

## Copolymerization of Dehydrated Castor Oil with Styrene: Determination of Reactivity Ratios

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### Synopsis

Dehydrated castor oil (DCO) has been used as a comonomer with styrene to determine reactivity ratios. The polymerization was a free-radical process in benzene, and the product was isolated by evaporation of the reaction mixture and by two precipitations into petroleum ether from benzene. The copolymer composition was determined by a saponification procedure. DCO was found to have a high chain transfer constant and a very low reactivity ratio (estimated at 0.086) compared to styrene (11.6). It was found that copolymerization is difficult to achieve in a system where the DCO concentration in the reaction mixture was above 20 mole-%.

### INTRODUCTION

One interesting area of copolymerization concerns the use of drying oils as comonomers. These oils, both natural and synthetic, must possess unsaturation to be capable of addition copolymerization. A drying oil is defined as an oil, containing two or more double bonds, which will absorb oxygen upon exposure to air to give peroxides, which catalyze polymerization of the unsaturated portion.<sup>1</sup> Polymerization renders the oil solid or semisolid and insoluble due to the crosslinking through the fatty acid chains of the glyceride. Drying oils form tough, elastic films when exposed in thin layers and are used extensively in paint manufacture.

In an effort to improve the properties and expand the usage of drying oils, copolymerization with vinyl monomers has been explored.<sup>1,2</sup> The demands of World War II led to the utilization of styrene-drying oil copolymers as substitutes for drying oils. The chemical inertness and quick-drying ability of polystyrene combined with the flexibility contributed by the oil have made this class of copolymers a leader in the area of coating materials.

Castor oil is a naturally occurring oil that possesses unsaturation. It exists naturally as glycerides of a mixture of fatty acids, ricinoleic acid comprising nearly 90% of the fatty acid portion. Castor oil is unique in possessing both unsaturation and hydroxyl functions; it is also one of the few natural or synthetic oils that approaches being a pure compound.<sup>3</sup>

Due to its unusual structure, castor oil has a wide range of applications. Despite being known primarily for its medicinal value, castor oil plays an important role in the field of polymer chemistry. Acting as a polyfunctional alcohol, castor oil reacts with polyfunctional isocyanates to form polyurethanes, which range from rigid foams to elastomers.<sup>4</sup> The hydroxyl functions of the oil also make it an important additive to impart plasticization in many polymer blends.

Castor oil also undergoes many familiar organic reactions to form useful derivatives. Epoxidized, hydrogenated, and hydroxylated oils are among the many derivatives. Epoxy derivatives have been found to stabilize PVC resins and hydroxylated oils yield quick-drying alkyds.<sup>5</sup> The hydrogenated derivatives are used as greases and paint vehicles. Sebacic acid, a product of the alkali fusion of castor oil, is used in the manufacture of nylon.

One of the more interesting derivatives of castor oil is obtained by heating the oil to temperatures above 200°C in the presence of catalysts (commonly sulfuric acid) to effect dehydration of the oil. The dehydration process involves the removal of an hydroxy function and an adjacent hydrogen, resulting in the formation of a second double bond. Since there are two adjacent hydrogen positions, the dehydrated castor oil (DCO) may possess both conjugated and nonconjugated unsaturation. This increase in unsaturation makes DCO a drying oil and useful as a surface-coating material.

The extent of conjugated unsaturation in DCO rarely exceeds 25%.<sup>6</sup> Since conjugated double bonds are more reactive, especially toward addition reactions, the degree of unsaturation will, to some extent, determine the copolymerization capability of DCO. Tewari and Aggerwal<sup>7</sup> have successfully used DCO (diene conjugation = 23.1%) as a comonomer with styrene, methyl methacrylate, acrylonitrile, and methyl acrylate. The film properties of the copolymers were found to be superior to those of films from DCO alone.

The exact nature of the copolymerization of styrene with DCO has not been determined. Hewitt and Armitage<sup>8</sup> polymerized styrene with DCO over a wide range of proportions and found that the homogeneity of the products was somewhat dependent upon the extent of conjugation in the oil. They proposed that two different mechanisms were involved: (1) styrene polymerizes with nonconjugated fatty acid radicals via a chain transfer process, and (2) styrene polymerizes with conjugated radicals through propagation of the styrene chain across the conjugated system, as in the styrene-butadiene reaction.

Crofts<sup>9</sup> drew similar conclusions for reactions of styrene with conjugated and nonconjugated triglycerides of DCO. Hoogstein and Young<sup>10</sup> reported a relationship between the viscosity and degree of dehydration of the oil and the film properties of the styrenated products. Whatever the nature of the reaction, styrene and DCO do form products that are useful as surface coatings. However, no attention has been paid to the actual ratios of combination in copolymers.

Even though the styrene-DCO reaction has been studied extensively, the reported experimental results dealing with product analysis have been determined without isolation of the product copolymer. The previous work has dealt with a "styrenated DCO" mixture, rather than the actual copolymer. Styrenated DCO is simply the product of a styrene-DCO reaction which may include homopolystyrene and unreacted DCO, as well as the copolymer. Valid characterization of the copolymer is impossible if complete isolation is not accomplished. Furthermore, the kinetics of the reaction have not been investigated. This study, therefore, was conducted to produce a styrene-DCO copolymer, isolate the product, and perform an experimental determination of the reactivity ratios for the styrene-DCO system. A typical grade of DCO was used so facile application of the results could be made. Reactivity ratios were determined in an attempt to shed some light on the products to be expected.

## EXPERIMENTAL

All chemicals used were analytical reagent grade. The DCO was Baker castor oil product Castung 103 G-H, Lot 10-192. Styrene was purified by vacuum distillation and stored under nitrogen, in a dark bottle, refrigerated, and used within one week.

### Copolymerization Procedures

Copolymerizations were carried out in 250-ml round-bottom flasks equipped with nitrogen inlets and water condensers. The general procedure consisted of adding DCO, styrene, initiator, and solvent to a pre-weighed flask which was heated to reflux after a condenser was attached. The reaction was terminated by the removal of heat, and the mixture was allowed to cool to room temperature.

A series of reactions was carried out to determine copolymer conversion rate. The series included a total of ten reactions with approximately the same monomer feed compositions. In each copolymerization in the series, the flask was charged with 25 ml DCO, 20 ml styrene, 1 g AIBN (azobisisobutyronitrile), and 50 ml benzene. Five copolymerizations were executed in an inert atmosphere ( $N_2$ ), and a second five were not. Under both conditions, reaction times of 1, 2, 4, 8 and  $21\frac{1}{2}$  hr were employed.

In the procedure to obtain reactivity ratio data, the reactants were added in the same manner. However, the monomer feed compositions were changed for each reaction. In each case, 50 ml benzene and 1 g ABIN were added as solvent and initiator, respectively. Furthermore, each reaction was allowed to run for 3 hr.

### Isolation and Purification of Copolymer

When the reaction mixture had cooled, the flask was placed on a rotary evaporator under reduced pressure (about 10 mm Hg) to evaporate the solvent and any unreacted styrene monomer. Evaporation was accom-

plished without the application of heat to protect against any further polymerization.

The remaining contents of the flask were poured slowly into 400 ml vigorously stirred petroleum ether. The precipitate that formed was allowed to settle until a clear supernate was obtained. The supernate was then decanted, and the precipitate, a creamy viscous mass, was redissolved in a minimum amount of benzene. A replicate precipitation was then performed, using 200 ml petroleum ether as nonsolvent. Following decantation, the residue was again dissolved in benzene and transferred quantitatively to a preweighed 250-ml round-bottom flask. The flask was placed on a rotary evaporator and the solvent removed by vacuum evaporation. A pressure of approximately 1 mm Hg was maintained for a minimum of 12 hr to ensure complete removal of solvent. At the end of the evacuation period, the residue was a white, glassy mass. The dry solid was weighed, transferred to a sample bottle, and placed in a refrigerator. It is important to note that all possible impurities (except polystyrene) are soluble in petroleum ether and are therefore excluded from the product.

The precipitation process was only performed twice since this was found to be adequate for purification. This conclusion was based on the fact that saponification data for one sample did not vary significantly beyond two purifications.

### Analyses

The procedures used for determining saponification numbers generally followed those outlined in ASTM Designation D 1962-67. Phenolphthaleine was used as an indicator and hydrochloric acid was used as back titrant.

Duplicate samples were weighed out to the nearest 0.0001 g and placed in 250-ml Erlenmeyer flasks. An adequate portion of benzene, to facilitate dissolution of the sample, was added to each flask. Approximately 10-15 ml standardized alcoholic potassium hydroxide solution (approximately 0.5*N*) was then added to each flask from a standard 50-ml burette. A third flask was charged with a similar volume of the alkaline solution for the purposes of a blank normality determination.

Each flask was subsequently equipped with a water condenser and placed on a hot plate. The sample solutions were allowed to remain at reflux temperature for 2 hr. After cooling to room temperature, the solutions were titrated against standardized hydrochloric acid (0.5229*N*) using six drops phenolphthalein solution as an indicator. It was important to keep the titration procedure constant for all samples in order to minimize the effect of hydrolysis of the weak fatty acids produced during saponifications. Titration endpoints were observed when the pink color of the solutions disappeared. The judgement of endpoints was somewhat obscured by the formation of white insoluble solids during back titration; therefore six drops of indicator were used to give a deeper color to the basic solution.

Saponification number is defined as the number of milligrams of KOH required to saponify 1 gram of a substance and was calculated as follows:

saponification number =

$$\frac{\left[ \text{vol. of KOH} - \frac{(\text{vol. of acid}) (N \text{ of acid})}{N \text{ of base}} \right] (\text{eq wt of KOH}) (N \text{ of base})}{\text{wt of sample}}$$

$$= \frac{\left[ (11.20 \text{ ml}) - \frac{(12.52 \text{ ml}) (0.5229)}{(0.6128)} \right] (56.12) (0.6128)}{1.6857 \text{ g}} = 10.54.$$

### Determination of Molecular Weight of DCO from Saponification

The average value of the saponification numbers for a series of samples of DCO was used to determine the molecular weight of DCO. Since DCO is a mixture of glycerides of fatty acids, it was necessary to obtain a value for the molecular weight for use in calculating monomer mole fractions. A comparison of the saponification number for a typical grade of similar castor oil and the experimental value of the saponification number of DCO was made to obtain a reasonable estimate of the molecular weight of DCO. Using the theoretical molecular weight and saponification number of castor oil, 928.5 and 180, respectively,<sup>3</sup> and the experimental value of 195.2 for the saponification number of DCO, the effective molecular weight of DCO used in this work was calculated to be 856, as shown below:

$$\text{mol wt of DCO} = \frac{(928.5) (180)}{195.2} = 856.$$

### Determination of Copolymer Composition

Saponification results were used to calculate the amount of DCO in the copolymer products. The saponification number for a particular sample was used in conjunction with the saponification number of DCO to determine the weight percentage of DCO in the copolymer. A sample calculation is given below:

$$\begin{aligned} \text{saponification number of copolymer} &= 10.54 \\ \text{saponification number of pure DCO} &= 195.2 \\ \text{weight percentage of DCO in sample} &= 10.54/195.2 = 5.40\% \\ \text{weight of sample} &= 1.6857 \text{ g} \\ \text{weight of DCO in copolymer} &= 0.0910 \text{ g} \end{aligned}$$

The styrene content of the copolymer samples was determined by difference.

## RESULTS AND DISCUSSION

## Rate of Copolymerization

The rate of copolymerization for the styrene-DCO system is depicted in Figure 1. Yields are expressed in weight percentages based on the total original monomer feed.

The conversion rate is quite low, as indicated by the graph, with yields less than 25% after 20 hr. The presence of a nitrogen atmosphere during polymerization resulted in slightly higher conversion rates, but the inhibition effect of atmospheric oxygen is small. Nevertheless, an inert atmosphere was used in the reactivity ratio copolymerizations to remove any doubt about oxygen interference.

Analysis of the copolymers resulting from this reaction showed a styrene mole fraction of 0.95. Since the original feed composition was approximately 0.88 styrene to 0.12 DCO on a mole fraction basis, inclusion of styrene in the copolymer was substantially greater than for DCO. The change in the initial styrene feed is therefore much greater than for the DCO feed. This result was expected, however, since the tendency toward polymerization is much greater with styrene than with DCO. Styrene will polymerize at room temperature, even in the absence of initiator, whereas DCO shows no tendency to polymerize. DCO was subjected to polymerization conditions similar to those for copolymerization, and no increase in the viscosity of the reaction mixture was noted after 3 hr.

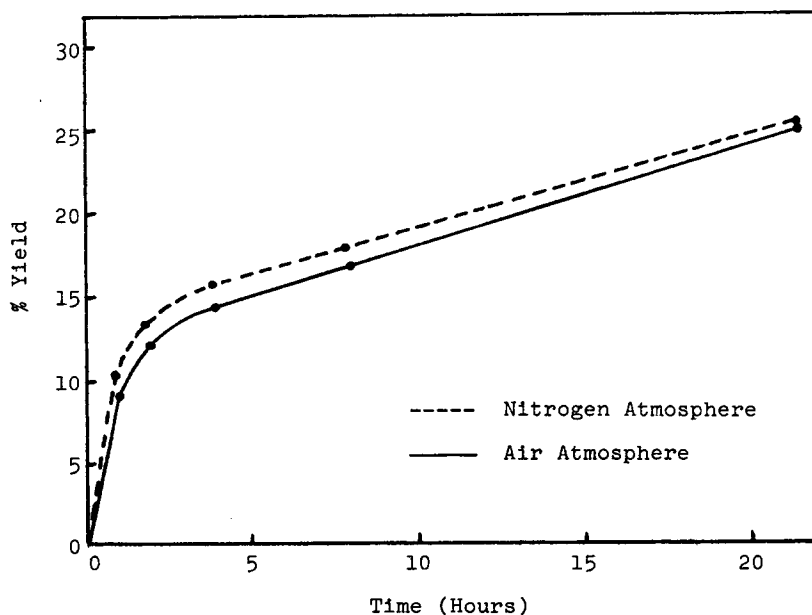


Fig. 1. Copolymerization rate.

Examination of the conversion plot led to the selection of a satisfactory reactivity ratio reaction period of 3 hr which shows a yield of approximately 15%. The decrease in the initial DCO feed is almost negligible, whereas the change in the styrene feed is somewhat more than desired. Also, the quantity of product at 3 hr should be ample for analyses.

### Stereoscopic Analysis

In order to confirm the presence of both monomers in the copolymer, infrared and ultraviolet spectra were taken. Infrared data from KBr pellets exhibited both ester carbonyl absorption at  $1742\text{ cm}^{-1}$  and a characteristic polystyrene peak at  $1601\text{ cm}^{-1}$  for the copolymer. Ultraviolet spectra taken in cyclohexane displayed peaks for DCO ( $\lambda_{\text{max}} 232\text{ nm}$ ) and polystyrene ( $\lambda_{\text{max}} 224\text{ nm}$ ), confirming again the coexistence of both species in the product. Unfortunately, the ultraviolet peaks were in too great a proximity to allow facile quantitative analysis by this method.

### Copolymer Composition

Complete saponification data for the copolymers are listed in Table I. It is apparent that the DCO content of the copolymer did not vary much as feed ratios changed. Even when the DCO feed mole fraction approached 0.2, the copolymer DCO mole fraction was still less than 0.2. The saponification numbers correspond favorably to those reported by Croft.<sup>9</sup> Furthermore, these numbers indicate saponification equivalent weights of 2200–5500 for the copolymer; the equivalent weight represents the weight of copolymer containing one ester function.

Molecular weights of several copolymer samples were determined by vapor phase osmometry. The samples were not taken from the reactivity ratio reactions, but represent products from typical feed compositions and identical reaction conditions. Molecular weights ranged from 1700–2300 for the products analyzed. The larger values were recorded for products from high styrene feeds (95 mole-% styrene) and/or lengthy reaction times

TABLE I  
Saponification Data

Sample no.	Mole fraction of DCO in feed ( $f_1$ )	Saponification number	DCO, %	Mole fraction of DCO in copolymer ( $F_1$ )
1	0.044	10.54	5.4	0.0069
		10.23	5.2	0.0067
2	0.085	16.85	8.7	0.0113
		16.99	8.7	0.0114
3	0.110	18.90	9.7	0.0128
		17.01	8.8	0.0115
4	0.141	23.44	12.0	0.0163
		24.16	12.4	0.0169
5	0.187	25.18	12.9	0.0177
		25.67	12.3	0.0181

(i.e., 10 hr). These values correspond favorably with the lower equivalent weights obtained from saponification data. However, the equivalent weights suggest much larger molecular weights. If the DCO molecule is considered a triglyceride, then the equivalent weight of the copolymer would be representative of one third of the molecular weight. Therefore, the molecular weights determined by osmometry are much smaller than the molecular weights derived from saponification data.

The discrepancy in these values could possibly be the result of two factors. First, the portion of DCO that reacts may not be a triglyceride, but rather a monoglyceride or diglyceride. According to Achaya,<sup>4</sup> the glyceride content of castor oil is comprised of 28% diricinolein and 3% monoricinolein. Since the glyceride content of DCO should show similar stratification, the inclusion of di- and monoglycerides of ricinoleic acid in the copolymer is highly probable. If this occurred, the equivalent weight of the copolymer would be the same as the molecular weight, or one half the the molecular weight.

Second, a portion of the products analyzed perhaps was not copolymer. Since the rate of styrene monomer consumption was much greater than for DCO, the production of homopolystyrene was possible. The saponification numbers for samples of copolymer containing homopolystyrene would not be representative of the actual copolymer compositions; the numbers would be smaller than those for a pure copolymer sample. Therefore, the equivalent weights of copolymer calculated from these numbers would be larger than the true values.

It is pertinent to note that a complete range of feed composition data is not listed. The monomer feeds where styrene concentration was less than 0.8 mole fraction did not yield copolymer products that could be isolated by the solvent/nonsolvent precipitation procedure used. Failure to obtain a precipitate is possibly a result of one of two factors: (1) copolymer is soluble in petroleum ether, or (2) no copolymer is formed. It is quite unlikely that no polymerization occurs, since viscosity tests showed a substantial increase in the viscosity of the reaction mixture containing such monomer feeds after 3 hr of reflux. However, similar solubilities of copolymer and monomers could result if low molecular weight products are formed, or if the DCO content of the copolymer increases sufficiently to give the copolymer solubility properties similar to that of DCO. The latter possibility seems doubtful, since the copolymer from a 0.187 DCO mole fraction feed revealed a DCO mole fraction of less than 0.02.

On the other hand, low molecular weight products were quite possible. As previously mentioned, extensive chain transfer may lead to low molecular weight products. The unsaturated portion of DCO lends a very susceptible site for chain transfer. Abstraction of a hydrogen by a growing radical chain would terminate that particular chain and yield a new radical. This new radical, however, might be quite stable and not entertain propagation. DCO contains both conjugated and nonconjugated unsaturation. The double bonds are flanked on either side by allylic hydrogens which are



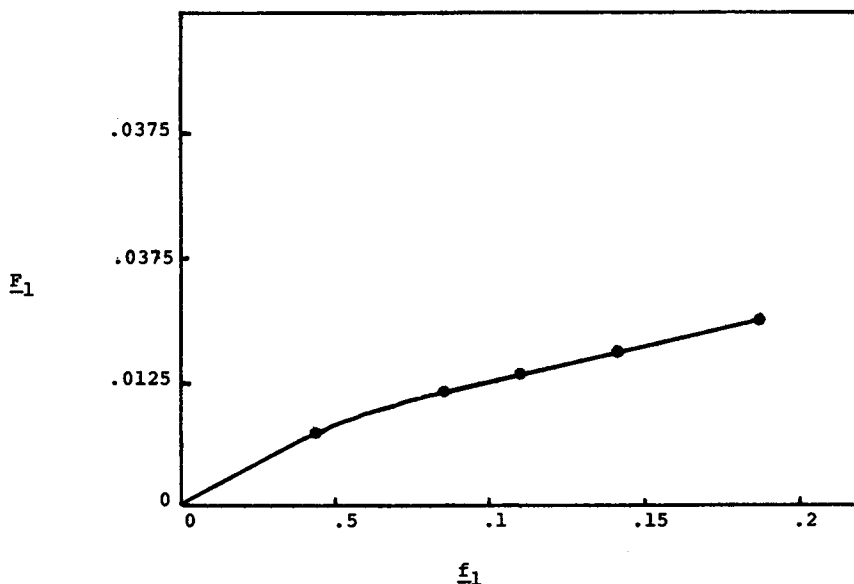
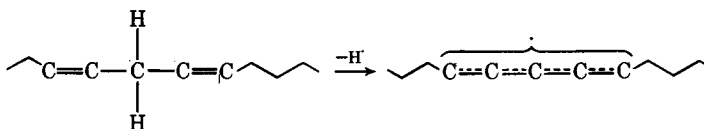


Fig. 2. Styrene/DCO copolymerization ( $M_1$  is DCO).

susceptible to abstraction. Moreover, the nonconjugated double bonds create a site which should be even more susceptible toward chain transfer. The two hydrogens on the carbon between the double bonds are allylic to both double bonds:



Since these hydrogens are "doubly allylic," they should be quite easily abstracted. If a hydrogen atom is abstracted, the radical thus created could be stabilized through resonance. If sufficiently stable, the radical would not continue propagation, and the overall result would be chain termination. Assuming such a reaction occurs, the rate of termination would be proportional to the degree of nonconjugation, hence the DCO feed concentration. Since the degree of conjugation rarely exceeds 25% and the DCO used in this study was typical, the "doubly allylic" sites are dominant. Therefore, chain transfer is most likely an important factor in this copolymerization.

The exact yields of the reactivity ratio reactions were not recorded. However, it was observed that as the feeds became richer in DCO, the yields became smaller. It is quite probable that chain transfer does occur; and with 0.2 DCO mole fraction feeds, this reaction becomes so dominant that only very low molecular weight products are obtained.

### Reactivity Ratios

A plot of the mole fraction of DCO in the copolymer ( $F_1$ ) versus the mole fraction of DCO in the feed ( $f_1$ ) is depicted in Figure 2. The initial slope of the line, where  $f_1 \rightarrow 0$ , is 0.086, which is  $1/r_2$ , or 11.6. The lack of data for  $f_1 \rightarrow 1$  feeds made the determination of  $r_1$  from a final slope impossible. However, if the composition curve is assumed to be symmetrical, final slope is equal to the inverse of the initial slope. Therefore, a reasonable approximation gives  $r_1 = 0.086$ .

The Fineman-Ross method<sup>11</sup> of reactivity ratio determination was attempted and proved to be inapplicable due to the lack of composition data at intermediate feed ratios.

The relative values determined for  $r_1$  and  $r_2$  reveal the copolymerization capability for the DCO-styrene pair. The value of  $r_2$  reveals that styrene tends to homopolymerize rather than copolymerize; and  $r_1$  reveals a copolymerization tendency for DCO. These values indicate that in this styrene-DCO copolymerization, the product will always consist primarily of styrene units. Furthermore, the amount of DCO incorporated is almost independent of monomer feed concentrations, at least up to the point where no copolymer was isolated.

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