Styrenation of Triglyceride Oils by Macromonomer Technique

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A novel macromer technique is described for the styrenation of triglyceride oils. Triglyceride oil-based macromers were prepared via successive transesterification and condensation reactions. The macromers were styrenated at 100°C using benzoyl peroxide as an initiator. The styrenation led to improved film properties with semidrying oils. Homopolymerization of the macromonomers failed due to the stearic hindrance of the bulky oil moieties. The results obtained were also evaluated by considering the degree of unsaturation.

INTRODUCTION

The use of renewable sources in the manufacturing of industrial products received much attention after the petroleum shortages in the 1970s and is now becoming even more important industrially due to environmental concerns. Today, natural oils and fats are considered to be the most important class of renewable sources. Drying and semidrying oils are used in making paints, varnishes, enamels, printing inks, and other protective and decorative coatings of an oil-based type.[1] However, quite often, desired properties are not attainable due to the somewhat deficient film properties of coatings prepared from unmodified oils. Various methods have been proposed to adjust the final properties of the products. One well-known method is the copolymerization of oils with vinyl monomers, such as styrene. This process is often termed styrenation. Styrenation reactions are generally accomplished in two ways depending on the mode of generation of radicals on the oils. In the classical method, radicals are formed by thermolysis either in the absence (conjugated oils) or in the presence (non-conjugated) of added initiators, such as dibenzoyl peroxide shown in *Scheme* 1.[2-11]

We have recently developed an alternative method for the styrenation of triglyceride oils without adding initiator or catalysis.[12-15] In this case, azo groups incorporated onto triglyceride oils can undergo decomposition upon heating to yield radicals capable of reacting with styrene. Moreover, homopolymer formation observed in the classical method was minimized.

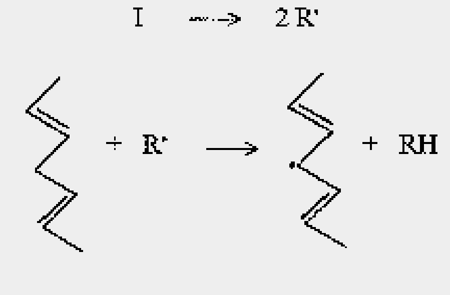
As part of our continuing interest in developing general approaches for styrenation of semidrying and drying oils, we report on a macromonomer (macromer) technique. The term macromer refers to short polymer molecules carrying a terminal polymerizable unsaturation.[16] Macromers based on oils are expected to copolymerize with styrene via conventional radical polymerization.

There are few studies in this area.[17,18] In these studies, styrene, methyl methacrylate, and acrylic acid monomer mixtures were used to modify the oil modified alkyd resin without preparing the acrylate glyceride separately.

EXPERIMENTAL

Materials

Commercially purchased linseed oil and sunflower oil were used. The main characteristics of these oils are presented in *Table* 1. The acrylic acid (AA) was analytical grade from Fluka. Styrene and solvents were purified according to conventional drying and distillation procedures.[19]



Scheme 1

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Table 1—Characteristics of the Triglyceride Oils Used in the Study[a]

Oil	Refractive Index, n_D^{20}	Acid Value	Saponification Value	Ester Value	Iodine Value[b]
Sunflower oil	1.4750	0.6	188.3	187.7	121.5
Linseed oil	1.4811	1.0	192.4	191.4	173.6

(a) Working procedure for the analytical methods were taken from reference 20 unless otherwise stated.
(b) Hanus method, reference 28.

Preparation of Partial Glycerides

Preparation of partial glycerides (PG) was carried out in a 250 ml four-necked flask equipped with a stirrer, a thermometer, a nitrogen inlet tube, and a condenser. One hundred grams of oil and 8.5 g of glycerol were placed into the reaction flask and heated. When the temperature reached 218°C, 0.01 g of CaO was added as the catalyst. The temperature was set at 232°C and maintained for 45 min. Acid and hydroxyl values of the resulting partial glycerides were determined.[20]

Esterification of PG with AA

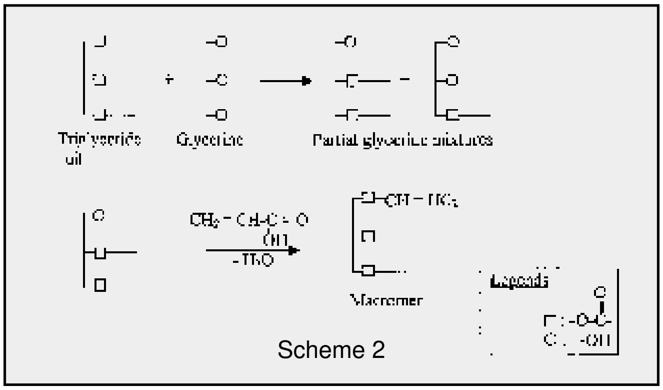
For the partial glyceride-acrylic acid (PG-AA) ester manufacture, the mixture of AA and PG was heated to 180°C for a period of four hours. The reaction was carried out in the same set of apparatus as that used for PG preparation except that a water trap was included. The initial mol ratio of hydroxyl groups to acid groups was set to 1:2. *p*-Toluenesulfonic acid was used as the esterification catalyst. To remove the water formed in the esterification reaction, the reaction was carried out in a benzene (90% of the AA) medium. To prevent homopolymerization of AA, 6.5% by weight of hydroquinone with respect to AA was added to the reaction flask. The reaction content was precipitated in methanol, and then hydroxyl and acid values of the precipitated portion were determined.

Copolymerization of PG-AA with Styrene

The mixture of PG-AA and styrene in a weight ratio of 1:1 was placed into a flask and sparged with N_2 for 15 min. The mixture was then heated to 100°C under inert gas atmosphere. Benzoyl peroxide (0.5 wt% with respect to styrene) was used as an initiator.

As the basis for comparison, homopolymerization of PG-AA was also achieved by using the same conditions.

Viscosities of the products of copolymerization and homopolymerization reactions were determined.



Scheme 2

Preparation of Comparative Sample

A conventional sample was prepared by using a solvent method according to the following formulation.[8]

Ingredient	Part by Weight
Oil	55
Styrene	45
Xylene	43
Benzoyl peroxide	1.1

The reactants were heated to refluxing temperature which was in the range 145° to 155°C for a period of 24 hr.

Determination of Film Properties

Film properties, such as drying time,[21] flexibility,[22] adhesion,[23] water resistance,[24] alkali resistance,[24] and acid resistance[24] were determined. For this purpose, each sample was thinned with xylene to 70 or 90% solid content. Lead naphthenate (0.5%) and cobalt naphthenate (0.05%) as metal based on solid content were added. Driers were added 24 hr before the film application. In drying time determinations, a Bird film applicator with 40 µm aperture was used for film application on glass plate; the dry film thickness being 7.5-12.5 µm. For the other tests, a dipping method was employed. For the flexibility, adhesion, and water resistance tests, tin plate panels were used as a substrate, while glass tubes were used for the alkali and acid resistance tests, as explained in the related standard methods. A water resistance test was performed 48 hr after the film application, while other tests were conducted after 72 hr.

RESULTS AND DISCUSSION

Triglyceride oil-based macromonomers were prepared by two successive steps. First, PGs were obtained by the transesterification of the corresponding triglyceride oils with glycerol. Subsequently, these PGs were esterified in the presence of an inhibitor with AA to afford the macromonomer, PG-AA. The overall reactions are described in *Scheme* 2.

The acid and hydroxyl values of PG and PG-AA are given in *Table* 2. As shown, the free acid content of PG-AA

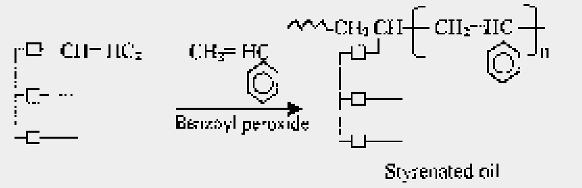
Table 2—Acid and Hydroxyl Values of PG and PG-AA

	PG		PG-AA	
By-Product Based on:	Acid Value	Hydroxyl Value	Acid Value	Hydroxyl Value
Sunflower oil	2.6	117.3	7.1	10.8
Linseed oil	2.8	126.7	11.4	15.6

Table 3—Viscosities of By-Products and Final Products

	Viscosity (St, 20°C) of:		
Oil	PG-AA	PG-AA / St	PG-AAh
Sunflower oil	1.4	17^{a}	1.4,^{a} 1.65^{b}
Linseed oil	1.8	5.5^{c}	2.5,^{a} 2.5,^{b} 2.8^{c}

The reaction was continued for: (a) 80 minutes
(b) 7 hours
(c) 10 hours



Scheme 3

fell to considerably lower values under the applied reaction conditions. Hydroxyl values of the PG-AA also decreased to a reasonable level, indicating successful incorporation of AA.

Macromonomers were then polymerized and co-polymerized with styrene in the presence of benzoyl peroxide at 100°C, thus yielding modified oils (*Scheme* 3).

In *Table* 3, viscosity values of PG-AA ester macromonomers, copolymer of PG-AA with styrene (PG-AA/St), and PG-AA homopolymer (PG-AAh) are given. The viscosity increase in the homopolymerization reaction is low for both sunflower and linseed oil-based homopolymers, probably due to the stearic hindrance of the bulky triglyceride oil moieties. In general, homopolymerization of the macromers of the linear polymers is less efficient than copolymerization. However, the linseed oil-based sample showed a slightly higher viscosity increase compared to sunflower oil. This small difference may be due to the thermal polymerization of the linseed oil moiety under the conditions used.

The sunflower oil-based copolymer showed a larger increase in viscosity than did the linseed oil-based sample. This indicates that the rate of polymerization decreases with increasing of unsaturation of the oil used. Previous reports have also shown that vinyl esters of unsaturated fatty acids either decrease the rate or stop the polymerization.[25-27] In our opinion, this behavior is due to the susceptability of the methylene hydrogen between two double bonds to abstraction resulting in stable free radical formation on the linolenic acid chain. These radicals most probably cause chain termination rather than chain extension because of recombination of the resonance stabilized free radicals.

The film properties of the styrenated oils together with those of the comparative samples are shown in *Table* 4. As can be seen, the product based on sunflower oil gave the best alkali and water resistance. Comparing drying times, the linseed oil-based product prepared by the conventional method has the shortest drying time. This result is related to the fatty acid composition of the oils. Sunflower oil is a semidrying oil rich in linoleic acid. Linseed oil is a drying oil rich in linolenic acid. Therefore, linseed oil-based surface coating materials have either an equal or shorter drying time than the materials based on sunflower oil. In this study, the sunflower oil-based polymer had a shorter drying time than that based on linseed oil, because the sunflower oil-based polymer was higher in molecular weight based on resin viscosities.

The results show that semidrying oils, such as sunflower oil, can be used for preparation of styrenated oil by using macromonomers based on oil and acrylic acid. On the other hand, this method is not suitable for the modification of drying oils.

CONCLUSION

The styrenation of triglyceride oils has been achieved by a macromonomer technique. For the preparation of macromer, triglyceride oil was converted to a partial glyceride, and this intermediate was esterified with acrylic acid. Macromer was homopolymerized and copolymerized with styrene. Film properties of the resulting products were determined and compared with those of classical styrenated oil samples. This technique was successful in the case of semidrying oils. Drying oils failed in the polymerization reaction due to the very slow polymerization rate. The semidrying oil-based sample exhibited good film properties with excellent water, alkali, and acid resistance.

Table 4—Film Properties of the Styrenated Oils

Styrenated Sample Based on:	Drying Time^{a} (set-to-touch)	Flexibility^{b}	Adhesion^{c}	Water Resistance^{d}	Alkali Resistance^{e}	Acid Resistance^{f}
Sunflower oil	30 min	2 mm	4B	nc	nc	nc
Linseed oil	75 min	2 mm	4B	25 min	40 min	nc
Linseed oil by conventional method	4 min	2 mm	5B	5 min	60 min	nc

(a) Test was carried out at 25°C and 60% relative humidity[21]
(b) The diameter of cylinder which caused no crack on the film[22]
(c) Test method B was applied[23]
(d) Ref. 24.
(e) The test was carried out at 25°C with 5% NaOH solution[24]
(f) The test was carried out at 25°C with 9% H_2SO_4 solution[24]
Legend : nc - no change

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