

## Copolymerization of Unsaturated Polyester with Styrene in Inverted Emulsion

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### Synopsis

Copolymerization of unsaturated polyester with styrene in water-in-oil (W/O) type emulsion was carried out with the use of various basic compounds as emulsifiers. It was found that a stable, gellike W/O type emulsion of unsaturated polyester resin is formed only when  $pK_a$ 's of the bases are above 6 and their concentrations are higher than some critical value. In these conditions, water can be dispersed in emulsion up to 900% to the resin. By polymerization, the stable W/O type emulsion is transformed to a white solid copolymer which is dry to the touch and which contains 90-95% of initially added water. It was confirmed that the basic compounds react with the carboxylic group of the polyester to form at the water-resin interface polyester salts, which act as true emulsifying agents. The stabilization mechanism of the emulsion at various concentrations of the polyester salt was investigated, mainly by microscopic observations, and an interpretation of the critical value of emulsifier concentration is proposed.

### INTRODUCTION

The polymerization of water-insoluble vinyl monomers in an inverted emulsion, i.e., in water-in-oil (W/O) type emulsion, has been investigated by Bartl and Von Bonin.<sup>1,2</sup> Using styrene-grafted poly(ethylene oxide) as an emulsifier, they have prepared emulsions of water in styrene or methyl methacrylate and after polymerization obtained solid polystyrene or poly(methyl methacrylate) containing up to 700% of water to the monomer. When monomer-soluble initiators were used, the rate of polymerization of styrene in inverted emulsion and the molecular weight distribution of the resulting polymer were similar to those obtained in bulk polymerization of styrene. As the mechanism of polymerization in inverted emulsion is not very different from that of ordinary radical polymerization, the most important factor in producing the water-containing polymers is to obtain stable emulsions by employing suitable emulsifiers.

Von Bonin and Göbel<sup>3</sup> have also proposed the addition of unsaturated polyester to the styrene monomer for obtaining a crosslinked polystyrene. In our preliminary experiments, however, it was found that when the grafted poly(ethylene oxide) type emulsifiers are used for common polyesters consisting mainly of unsaturated polyester and containing only 20-40%

styrene, water cannot be emulsified sufficiently and most of the water initially added is lost during polymerization of the unstable emulsion.

The present paper deals with a new emulsifying method which is very effective for the formation of inverted emulsions of the common polyesters. The method consists simply of adding bases to the polyester to form *in situ* a polyester salt which acts as a true emulsifying agent. The mechanism and the necessary conditions for the formation of inverted emulsion by this method are also discussed.

## RESULTS AND DISCUSSION

### Preparation of Water-Containing Unsaturated Polyester-Styrene Copolymers

As mentioned above, the styrene-grafted poly(ethylene oxide) was not an effective emulsifier for the polymerization of unsaturated polyester resins in inverted emulsion.

The graft copolymer was prepared and added to a commercial general-purpose unsaturated polyester resin (Estar D-32, styrene content: 30%). Even if 10% of this W/O type emulsifier was used, water could be emulsified into the resin only up to 100% with respect to the resin. When more water was added, it remained as a separate phase. If the unstable emulsion containing 100% water was heated at 60°C. with benzoyl peroxide (BPO), it turned to a white solid copolymer of unsaturated polyester and styrene which is dry to the touch and which contained, however, only 52% of water added. The water content of the copolymers decreased gradually at room temperature, as is shown in Figure 1.

In order to increase the lipophilic affinity of the emulsifier for the unsaturated polyester, methyl methacrylate-styrene-grafted poly(ethylene oxide) as well as vinyl acetate-grafted poly(ethylene oxide) was prepared and used for emulsification of water into the unsaturated polyester resin. However, these graft copolymers proved ineffective in the enhancement of the water content of the copolymers (Fig. 1).

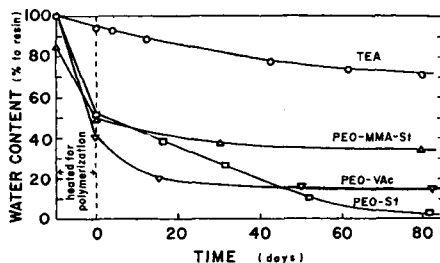


Fig. 1. Time dependence of water content of water-containing polymers at room temperature. Emulsifiers used are indicated above the curves: TEA = triethanolamine; PEO-MMA-St = methyl methacrylate-styrene-grafted poly(ethylene oxide); PEO-VAc = vinyl acetate-grafted poly(ethylene oxide); PEO-St = styrene-grafted poly(ethylene oxide).

Von Bonin and Göbel<sup>3</sup> made some experiments on the polymerization of styrene with unsaturated polyester in inverted emulsion with graft copolymers as an emulsifier. However, the proportion of unsaturated polyester to styrene monomer was not disclosed in their paper.

W/O type emulsions of unsaturated polyester resins with various styrene contents were prepared by using styrene-grafted poly(ethylene oxide) as an emulsifier; then the polyester was copolymerized with styrene by heating at 60°C., and the water contents of the resulting polymers were measured. Figure 2 shows the dependence of the water contents on the heating time at 60°C. The styrene-grafted poly(ethylene oxide) is a powerful W/O type emulsifier when styrene is much richer in monomer composition than unsaturated polyester. However, the increase in the proportion of unsaturated polyester makes the emulsifier less effective. The graft copolymer seems to have only a weak effect on a commercial general-purpose unsaturated polyester resin which contains 20–40%

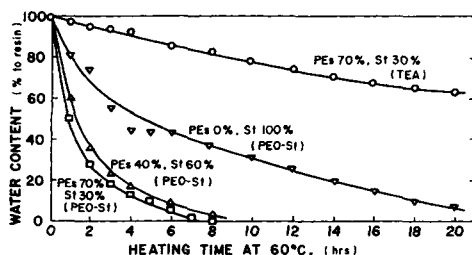


Fig. 2. Effect of polyester resin compositions on the water content of polymers heated at 60°C. Emulsifiers: PEO-St or TEA.

styrene. In this respect, Molau's<sup>4</sup> recent observation that in order to obtain a stable polymeric oil-in-oil type emulsion the components of the graft copolymer type emulsifiers must be identical with the polymers in each phase is worthy of note.

In Figures 1 and 2 are also shown, for comparison, water contents of a copolymer prepared by using triethanolamine as a W/O type emulsifier, which will be discussed later.

In order that water may have a selective affinity to the emulsifier which is dissolved in the unsaturated polyester resin, the polarity of the hydrophilic backbone of the emulsifier must be stronger than that of the unsaturated polyester. In addition, so as to form W/O type emulsion it is necessary that the lipophilic affinity of the emulsifier to the polyester is stronger than its hydrophilic affinity to water. Poly(ethylene oxide) has nearly the same polarity as the polyester, and therefore the graft copolymers with poly(ethylene oxide) backbone seem to be unfavorable as W/O type emulsifiers for unsaturated polyester emulsions. From these considerations, it seems that the salts of the polyester itself may be effective emulsifiers for inverted emulsions. This proved to be the case.

The polymerization of unsaturated polyester resins was carried out in inverted emulsion stabilized by *in situ* formation of polyester salts of various bases which were added as W/O type emulsifiers.

The basic emulsifiers are summarized in Table I.

TABLE I  
Effectiveness of Basic Emulsifiers for the Polymerization of the Unsaturated Polyester Resin (Estar D-32) in W/O Type Emulsion

Compound	Emulsifier	Minimum concentration, mmole/g. <sup>a</sup>	State of emulsion	Polymer		
				Color	Water content, % <sup>b</sup>	Hardness after heating, (Barcol 935)
Sodium hydroxide	Strong base	0.38-0.60	W/O gel	White	95	3
Potassium hydroxide	Strong base	0.46-0.55	W/O gel	White	94	3
Calcium hydroxide	12.7	0.24-0.40	W/O gel	White	94	10
Diethylamine	11.0	0.39-0.47	W/O gel	White	91	9
Triethylamine	10.7	0.66-0.72	W/O gel	Brown	81	48
Monoethylamine	10.6	0.44-0.55	W/O gel	White	70	69
Monoethanolamine	9.5	0.26-0.34	W/O gel	White	81	29
Ammonia	9.2	0.44-0.57	W/O gel	White	84	55
Diethanolamine	8.8	0.30-0.36	W/O gel	White	83	14
Hydrazine	8.1	0.36-0.88	W/O gel	Yellow	78	—
Triethanolamine	7.8	0.32-0.40	W/O gel	White	94	33
Ethylenediamine	7.0	0.40-0.59	W/O gel	White	67	—
Diethylaniline	6.5	0.29-0.38	W/O gel	Yellow	84	—
Pyridine	5.2		W/O unstable		Separated	
Aniline	4.6		W/O unstable		Separated	
Diphenylamine	0.5		W/O unstable		Separated	

<sup>a</sup> Minimum concentration of emulsifier necessary to form the gellike emulsion.

<sup>b</sup> Initial water content: 100%. All percentages are based on the weight of the unsaturated polyester resin.

A stable, semitransparent W/O type emulsion of unsaturated polyester containing the same amount of water was prepared easily by using basic compounds having  $pK_a'$  values above 6. Heating of the emulsion at 60°C. for a few hours with BPO resulted in an apparently homogeneous and dry-to-the-touch solid polymer containing 90-95% of initially added water. States of the emulsions and properties of the copolymers formed were not affected by the method of adding water and the basic emulsifier.

Table II shows that it was possible to get a white unsaturated polyester-styrene copolymer containing up to 900% water based on the resin by using triethanolamine.

TABLE II  
 Polymerization of Unsaturated Polyester Resin (D-32) Containing Various Amounts of Water with Triethanolamine as an Emulsifier

Water added, % on resin	Concentration of emulsifier, mmole/g.	Emulsion		Water content of polymer after heating, % on resin <sup>a</sup>
		Volume fraction of water, %	State	
100	0.40	53	W/O gel	94
200	0.54	69	W/O gel	190
300	0.55	77	W/O gel	272
400	0.83	82	W/O gel	339
500	0.79	85	W/O sol	416
600	0.84	87	W/O sol	490
900	1.03	91	W/O sol	720

<sup>a</sup> Polymerization was carried out at 60°C. for a few hours with 2% BPO.

In addition to the compounds given in Table I, triethanolamine hydrochloride, urea, aniline, *N,N*-dimethylformamide, diethyl sulfate, diethylene glycol, and glycerine were tested as W/O type emulsifiers for the resin. These compounds, like the emulsifiers in Table I, contain nitrogen atoms or hydroxyl groups in their chemical structure but all of them are neutral. When one of these neutral compounds or a base of lower  $pK_a'$  value in Table I was employed as an emulsifier, an unstable W/O type emulsion was formed which disintegrated immediately on heating. The similar unstable W/O type emulsion was formed even without emulsifier.

Acids and bases ionize when dissolved in water and from the equilibrium conditions the following relation holds, in which  $K_a$ ,  $K_b$ , and  $K_w$  are dissociation constants of the acid, base, and water, respectively.

$$[\text{HA}][\text{BOH}]/([\text{A}^-][\text{B}^+]) = K_w/K_aK_b \quad (1)$$

For polyester salt to be formed in appreciable amount,  $K_w/K_aK_b$  must be smaller than unity in a very rough approximation and this condition will be transformed to eq. (2).

$$pK_a < pK_a' \quad (2)$$

where

$$pK_a' = pK_w - pK_b$$

The polyester salt seems to be formed when  $pK_a'$  value is larger than 6. Thus, the dissociation constant of the polyester acid  $K_a$  may be supposed to be about  $10^{-6}$ . This value is reasonable, since the equilibrium at the interface instead of the equilibrium in a dilute solution is concerned here.

The infrared spectra of the interfacial layer between polyester and aqueous solution of bases supported the formation of carboxylate anion, showing intense absorption bands at 1585 and 1385  $\text{cm.}^{-1}$ .

It is clear from Table I that minimum concentrations of emulsifiers necessary to form a stable emulsion lie in the range of 0.3–0.5 mmole/g.

TABLE III  
 Polymerization in Inverted Emulsion of Unsaturated Polyester Resins with Various Chemical Structures.

Polyester resin		Emulsifier			State of emulsion <sup>a</sup>	Color	Water content after heating, %	Hardness (Barcol 935)
Resin	Concentration of carboxylic group, mmole/g.	Nature	Concentration, mmole/g.					
HR-150	0.50	TEA	0.43	W/O gel	White	95	30	
D-32	0.46	TEA	0.40	W/O gel	White	94	33	
S-34	0.5	TEA	0.39	W/O gel	White	79	38	
G-40	0.4	TEA	0.55	W/O gel	White	89	—	
XE-499	0.4	TEA	0.40	W/O gel	Yellow	85	22	
M-2	0.27	TEA	0.27	O/W		Separated		
XE-661	0.04	TEA	0.50	W/O unstable		Separated		
XF-661	0.04	Polyester salt	0.60	W/O gel	White	83	10	

<sup>a</sup> Initial water content: 100% based on the resin.

<sup>b</sup> Polymerization was carried out at 60°C. for a few hours with 2% BPO.

of resin, regardless of the chemical structure. The meaning of the critical value is discussed below.

Water-containing polymers were obtained by polymerization in inverted emulsion of different unsaturated polyester resins with the basic emulsifier regardless of the chemical structure of polyesters (Table III). In the case of unsaturated polyester resins with a low acid value (Estar XE-661, acid value 2.2; and M-2, acid value 15) stable emulsions were never realized at any concentrations of the basic emulsifier. The unstable emulsions disintegrated on heating. The concentrations of carboxyl groups at the chain end in the resin are 0.04 and 0.27 mmole/g. for these two polyesters and smaller than the critical value. Even for these resins with a low acid value, stable W/O type emulsions and water-containing polymers were obtained by addition of a saturated polyester salt prepared beforehand as an emulsifier (Table III).

The basic emulsifiers are also effective even when styrene is richer than unsaturated polyester in monomer composition, as long as the concentration of the carboxyl groups at the chain ends is above the critical value (Table IV).

TABLE IV  
Effect of Monomer Composition in Unsaturated Polyester Resin on the State of Emulsion Containing 100% Water

Monomer composition of resin		Concentration of carboxylic group, mmole/g.	Minimum concentration of triethanolamine, mmole/g.	State of emulsion
Polyester, %	Styrene, %			
70	30	0.46	0.32-0.40	W/O gel
64	36	0.41	0.35-0.36	W/O gel
54	46	0.35	0.31-0.34	W/O gel
46	54	0.30	0.30-0.35	W/O sol
20	80	0.13		O/W

It can be concluded from the above results that the basic emulsifiers react with the carboxyl groups of polyesters to form polyester salts, which accumulate at the water-resin interface and therefore stabilize the W/O type emulsions.

### Mechanism of Formation of the Water-in-Polyester Emulsion by Polyester Salts

The state of unsaturated polyester emulsions varies markedly with increasing concentration of basic emulsifiers. At lower concentrations of bases, emulsions are of the unstable W/O type, and these disintegrate immediately on heating. At medium concentrations the O/W type emulsions are formed. Only when the concentration of bases is above some critical value are the stable gellike W/O emulsions obtained. Emulsions

consisting of unsaturated polyester resin (Estar D-32) and the same amount of water stabilized by triethanolamine (TEA) were investigated by the measurements of viscosity and interfacial tension as well as by optical and electron microscopic observations.

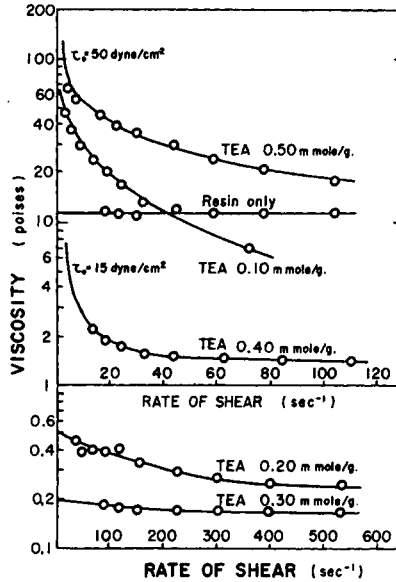


Fig. 3. Non-Newtonian viscosity and yield value ( $\tau_0$ ) of emulsions of unsaturated polyester resin at 30°C. with various concentrations of TEA as emulsifier.

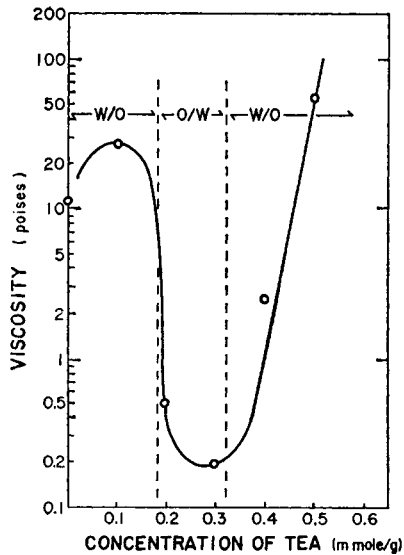


Fig. 4. Effect of TEA concentration on the type and viscosity (at 10 sec.<sup>-1</sup>) of the emulsions.





Fig. 5. O/W type emulsion of unsaturated polyester resin. [TEA] = 0.24 mmole/g.

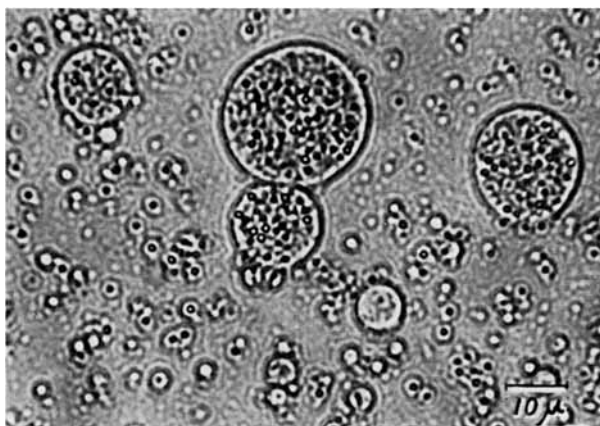


Fig. 6. Multiple W/O/W type emulsion of unsaturated polyester resin. [TEA] = 0.28 mmole/g.

The non-Newtonian viscosity of the emulsions with various concentrations of TEA as an emulsifier is shown in Figure 3. The viscosity of the original resin was 11.5 poise. By adding 100% water and 0.10 mmole/g. TEA, the viscosity of the resulting emulsion increased to 27 poise at a shear rate of 10 sec.<sup>-1</sup>. An increase in concentration of TEA (0.20–0.30 mmole/g.) resulted, however, in a marked decrease in viscosity of the emulsion, as is shown in Figure 4. When the TEA concentration was increased further (>0.40 mmole/g.), the emulsion became a white semitransparent gel with a high viscosity showing a yield value.

By means of the microscopic observations with methyl orange as a water-soluble dye, the emulsions were identified as O/W type at medium TEA concentrations (0.18–0.32 mmole/g.). The sudden decrease in viscosity in this range of TEA concentration can be explained by the fact that water is the continuous phase.

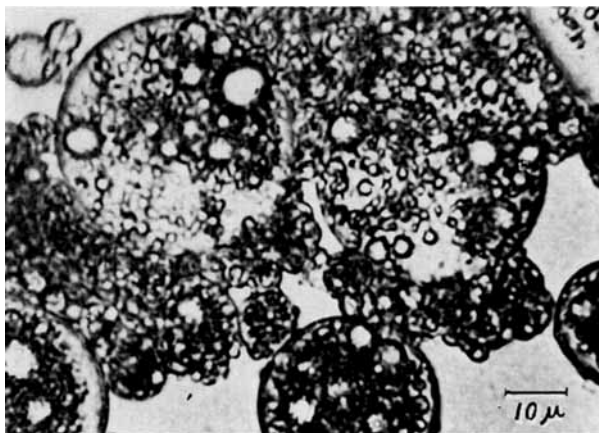


Fig. 7. Phase inversion of the emulsion from O/W to W/O type. [TEA] = 0.32 mmole/g.

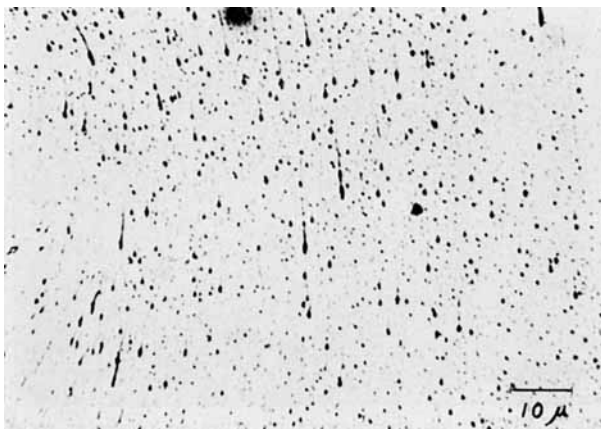


Fig. 8. W/O type emulsion of unsaturated polyester resin. [TEA] = 0.36 mmole/g.

Microphotographs of unsaturated polyester emulsions with the same amount of water formed with various concentrations of TEA are shown in Figures 5-8. At 0.24 mmole/g. where emulsions are of the O/W type, uniform polyester droplets, about  $1\ \mu$  in diameter, are observed (Fig. 5). Figure 6 also shows an O/W type emulsion, but a small increase in TEA concentration induces the appearance of multiple W/O/W type emulsion. Further increase in the proportion of the multiple emulsion results in phase inversion from O/W to W/O type (Fig. 7), and the water droplets in the W/O type emulsion are dispersed more finely with increasing TEA concentration (Fig. 8). At 0.40 mmole/g. of TEA the water droplets were too small to be observed by the optical microscope.

Figure 9 is an electron microphotograph of a section of the solid polymer obtained from a stable W/O type emulsion (at [TEA] = 0.40 mmole/g.). Spaces between the shadows in Figure 9 are thought to be the marks of

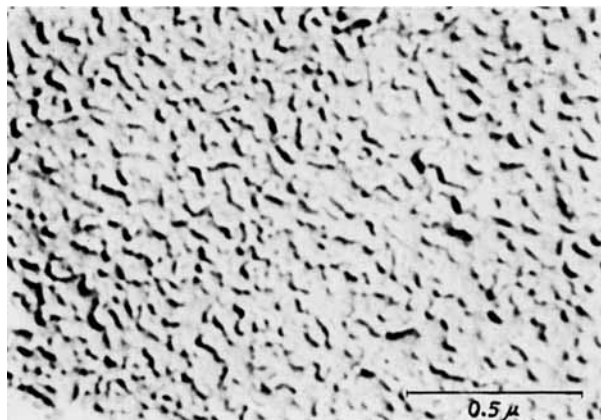


Fig. 9. Electron microphotograph of a section of a water-containing polymer. [TEA] = 0.40 mmole/g.

the vaporized water droplets. Distortions of the shadows may be due to the dimensional contraction of the unsaturated polyester during polymerization. The diameter of a number of the water droplets was measured and the mean value was found to be about  $0.13 \mu$ .

When 0.10 mmole/g. of hydrochloric acid was added to a gellike W/O type emulsion ([TEA] = 0.40 mmole/g.), the emulsion immediately inverted to O/W type because of the salt exchange reaction at the interface. This O/W type emulsion inverted again to a gellike W/O type one on addition of another 0.10 mmole/g. of TEA. From this experiment it is clear that the phase inversion occurs reversibly and depends solely upon the concentration of the polyester salt.

A gellike W/O type emulsion ([TEA] > 0.32 mmole/g.) and an O/W type emulsion ([TEA] = 0.18–0.32 mmole/g.) are formed easily by stirring, regardless of the method of adding water. However, an unstable W/O type emulsion ([TEA] < 0.18 mmole/g.) was obtained only when water was added little by little to the resin. It is noteworthy that by such careful mixing a similar W/O type emulsion was formed, even in the absence of the basic emulsifier.

As is shown in Figure 10, the interfacial tension between the unsaturated polyester resin and aqueous solution of TEA rapidly decreases with increasing TEA concentration and approaches zero at 0.3–0.4 mmole/g. of TEA. The decrease of interfacial tension is considered to cause a finer emulsification of water droplets.

From the above results the stabilization mechanism of the emulsions formed with basic emulsifiers is considered to be as follows.

At the low concentrations of basic emulsifiers (0–0.18 mmole/g. in the case of TEA), free carboxylic acid at the chain ends of polyester acts as a weak W/O type emulsifier. The fact that the unstable emulsions can be formed even without bases indicates that the polyester salt plays no sig-

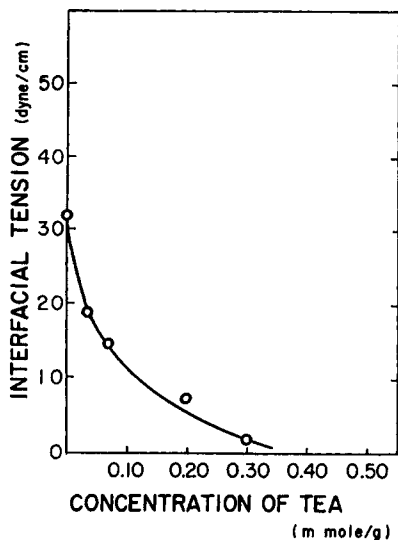


Fig. 10. Interfacial tension between the resin and aqueous solution of TEA at 30°C.

nificant role at this stage of emulsification. The first phase inversion (at about 0.18 mmole/g. of TEA) occurs when the one of the two sorts of emulsifier, that is the polyester salt, prevails over the other, free polyester acid, as the increase in the concentration of a basic additive. At medium concentrations (0.18–0.32 mmole/g. in the case of TEA) polyester salt acts as an O/W type emulsifier. At 0.24 mmole/g. of TEA there are formed uniform polyester droplets in the continuous water phase. The polyester salt formed by additional TEA does not contribute to dividing the polyester droplets more finely, but it dissolves into the water phase and associates into micelles. The solubility of the polyester salt in water was determined to be 0.08 mmole/ml., supporting the above consideration. When micelles are formed in sufficient concentration, they begin to combine polyester droplets into networks, including water in them, and induce the partial formation of multiple W/O/W type emulsion. Then the proportion of the multiple emulsions increases and finally the second phase inversion from O/W to W/O type occurs at 0.32 mmole/g. of TEA concentration.

After the phase inversion, an increase in polyester salt emulsifier causes the finer dispersion of water droplets. The decrease of interfacial tension may play a role in this stage. When the diameter of water droplets has become of the order of 0.1  $\mu$ , further formation of micelles and consequent emulsification of water droplets is very difficult, since the water droplets are comparable in volume to the micelles. By a calculation based on the approximation that the water droplets are uniform spheres with a mean diameter of 0.13  $\mu$  at 0.40 mmole/g. of TEA concentration, it is shown that the mean interfacial area per molecule of polyester salt is equal to 19  $\text{A}^2$  at the water-polyester interface. This value corresponds successfully to

mean areas per molecule of soaps which form aggregated monomolecular films at the interface.<sup>5</sup> When more than 0.40 mmole/g. of TEA is added, water droplets are not changed markedly in size, and polyester salt presumably forms a multiple layer at the interface.

It is confirmed from the above that the critical concentration of basic emulsifiers for obtaining water-containing polymers is the concentration necessary for polyester salt to form the aggregated monomolecular film at the water-polyester interface, when further effective emulsification of water droplets is restricted by the difficulty of formation of micelles due to their equality in volume to the water droplets.

## EXPERIMENTAL

### Preparation of Emulsifiers

Styrene-grafted poly(ethylene oxide) was prepared according to the method described by Bartl and von Bonin.<sup>1</sup> Vinyl acetate-grafted poly(ethylene oxide) was prepared from 100 g. of poly(ethylene oxide) (M.W. 1500) and 200 g. of vinyl acetate by heating at 60°C. for 12 hr. in 2-propanol with 1.0 g. of azobisisobutyronitrile. Methyl methacrylate-styrene-grafted poly(ethylene oxide) was prepared from 100 g. of poly(ethylene oxide) (M.W. 1500), 120 g. of methyl methacrylate, and 60 g. of styrene by heating at 90°C. for 10 hr. in toluene with 1.0 g. of BPO. Preparations of the graft copolymers were all carried out in an atmosphere of nitrogen.

Basic compounds were guaranteed-grade commercial products and used without purification.

Saturated polyester was prepared from 1.6 mole of diethylene glycol, 1.0 mole of adipic acid, and 1.0 mole of succinic acid by heating at 180–190°C. for 20 hr. in nitrogen atmosphere. The acid value of the resulting polyester was 110 and the number-average molecular weight was about 1000. Addition of sodium hydroxide equivalent to the carboxylic concentration of the polyester provided a saturated polyester salt, which was also used as a W/O type emulsifier.

### Preparation of Water-Containing Unsaturated Polyester-Styrene Copolymer

An aqueous solution of basic emulsifier of more than the critical concentration was added to 20 g. of the unsaturated polyester resin and immediately a stable W/O type emulsion was formed by stirring. When independently prepared polyester salts were used as an emulsifier, it was necessary to add the emulsifier beforehand to the polyester resin. Heating of the emulsion at 60°C. with 0.4 g. of BPO resulted in a white solid polymer of unsaturated polyester containing water which was dry to the touch. The water contents were evaluated by the weight loss measurements of the polymers. The hardness of the polymers was measured by a Barcol Impressor (935), their heterogeneous structures being ignored.

With lower concentrations of basic emulsifier or graft copolymers and no emulsifier, unstable W/O type emulsions could be prepared only when water was added little by little to the resin under careful stirring.

### Viscosity and Interfacial Tension Measurements

The viscosity of the emulsions was measured at 30°C. with a rotational cylindrical viscometer. Yield values were found from the shear stress-shear rate curves.

The interfacial tension between the unsaturated polyester resin and aqueous solutions of TEA was measured at 30°C. with a Donnan pipet since the density of the resin was larger than that of the solution.

### Microscopic Observations

For the optical microscopic observation the emulsions were colored by methyl orange as a water-soluble dye.

Electron microphotographs were taken of the fractured surface of the polymer containing water. Acetyl cellulose-chromium-shadowed carbon replica was chosen and examined with a JEM-6 electron microscope.

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### Résumé

La copolymérisation d'un polyester insaturé avec du styrène dans des émulsions du type eau-dans-l'huile (W/O) a été effectuée en utilisant différents composés basiques comme émulsifiants. On a trouvé que l'on obtient une émulsion du type W/O, du type gel, de la résine polyester insaturé lorsque les  $pK_a$  des bases sont supérieures à 6 et la concentration supérieure à une certaine valeur critique. Dans ces conditions l'eau peut être dispersée en émulsion jusque 900% par rapport à la résine. Par polymérisation, l'émulsion W/O stable se transforme en un copolymère solide de toucher sec qui contient 90 à 95% de l'eau initialement ajoutée. On confirme que les composés basiques réagissent avec les groupes carboxyliques du polyester en formant des sels polyesters à l'interface eau/résines qui réagissent comme de véritables agents émulsifiants. Le mécanisme de stabilisation de l'émulsion aux diverses concentrations de sels polyesters a été étudié principalement par observations microscopiques et une interprétation de la valeur critique de la concentration en émulsifiant est également proposée.

### Zusammenfassung

Die Copolymerisation ungesättigter Polyester mit Styrol wurde in Wasser-in-Öl-Emulsion (W/O) mit verschiedenen basischen Verbindungen als Emulgatoren durchge-

führt. Eine stabile W/O-Emulsion des ungesättigten Polyesterharzes bildet sich nur, wenn der  $pK$ -Wert der Basen oberhalb 6 und ihre Konzentration höher als ein bestimmter kritischer Wert ist. Unter diesen Bedingungen, kann Wasser in einer Menge bis zu 900% des Harzes als Emulsion dispergiert werden. Durch Polymerisation verwandelt sich die stabile W/O-Emulsion in ein weisses, sich trocken anführendes Copolymeres, das 90–95% des anfänglich zugesetzten Wassers enthält. Es wurde festgestellt, dass die basischen Verbindungen mit der Carboxylgruppe des Polyesters unter Bildung von Polyestersalzen an der Wasser-Harzgrenzfläche reagieren und die Polyestersalze als die wahren Emulgatoren wirken. Der Stabilisierungsmechanismus der Emulsion bei verschiedenen Konzentrationen des Polyestersalzes wurde hauptsächlich mikroskopisch untersucht; eine Interpretation des kritischen Wertes der Emulgatorkonzentration wurde gegeben.

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