

## Hydrolysis Rates of Unsaturated Esters in Alkaline Emulsion Systems of the GR-S Type\*

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One of the main difficulties in employing unsaturated esters of the acrylate type in the preparation of synthetic rubber arises from the tendency of such esters to hydrolyze in the common alkaline emulsion system. In the copolymerization of butadiene and styrene the pH of the system does not change to any large degree during the reaction. However, when methyl acrylate is present, the pH of the system drops considerably as the copolymerization proceeds. This may lead to a decrease in the rate of polymerization and a change in the properties of the polymer, usually in an undesirable manner. While these results have been established qualitatively by various workers (2, 7), little of a quantitative nature is known concerning the rates or degrees of hydrolysis of acrylate esters in alkaline emulsions. In this work a study has been made of these hydrolysis rates, and certain factors governing them have been determined.

Much literature is available concerning the rates of hydrolysis of esters in alkaline systems (1, 4, 5, 6), but in all cases the systems have been simple. Usually the ester is in solution and the alkali used is sodium or potassium hydroxide. In these cases the amount of hydrolysis is frequently determined by withdrawing a sample and titrating it with standard acid. This technique is not easily adaptable to a complex emulsion system containing ingredients which may interfere with indicator end points. Therefore it was decided to prepare an emulsion as used in polymerizations and to follow the pH of the system over a period of time, with a glass electrode pH meter.

By plotting the pH of the system against reaction time, the rate and degree of hydrolysis can be determined. The relationship between structure of monomer and hydrolysis rate can also be determined, and the results used to select satisfactory esters and emulsion systems for copolymerizations.

### Experimental Procedure

Five acrylate and methacrylate esters which are readily available commercially were selected for study. Methyl acrylate, ethyl acrylate and butyl methacrylate were obtained from the Rohm and Hass Company.

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Methyl and ethyl methacrylate were obtained from E. I. du Pont de Nemours and Company.

Two different types of emulsion recipes were employed; one, the "unactivated" system commonly used in the production of GR-S, the other, the "activated" system frequently used in laboratory polymerization studies. The recipes for these two systems are presented in Table I.

TABLE I.

Unactivated	POLYMERIZATION RECIPES	Activated
180 ml.	Water	190 ml.
5 g.	Soap	3 g.
0.5 g.	Potassium persulfate	1 g.
0.65 g.	O.E.I.	0.65 g.
	Potassium ferricyanide	0.15 g.
	Sodium hydroxide (5% soln.)	10 ml.
25 g.	Comonomer	25 g.
75 g.	Butadiene*	75 g.

The reaction vessel consists of a three-neck, round bottom, 500 ml. flask equipped with stirrer and condenser. The third neck is stoppered and is used for withdrawal of samples. The flask is heated by an electric heating mantle equipped with a variable transformer for temperature control.

The soap is dissolved in the water at 50° C., and after the solution has cooled to 35-40° C. the potassium persulfate and ferricyanide are added. The soap and sodium hydroxide solutions are then added to the reactor and the stirrer started. O.E.I. is added from a calibrated micro-dropper at this time. The reaction mixture is then brought to 40° C. (the reaction temperature) before the monomer is introduced.

It is advisable to take a zero time sample and to determine its pH. With the "unactivated" system a value of 10.2 is obtained for all such zero time samples. The ester is added and samples are taken at time intervals of 15-30 minutes for the first 3 hours and then at intervals of 1-3 hours for the remaining time.

A 10 ml. sample, taken by means of a suction pipette and water aspirator, is sufficient for a satisfactory pH reading. Part of the sample is used in rinsing the glass cup of the pH meter, and the remainder for the pH determination. If there is any of the sample unused it can be returned to the reactor.

A Coleman pH meter with a glass electrode was used throughout the entire hydrolysis study. This unit was modified for the titration of the "unactivated" and the "activated" systems. The glass electrode was immersed directly into the solution being titrated, and the calomel cell was connected to the soap emulsion by means of a saturated potassium chloride bridge.

\* Butadiene was ordinarily omitted from the recipes to allow the use of simple laboratory equipment.

## Discussion

## pH Versus Reaction Time.

**Unactivated System.** Probably the most familiar formula for the preparation of butadiene-styrene copolymers is the one used in the production of GR-S. This is well known for its simplicity and general utility. Table I shows the amounts of ingredients based on 100 g. of monomers for a similar recipe which is referred to as an "unactivated" system. In this system the butadiene was omitted to eliminate the need for pressure equipment and to simplify the sampling procedure. The presence of butadiene would have only a minor effect on the resulting pH data by decreasing somewhat the amount of ester dissolved in the water phase. Therefore, the rates of ester hydrolysis would be slightly larger in the absence of butadiene than in its presence. This effect would not modify seriously any correlation obtained between the structure of an acrylate ester and its rate of hydrolysis. Proof of this was obtained directly by comparing the pH of an emulsion containing butadiene with the pH of a system not containing butadiene. After several hours of reaction the pH values of the two systems were identical as determined.

The pH data resulting from the rate studies of these five esters in the "unactivated" system are shown in figure 1. These data indicate

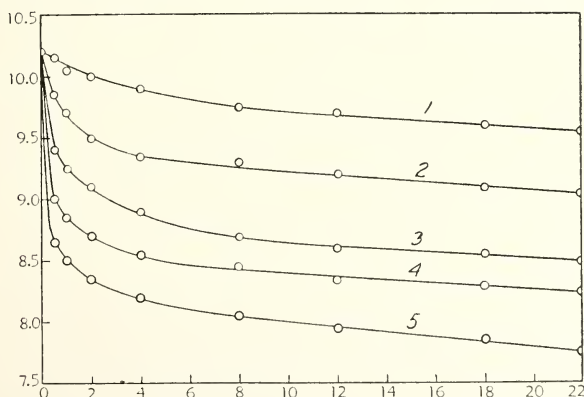


Fig. 1. pH Versus Hours of Reaction Time for Esters in the "Unactivated" System. Curve 1. Butyl methacrylate; Curve 2. Ethyl methacrylate; Curve 3. Methyl methacrylate; Curve 4. Ethyl acrylate; Curve 5. Methyl acrylate.

that the largest change in pH occurs during the first 2-4 hour period, after which the rate of pH change becomes small and nearly constant for all of the esters studied. It is evident that systems containing esters of low molecular weight have larger initial drops in pH than those containing esters of high molecular weight. The explanation for the change in pH becoming nearly constant for all esters after the initial drop in pH could be either a buffering action caused by the organic salts formed during hydrolysis or an actual slowing down of the hydrolysis. Additional studies relative to this effect will be discussed in a subsequent section.

**Activated System.** Although an "unactivated" system is very useful in exploratory work, other types of polymerization recipes are often utilized to obtain faster reaction rates and also to obtain improved products. These are often referred to as "activated" systems. The second system studied falls in this class. The chief difference between the two recipes other than slight changes in the amount of water, soap, and per-sulfate is the addition of potassium ferricyanide and sodium hydroxide. Table I shows the amounts of ingredients based on 100 g. of monomers for such a recipe. As in the hydrolysis study of the "unactivated" system, the butadiene was omitted.

The pH data resulting from studies of methyl acrylate, methyl methacrylate, and butyl methacrylate in the "activated" system are

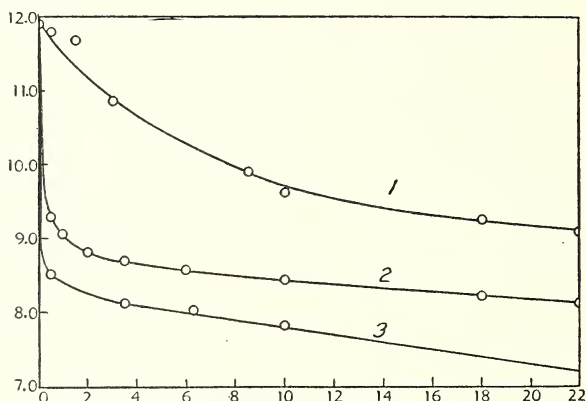


Fig. 2. pH Versus Hours of Reaction Time for Esters in the "Activated" System. Curve 1. Butyl methacrylate; Curve 2. Methyl methacrylate; Curve 3. Methyl acrylate.

shown in figure 2. These data show the same immediate drop in pH and leveling off to a constant pH change as was noted for the esters in the "unactivated" system. The most interesting result is that although the initial pH lowering is much larger, the pH of the system after 2-4 hours is only slightly lower than for the same ester in the "unactivated" system. This indicates that the excess sodium hydroxide is neutralized very quickly by the hydrolysis products of the ester, and that after this reaction has taken place the two systems are comparable in pH.

#### Titration of Emulsion Systems with Acetic Acid.

There are two possible explanations for the change in the rate of pH drop with time. First, the hydrolysis could have continued at its initial rate without an accompanying change of pH because of a buffering action by the organic salts formed. Second, the hydrolysis could have actually slowed down because the lower pH of the system no longer promoted rapid hydrolysis.

It was decided to determine the extent of the buffering action of the organic salts on the pH change by directly titrating the emulsion

systems with acetic acid, which is comparable in strength to acrylic and methacrylic acids. If buffering action were appreciable the pH of the system titrated would level off in the same range (pH of 7.5-9.5) as in the ester hydrolysis studies. If such an action did not occur, the pH of the titrated system would continue to drop as acid was added until a pH of 4-5 was attained.

Figure 3 and 4 were obtained by plotting the data obtained on titrating each system with acetic acid of known strength and following the pH. It is evident from these curves that the pH continues to decline as acid is added to the system and that no buffering action occurs within the pH range of 7.5-9.5. Therefore, the change of rate of the pH lowering in the original studies of the acrylate esters in the "unactivated" and

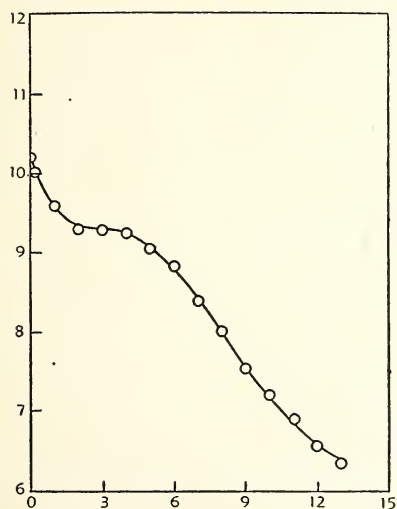


Fig. 3. Titration of the "Unactivated" System with 1 N Acetic Acid.

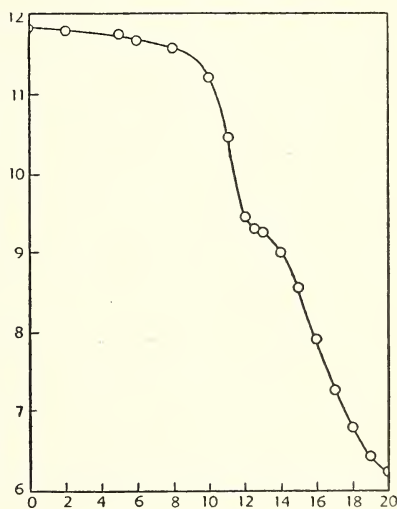


Fig. 4. Titration of the "Activated" System with 1 N Acetic Acid.

"activated" systems must be due to an actual slowing down of the rates of hydrolysis.

#### Development of Rate Curves.

Acetic acid was used in the titration of the emulsion systems because of its ease of handling as compared to acrylic or methacrylic acid. Acetic and acrylic acids have ionization constants of the same order of magnitude ( $1.8 \times 10^{-6}$  and  $5.5 \times 10^{-5}$  respectively) (3), and because of this it can be assumed that if acrylic acid had been used in the titration of the "unactivated" and "activated" systems, approximately the same curves would have been obtained.

By combining the data obtained in the pH studies of esters in the two systems with the data obtained in the titration of the same systems,

a series of curves can be drawn which show approximately the amount of hydrolysis after various periods of reaction. This can be explained in the following manner. The first series of studies give data showing the relationship of pH with time of reaction. The second series of studies give data showing the relationship of pH with the amount of acid used in the titration. As the ester is hydrolyzed, acid and alcohol are produced, and the liberated acid causes a lowering of pH. Therefore, it is possible to obtain a relationship between the amount of acid used in the titration and the time of reaction. This is the same as the relationship between the amount of acid liberated by hydrolysis and the reaction time, or the actual rate of hydrolysis curve.

The specific example of ethyl acrylate in the "unactivated" system will clarify this relationship. First, (Figure 1) the pH after three hours of reaction is found to be 8.6. Second, (Figure 3) it is seen that 6.5 ml.

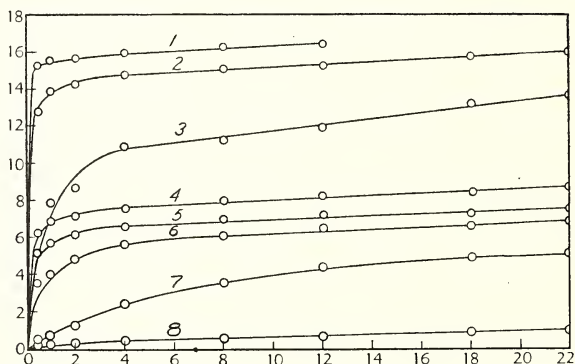


Fig. 5. Rates of Hydrolysis of Esters in the "Unactivated" and "Activated" Systems. Curve 1. Methyl acrylate "Activated"; Curve 2. Methyl methacrylate "Activated"; Curve 3. Butyl methacrylate "Activated"; Curve 4. Methyl acrylate "Unactivated"; 5. Ethyl acrylate "Unactivated"; Curve 6. Methyl methacrylate "Unactivated"; Curve 7. Ethyl methacrylate "Unactivated"; Curve 8. Butyl methacrylate "Unactivated".

of 1 N acetic acid must be added to the same system before a pH of 8.6 results. Therefore, it is reasoned that 6.5 milliequivalents (ml. x normality) of acid is liberated by ester hydrolysis in three hours. By following this same procedure for other reaction times the actual rate of hydrolysis curve is found for ethyl acrylate in the "unactivated" system. Figure 5 includes the rates of hydrolysis curves for the various esters in the "unactivated" and "activated" systems.

### Conclusions

The conclusions that can be drawn from this rate of hydrolysis study are as follows:

1. The greatest amount of hydrolysis takes place within the first 2 to 4 hours for most esters in either "unactivated" or "activated" systems.

2. The rate of hydrolysis after 2 to 4 hours is quite uniform for all esters in both systems.

3. The excess alkali of the "activated" system is neutralized very quickly when methyl acrylate or methyl methacrylate is present, but with butyl methacrylate the reaction is much slower. Therefore, it is questionable whether the excess alkali is able to play its usual accelerating role in systems containing low molecular weight acrylate and methacrylate esters.

4. Acrylate esters are more easily hydrolyzed than methacrylate esters of the same molecular weight (e.g. ethyl acrylate and methyl methacrylate). This may be attributed to steric hindrance in the alpha-substituted acid.

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