

The Kinetics of Thin Film Polyesterification*

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Synopsis

The goal of this work was to investigate the increase in the rate of polyesterification that takes place as surface-to-volume ratio is increased. The polymer used in this reaction was derived from the esterification of adipic acid (hexanedioic acid) and propylene glycol (1,2-propanediol). The effect of three variables—film thickness, water concentration of the nitrogen atmosphere, and temperature—was studied to determine their effect on the reaction rate. The water content of the atmosphere was found to severely retard the progress of the esterification and this fact reaffirms that the reverse reaction, hydrolysis, is much more important than was realized by earlier investigators. The reaction in the film was found to have an activation energy of 22,600 cal/mole compared to 12,600 cal/mole in the batch reaction, indicating a possible change in controlling rate from the batch to the film system. New evidence was found which illustrates the possible role of reactant mobility at high conversions. It is suggested that a possible explanation for the change in controlling rate may be due to a complex surface phenomenon such as the alignment of reactive groups at the surface or the orientation of water molecules at the gas-liquid interface.

INTRODUCTION

Recent textbooks^{1,2} dealing with polymer chemistry treat polyesterification as a simple third-order irreversible reaction as originally proposed by Flory.³ The familiar rate equation $d[A]/dt = -k[A][B][H^+]$ is considered by Flory to be valid for the first 92% of the reaction when the viscosity is low enough to allow the removal of water from the system as fast as it is formed. The use of irreversible kinetics implies that for the first 92% of the reaction the hydrolysis reaction rate is essentially zero in polyesterification.

During the past 20 years, several investigators have published data which appear to show that this assumption is invalid. Sunderland,⁴ while studying the formation of an alkyd resin, reported that conducting the reaction in a falling film reactor gave a 30-fold increase in rate over that observed in a batch system. Sunderland concluded that the increased rate was due to the more favorable conditions for the removal of water in the film reactor system. Davis⁵ reported that polyesterification data, including Flory's,

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best fit second-order kinetics for the first 85% of the reaction. Also Davis,⁶ after conducting reactions in sealed glass tubes and observing a decreased rate compared with that found in an open system, concluded that the reaction was probably quite reversible.

Bobalek et al.⁷ used a falling film reactor to study the kinetics of polyesterification. Their conclusion was that the increased reaction rate observed in film reactors could be due at least in part to the improved conditions for the removal of the water from the system. They suggest that the rate is in the mixed regime with the reaction rate constant a combination of both physical and chemical rate constants. Smith,⁸ in a statistical analysis of literature data, found that mixed models where rate control was shared by diffusion and reaction gave the best fit to the data. He believed, however, that this might have been derived from the inherently better empirical fit possible with two-constant models over one-constant model.

EXPERIMENTAL

Apparatus

To investigate the rate-controlling step of thin film polyesterification, a thin film reactor in the form of a rotary cone was constructed. This reactor was designed to give precise control of process variables.

The film reactor system can be broken down into three subsystems: the purge system, the reactor, and the feed system. The purge system (Fig. 1) consisted of a nitrogen source which was connected to the reaction chamber through a rotameter and a constant temperature bath maintained at 182.5°C. There was also a water source which was metered in a fine stream into a 50-ft heating coil in the purge line, to provide water vapor for the humidity tests.

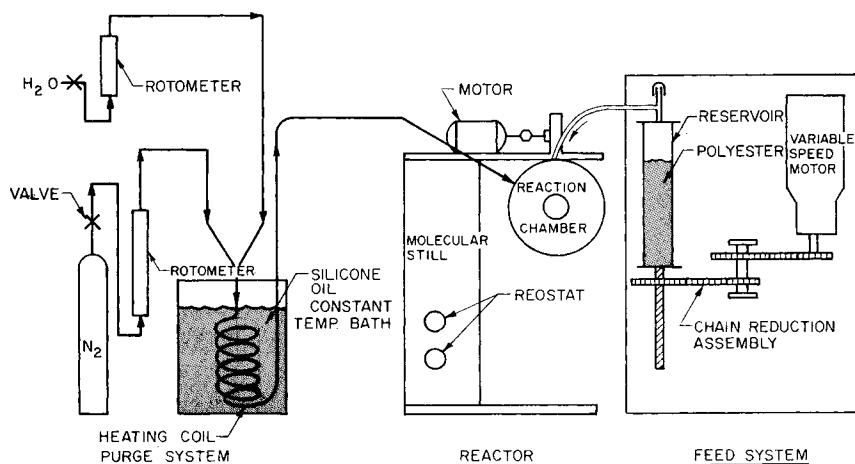


Fig. 1. Flow reactor system.

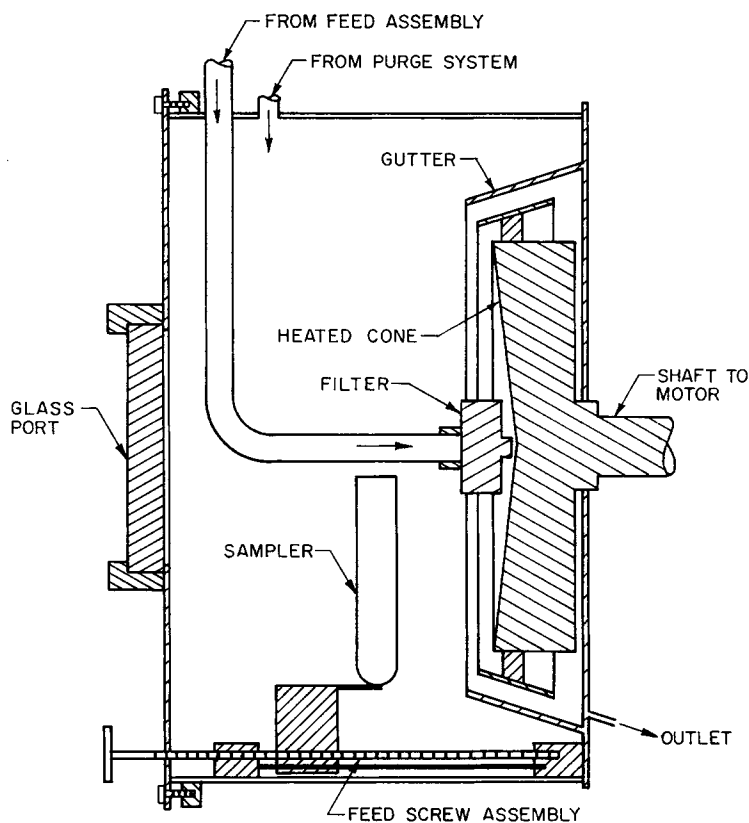


Fig. 2. Reaction chamber for the flow reactor.

The feed system (Fig. 1) contained the following elements: a variable speed motor, a chain and sprocket reduction assembly, and a heated reservoir with a screw feed piston. The Zero-Max variable speed motor had a range of from 0 to 400 rpm and was equipped with a digital counter so that the speed setting could be reproduced. This motor was connected to the drive screw by a chain and sprocket reduction assembly to provide a positive nonslip-drive feed metering system. The piston traveled in a 316 stainless steel heated reservoir with a volume of 150 ml.

The feed assembly was used to meter feed precisely onto the rotary cone reactor which is shown in Figure 2. The reactor, a modified 5-in. centrifugal still made by Consolidated Vacuum Corporation, is an internally heated rotating cone. This was enclosed in a stainless steel chamber so that the purge humidity could be controlled. The gutter-collecting system was modified so that the sampler could be used to obtain samples as the reacting fluid left the cone. The sampler was a water-cooled semicircular gutter which could be moved by the use of a screw assembly to the edge of the cone to take a sample after the system had reached steady state. There was a filter in the feed tube to keep any small dust particles away from the

0.01-cm orifice through which the feed was forced onto the cone. Two thermocouples were positioned on the face of the cone to determine the temperature of the reactants, one at the center of the cone and another on the outer edge. A glass port was installed in the cover so that the reactor could be observed.

Procedure

Prepolymer which was used as a feed to the rotary cone reactor was prepared in a heated, 2-liter reaction kettle which was fitted with a heated, modified Vigreux distillation column with distillation head.

A typical experiment was conducted as follows: The heaters for the reservoir, feed tube, cone, and nitrogen purge were turned on and adjusted. Then the prepolymer of partially polymerized adipic acid and propylene glycol was placed in the reservoir and raised to 165.8°C. When the cone and reaction chamber reached their respective temperatures, the feed motor was started and its output speed was adjusted so that desired feed rate of prepolymer to the cone was maintained. The polymer was raised to reaction temperature in the feed line so that when it emerged onto the cone it was at the same temperature as the cone. This temperature was monitored at the center of the cone and at the periphery to insure that the reaction mass was maintained at a constant temperature for the duration of the reaction. After steady state was reached, the system was allowed to run for 5 min to smooth out fluctuations, after which a sample was taken at the edge of the cone with the sampler. It was found that the acid number of this sample was the same as that of samples taken from the outlet. Because it is more convenient to tap a sample at the outlet, this is where the samples were taken thereafter. Samples were also taken from the reservoir as soon as the cone sample was taken. The difference in these two acid values was recorded as the change in the degree of reaction as the material crossed the cone. A nitrogen atmosphere was maintained at 160.0°C at a flow rate of 28.3 liters/min to act as a quench for the reaction.

To find the effect of atmosphere humidity on the reaction, water was metered into the purge heating coil where it evaporated to add water vapor to the purge gas. The reactor was then operated at constant film thickness and the rates of reaction were compared for both dry and humid atmospheres of variable water content.

Endgroup Analysis

It would be advantageous to be able to determine the concentrations of acid, base, and water in the system. However, because of the extreme difficulty and inaccuracy of determining free hydroxyl and water concentrations, the reaction was followed by the amount of residual acid in the melt. This is the so-called acid number, and it is defined as the number of milligrams of KOH necessary to neutralize one gram of the melt.

One gram of polymer melt was weighed in a 150-ml beaker and dissolved in a neutral 50-50 mixture of ethanol-benzene. A Fisher titrimeter was

used to detect the endpoint, which was found to be at a pH of 8.4. This technique gave reproducibility of acid number to a precision of better than $\pm 0.5\%$. By comparison, the precision obtained by the phenolphthalein endpoint is approximately $\pm 5\%$.

Extreme care must be exercised in cleaning the analytical glassware. It was found that this polymer tends to adhere to the glass and cannot be washed off by either solvents or soap and water. This adherent ester contamination on improperly cleaned glassware will cause erroneous acid values. To overcome this problem, the glassware was first washed thoroughly, then cleaned by pyrolysis at 500°C to remove all organic residue from the glass.

RESULTS AND DISCUSSION

Nature of the Flow on the Rotating Cone

The conditions of flow on the conical reactor were examined by using high-speed cinematography to follow the behavior of a dye tracer injected into the feed stream. Over the range of variables studied in this investigation, the residence time was found to be approximately constant at 0.83 sec and independent of the feed rate. Thus, because the surface area of the disk and density of fluid are constant, the volume and thickness of the reacting fluid held by the disk are linear functions of the mass flow rate. For flow rates of 5.66 g/min and 17.0 g/min, the film thicknesses were 0.00077 and 0.0023 cm, respectively. The rotating cone reactor, therefore, represents a convenient device for maintaining nearly constant residence time while variations are made in surface-to-volume ratio.

Reaction Rates in the Film Reactor

Figures 3 and 4 show the rate data that were taken on the rotary cone reactor. Because of the uniformity of residence time over the range of experimentation, the average rate of reaction can be reported as the acid number change per pass through the reactor.

Comparison of the reaction rates on the rotating cone with the batch reaction rates of Geittmann,⁹ the semibatch rates of Chae,¹⁰ and the rates of formation of the prepolymer used for this study shows the rate of reaction on the rotating cone to be approximately 3 orders of magnitude greater than the rate of reaction obtained in these other studies.

Chae believed that the rate acceleration in the thin film reactor resulted from a reduction of the diffusional resistance to water removal from the system. Geittmann's data, however, present a strong counterargument to the proposed diffusional limitation because they were obtained in a closed system and could not have been affected by diffusion of water.

Although Geittmann's results only cover the range from zero to 50% conversion, they illustrate that the reaction on the rotating cone is unique and that rate limitations of water diffusion cannot be used to explain all

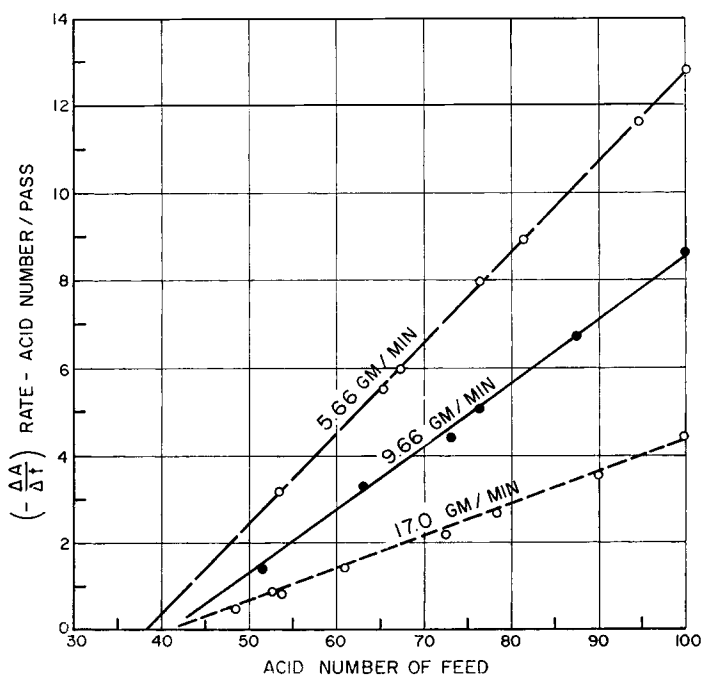


Fig. 3. Effect of feed flow rate (grams per minute) on the reaction rate for the film reactor.

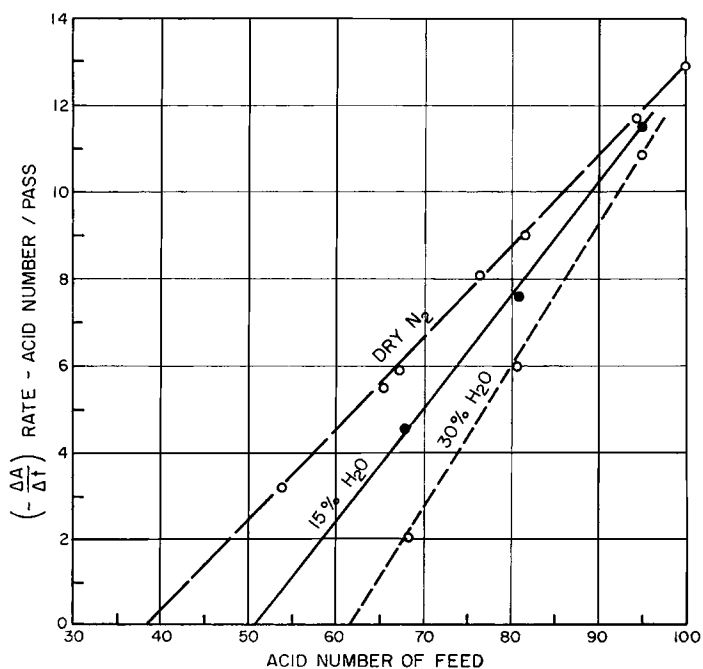


Fig. 4. Effect of purge water concentration on reaction rate for the film reactor.

of the observed rate enrichment. Some alternate explanations which could be applied to the observation are listed as follows: (1) the possible catalytic effect of the surface of the cone; (2) a previously unobserved autocatalytic effect at high conversions which is masked in the semibatch system by diffusional limitations; (3) orientation of reactants to a preferred mode of reactive functions at the liquid-gas or liquid-solid interface; (4) improved mobility of reactants deriving from internal stresses in the fluid.

Effect of Film Thickness

Figure 3 illustrates the effect of feed rate on the relationship between reaction rate and feed concentration. These data were taken at 187.5°C on the rotary cone reactor while introducing dry nitrogen into the reaction chamber as a purge gas. It is interesting to note that while the residence time on the cone was found to be independent of feed rate, the amount of reaction per pass over the cone is clearly influenced by feed rate.

Since the film thickness is linear with feed rate, Figure 3 shows the rate of reaction to increase as the film thickness is decreased. This fact would be consistent with any of the possible explanations for rate enrichment mentioned earlier, including as well the case for diffusion control.

A simplified derivation of a rate equation, based on either diffusional control or a possible surface reaction, would show that the reaction rate should be proportional to the reciprocal of film thickness. Comparison of the rates at equal feed composition shows that this relationship can neither be proved nor disproved. This could likely be the result of irregularities in the pattern of fluid flow.

Effect of Purge Gas Humidity

The effect caused by variation of purge gas humidity is shown in Figure 4. These data were all taken at 187.5°C and at a flow rate of 5.66 g/min. The pronounced effect of humidity on reaction rate illustrates the importance of the reverse reaction.

The apparent tendency of the lines in Figure 4 to intercept the abscissa is characteristic of reversible reactions. Increasing the vapor pressure of water in the atmosphere has the effect of increasing the rate of the reverse (hydrolysis) reaction.

The line for dry nitrogen, however, shows an anomalous behavior. When dry nitrogen is used as a purge, the only atmospheric water present should be that which is volatilized during reaction. This reaction-caused humidity should decrease linearly as reaction rate decreases, and the normal expectation is that data from the dry nitrogen experiments should pass through the origin. Extrapolation of the data from the dry nitrogen experiments does not bear this out.

It is unlikely that the intercept of the dry nitrogen experiments could have been caused by a deficiency of propylene glycol in the reacting mass. This conclusion is based on the following experimental observations,

First, in the production of the prepolymer, great care was taken to prevent loss of propylene glycol and these losses were found, by analysis of the condensed water of reaction, to be less than 0.4% of the glycol originally charged to the reactor. Yet, it would have required a loss of about 7.5% of the glycol to cause an intercept as high as the one found experimentally. The second set of experimental evidence was obtained to test the argument that because of the acceleration of the reaction on the conical reactor, the reverse reaction is similarly accelerated and could result in the liberation of glycol by hydrolysis and evaporation into the purge gas. This was shown to be an unimportant effect by a series of experiments in which polymer was recycled and used repeatedly for five rotating cone experiments. The results of the recycle experiments were identical to those of a series of experiments in which fresh feed was used for each determination. Clearly, if 7% of the glycol could be hydrolyzed and volatilized by one pass over the cone, four or five passes would have shown measurably more volatilization and a higher apparent intercept would have been observed in the recycle experiments. Thus, the conclusion must be that the intercept of the dry nitrogen experiments does not come from a loss of propylene glycol during reaction.

Of the possible explanations that might be proposed to explain the intercept of the dry nitrogen experiments, one is that the high viscosity of the polymer melt at high conversion causes an immobilization of reactive chain ends imposing, in effect, a diffusion limitation on the reactants and thus slowing the reaction. This has been called the *gel effect* and is discussed by Boudart.¹¹ Additional support for this concept can be found in the melt viscosity data obtained by Chae.⁹ At the temperature used for this set of experiments, Chae's data show that at acid numbers of about 40 to 50 the melt viscosity begins to show a very large rate of increase with further conversion.

At a temperature of 187.5°C, the reaction on the cone can be imagined to progress to a point at an acid number of about 40 or 50 where the control of reaction rate undergoes a transition toward control by reactant diffusion. The thermodynamics remain unviolated, but the rate is too small to be observed in rotating cone experiments.

The lines in Figure 4 appear to converge on a single value of rate at an acid number of about 105. This is an unexpected finding because normally this would not be expected except under the initial conditions of reaction, in this case, at an acid number of 503. When experiments were attempted to feed prepolymer having acid numbers of 150 and 120 to the conical reactor, reliable data could not be obtained because water vapor formed in the feed line caused spurting and boiling of the feed. Similar behavior was observed in the semibatch reactions conducted in the 2-liter kettle and suggests the reason for the convergence of the lines in Figure 4.

There are two rate processes involved in this reaction, the rate of chemical change and the rate of water removal. Early in the reaction, the rate of chemical change is fast enough to keep the inventory of water in the

system at a high enough concentration so that its vapor pressure is one atmosphere. Thus, at this stage of the process, water removal occurs by the parallel paths of diffusion and boiling. At higher conversions, the rate of chemical change slows down enough so that diffusion is able to keep pace with the rate of water production, the water inventory begins to decline, and boiling stops. Now the process has lost one of its paths for water removal and diffusion of water becomes a more important factor in setting the overall rate of reaction. A set of experiments was conducted in the 2-liter kettle in which agitation was shown to have no effect on reaction rate while boiling was taking place but it increased the reaction rate after boiling stopped. This type of behavior accounts for the apparent convergence of the lines in Figure 4. At the temperature of 187.5°C, the acid number of 105 is believed to correspond to the point at which the water inventory of the prepolymer feed is in Henry's Law equilibrium with one atmosphere of pressure and fixes the net rate of reaction, regardless of the water composition of the purge gas. The convergence of these lines supports the argument that diffusion has a role in determining the overall reaction rate on the cone but is not the sole rate determining step.

Effect of Temperature

The effect of temperature on reaction rate was studied at a feed rate of 5.66 g/min and using dry nitrogen as the purge gas. The activation energy for the reaction on the conical reactor was determined to be 22,600 cal/mole. For comparison, an activation energy of 12,600 cal/mole was found in the semibatch experiments; Geittmann⁹ found an activation energy of 13,200 cal/mole in his closed system; and Chae¹⁰ reported 15,400 cal/mole for the reaction in the falling film reactor. Thus the evidence shows a tendency for the experimental activation energy to increase with surface-to-volume ratio and indicates an apparent shift in reaction mechanism.

SUMMARY

The preceding evidence has shown that the high reaction rate obtained in the rotating cone experiments is not likely the result solely of the lowering of the resistance to water removal by diffusion as has been previously supposed. Yet, the tendency for the activation energy to increase as surface-to-volume ratio is increased indicates that a transition of controlling resistances does indeed take place. The nature of this transition is not exactly known but it might be related to a surface effect or, possibly, to an enrichment of the reaction rate constant by improved mobility of reactants. The diffusion of water does appear to play some role in the reaction rate on the cone, presumably because the resistances of all pertinent rate processes, chemical change as well as diffusion, are lowered in the thin film reactor. In addition, the apparent limiting conversion shown by the intercept of the dry nitrogen experiments points to the possible effect of

reactant mobility at high conversions in accordance with the so called *gel effect*.

One possible hypothesis to explain the increased rate with increased surface-to-volume ratio supposes the existence of a surface reaction or some unique surface phenomenon such as concentration or orientation to a preferred mode of reactive functions at the film-gas or film-solid interface. There are several surface-related mechanisms which theoretically could affect the dependence of rate on surface-to-volume ratio which was observed in these films on the rotary cone reactor. One possible explanation is an ordering of the surface molecules to produce a high surface concentration and thus producing a favorable condition for the reaction to occur. Secondly, Kavanau¹² has stated that water tends to orient itself at the surface of a polymer and that the mobility of a proton in this structured water is greatly increased over that of a proton in solution. Assuming that the reaction is general acid catalyzed, this increased proton mobility at the surface would also cause the averaged rate of reaction to be dependent upon surface-to-volume ratio.

CONCLUSIONS

The following conclusions may be drawn from this work:

(1) The reaction of adipic acid (hexanedioic acid) and propylene glycol (1,2-propanediol) to form a polyester is a reversible reaction the rate of which is very sensitive to water concentration at all levels of reaction.

(2) The Arrhenius activation energy increases from about 12,600 cal to 22,600 cal from the batch to the film system, indicating a change in controlling resistance as the surface-to-volume ratio is increased.

(3) On the film reactor used in this study, the rate is not limited solely by the resistance to diffusion of the water from the bulk polymer through the gas-liquid interface.

(4) At high conversions on the film reactor, reactant mobility appears to restrict the rate of reaction.

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