

# Drying and Semidrying Oil Macromonomers. III. Styrenation of Sunflower and Linseed Oils\*

T. Akbas,<sup>1</sup> Ü. G. Beker,<sup>1</sup> F. S. Güner,<sup>1</sup> A. T. Erciyes,<sup>1</sup> Y. Yagci<sup>2</sup>

<sup>1</sup>Istanbul Technical University, Chemical Engineering Department, 80626 Maslak, Istanbul, Turkey

<sup>2</sup>Istanbul Technical University, Department of Chemistry, 80626 Maslak, Istanbul, Turkey

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**ABSTRACT:** Styrenation of drying and semidrying oils, namely sunflower and linseed oils, via the macromer technique was studied. For this purpose, the macromonomers of the oils were prepared by transesterification of methyl methacrylate (MMA) with the corresponding partial glycerides (PG). Subsequent styrenation was achieved by free radical copolymerization of the macromonomers with sty-

rene using benzoyl peroxide as the initiator. The viscosity and the film properties of the products were studied and compared. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2373–2376, 2003

**Key words:** macromonomers; polystyrene; coatings; copolymerization

## INTRODUCTION

Drying and semidrying oils have been used in the manufacture of paints, varnishes, printing inks, and other protective and decorative coatings for years.<sup>1</sup> Because desired film properties such as drying time, adhesion, and resistance to alkali, acid, water are not attainable, various modifications have been applied to the triglyceride oils. One of those modifications is the copolymerization of oils or alkyds with vinyl monomers, such as styrene. This method is also known as styrenation.<sup>2–4</sup> There are generally two methods of styrenation of oils depending on the mode of the generation of radicals on the oils. In classical method, radicals are formed by thermolysis either in the absence (conjugated oils) or in the presence (nonconjugated oils) of added initiators such as dibenzoyl peroxide. In this method, degree of saturation and conjugation have an important effect on the formation of free radicals on the oil molecules. Because of this reason, semidrying and nonconjugated drying oils are need to be mixed with conjugated drying oils to have better styrenated products.<sup>5–8</sup>

In the literature, studies related with this area are limited. Most of these studies are covered as patents. The general procedure for this vinyl modification of alkyd or oil were explained as follows. First, hydroxyl containing oil species were obtained by reacting triglyceride oils (i.e., linseed, soybean, castor, safflower) with a polyalcohol (i.e., glycerol, pentaerythritol). These alcoholysis products were then treated with the

mixture of methyl methacrylate–styrene,<sup>9</sup> methacrylic acid–styrene,<sup>10</sup> acrylic acid–methyl methacrylate–styrene,<sup>11</sup> and methyl methacrylate–methacrylic acid–styrene.<sup>12</sup> As seen in this procedure, the conditions and the extent of the reaction for a specific monomer was not determined. The quality of the products were determined finally with regard to their film properties.

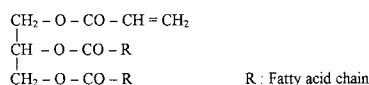
We have recently developed an alternative method for the styrenation of triglyceride oils without requirement of added initiator or catalyst.<sup>13–16</sup> In this method, azo groups that yields radicals upon heating were incorporated onto glyceride oils. This macroinitiator thus obtained was activated in the presence of styrene monomer by heating the mixture at an appropriate temperature. In this way, homopolymer formation observed in the classical method was minimized. Another method, namely the macromonomer (macromer) technique, has been reported. In this method, first the macromer of the following structure (Scheme 1) was obtained through the reaction of hydroxyl containing oil specimens with a vinyl monomer such as acrylic acid and then this macromer was homopolymerized and copolymerized with styrene.<sup>17</sup>

In an another study, macromers were prepared through the interesterification of castor oil with linseed oil followed by esterification with acrylic acid. The macromers thus obtained contain vinyl groups to facilitate subsequent styrenation.<sup>18</sup>

As a part of our continuing interest in developing general approaches for styrenation of semidrying and drying oils, we now report the preparation of methyl

Correspondence to: A. T. Erciyes.

\*For parts I and II see references 17 and 18, respectively.



Scheme 1

TABLE I  
Some Characteristics of the Triglyceride Oils Used in the Study<sup>a</sup>

Oil	Refractive index, $n_D^{20}$	Acid value	Saponification value	Ester value	Iodine value
Sunflower oil	1.4750	0.6	188.3	187.7	121.5
Linseed oil	1.4811	0.1	192.4	191.4	173.6

<sup>a</sup> Working procedure for the analytical methods was taken from ref. 20 unless otherwise stated.

<sup>b</sup> Hanus method, ref. 27.

methacrylate-type macromer synthesized by a transesterification reaction instead of direct condensation. The macromer thus formed was then reacted with styrene to give styrenated oils. Finally, film properties were determined and the modified oil samples were evaluated as oil-based binders.

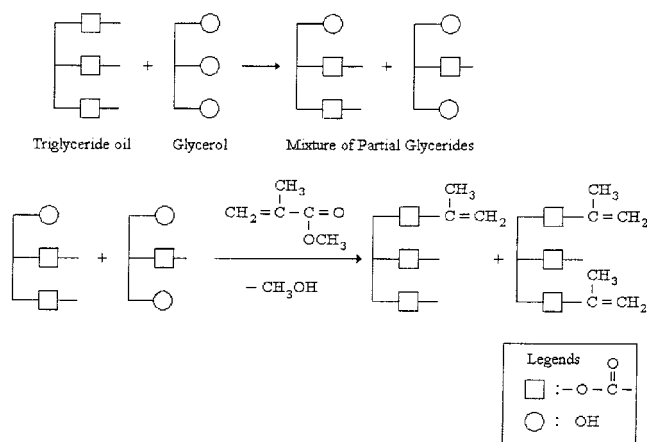
## EXPERIMENTAL

### Materials

Sunflower oil and linseed oil were purchased commercially. The main characteristics of these oils are presented in Table I. Methyl methacrylate (MMA) and styrene (St) were purified according to conventional drying and distillation procedures.<sup>19</sup>

### Preparation of partial glycerides (PG)

Preparation of PG was carried out in 250-mL four-necked flask equipped with a stirrer, a thermometer, a nitrogen inlet tube, and a condenser. One hundred twenty grams of oil and 10.2 g of glycerol were placed into the reaction flask and heated. When the temperature reached 218°C, 0.12 g of CaO was added as a catalyst. The temperature then was set at 232°C and the reaction was continued at this temperature for 45 min under inert gas atmosphere. Acid and hydroxyl values of the resulting PG were determined.<sup>20</sup>



### Transesterification of PG with MMA

The reaction was carried out in the same set of apparatus used for PG preparation. The mixture of MMA and PG was heated to 200°C. The initial mol ratio of hydroxyl groups to MMA was set to 1:2, CaO was added in the amount of 0.2% wt of the PG portion as a catalyst. To prevent homopolymerization of MMA, 6% by weight of hydroquinone with respect to MMA was added to reaction flask. The system was carried out under nitrogen flow to remove the methanol formed in the transesterification reaction. Acid and hydroxyl values of macromers were determined.

### Copolymerization of macromer with styrene

The mixture of macromer and styrene in a weight ratio of 1:1 was placed into a flask and sparked with N<sub>2</sub> for 15 min. The mixture was heated to 100°C under inert gas atmosphere. Benzoyl peroxide (0.5% wt with respect to styrene) was used as an initiator. Reaction times were stopped when the predetermined viscosity was reached.

### Determination of viscosities and film properties

Film properties such as drying time,<sup>21</sup> flexibility,<sup>22</sup> adhesion,<sup>23</sup> water resistance,<sup>24</sup> alkali resistance,<sup>24</sup> acid resistance,<sup>24</sup> and hardness<sup>25</sup> were determined. For this

TABLE II  
Hydroxyl and Saponification Values of Partial Glycerides (PG) and Macromers

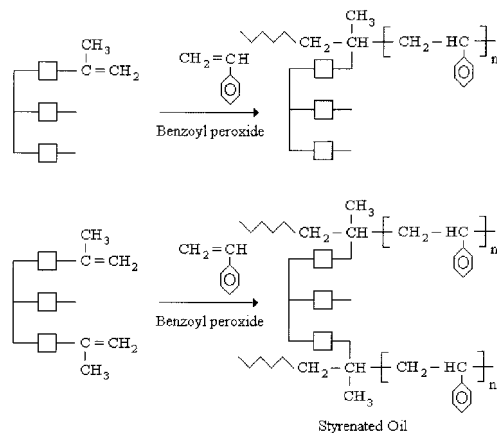
Product <sup>a</sup>	Reaction time (h)	Hydroxyl value	Saponification value
PG of sunflower oil	—	124.5	81.6
PG of linseed oil	—	119.4	86.6
(S-MMA) <sub>1</sub>	4	54.3 (86.2) <sup>b</sup>	196.0 (297.8) <sup>b</sup>
(S-MMA) <sub>2</sub>	8	44.5 (68.5) <sup>b</sup>	200.5 (273.8) <sup>b</sup>
(S-MMA) <sub>3</sub>	8	34.7 (45.2) <sup>b</sup>	199.2 (255.3) <sup>b</sup>
(L-MMA) <sub>1</sub>	4	54.1 (83.6) <sup>b</sup>	198.7 (194.8) <sup>b</sup>
(L-MMA) <sub>2</sub>	8	32.5 (45.3) <sup>b</sup>	196.3 (257.0) <sup>b</sup>

S-MMA : sunflower oil-based macromer.

L-MMA : linseed oil-based macromer.

<sup>a</sup> The macromers having different hydroxyl values are stated by 1, 2, 3 indices.

<sup>b</sup> The hydroxyl and saponification values of macromers purified are given in the brackets.



Scheme 3

purpose, each sample was thinned with xylene to 55% solid content. Viscosities of thinned samples were determined using a Brookfield model viscometer at 15°C; 0.5% lead naphthenate and 0.05% cobalt naphthenate as metal based on solid content were added 24 h before the film application. For drying time determinations a Bird film applicator with 40 μm aperture was used for film application on glass plate; dry film thickness being 22.0–25.0 μm. For hardness test, Bird film applicators with 40- and 60-μm apertures were used for film applications on glass plates; dry film thickness being, respectively, 23.3–26.7 and 35.0–38.3 μm. For the flexibility, adhesion and water resistance tests, tin plate panels were used as the substrate, while glass tubes were used for the alkali and acid resistance tests as explained in the related standard methods. Tests were performed 7 days after the film application.

RESULTS AND DISCUSSION

Triglyceride oil-based macromers were prepared by two successive steps. First, partial glycerides (PG)

TABLE III  
Viscosities and Molecular Weight Characteristics of Macromers and Copolymers

Product	Viscosity <sup>a</sup> , cP	M <sub>w</sub>	M <sub>w</sub> /M <sub>n</sub>
(S-MMA) <sub>1</sub>	169.0	1505	1.12
(S-MMA) <sub>2</sub>	182.0	1488	1.10
(S-MMA) <sub>3</sub>	220.5	1563	1.20
(L-MMA) <sub>1</sub>	116.0	1366	1.03
(L-MMA) <sub>2</sub>	123.0	1489	1.12
(S-MMA) <sub>1</sub> /St <sup>a</sup>	134.0	31423	1.87
(S-MMA) <sub>2</sub> /St <sup>a</sup>	68.5	32436	2.02
(S-MMA) <sub>3</sub> /St <sup>a</sup>	110.5	56469	2.36
(L-MMA) <sub>1</sub> /St <sup>a</sup>	63.5	52597	2.07
(L-MMA) <sub>2</sub> /St <sup>a</sup>	68.0	62229	2.31

(S-MMA): sunflower oil-based macromer.

(L-MMA): linseed oil-based macromer.

(S-MMA)/St: sunflower oil-based polymer.

(L-MMA)/St: linseed oil-based polymer.

<sup>a</sup> Copolymers were thinned with xylene to 55% solid content.

were prepared by glycerolysis reaction between each triglyceride oil and glycerol. Subsequently, macromer was obtained by the transesterification reaction of PGs with MMA in the presence of a catalyst. The chemical reactions of two steps are depicted in Scheme 2.

In Table II, hydroxyl and saponification values of PG and macromers are given. By evaluating the table, it was understood that the changing of hydroxyl and saponification values of macromers indicates the successful incorporation of methacrylate moiety. Low hydroxyl value indicates that more hydroxyl groups of PG were reacted with MMA for the same oil-based macromers.

Macromers prepared were then copolymerized with styrene in the presence of benzoyl peroxide at 100°C, thus yielding modified oils (Scheme 3).

The viscosity values of macromers and the corresponding copolymers are given in Table III. The macromers having smaller hydroxyl values are more vis-

TABLE IV  
Some Film Properties of Copolymers

Film properties	(S-MMA) <sub>1</sub> /St	(S-MMA) <sub>2</sub> /St	(S-MMA) <sub>3</sub> /St	(L-MMA) <sub>1</sub> /St	(L-MMA) <sub>2</sub> /St	Linseed oil by solvent method <sup>f</sup>	Linseed oil by Dow method <sup>f</sup>
Drying time <sup>a</sup> (set-to-touch)	4.5 min	5.0 min	2.5 min	6.0 min	4.5 min	2.5 min	2.5 min
Alkali resistance <sup>b</sup>	nc	nc	nc	6 hr	2 hr	60 min	31 min
Acid resistance <sup>c</sup>	nc	nc	nc	nc	nc	nc	nc
Water resistance	60 min	180 min	30 min	45 min	45 min	5 min	9 min
Adhesion	0B	4B	0B	3B	4B	5B	5B
Flexibility <sup>d</sup>	2 mm	2 mm	2 mm	2 mm	2 mm	2 mm	2 mm
Hardness <sup>e</sup>	18	14	34	46	34	—	—

<sup>a</sup> The test was carried out at 21°C and 65% relative humidity.

<sup>b</sup> The test was carried out at 21°C with 5% NaOH solution.

<sup>c</sup> The test was carried out at 21°C with 9% H<sub>2</sub>SO<sub>4</sub> solution.

<sup>d</sup> The diameter of cylinder which caused no crack on the film.

<sup>e</sup> Rocker Hardness Tester was used. Film was applied by 60 μm Bird applicator.

<sup>f</sup> The products obtained by classical method and were thinned with xylene to 60% solid content.<sup>13</sup>

cous than the ones having greater hydroxyl values. This indicates the degree of MMA incorporation. If the macromers based on the same oil base are compared with one another it can be seen that the viscosities increase with decrease in hydroxyl values. This is an expected result.

It should also be noted that, although the hydroxyl content of the sunflower and linseed oil-based macromers were different from each other, they gave the copolymers having practically the same molecular weights. Molecular weight characterization of the macromers as well as the copolymers were also tabulate in Table III. As can be seen, the polydispersity of the copolymers were in the range of 1.87–2.36, which is expected for conventional free radical polymerization.

The film properties of the products<sup>26</sup> styrenated by classical methods have also been given in Table IV to make a comparison with the copolymers obtained.

It can be concluded that both sunflower and linseed oil-based copolymers gave the best alkali resistances than the products styrenated by classical methods. In our opinion, this is probably due to the steric hindrance of the ester groups by the long styrene segment attached to the oil molecule through MMA.

In comparison of drying times, samples prepared by the classical methods have the shortest drying time. This result is related to the fatty acid composition of the oils. Linseed oil is a drying oil rich in linolenic acid, while sunflower oil is a semidrying oil rich in linoleic acid. Therefore, linseed oil-based surface coating materials should have shorter drying times than those based on sunflower oil. In this study, sunflower oil-based copolymers have shorter drying times than linseed oil-based copolymers, in contrast to expectation. As seen in Table III, sunflower oil-based samples namely (S-MMA)<sub>1</sub>/St and (S-MMA)<sub>3</sub>/St have greater viscosities compared to those of linseed oil-based samples, namely (L-MMA)<sub>1</sub>/St and (L-MMA)<sub>2</sub>/St. This shows that in the case of sunflower, products with longer polystyrene segments have been obtained. In the case of linseed oil, linoleic acid chain generated free radicals more easily, and most probably these radicals serve as a chain terminator.

Film properties of the obtained copolymers such as acid resistance and flexibility do not show any difference compared with those obtained by the classical methods.

## CONCLUSION

In this study, macromers based on transesterification product of each linseed oil and sunflower oil with

methy methacrylate were prepared. The macromer thus obtained contains vinyl groups to facilitate subsequent styrenation. Results obtained show that semi-drying oils such as sunflower oil can be used for preparation of styrenated oil by using macromers based on an oil and methyl mathacrylate.

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