hours at 80-100 $^{\circ}\text{C}$ is shown in Figure 3.9. for comparison. Thus we believe that there is some premature dimerization or polymerization of the maleates during this reaction which can be substantially prevented by the addition of a free radical inhibitor.

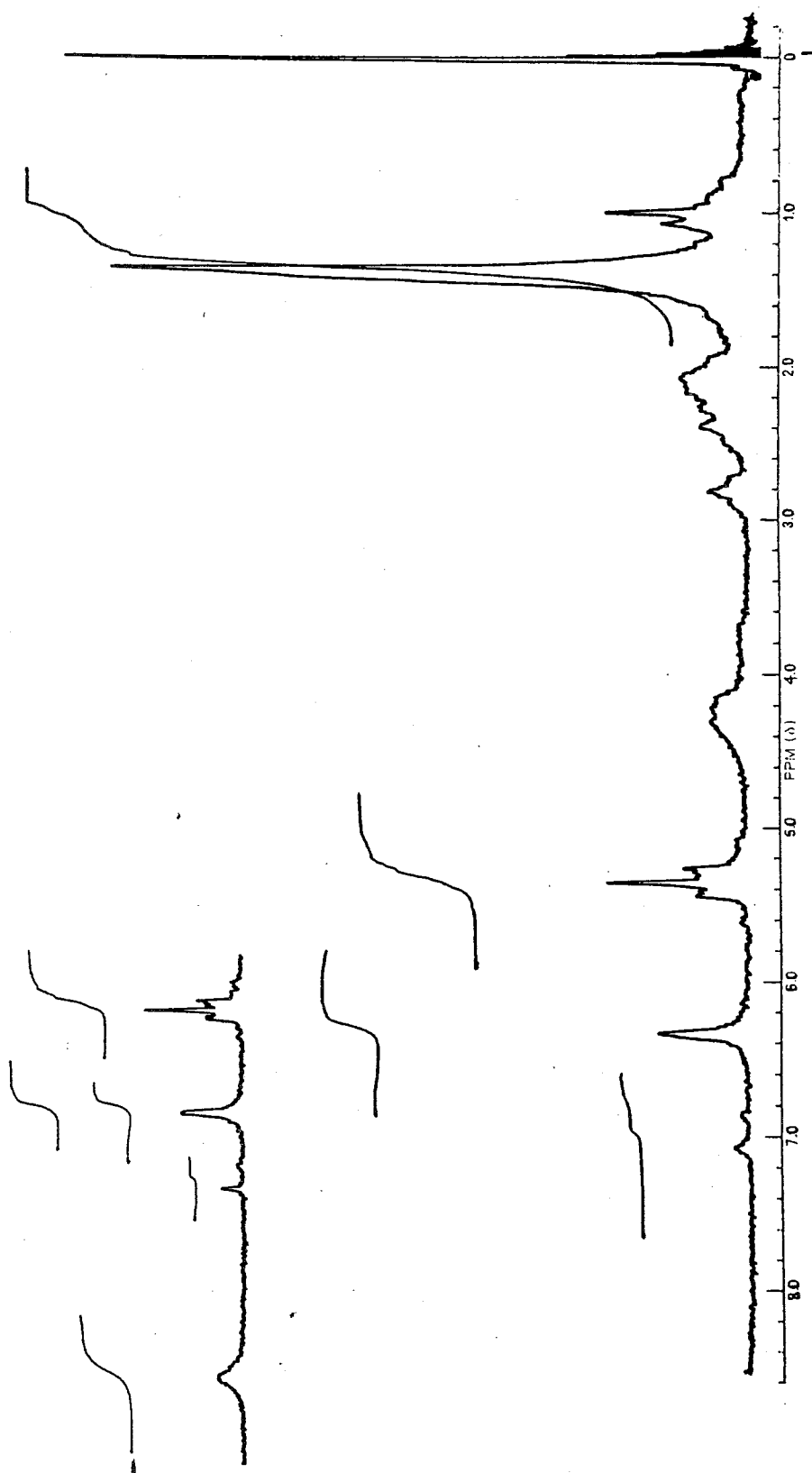


FIGURE 3.8. ^1H -NMR spectrum of SOMG/MA (CDCl_3).

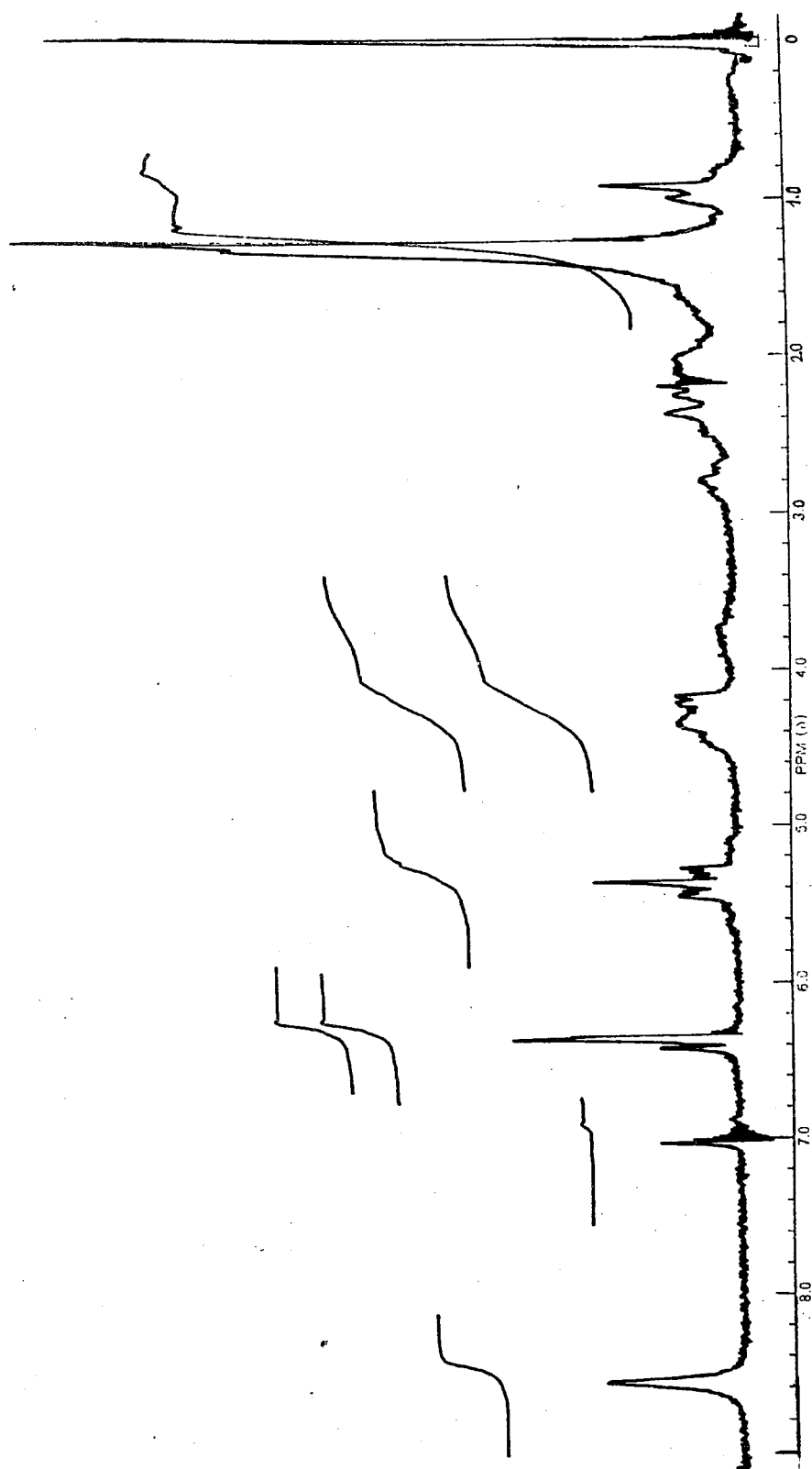
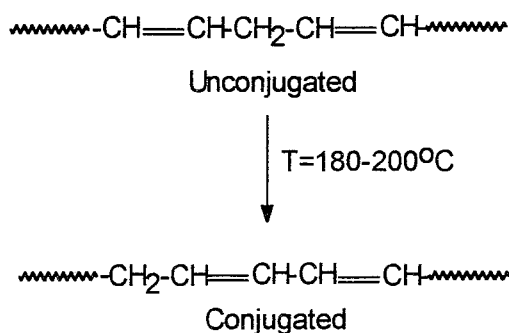


FIGURE 3.9. ^1H -NMR spectrum of SOMG/MA (Run no : 9, end of reaction) (CDCl_3).

Another possible side reaction that may explain the consumption of the reactive double bonds during the maleinization reactions might be the addition of the alcohol segments to the double bonds of maleate and fumarate half esters. The addition of alcohols to esters of maleic anhydride through the double bonds was previously mentioned in Section 1.3.1. and the related reaction was shown in Figure 1.7. In fact, Cristball J. and co-workers, in a series of separate works [25,26,27] carried on the preparation of unsaturated polyesters from maleic anhydride and various diols including ethylene glycol, 1,4 butylene glycol and 1,6 hexane diol observed the addition of glycol segments to double bonds. He also showed that, the fumarate fumarate double bond reactions that occur through a radical mechanism may lead to limited polymerization and cause gelation before cross-linking of the unsaturated polyesters takes place. However it must be noted here that, the temperature that these polyesterification reactions take place is between 160-190°C and is much higher than the temperature of the monoesterification reactions that we carried out.

The Diels Alder type of addition of maleic anhydride or maleate half esters to double bonds of the fatty acid residue on the triglyceride molecule may be another possible side reaction that accounts for the consumption of the reactive double bonds. Maleic anhydride functions as a dienophile in the Diels Alder reaction and adds to conjugated double bond systems of the fatty acids or of unsaturated fatty acids capable of generating them, as shown in Figure 3.10.



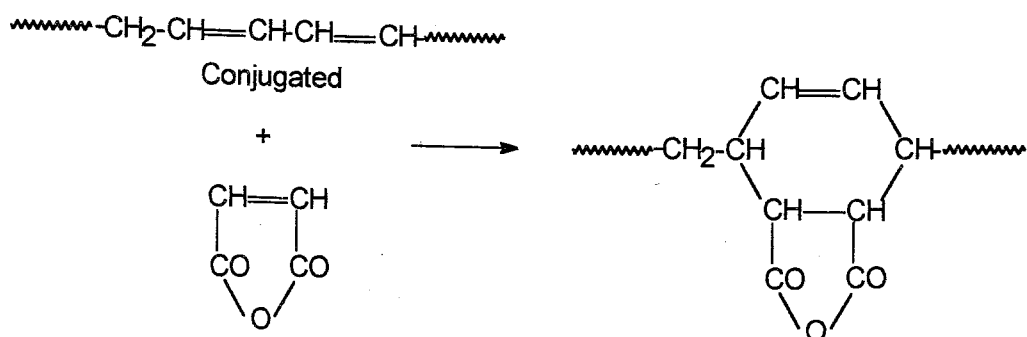


FIGURE 3.10. The Diels Alder type of addition of maleic anhydride to unsaturated fatty acids or their esters.

The reaction of maleic anhydride with conjugated dienes such as 9:11 or 10:12 fatty acids, proceeds readily at temperatures as low as 80°C provided that the double bonds of the oil are in a trans: trans configuration [4]. However by proposing this mechanism as a possible side reaction, we assume that at least some of the unconjugated unsaturation of soybean oil is isomerized to conjugated unsaturation and that the interconversion of cis to trans isomers also takes place during the glycerolysis of soybean oil, since the oil is processed at a temperature above 200°C for five and half hour. Unfortunately, no spectral evidence can be given for the above suggestions.

In acid catalyzed reactions, on the other hand we observed that, both p-toluene sulfonic acid and H₂SO₄ hydrolyze a certain amount of maleic anhydride to maleic acid which is insoluble in the reaction mixture and therefore separates from the mixture as a precipitate. The formation of maleic acid was confirmed in the ¹H-NMR analysis, with a sharp peak at 6.5 ppm in D₂O and a peak at 6.3 ppm in DMSO-d₆ which are both characteristic for maleic acid. The N_m / N_{fa} values obtained for reactions Run no: 5 and Run no: 6 were therefore very low as shown in Table 3.2. since the ¹H-NMR analysis were performed on the viscous liquid part of the crude reaction mixtures.

The hydrolysis of maleic anhydride to maleic acid in acid catalyzed reactions suggested that the SOMG product may contain a trace amount of water although in the IR spectrum of the SOMG product there was no sign of a fatty acid that would result from the hydrolysis of the triacylglyceride if water was present. We therefore dried the SOMG over Na_2SO_4 and carried out the maleinization reaction (Run no: 12) in Table 3.2. In this reaction, it was found out that maleic anhydride was consumed much slower than the other reactions and that at any time of the reaction, the product was much richer in terms of maleic anhydride when compared to other reactions carried out under the same conditions. Thus a comparison of the ^1H -NMR spectra of the reaction mixtures (Run no: 9) and (Run no: 12) about thirty minutes after maleic anhydride addition that are shown in Figure 3.11. and Figure 3.12. respectively, clearly demonstrate this difference. The product of the reaction carried over dried SOMG (Run no: 12) at the end of four hours reached a high maleate yield as can be figured out from the N_m/N_{fa} value in Table 3.2. although it still contained a certain amount of maleic anhydride. The ^1H -NMR spectrum of this reaction product is shown in Figure 3.13.

Another very important feature, that the ^1H -NMR data of these two reactions (Run no:9) and (Run no: 12) show is that , the maleate half ester formation proceeds very fast, especially at the beginning of the reactions, since the N_m/N_{fa} value in reaction (Run no: 9), for example, reaches 0.8 only in 30 minutes after maleic anhydride addition; this value then hardly increases to 0.85 in the following four and half hours. The same type of behaviour is also observed in reaction (Run no: 12). A possible explanation for this behavior may be that the primary hydroxyls of the mono- and diglycerides and glycerol readily react with maleic anhydride and form the huge amount of the product and that the secondary hydroxyls react slowly and thus increases the maleate yield only to a lower extent. This is in agreement with the known differences of reactivity of the primary and secondary hydroxyls towards esterification.

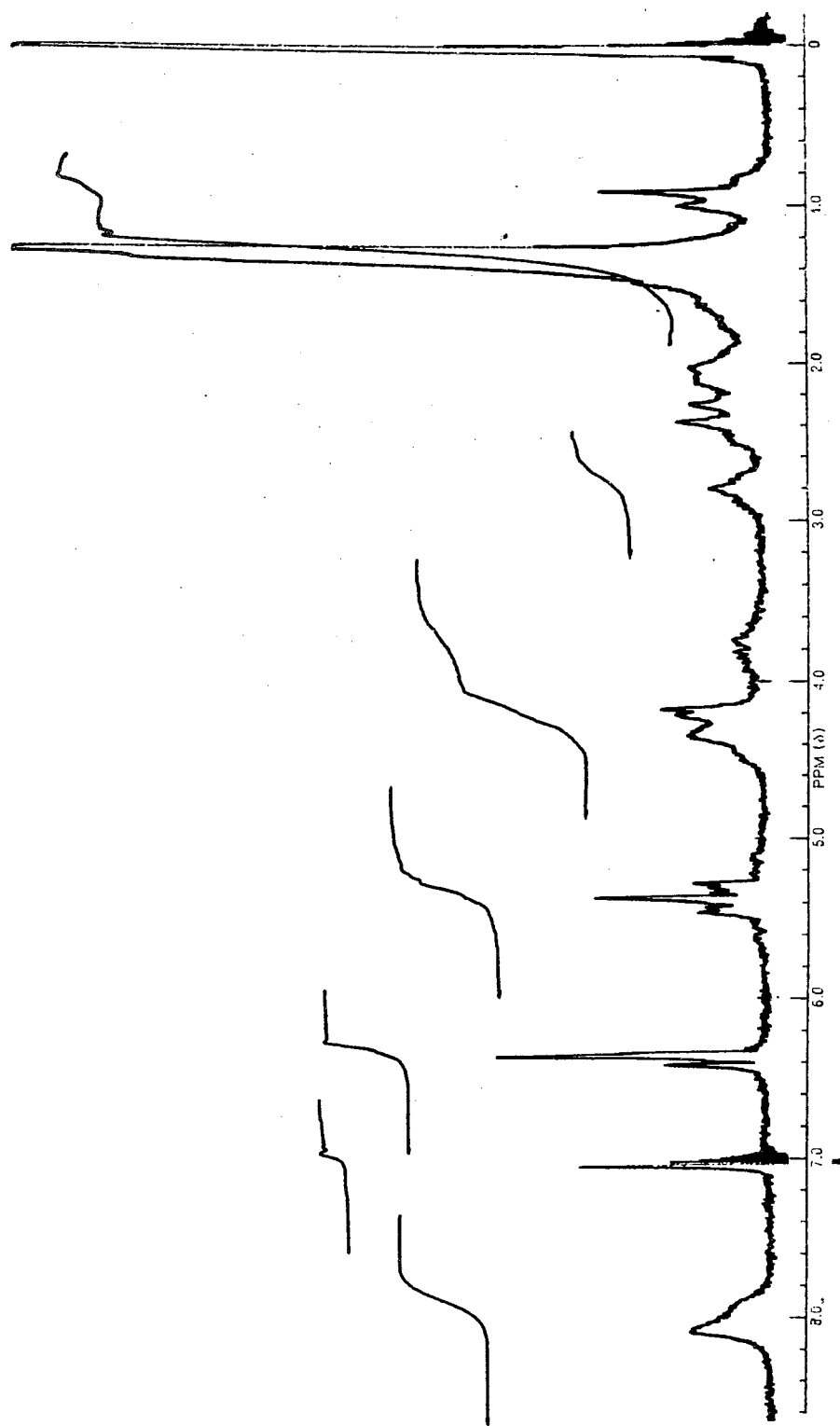


FIGURE 3.11. ^1H -NMR spectrum of SOMG/MA (Run no : 9, beginning of reaction) (CDCl_3).

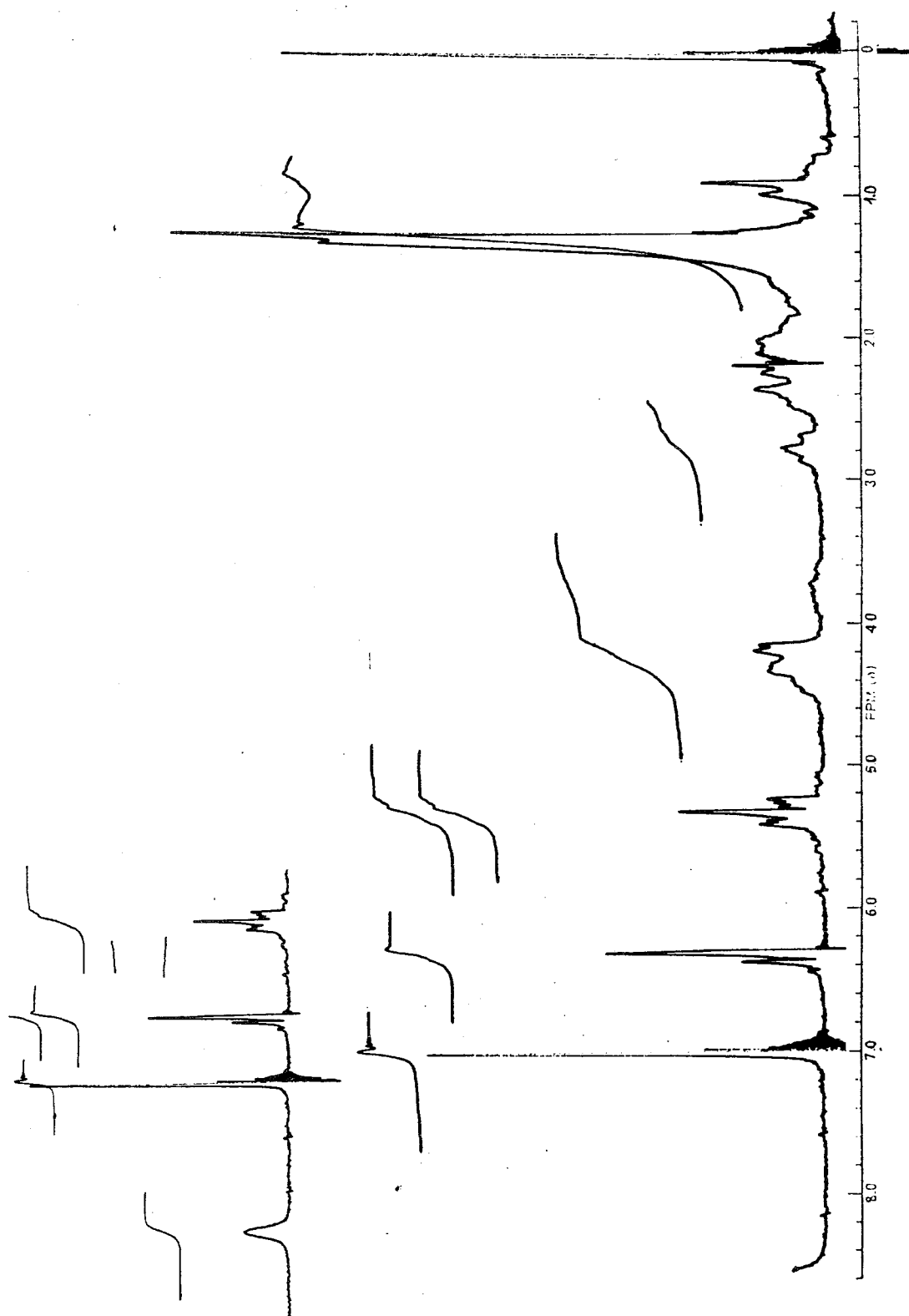


FIGURE 3.12. ^1H -NMR spectrum of SOMG/MA (Run no : 12, beginning of reaction) (CDCl_3).



FIGURE 3.13. ^1H -NMR spectrum of SOMG/MA (Run no : 12, end of reaction) (CDCl_3).

3.2.1. Maleate (Cis) – Fumurate (Trans) Isomerization

Much work had been carried out on the (cis) maleate – trans (fumurate) isomerization of unsaturated polyesters prepared from maleic anhydride and various polyols. J. Grobelney studied the maleate fumurate isomerism of dicarboxy diesters prepared from maleic anhydride and various diols and utilized the results to interpret the isomerism of unsaturated polyesters [20]. In the case of 1,2-propylene glycol direct evidence was provided of the preference of CH- over CH₂- groups in promoting the trans isomer. V. Lorez, on the other hand, based on his previous works on unsaturated polyesters prepared from maleic anhydride and various methylene glycols, claims that the linear glycols with an even number of carbon atoms gives rise to a higher percentage of maleate to fumurate isomerization than do the odd ones, if the polycondensation is carried out under the same conditions. He also adds that the temperature is one of the most important parameters that must be taken into account and that the time of the reaction plays its part, though only in the initial steps of polycondensation [26]. Thus, in our work we found out that, at the temperature range between 80-100⁰C, the maleate form is the predominant isomer and that a considerable increase in the fumurate content can only be observed in the case of extended heating, such as in reaction (Run no: 4). This result seems logical since, the SOMG is most probably richer in primary hydroxyls rather than the secondary hydroxyls, when considering the structures of mono- and diglycerides and also glycerol and that if any isomerization takes place at this low temperature range, it will result from the less reactive secondary hydroxyls present in the SOMG product.

When the reaction temperature is increased to 180-200⁰C, on the other hand, it is found out that, the fumarate is the predominant isomer at the end of ten minutes, as can be figured out from the ¹H-NMR data of reaction (Run no: 13) in Table 3.2. This result is expected, since as was mentioned in Section 1.3.4. the maleate esters are characterized with higher strain energy across the double bond because of steric hindrance and that at lower reaction temperatures of polyesterification ie, 160⁰C, the maleate esters remain in this condition, but as reaction temperatures exceeds 180⁰C, they effectively relieve the strain by

transforming to more planar trans- fumurate isomer which reduces steric congestion as was shown in Figure 1.15.

The result of reaction (Run no: 13) was very promising, since the highest product yield was found to be obtained from this reaction with $N_m + N_f / N_{fa} = 1.026$. The very high fumurate content of this product was also very advantageous in the next copolymerization step with styrene owing to a higher reactivity of the trans isomer in copolymerization with vinyl monomers. Unfortunately, this product was found to be insoluble in styrene and was thus useless for our purpose. In this reaction procedure, 1.5 g SOMG was heated to about 200°C and then 1g. maleic anhydride was added and the mixture was kept at this temperature for ten minutes. At the end of this time, the product was rapidly cooled to RT in five minutes. The resulting product was much more viscous than the other reaction products. The ¹H-NMR spectrum of this reaction product is given in Figure 3.14. The absorptions at 6.3 ppm and 6.9 ppm correspond to maleate and fumurate half esters respectively, the peak at 7.8 ppm belongs to the acid protons, thus it was found out that this peak disappears upon D₂O exchange as shown in Figure 3.15. We believe that, in addition to monoesterification, the polyesterification reaction also occurred to a limited range resulting in a higher molecular weight and viscosity of this product compared to products of previous reactions.

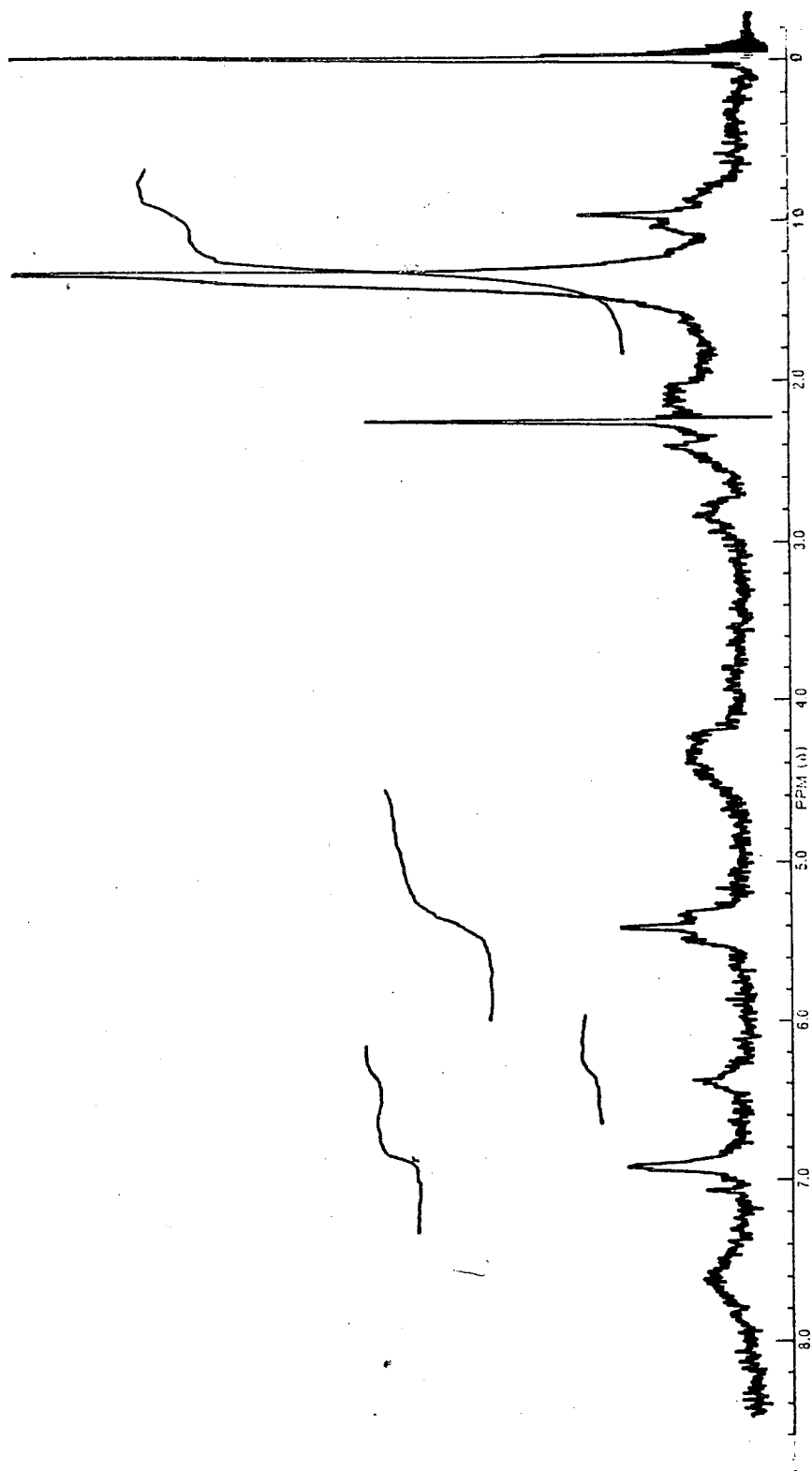


FIGURE 3.14. ^1H -NMR spectrum of SOMG/MA (Run no : 13, end of reaction) (CDCl_3).

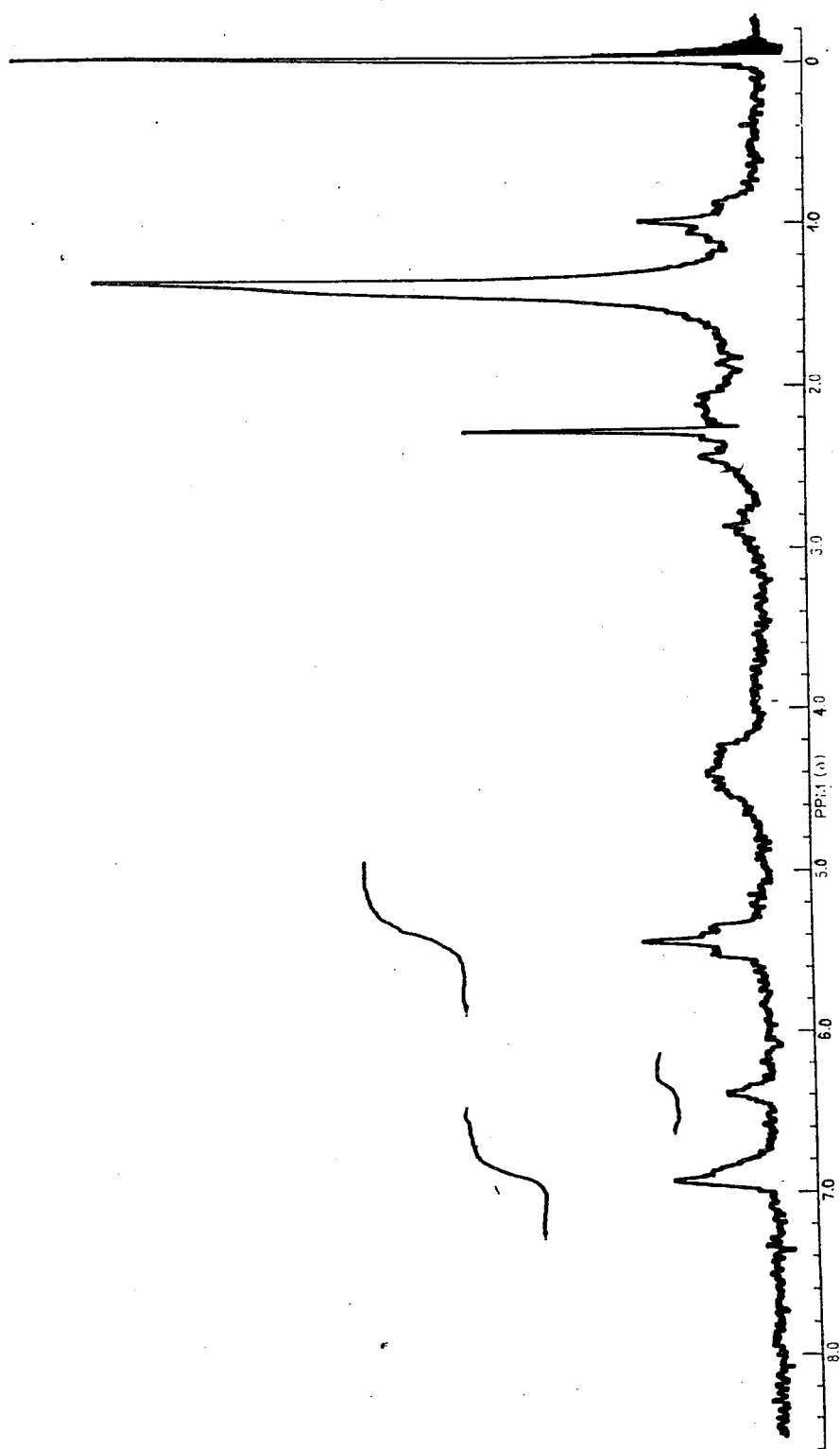


FIGURE 3.15. ^1H -NMR spectrum of SOMG/MA (Run no : 13, end of reaction) ($\text{CDCl}_3 + \text{D}_2\text{O}$).

3.2.2. Mass Spectral Analysis of Maleinized SOMG

Apart from the maleinization reactions, previously mentioned in section 3.2., maleinization of the SOMG that is prepared from the $\text{Ca}(\text{OH})_2$ catalyzed glycerolysis of soybean oil was also carried out in a non-catalyzed system at different SOMG : MA weight ratios for mass spectral analysis. Therefore, four separate reaction mixtures with the SOMG : MA weight ratios; (1:1), (1:1.5), (1:2), (1:2.5) were prepared at 120°C , without a catalyst and then each reaction mixture at the end of two and half hours was analyzed by mass spectroscopy for the identification of the possible reaction products. The related mass spectra are given in Figure 3.16., 3.17., 3.18., and 3.19. The structure of the possible reaction products and the assigned molecular weights from the mass spectra are shown in Figure 3.20.

In the mass spectrum of the maleinized SOMG product (SOMG : MA = 1:1) shown in Figure 3.16., the peaks at 454 and 436 with the highest intensities represent the monoglyceride monomaleate and dehydrated monoglyceride monomaleate whereas the peaks at 356 and 338 represent the monoglyceride and the dehydrated monoglyceride and therefore show the presence of unreacted monoglycerides. The peak with low intensity at 552, on the other hand, corresponds to monoglyceride bismaleate.

In the mass spectrum of the maleinized SOMG product (SOMG : MA = 1:1.5), shown in Figure 3.17., the monoglyceride monomaleate and the dehydrated monoglyceride monomaleate peaks at 454 and 436 are still the peaks with the highest intensity, whereas the peak of monoglyceride still exists but with a lower intensity. An increase in the intensity of the peak at 552 that represents the monoglyceridebis maleate is also observed.

In the mass spectrum of the maleinized SOMG product (SOMG : MA = 1:2) shown in Figure 3.18., the monoglyceride monomaleate and the dehydrated monoglyceride monomaleate give out a peak at the same molecular weights; at 454 and 436 respectively.

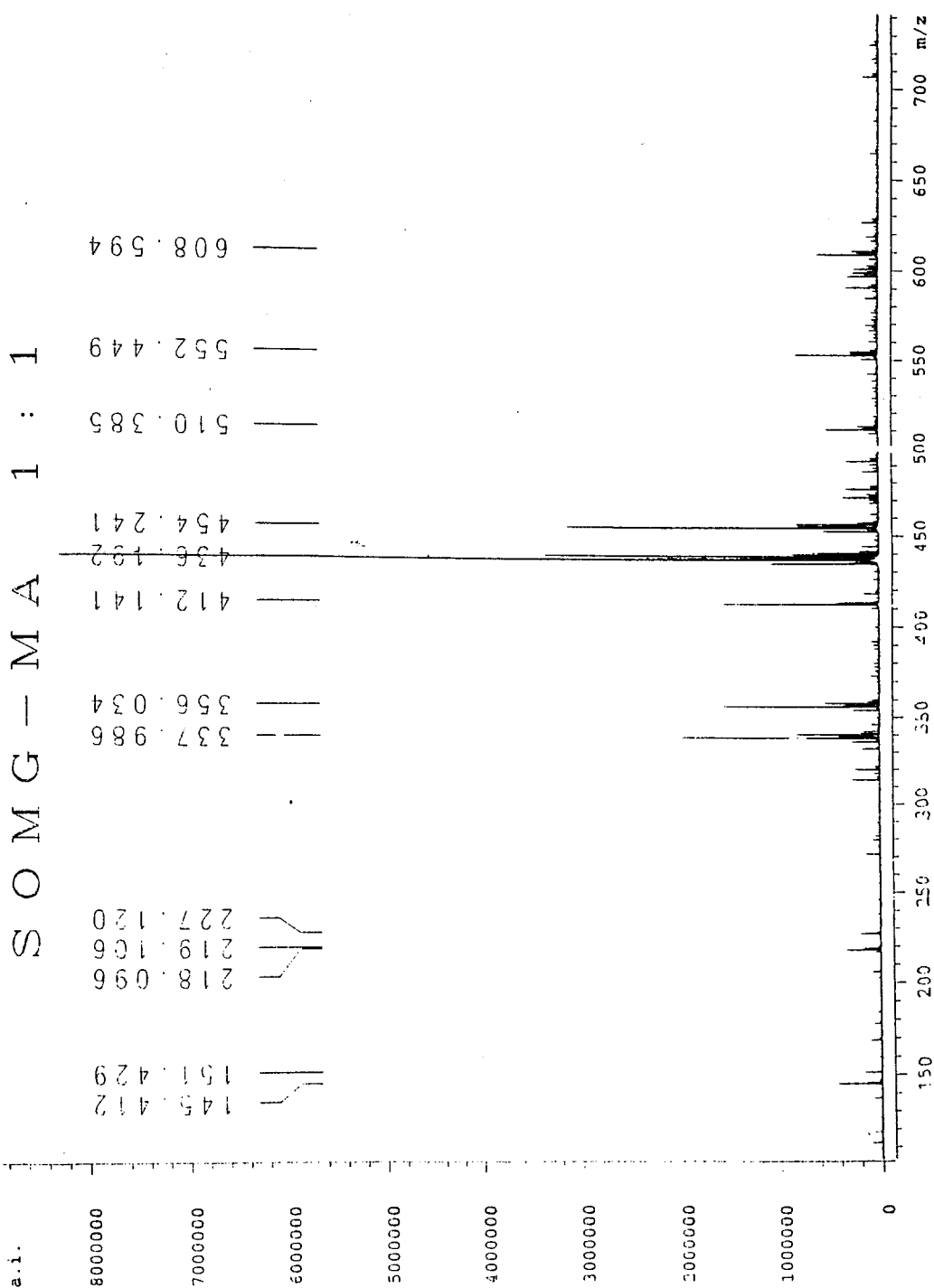


FIGURE 3.16. Mass spectrum of SOMG/MA (1 : 1).

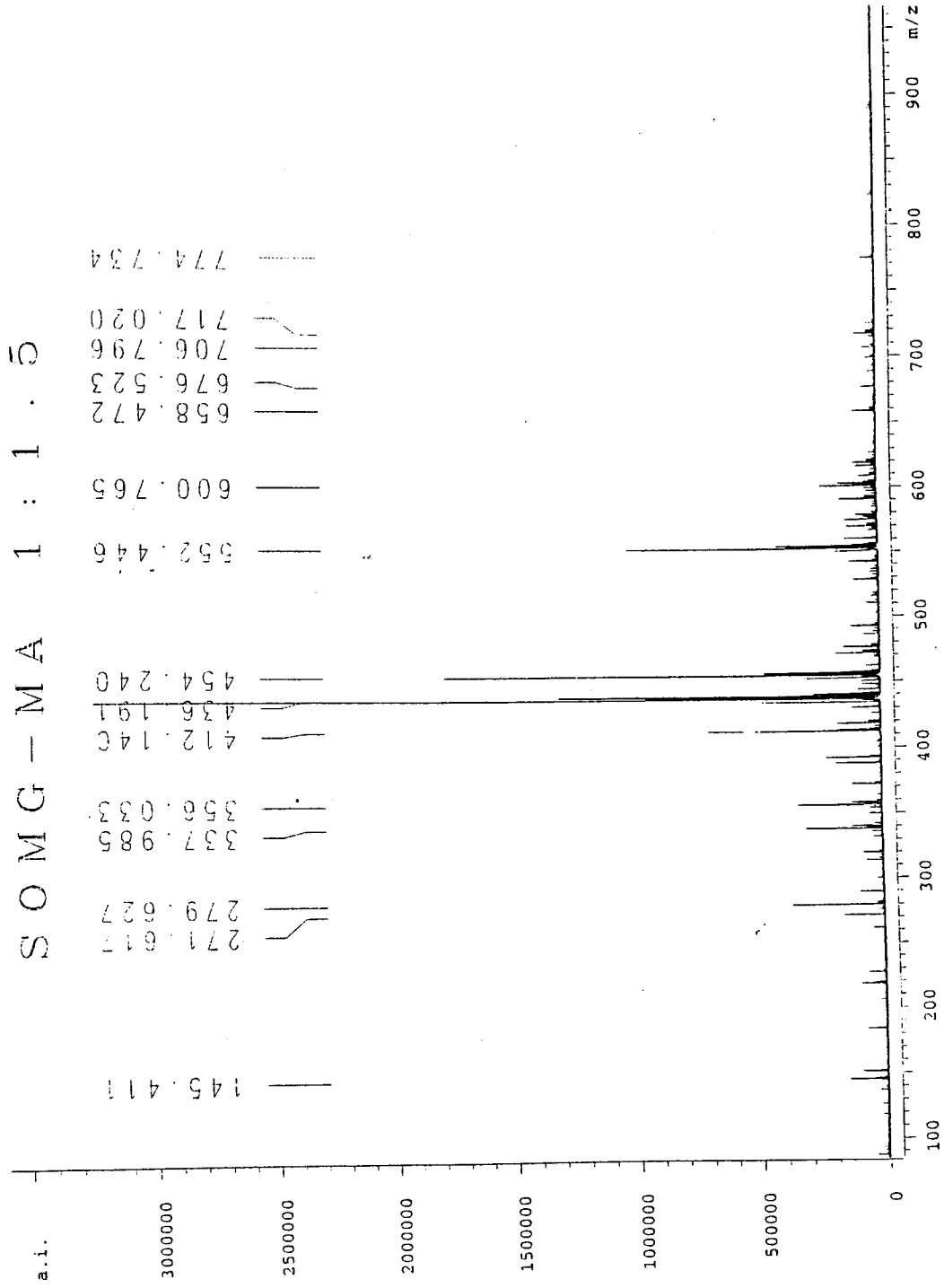


FIGURE 3.17. Mass spectrum of SOMG/MA (1 : 1.5).

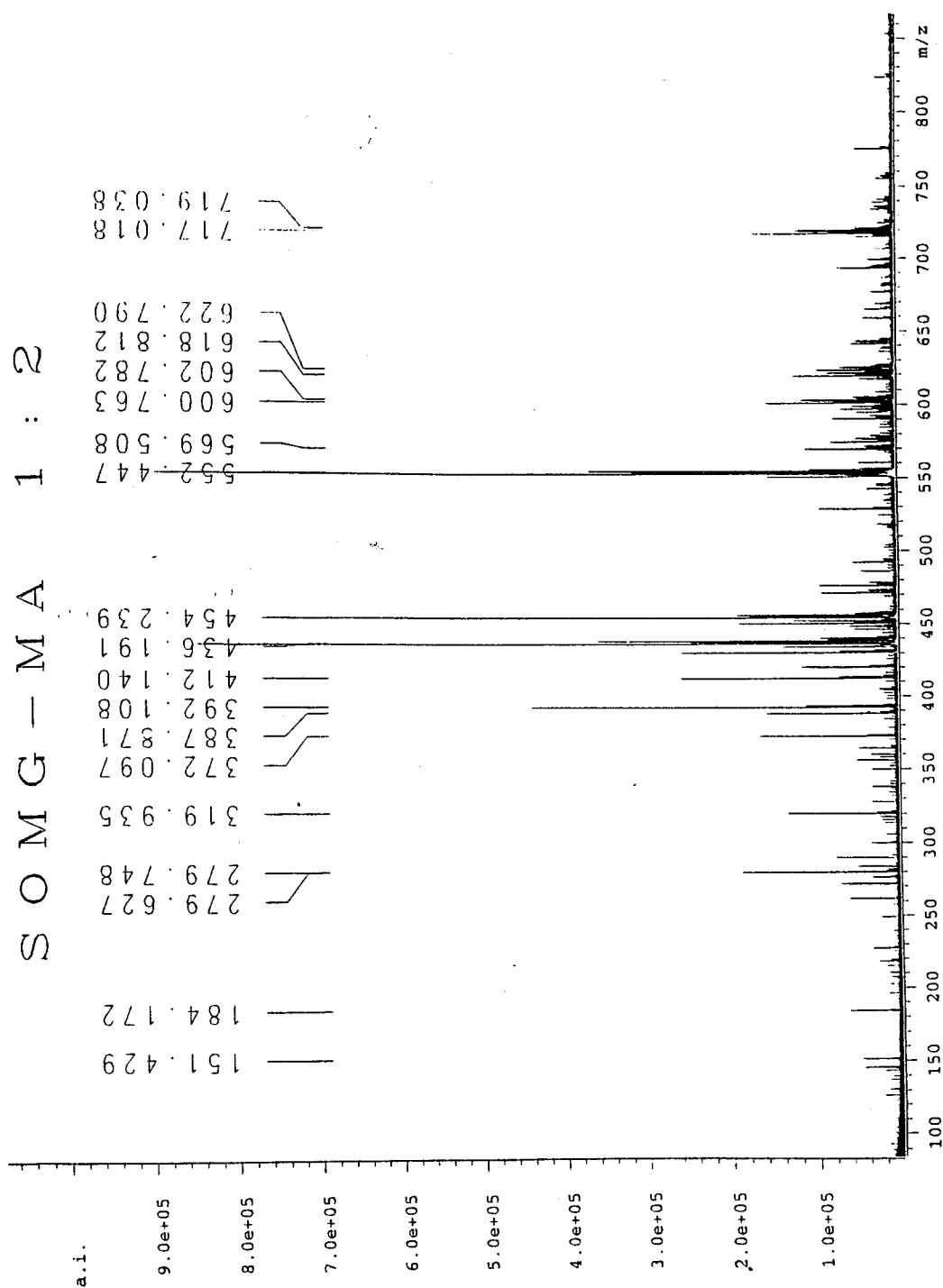


FIGURE 3.18. Mass spectrum of SOMG/MA (1 : 2).

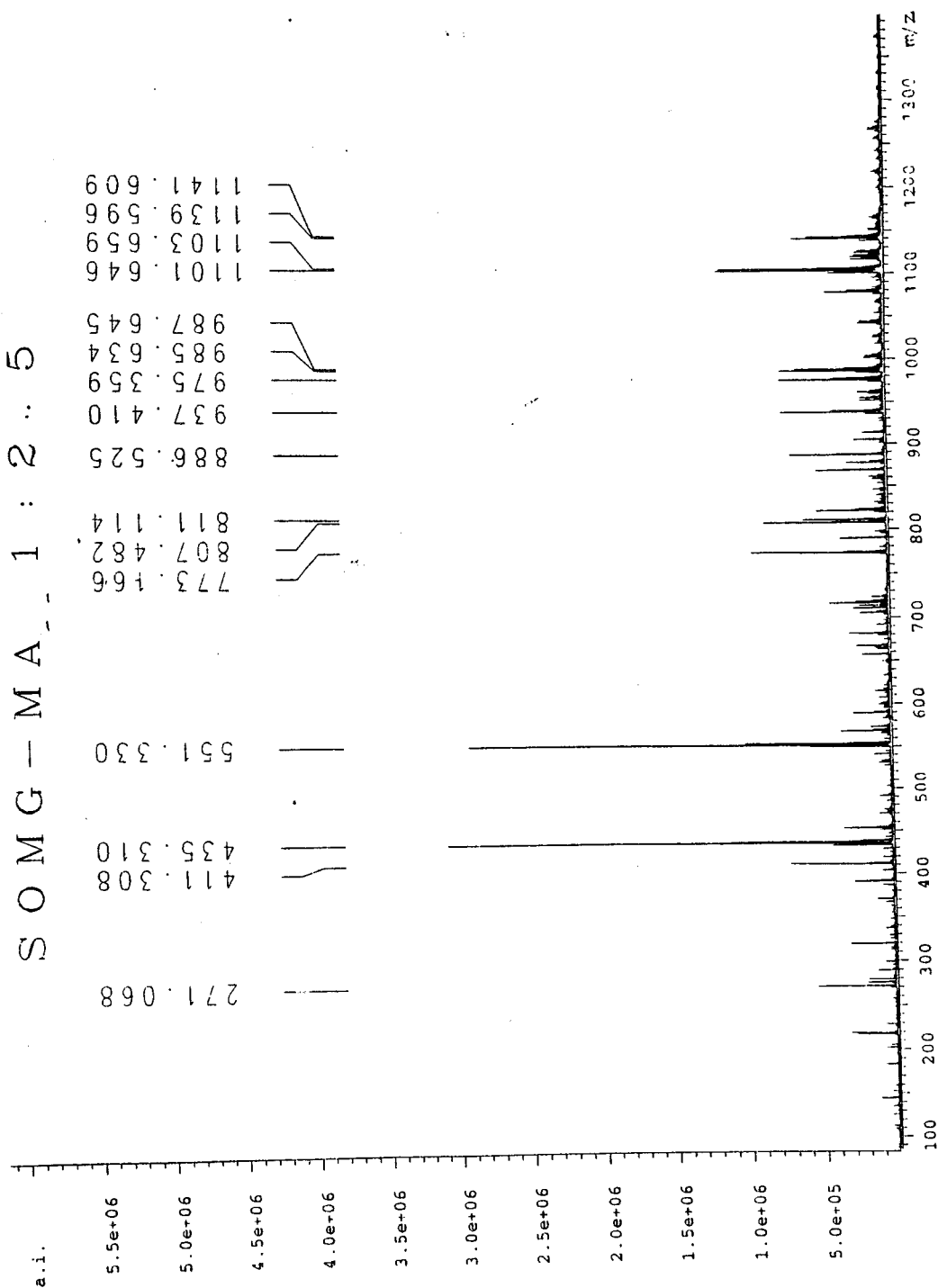
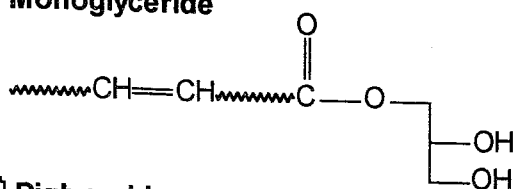


FIGURE 3.19. Mass spectrum of SOMG/MA (1 : 2.5).

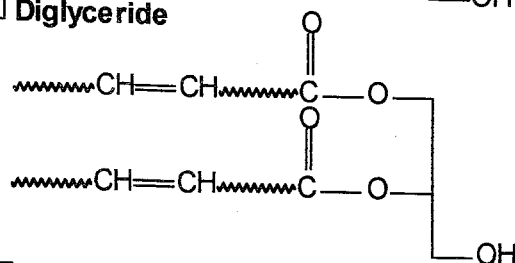
☐ Monoglyceride



$$M_{\text{monoglyceride}} = 356$$

$$M_{\text{monoglyceride}} - 18 = 338$$

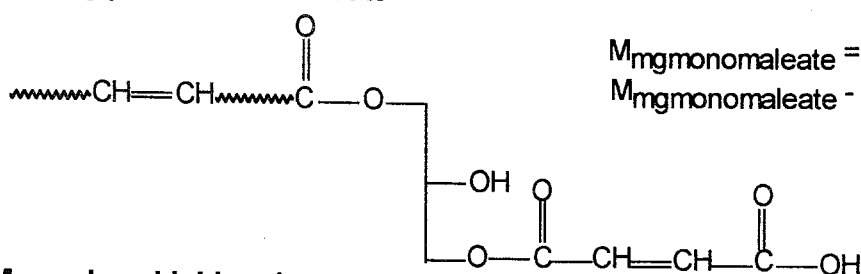
☐ Diglyceride



$$M_{\text{diglyceride}} = 618$$

$$M_{\text{diglyceride}} - 18 = 600$$

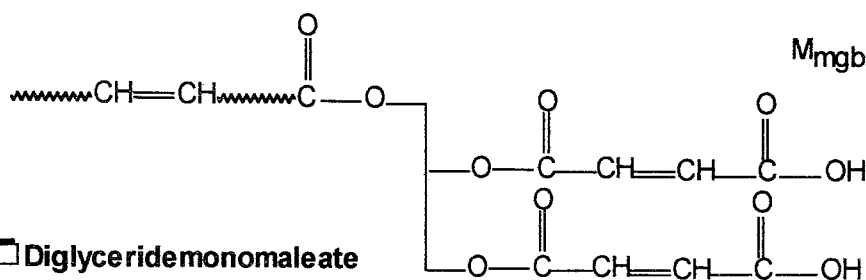
☐ Monoglyceridemonomaleate



$$M_{\text{mgmonomaleate}} = 454$$

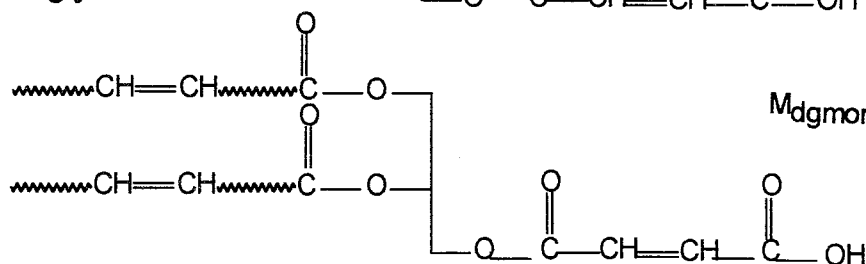
$$M_{\text{mgmonomaleate}} - 18 = 436$$

☐ Monoglyceridebismaleate



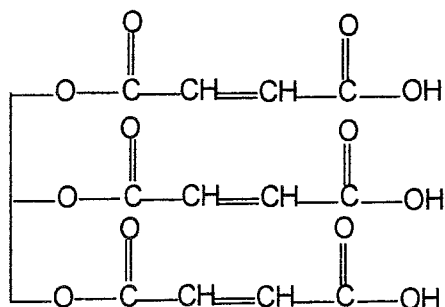
$$M_{\text{mgbismaleate}} = 552$$

☐ Diglyceridemonomaleate



$$M_{\text{dgmmonomaleate}} = 717$$

☐ Glyceroltrismaleate



$$M_{\text{glyceroltrismaleate}} = 387$$

FIGURE 3.20. Assigned molecular weights for the possible maleinized SOMG products.

However, the peak with the highest intensity of this spectrum belongs to monoglyceride bismaleate at 552. The peak with middle intensity at 387 represents glycerol trismaleate, whereas the peak at 717 represents the diglyceride monomaleate.

Finally, the mass spectrum of the maleinized SOMG product (SOMG : MA = 1:2.5) shown in Figure 3.19. is characterized mainly with the peaks at 436 and 454 that represent the dehydrated monoglyceride monomaleate and monoglyceride monomaleate respectively and with the peak at 552 that represents the monoglyceride bismaleate. The peak at 717 that belongs to diglyceride monomaleate, on the other hand still exists but with very low intensity in this spectrum.

The mass data obtained from maleinization reactions performed with increasing maleic anhydride weight ratio gave some interesting results. A summary of this data is therefore is given in Table 3.3. which shows the changes in the intensities of the peaks in the mass spectra of the SOMG + MA reaction products with increasing maleic anhydride weight ratio.

TABLE 3.3. Peak intensities in the mass spectra of SOMG +MA reaction products with increasing maleic anhydride feed ratio.
(Mg = Monoglyceride Dg = Diglyceride)

Assigned MWs for SOMG : MA Reaction Products ⇒	SOMG : MA WEIGHT RATIOS			
	SOMG : MA 1 : 1	SOMG : MA 1 : 1.5	SOMG : MA 1 : 2	SOMG : MA 1 : 2.5
338 (Mg-18)	39	15	5	2
356 (Mg)	30	16	8	—
387 (Glyceroltrismaleate)	—	9	25	2
436 (Mgmonomaleate – 18)	162	157	139	89
454 (Mgmonomaleate)	62	87	126	10
552 (Mgbismaleate)	16	50	147	84
717 (Dgmonomaleate)	1	4	28	12

Although the peak intensity in a mass spectrum, is not absolutely proportional to the direct quantity of that molecule in the mixture, the data in this table give a good idea about the composition of the reaction mixtures. A quick examination of the table shows that, as maleic anhydride feed ratio is increased, the intensity of the monoglyceride peak decreases and finally diminishes, whereas the peak intensity of all the possible reaction products including monoglyceride monomaleate, monoglyceride bismaleate, diglyceride monomaleate and glycerol trismaleate increase. The decrease in the intensity of the dehydrated monoglyceride monomaleate peak, on the other hand is attributed to the increase in the peak intensity of the monoglyceride bismaleate. Unfortunately, we are not able to explain these sudden decreases in the last weight ratio (SOMG : MA = 1:2.5), however it must be noted here that maleic anhydride is in a huge excess amount in this reaction and the reaction in this weight ratio is therefore an extreme case.

3.3. Radical Copolymerization of the SOMG Maleates with Styrene

The radical copolymerization of the SOMG maleates with styrene is similar to cross-linking reactions of unsaturated polyesters with styrene in presence of free radical initiators, which was previously explained in section 1.3.3. But our copolymerization system differs from that of unsaturated polyesters in that, SOMG maleates are macromolecular monomers and not short chain polymers that copolymerize with styrene. It was critical for us that, the maleinized SOMG products are all soluble in styrene forming a liquid molding resin. Thus, we found out that, all the maleinized SOMG products obtained from reactions cited in Table 3.2. were soluble in styrene.

We used benzoyl peroxide and methyl ethyl ketone hydroperoxide (MEKP) as radical initiators. Benzoyl peroxide decomposes thermally and necessitates a processing temperature range of 80-95°C. MEKP, on the other hand, can be used at ambient temperatures, in presence of a multi valent salt accelerator such as cobalt naphthanate. Free

radicals are produced from hydroperoxides by Cobalt in either valent state by redox reactions shown in Figure 3.21. [5].

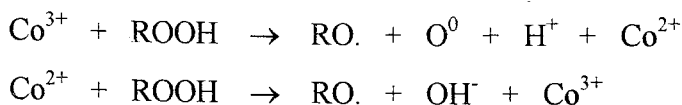


FIGURE 3.21. Production of free radicals from hydroperoxides by cobalt by redox reactions,

The copolymerization of the SOMG maleates with styrene were carried out for the different SOMG + MA reaction products cited in Table 3.2. The polymerization of each reaction product differs in terms of curing time depending on the maleate half ester ratio of the maleinized SOMG product. The products with the higher maleate half ester ratios naturally reached a solid state quicker than the ones with a lower maleate ratio. The presence of residual hydroquinone traces, in some of the maleinized SOMG products may also retard curing, since in presence of such an inhibitor, the free radicals are initially consumed by quinone stabilizers and polymerization does not proceed until the inhibitor system is completely neutralized. Such a case was observed in the copolymerization of the maleinized SOMG product obtained from reaction (Run no: 9) because of the use of an excess amount of hydroquinone. The best result was obtained from the copolymerization of the maleinized SOMG product obtained from reaction (Run no: 12) in presence of MEKP and cobalt naphthanate. The liquid mixture of the SOMG maleates and styrene was transformed into a soft rubbery gel in 20 minutes and at the end of one and half hour, the polymer obtained was a transparent, light yellow colored hard solid. An exotherm volumetric shrinkage upon curing was also observed as expected from a radical polymerization system.

Unfortunately, it was impossible to analyze the polymers obtained by ^1H -NMR, since the polymers were insoluble in the common deuteriated solvents. ^1H -NMR of the essentially the same polymer was possible when the monomers were emulsion polymerized. This spectrum and its interpretation is given in Section 3.4. IR was taken, by preparing a

thin film of the polymer on a microscopic slide. The IR spectrum of the copolymer shown in Figure 3.22., was characterized with a broad carboxylic acid O-H band between 2500-3700 cm^{-1} . The peak at 820 cm^{-1} , with low intensity also shows the O-H out of plane bending vibrations of the acid groups. Unfortunately, the very intense overtone or combination bands of the phenyl ring shields the 1640 cm^{-1} region that is characteristic for the C=C double bond stretching vibrations of the maleate half esters, thus the disappearance of this peak can not be visualized in this spectrum. The peaks at 1491 and 1455 cm^{-1} show the C=C ring stretching vibrations and the peaks at 752 and 702 cm^{-1} show respectively the aromatic C-H out of plane bending and C=C bending vibrations of the phenyl ring.

In an attempt to prove the cross-linked network structure of the polymers obtained, we tried to examine the swelling behaviours of the polymers in different solvents. Generally if a solvent dissolves a linear polymer, it should swell the cross-linked polymer made with the same repeating unit. We found out that, the polymers obtained swell in most of the polar organic solvents such as CHCl_3 , DMSO or acetone to some extent and then fragment.

In CCl_4 , which is a non polar solvent, on the other hand, it was found out that, the polymer absorbs a certain amount of solvent and then the solvent uptake ceases and that the polymer is not fragmented at the end of six days. Thus for our purpose, the polymer sample was first weighed and this value was taken as W_0 and then put into a closed tank that contains CCl_4 . The polymer sample was then weighed at certain time intervals. The W/W_0 value referring to the ratio of the weight of the swollen material over the weight of the dry state of the polymer versus time graph is shown in Figure 3.23.

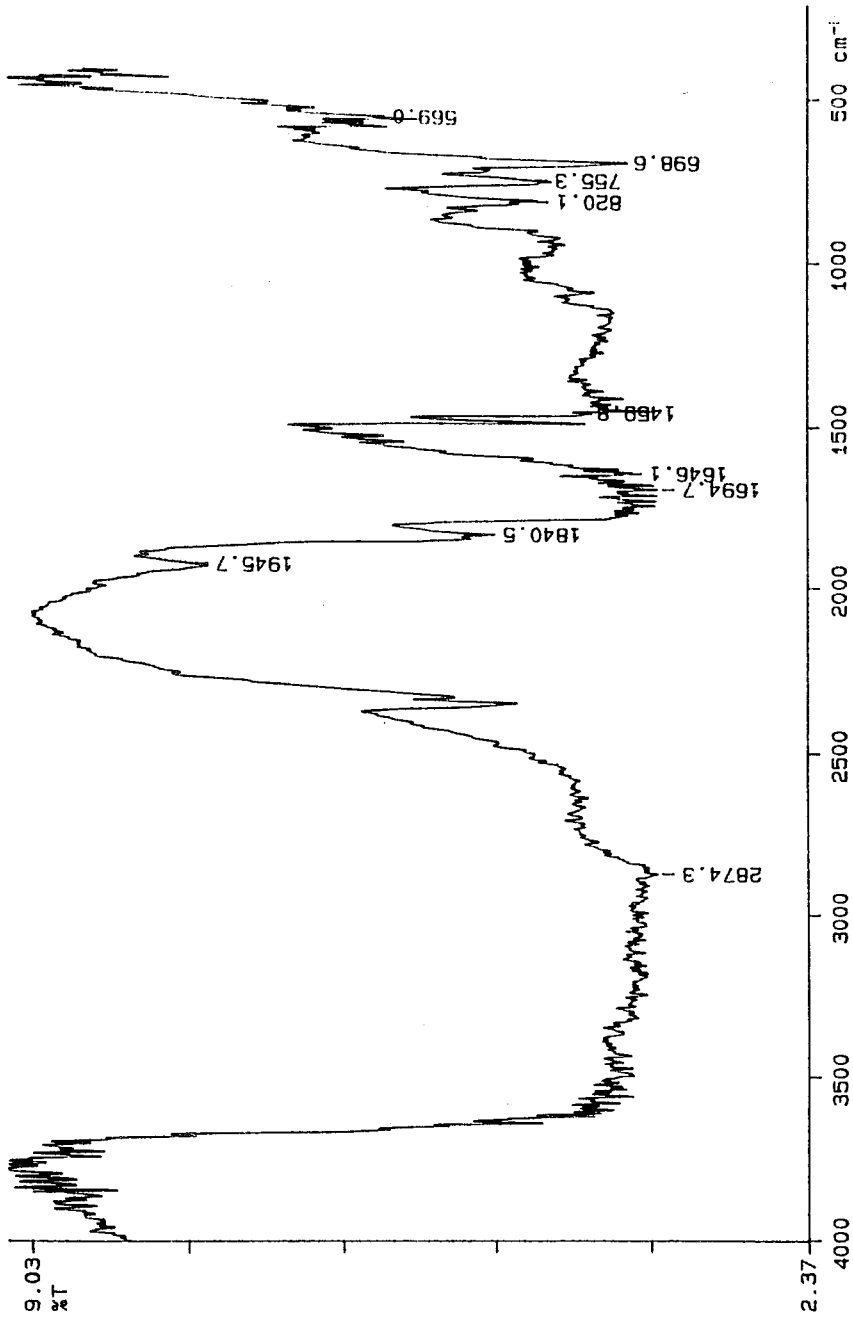


FIGURE 3.22. IR spectrum of SOMG/MA - styrene copolymer.

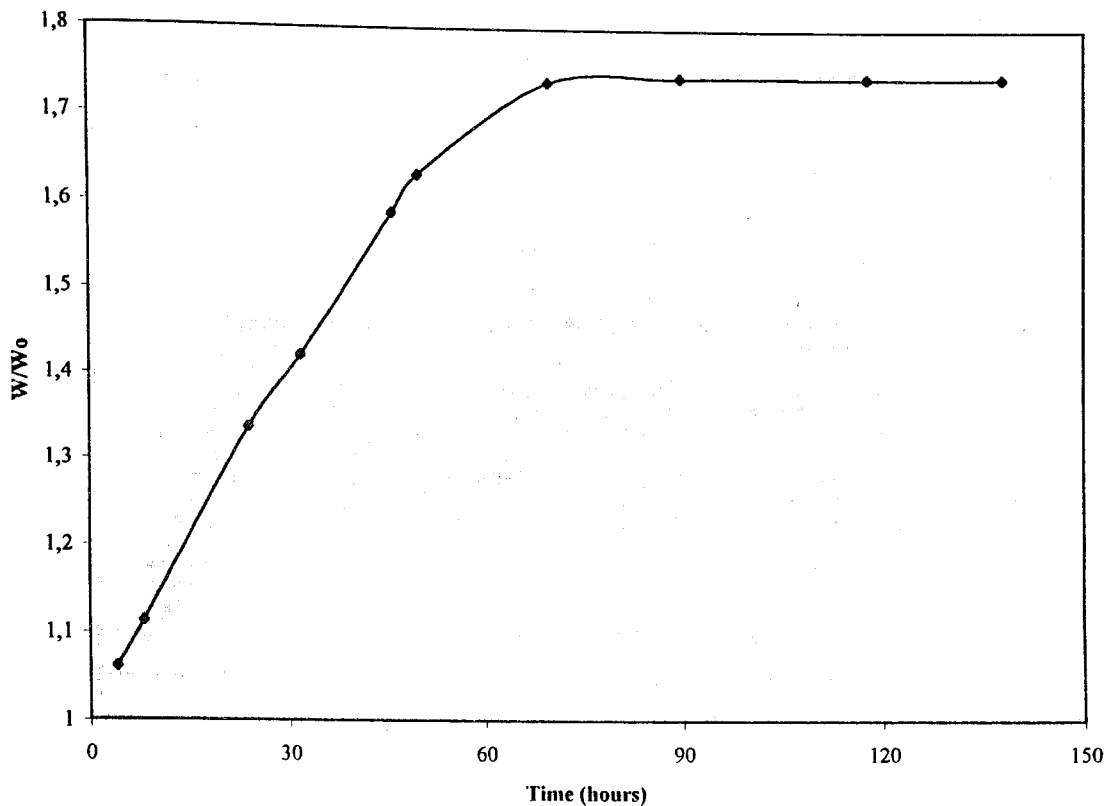


FIGURE 3.23. W/W_o versus time graph of the SOMG maleate styrene copolymer in CCl_4 .
(W = weight of the swollen polymer , W_o = weight of the dry polymer)

As can be seen, in Figure 3.23., the W/W_o value increases with time and then reaches a plateau at a certain ratio. This behaviour is typical for a cross linked polymer network structure because all structural units in the polymer network are interconnected with chemical bonds, that there is a point beyond which the units can not be further dispersed with the continued addition of solvent.

The extent of water absorption of the obtained polymers was also critical for us, since the copolymers of the SOMG maleates with styrene were very rich in terms of hydrophylic groups. Therefore we determined water absorption of the copolymers according to the standard TSE procedures [28,29]. Thus, the water absorbtions of the resulting polymers after being kept for 30 minutes in boiling water was found to be 4.7 per cent whereas the

water absorption at the end of 24 hours at RT was found to be 1.05 per cent. These figures compare very well with those obtained from commercial polyesters.

3.4. Emulsion Copolymerization of the SOMG Maleates with Styrene

An ideal emulsion polymerization system contains water, a water insoluble monomer, emulsifier, and a free radical initiator as the essential ingredients. In dilute aqueous solution at concentrations above the critical micelle concentrations (cmc), the molecules of an emulsifier forms aggregates. These aggregates called micelles contain a hundred or so molecules and take on a roughly spherical form with the hydrophobic portion of each molecule directed toward the center of the micelle. Addition of a water insoluble hydrocarbon monomer such as styrene to this, particularly under some agitation, leads to most of the latter's being dispersed in the form of fine droplets stabilized by the emulsifier.

In the ideal system, it is assumed that, the initiating free radical is generated in the water phase. Since $\approx 10^{13}$ free radicals /ml /sec may be produced from a typical persulfate initiator at 50°C , it can be readily seen that within a very short time radicals will meet the monomer swollen micelles in which the polymerization then starts. After initiation therefore a new phase is produced, namely a polymer latex particle swollen with monomer. After initiation, polymerization inside the micelles proceeds rapidly and the latex particles grow rapidly from within. The emulsifier is adsorbed on the surface of the growing latex particles, and functions as a protective colloid preventing the latex particles from flocculating. After a certain conversion (10%-20%) of monomer to polymer has been reached no micelles are left since the concentration of the emulsifier in the aqueous phase has been reduced to below the cmc. All the emulsifier in the system is adsorbed on the latex particle water interphase. After this stage has been reached, no fresh latex particles can be formed since initiation of the polymerization reaction can take place only in a monomer swollen micelle. The number of latex particles is thus fixed from this point and

further polymerization occurs only inside these latex particles. Polymerization will cease completely when all monomer in the particle is consumed.

In our work, the emulsion copolymerization of the SOMG maleates with styrene is different from an ideal emulsion polymerization system in that, in our system the comonomer SOMG maleate is itself a perfect emulsifier, and the other co reactant monomer styrene is the water insoluble monomer, therefore the addition of an emulsifier is unnecessary. However, the use of the maleate half ester as the emulsifier necessitates the conversion of the maleates to the corresponding sodium salts. Thus the maleinized SOMG product was first mixed with 5% NaOH solution, forming a slightly acidic medium with a Ph of 6.9. It was critical that not all the maleate half esters is converted to the sodium salts and that a slightly acidic solution must be prepared, since it is known that peroxides often decompose more easily under acid conditions. The structure of the sodium salt of the monoglyceride bis maleate halfester and its function as an emulsifier is depicted in Figure 3.24. The monoglyceride monomaleate and the diglyceride monomaleate half esters will function in a similar manner.

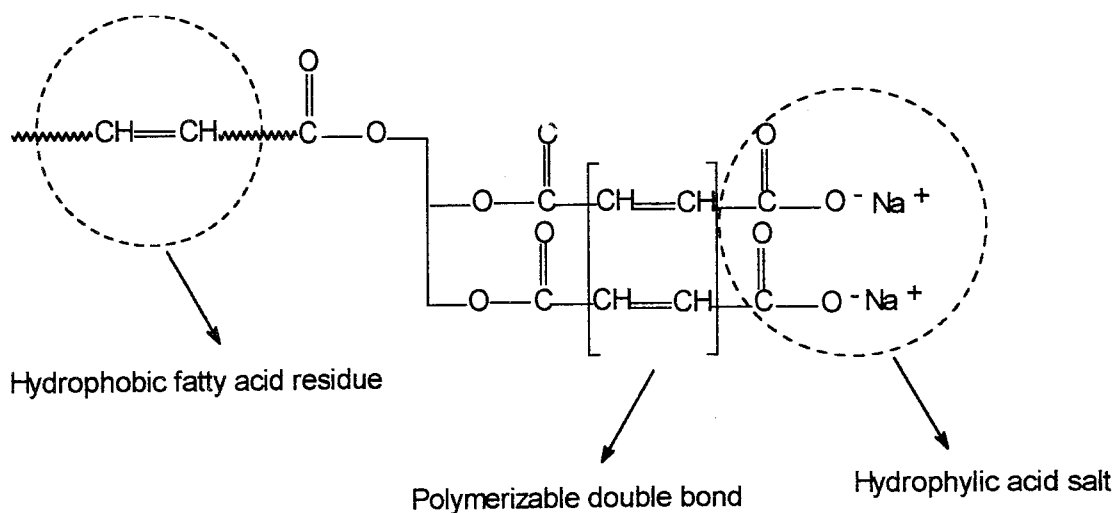


FIGURE 3.24. Structure of the Na^+ salt of monoglyceride bismaleate halfester and its function as an emulsifier in the polymerization system.

$K_2S_2O_8$ was used as radical initiator in our system. The peroxy disulfate which may be used as the sodium, potassium or ammonium salt is widely employed in emulsion polymerization. The peroxy disulfate decomposes thermally to give sulfate ion radical ($\cdot SO_4$) as initiating species. The mixture of the sodium salt of the SOMG maleates with styrene formed a very stable emulsion. After the addition of $K_2S_2O_8$ to this emulsion, at the end two and half hours at $75-85^\circ C$ with magnetic stirring, a suspension separated from the emulsion as an upper layer. A trace amount of this suspension was then analyzed with IR and 1H -NMR after the evaporation of the residual water.

In the IR spectrum of the product shown in Figure 3.25., the peak at 1571 cm^{-1} belongs to carbonyl stretching vibrations of the sodium salt of the acids and the peak at 1740 cm^{-1} represents the ester carbonyl stretching vibrations. The presence of polystyrene, can be rationalized with the peak at 699 cm^{-1} showing the C-H out of plane bending vibrations of the mono substituted benzene ring and also with the peaks at 1493 and 1456 cm^{-1} showing the C=C stretchig of the phenyl ring. The presence of O-H band at 3360 cm^{-1} , on the other hand may be explained with unneutralized remaining acid groups or with the hydroxyls left unreacted in the starting maleinized SOMG product. In the 1H -NMR spectrum of the product shown in Figure 3.26., the disappearance of the 6.3 ppm peak that belongs to maleate vinylic protons and the appearance of the 6.7 and 7.1 ppm peaks that are charecteristic for polystyrene, are the signs for the copolymerization of the maleate half esters with styrene.

3.5. Radical Homopolymerization of the SOMG Maleates

The homopolymerization of the SOMG maleates was also carried out in presence of MEKP and benzoyl peroxide as radical initiators. In each system, the polymerization of the SOMG maleates was observed with a slow viscosity increase. The radical polymerization of the maleate groups was incomplete since only a limited decrease in the maleate vinylic protons' peak intensity was observed in the 1H -NMR spectrum of the products obtained. We believe that the bulkiness of the acyl groups attached to one side of

the reactive maleate double bond is the main factor preventing the complete homopolymerization of the SOMG maleate half esters to long molecular weight polymers

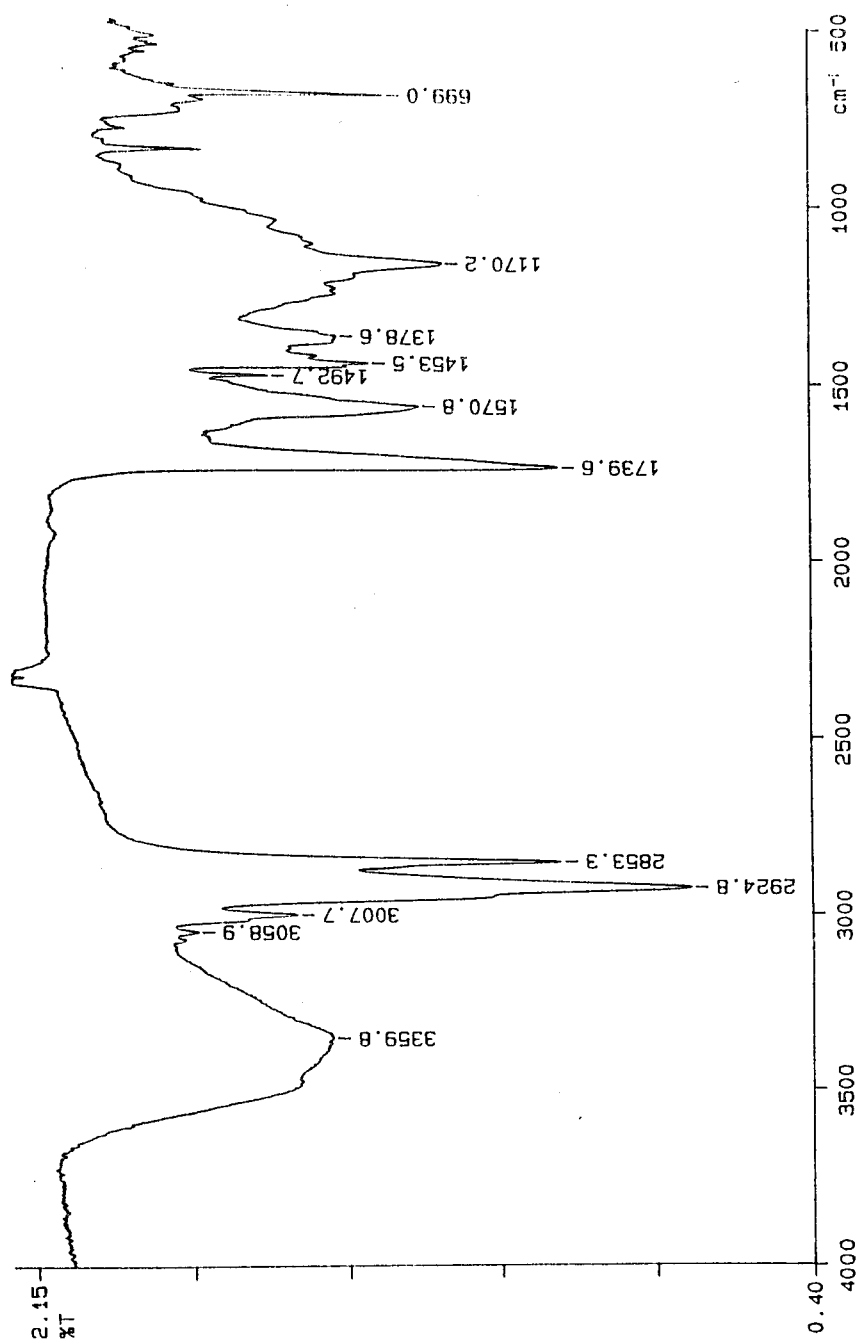


FIGURE 3.25. IR spectrum of SOMG/MA (Na^+ salt) - styrene copolymer.

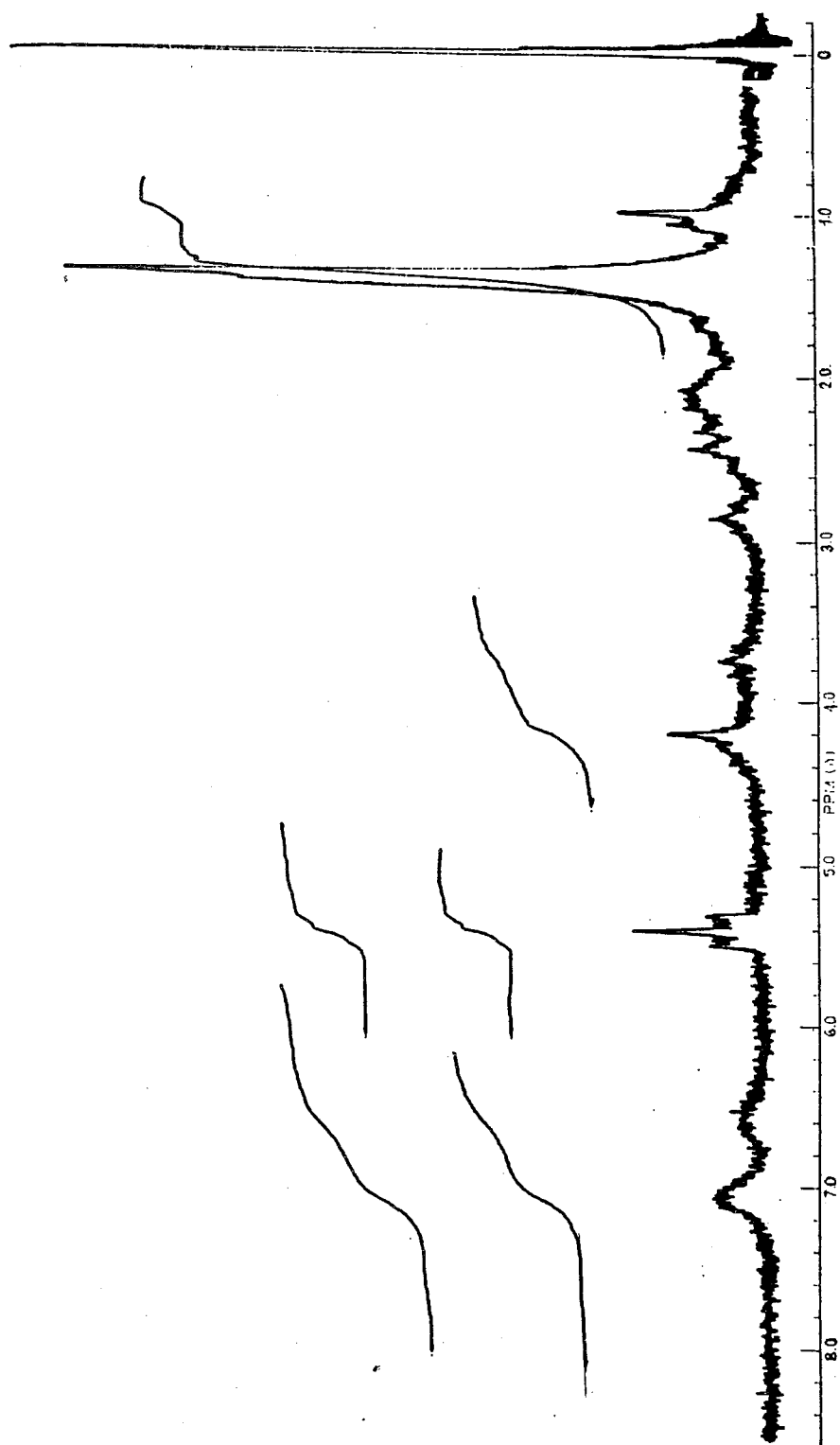


FIGURE 3.26. ^1H -NMR spectrum of SOMG/MA (Na^+ salt) - styrene copolymer (CDCl_3).

4. EXPERIMENTAL

4.1. Chemicals and Apparatus

4.1.1. Chemicals

Chemicals that are used in this research project are given in Table 4.1.

4.1.2. Apparatus

The IR analysis was performed on a Perkin Elmer 1600FT-IR spectrometer using KBr windows. ^1H -NMR spectra were obtained on a Varian T-60A NMR spectrometer. Mass spectra were obtained on a Du Pont 1200 quadrapole mass spectrometer operated in secondary ion (SIMS) mode.

TABLE 4.1. The chemicals used, their suppliers and their purities.

NAME	FORMULA	SUPPLIER	PURITY
Glycerol	$C_3H_8O_3$	Atabay	Pure
Maleic anhydride	$C_4H_2O_3$	Fluka	97%
2-methyl imidazole	$C_4H_6N_2$	Aldrich	99%
N,N-dimethyl aniline	$C_8H_{11}N$	Fisher	Reagent grade
p-Toluene sulfonic acid	$CH_3\text{O}SO_3H$	Fisher	Not defined
Sulfuric acid	H_2SO_4	Akkimya	98%
Sodium hydroxide	$NaOH$	Hannover	Pure
Sodium sulfate	Na_2SO_4	Merck	Extra pure
Potassium persulfate	$K_2S_2O_8$	Fisher	Not defined
Hydroquinone	$C_6H_6O_2$	Fisher	Not defined
Benzoyl peroxide	$C_{14}H_{10}O_4$	Fisher	Reagent grade
MEKP	$C_8H_{18}O_4$	Lucidal	Not defined
Chloroform	$CHCl_3$	Akkimya	99.5%
Carbon tetrachloride	CCl_4	Aksın	Not defined
Dimethyl sulfoxide	$(CH_3)_2SO$	Crown Zellerbach	Spectrometric grade
Diethyl ether	$C_4H_{10}O$	Merck	Extra pure
Deutero chloroform	$CDCl_3$	Aldrich	Spectrometric grade
Deuterium oxid	D_2O	Merck	99.75 %
Soybean oil	*	MarSA	Not defined

* Structure and composition of soybean oil given in Table 1.1

4.2. Glycerolysis of Soybean Oil

4.2.1. Soap Emulsified Glycerolysis of Soybean Oil (SOMG)

175 gr (1.90 mole) glycerol was put into a 1l, 3 necked round bottom flask, equipped with a mechanical stirrer, a N₂ gas tube and with an adaptor connected to a distillation apparatus. Glycerol was then heated to about 220-230⁰C under N₂ atmosphere and kept at this temperature for 2 hours during which time 3 ml of water with glycerol was distilled. Following this, 350 g. (0.40 mole) soybean oil was added to the glycerol at 220⁰C in five portions in order to create a larger amount of excess glycerol in each addition. The first portion of soybean oil was added with 3.5 g. of commercial soap as emulsifier catalyst. The soap firstly formed an insoluble white layer on the yellow colored solution but in about 15 minutes of time, it became emulsified in the solution, and the solution became homogenous. Each portion of soybean oil was added at 1 hour intervals, so the solution was heated for 5,5 hours at about 220-240⁰C with mechanical agitation and nitrogen gas sparging. At the end of this time, the heater was replaced with an ice and salt mixture, and the solution at 230⁰C was rapidly cooled to RT. During this rapid cooling process, some of the excess glycerol in the product separated as a lower layer. The glycerol separated and weighed was 45g. The remaining product containing the glycerides and glycerol was a light brown colored viscous mixture weighing 476 g. The IR and ¹H-NMR data showed the characteristic peaks of both the alcohol and the oil.

IR (cm⁻¹): 3384.5 (broad) (O-H stretching); 3008.4 (weak) (C=C-H stretching); 2923.2 , 22853.3 (strong) (aliphatic C-H asymmetric and symmetric stretching); 1738.7 (strong) (C=O stretching); 1653.8 (weak) (C=C stretching); 1456.7 (aliphatic C-H bending); 1175.8 (O=C-O stretching); 1046.4 (-CH₂-O stretching); 723.8 (-CH=C-H (cis) out of plane bending)

¹H-NMR (ppm): 0.95 (CH₃-); 1.3 (-CH₂-); 2.0 (-CH₂-CH=CH-); 2.3 (-CH₂-(C=O)-O); 2.8 (-CH=CH-CH₂-CH=CH-); 4.2 (-CH₂-O-(C=O)-); 5.2 (-CH₂-CH-O-(C=O)-); 5.3 (-CH=CH-)

4.2.2. Base ($\text{Ca}(\text{OH})_2$) Catalyzed Glycerolysis of Soybean Oil (SOMG)

350 g. (0.40 mole) soybean oil and 100 g. (1.09 mole) glycerol were put into a 1 l round bottom flask equipped with a thermometer, N_2 gas tube and magnetic agitation. The soybean oil glycerol mixture was heated to 230°C and held at this temperature for 15 minutes with agitation and nitrogen gas sparging. 0.22 g. $\text{Ca}(\text{OH})_2$ whose metal content based on the weight of glycerol was 0.12 per cent was then added. The reaction was followed with the methyl alcohol solubility test. As more and more monoglycerides are formed, methyl alcohol becomes more soluble in the alcholysis product and the glycerolysis reactions are generally considered to be completed when 1 ml of the glycerolysis product is soluble in 3-4 ml of methanol. The reaction mixture was therefore agitated under N_2 atmosphere for 9.5 hours at 230°C untill the resulting product was soluble in 3.5 ml of methanol and left for cooling. The glycerolysis product at RT was a light brown colored viscous mixture weighing 444 g. The IR and ^1H -NMR spectra showed the same characteristic peaks of the soap emulsified glycerolysis product outlined in Section 4.2.1.

4.3. Maleinization of the SOMG

4.3.1. Maleinization of the SOMG (Soap Emulsified)

The SOMG maleinization was performed under various conditions in which the SOMG : Maleic anhydride (MA) weight ratio, catalyst and temperature were the changing parameters. The related reactions' conditions and ^1H -NMR data are given in Table 3.2. in Section 3.2., however only one of the best procedures that results in the highest maleate half ester ratio will be described here as the best procedure.

SOMG : MA (Wt) = 1.5 : 1 Catalyst: 2-methyl imidazole $T = 80-100^{\circ}\text{C}$

10 g. SOMG was put into a 50 ml. round bottom flask equipped with a thermometer and a magnetic stirrer and heated to about 80°C . 6.67 g. (0.068 mole) maleic anhydride was then added and as maleic anhydride melted 0.1 g. 2-methyl imidazole was added to the mixture. With the addition of 2-methyl imidazole, the color of the solution changed from yellow to orange and small dark orange colored particles were also observed. Following the addition of the catalyst, a trace amount of hydroquinone was also added and the reaction was then followed with IR and $^1\text{H-NMR}$. Both IR and NMR data showed that maleic anhydride was totally consumed in 5.5 hours at $80-100^{\circ}\text{C}$. The formation of the maleate half esters was proven by the broad carboxylic acid O-H band in the IR spectrum and with the appearance of the maleate vinylic protons' peak at 6.3 ppm and also the acid proton's peak at around 8.2 ppm in the $^1\text{H-NMR}$ spectrum. The product obtained at the end of reaction weighed 15.6 g. Maleic anhydride sublimation on the walls of the flask was observed throughout the reaction. The reaction product was a red orange viscous liquid that crystalizes upon keeping.

IR (cm^{-1}): 3446.2 (broad) (carboxylic acid O-H stretching); 3007.7 (weak) ($\text{C}=\text{C}-\text{H}$ stretching); 2924.7, 2853.8 (aliphatic C-H asymmetric and symmetric stretching); 1734.0 (strong) ($\text{C}=\text{O}$ stretching); 1636.5 ($\text{C}=\text{C}$ stretching); 1457.7 (aliphatic C-H bending); 1213.5, 1169.5 (C-O-C asymmetric and symmetric stretching ester); 821.7 (O-H bending acid); 720.7 ($\text{CH}=\text{C}-\text{H}$ (cis) out of plane bending)

$^1\text{H-NMR}$ (ppm) : 0.95 (CH_3-); 1.3 ($-\text{CH}_2-$); 2.0 ($-\text{CH}_2-\text{CH}=\text{CH}-$);
2.3 ($-\text{CH}_2-(\text{C}=\text{O})-\text{O}-$); 2.8 ($-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-$); 4.2 ($-\text{CH}_2-\text{O}-(\text{C}=\text{O})-$);
5.2 ($-\text{CH}_2-\text{CH}-\text{O}-(\text{C}=\text{O})-$); 5.3 ($-\text{CH}=\text{CH}-$); 6.3 ($-\text{CH}=\text{CH}-\text{COOH}$);
8.2 ($-\text{CH}=\text{CH}-\text{COOH}$)

4.3.2. Maleinization of the SOMG (Base $\text{Ca}(\text{OH})_2$ catalyzed) for Mass Spectral Analysis

Apart from the reactions mentioned in Section 4.3.1., maleinization of the SOMG (base $\text{Ca}(\text{OH})_2$ catalyzed) was also carried out in a non-catalyzed system at different SOMG : MA weight ratios for mass spectral analysis. Therefore four separate SOMG + MA mixtures with the SOMG : MA weight ratio; (1:1), (1 : 1.5), (1 :2), (1 : 2.5) were agitated at 120°C without a catalyst for 2.5 hours and then each reaction mixture at the end of this time was analyzed by the Mass Spectrometry for the identification of the possible reaction products. The assigned molecular weights for the different SOMG + MA reaction products from the mass spectra and the related peak intensities are given in Table 3.3.

4.4. Radical Copolymerization of the SOMG Maleates with Styrene

The copolymerization of the SOMG maleates with styrene were carried out for the different SOMG + MA reaction products cited in Table 3.1. in presence of either benzoyl peroxide or methylethylketone peroxide (MEKP) as radical initiators. The polymerization of each reaction product differs in terms of the curing time and the physical properties of the polymers obtained. For convenience, only two of the polymerization procedures that are carried out with the SOMG + MA reaction products (Run no :3) and (Run no :12) will be described here.

4.4.1. Copolymerization of the SOMG + MA Reaction Product (Run no: 3) With Styrene [Initiators: Benzoyl peroxide, MEKP]

6.01 g. maleinized SOMG product was mixed with 2.10 g. styrene forming a yellow colored fluent mixture. 3.33 g. of this mixture was then transferred to a test bottle and

0.0184 g. benzoyl peroxide was added. After the addition of benzoyl peroxide, N_2 gas was sparged into the mixture for 30 minutes. The test bottle was then closed and the mixture was heated in an oil bath to about $90^{\circ}C$. At the end 4.5 hours at this temperature, a light yellow colored hard polymer was obtained. Shrinkage upon curing was observed on the walls of the bottle. Some small whitish insoluble particles also floated down the tube showing that benzoyl peroxide was not totally soluble in the maleinized SOMG and styrene mixture.

3.57 g. of the maleinized SOMG and 1.25 g. styrene were mixed and 2.40 g. of this fluent mixture was transferred into a test bottle. 0.0515 g. MEK peroxide with 0.0124 g. cobalt naphtanate as the accelerator was also added to this mixture. The mixture was held under vacuum for 15 minutes and then left for cure at RT. In about 1 hour the mixture became a soft rubber and at the end of 5 hours the polymer obtained was totally hard.

4.4.2. Copolymerization of the SOMG + MA Reaction Product (Run no : 12) With Styrene [Initiator: MEKP]

2.46 g. maleinized SOMG product which was a reddish brown viscous liquid at RT was mixed with 0.89g. styrene. 0.07g. MEKP with 0.014 g. cobalt naphtanate was then added to this mixture. After the addition of MEKP and cobalt naphtanate, the mixture was quickly transferred into a teflon mold and the mixture in the mold was covered with a microscobic slide to prevent contact with air. The sample was then left for cure at RT. In 20 minutes, the liquid mixture was transformed into solid resin. The polymer obtained at the end of 1.5 hour was a transparent light brown colored hard solid. IR showed both the succinate half ester's acidic O-H broad band and the characteristic peaks of polystyrene.

IR (cm^{-1}): 2000-3500 (broad) (O-H stretching acid); 2000-1600 (overtone or combination bands phenyl ring); 1491.3, 1454.9 ($C\approx C$ ring stretching); 820 (O-H out of plane bending acid); 752 (aromatic C-H out of plane bending); 701.7 ($C\approx C$ bending pheyl ring)

4.5. Emulsion Copolymerization of the SOMG Maleates With Styrene

2.55 g. of the maleinized SOMG product (Reaction run no : 9) was added to 10 ml 5% NaOH drop by drop, forming a slightly acidic solution with a Ph of 6.9. The maleinized SOMG product and the NaOH solution had formed a yellow colored milky emulsion. 0.9042 g. styrene 35% based on the maleinized SOMG product was then added and with the addition of styrene the yellow color of the emulsion suddenly changed into milky white. The stable emulsion was then put into a 50ml round bottom flask equipped with a condenser and magnetic stirrer and was heated to about 80°C. 0.0370 g. K₂S₂O₈ dissolved in 3 ml water was added drop by drop to this emulsion. At the end of 2.5 hours at 75-85°C with magnetic stirring, a light yellow colored suspension separated as an upper layer from the emulsion. A trace amount of this suspension which was a whitish creamy wax at RT was then put on a watch glass and heated to about 100°C for 30 minutes to evaporate the residual water and the sample was then analyzed with IR and ¹H-NMR. The copolymerization of the maleate half esters with styrene was proven with the disappearance of the 6.3 ppm peak that belongs to maleate vinylic protons and the appearance of the 6.7 and 7.3 ppm peaks that belong to polystyrene.

IR (cm⁻¹) : 3359 (O-H stretching); 3007.7 (aromatic and vinylic C-H stretching); 2924.8 , 2853.3 (aliphatic C-H stretching) ; 1739.6 (C=O stretching ester); 1570.8 (Na⁺ O-(C=O)- asymmetric stretching); 1492.7 , 1455.7 (C=C stretching phenyl ring); 1170.2 ((O=C)-O stretching); 699.0 (C-H out of plane bending mono substituted benzene)

¹H-NMR (ppm) : 0.95 (C-H₃); 1.3 (-CH₂-); 2.0 (-CH₂-CH=CH-); 2.3 (-CH₂-(C=O)-O-); 2.8 (-CH=CH-CH₂-CH=CH-); 4.2 (-CH₂-O-(C=O)-); 5.3 (-CH=CH-); 6.7 (C₆H₅-CH-CH₂-); 7.3 (C₆H₅-)

4.6. Radical Homopolymerization of the SOMG Maleates

The radical initiated homopolymerization of the maleinized SOMG product was carried in presence of benzoyl peroxide and MEKP as radical initiators. In a simple procedure, 5.94 g. of the maleinized SOMG product was mixed with 0.22 g. MEKP and 0.028 g. Cobalt naphtanate. The reddish brown viscous liquid mixture placed in a closed teflon mold was then left for cure at RT. The polymerization was observed with a slow viscosity increase. IR and ^1H -NMR showed a decrease in maleate peak intensities, however the homopolymerization of the maleate half esters only occurred to a limited extent.

4.7. Swelling Tests

Rectangular pieces of dimensions about 2mm*5mm*10mm were cut from the solid samples. The samples were weighed and this value was recorded as W_0 and put into a closed tank that contains the solvent. The polymer samples were then reweighed at certain time intervals and the weight of the swollen polymer was recorded as W_t . The procedure was continued until the polymer was fragmented or the solvent uptake ceased and W_t stayed constant.

4.8. Determination of Water Absorption

The polymer samples with a diameter around $10 \text{ mm} \pm 1$ and width of 2 mm were dried for 24 hours in the oven controlled at $50 \pm 3^\circ\text{C}$. At the end of this time, they were allowed to cool to ambient temperature in the dessicator and then each specimen was weighed to the nearest 1 mg. This value was recorded as W_0 . The three specimens were

then put into a container containing distilled water at RT. After immersion for 24 hours, the specimens were taken from the water and the surface water was removed with a dry clean cloth. The three specimens were then reweighed to the nearest 1mg and this value was recorded as W_1 . The per cent water absorption of the polymers were then calculated according to the formula $[(W_1 - W_0)/W_0] * 100$.

In determination of the boiling water absorption, the same procedure was applied but the polymers after being dried in the oven and cooled in the dessicator to RT, were kept for 30 minutes in boiling water. At the end of this time the polymer samples were transferred into another tank that contains distilled water at RT and cooled for 15 minutes in this tank and then taken out from this tank and reweighed. The per cent boiling water absorption was then calculated accordingly.

5. CONCLUSIONS

In this study, soybean oil monoglycerides (SOMG) were obtained by the glycerolysis of soybean oil. The SOMG product which is a mixture of glycerides containing mainly the monoglycerides were then reacted with maleic anhydride at temperatures around 100°C to produce the SOMG maleate half esters. The resulting SOMG maleates were soluble in styrene and the radical initiated copolymerization of the SOMG maleates with styrene produced rigid, thermoset polymers. The polyesterification reactions of monoglycerides with maleic anhydride and other types of anhydrides are known and widely used in the production of alkyd resins which are surface coating materials. However the synthesis of the SOMG maleate half esters and their radical copolymerization with styrene is new and results in a much more rigid polymer than that of the alkyd resins.

The glycerolysis of soybean oil was carried out with the use of a large amount of excess glycerol, in presence of a sufficient amount of soap as catalyst. The reverse reaction was prevented with a rapid cooling process at the end of reaction. Thus, with these optimizations the monoglyceride yield was maximized whereas the amount of unreacted triglyceride was minimized in the final SOMG product. IR and ¹H-NMR spectra of the product showed the characteristic peaks of both the alcohol and the oil and thus confirmed the formation of the mono- and diglycerides.

Maleinization of the SOMG product was carried out under various conditions in which the SOMG : MA weight ratio, catalyst and temperature were the changing parameters to maximize the maleate half ester's yield. It was found out that the highest maleate half ester yield can only be obtained when the SOMG is in excess. Different catalysts including NaOH, N,N dimethylaniline, 2-methyl imidazole, H₂SO₄ and p-toluene sulfonic acid were used in the maleinization reactions. 2-methyl imidazole was the best among the base catalysts used. Acid catalysts were not preferred since it was found out

that, both H_2SO_4 and p-toluene sulfonic acid hydrolyze a certain amount of maleic anhydride to maleic acid.

The course of maleinization reactions was followed with both IR and ^1H -NMR. In the IR, the disappearance of the 1779, 1849 and 696 cm^{-1} peaks that are characteristic for maleic anhydride and the appearance of the broad acid band between $2500\text{--}3600\text{ cm}^{-1}$ indicate the formation of the maleate half esters. In ^1H -NMR, the formation of maleate half esters was proven with the appearance of a new peak at 6.35 ppm that belongs to maleate vinylic protons and also a new acid peak at around 9 ppm. Higher reaction temperatures and longer reaction times resulted in the formation of trace amounts of fumarate half esters produced by cis to trans isomerism of the maleate double bonds whose chemical shift appears around 6.9 ppm. At the end of maleinization reactions it was found out that the reactive double bonds of maleate or fumarate half esters were consumed by some side reactions. Thus, in reactions performed in presence of a trace amount of hydroquinone; a known free radical inhibitor, a considerable increase in the maleate half ester yield was observed. The premature dimerization or polymerization of the maleates which can be substantially prevented by the addition of a free radical inhibitor is therefore suggested as a possible side reaction. The mass spectral analysis of the maleinized SOMG product, on the other hand showed the presence of different types of maleates in the product. Thus, the presence of monoglyceride monomaleate, monoglyceride bis maleate, diglyceride monomaleate and finally glycerol trismaleate was confirmed with the corresponding peaks at 454, 552, 717 and 387 respectively in the mass spectra of the maleinized SOMG products.

The free radical initiated copolymerization of the SOMG maleates with styrene produced yellow colored, transparent rigid polymers. The IR spectrum of the polymers obtained was characterized with a broad acid band between $2500\text{--}3700\text{ cm}^{-1}$ and with the characteristic peaks of styrene ring. ^1H -NMR analysis of the obtained polymers was impossible since the polymers were insoluble in the common deuteriated solvents. The cross-linking network structure of the polymers obtained is indicated by the insolubility of the polymers in most of the common solvents. It was found out that, the polymers are not

dissolved but swell in most of the organic solvents such as CHCl_3 , DMSO, CCl_4 , and acetone.

The emulsion copolymerization of the SOMG maleates with styrene was also carried out in presence of $\text{K}_2\text{S}_2\text{O}_8$ as radical initiator. The sodium salt of the SOMG maleates formed very stable emulsions with styrene and their copolymerization produced a suspension separated from the emulsion as an upper layer. The IR and ^1H -NMR analyses performed on this product confirmed the copolymerization of the sodium salts of the SOMG maleates with styrene.

The resulting copolymers of SOMG maleates with styrene are abundant with the hydrophylic acid groups and are therefore very suitable for fiber reinforcement. Thus, the mechanical properties of the obtained polymers can further be improved with suitable fiber reinforcement and these polymers can serve as an alternative to the petroleum based unsaturated polyesters.

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