A Study of Interfacial Polycondensation in a Continuous Reaction System

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Synopsis

A study was made of the interfacial polycondensation of nylon 6-10 in a continuous reaction system since no previous detailed work of this type was reported in the literature. An experimental stirred-flow reactor was used to determine both yield and intrinsic viscosity (molecular weight) as functions of reactant ratio (sebacoyl chloride/ hexamethylenediamine) and Reynolds number. It was found that mass transfer was the controlling factor in the reaction system. The yield as a function of Reynolds number correlated directly with the behavior of mass transfer coefficient. In addition, reactant ratio effects on yield were shown to relate to change in organic phase volume. Intrinsic viscosity was a maximum in the same reactant ratio range as for batch and continuous cascade systems studied earlier. Intrinsic viscosity behavior was also shown to relate to mass transfer. The j_D data for the reactor systems were also determined. These values were shown to correlate if normalized for reactant ratio.
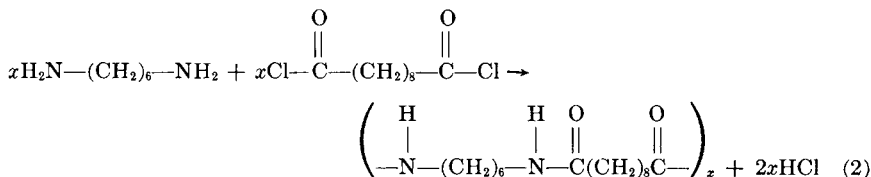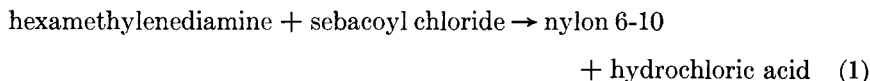
INTRODUCTION

Interfacial polycondensations have aroused considerable interest since they represent a rapid, low-temperature technique for producing polymeric material at atmospheric pressure. The process involves contacting two immiscible phases. One of the phases is aqueous and contains a diamine or diol as well as a base used to neutralize the acid formed as a by-product of the polymerization reaction; the other comprises an organic liquid and a diacid halide. Polymerization takes place at or near the interface of these phases.

Morgan[1,2] has written two excellent reviews that describe research on interfacial polycondensation up through 1965. Most of this work was done in either unstirred or stirred batch reactors.[1-4] In his book,[2] Morgan does mention some work done with continuous reactors.[1,5-9] Basically, this involved the description of various laboratory devices (a T-tube, injection polymerizer, a U-tube, and a centrifugal polymerizer) for continuous interfacial polymerization, together with some product data. In addition, some research was done in the Soviet Union[10-12] on the topic of continuous interfacial polymerization reactors. Continuous cascade reactor systems have also been studied by Kispert and Griskey[13] as well as Schnell and coworkers.[14]

The preceding references[1-9,13] have stressed the importance of mass transfer as the controlling step in interfacial polycondensations. The predominating influence of mass transfer becomes apparent when it is realized that reaction rate constants in interfacial polycondensation systems are of the order of 10^2 to 10^6 l./mole-sec.[1,3,4,5,6,17]

The present work was undertaken to study in more detail interfacial polycondensation in continuous stirred units. In addition, another of the goals was to consider in a more detailed and fundamental sense the hydrodynamic and mass transfer aspects of the interfacial polycondensation.

The polycondensation system studied was that for nylon 6-10. This reaction

hexamethylenediamine + sebacoyl chloride → nylon 6-10

$$+ \text{ hydrochloric acid} \quad (1)$$

$$x\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2 + x\text{Cl}-\overset{\overset{\text{O}}{\|}}{\text{C}}-(\text{CH}_2)_8-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{Cl} \rightarrow$$

$$\left(\overset{\overset{\text{H}}{|}}{-\text{N}}-(\text{CH}_2)_6-\overset{\overset{\text{H}}{|}}{\text{N}}-\overset{\overset{\text{O}}{\|}}{\text{C}}(\text{CH}_2)_8\overset{\overset{\text{O}}{\|}}{\text{C}}- \right)_x + 2x\text{HCl} \quad (2)$$

EXPERIMENTAL

A schematic diagram of the overall experimental apparatus is given in Figure 1. Solutions of reactants (hexamethylenediamine in water and sebacoyl chloride in carbon tetrachloride) were stored in constant head reservoirs (A). The reactant streams passed through ¼ in. poly(vinyl chloride) valves to a poly(vinyl chloride) duplex pump (i.e., streams were kept separate). The exiting reactant streams were split so that a portion of each reactant was recycled back to the reservoirs. The remainder of the reactants then passed through check valves (F) to a Durallin block (G) which supported the reactor.

The reactor (H of Fig. 1) is shown in greater detail in Figure 2. The thick-walled glass reactor was 6 in. long and ¾ in. in diameter with conical ends. It was attached to the Durallin block by means of a flange-and-gasket arrangement. A stainless steel paddle with a pitch of 45° and a ³/₈ in. diameter was used to agitate the reactor. The stirrer extended ½ in. into the reacting zone. A variable-speed motor equipped with a hand tachometer was used to drive the stirrer. A U-shaped glass overflow tube was attached to the end of the reactor.

In an actual run, the pump was primed for 1 hr before the reaction was studied. The reactor was first filled with hexamethylenediamine and the desired rpm set on the stirrer. The acid chloride was then allowed to enter the reactor where polymer was formed. After steady state was achieved, polymer and unreacted materials were collected in a 4-liter beaker contain-

FLOW CHART OF THE APPARATUS

A – RESERVIOR   H – REACTOR

B – PUMP   I – SLURRY

C – TWO WAY VALVE   J – STIRRER

E – NEEDLE   "   K – HCl SOLUTION

F – BALL   "   L – BEAKER
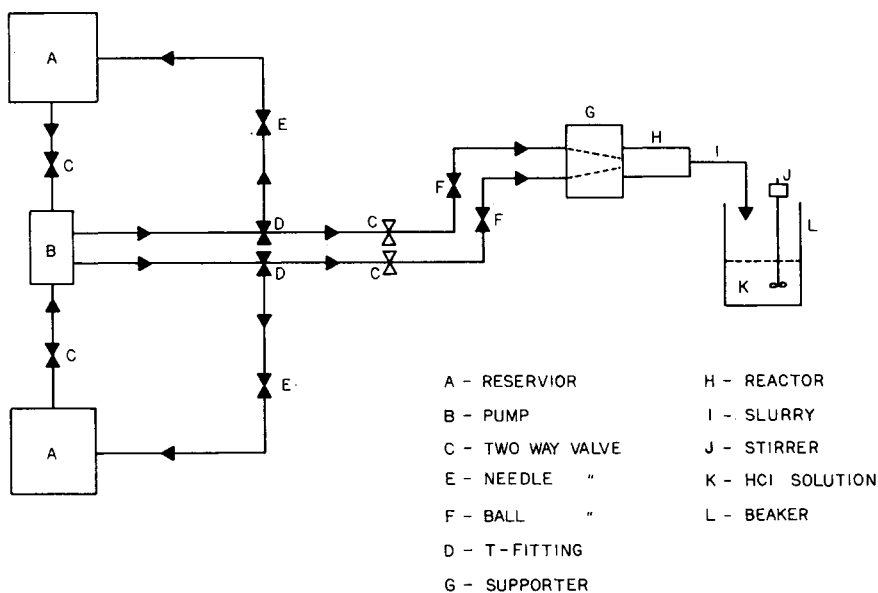
D – T–FITTING
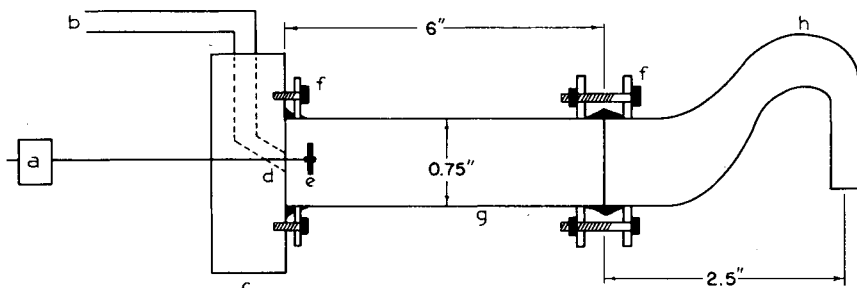
G – SUPPORTER

Fig. 1. Schematic of apparatus.

Fig. 2. Reactor.

ing 1 liter dilute hydrochloric acid.   This solution was stirred to react the
acid with unreacted hexamethylenediamine.   This stopped further poly-
merization.

The entire mixture was stirred for about 5 min.   Then, the polymer was
filtered out and washed with distilled water.   The polymer was then oven
dried for 12 hr.   This product was then weighed so that the yield could be
determined.   Next, the sample's intrinsic viscosity was determined.   This
was done by first dissolving the polymer in an appropriate solvent (m-cresol
for nylon 6-10).   Efflux times were then measured for various solutions.
These data were then used to calculate intrinsic viscosities.

RESULTS AND DISCUSSION

Figures 3 and 4 present polymer yield data versus Reynolds number for nylon 6-10. The Reynolds number (Re) in this case is

$$Re = \frac{D^2 N \rho}{\mu} \tag{3}$$

where D = stirrer diameter; N = agitator speed, in rpm; ρ = slurry density; and μ = slurry viscosity. As can be seen, the yield (at a constant reactant ratio of sebacoyl chloride/hexamethylenediamine) first increases and then drops or levels off with increasing Reynolds number. A consideration of this behavior will be deferred until some other experimental data are presented.

In Figure 5, the yield is plotted against reactant ratio at constant Reynolds number. These data first show an increasing yield with reactant ratio until a maximum is reached in the vicinity of sebacoyl chloride/hexamethylenediamine of 2.5. Then, the yield decreases with increasing values of reactant ratios.

Next, let us consider the behavior of polymer intrinsic viscosity with Reynolds number and reactant ratio. However, before doing so, it is well to note that intrinsic viscosity is a measure of the polymer's average molecular weight. It is especially important to remember that yield and intrinsic viscosity are not necessarily complimentary functions. In other words, the reaction system could produce a large yield of short chain (low molecular weight) polymer or a small yield of high molecular weight polymer.
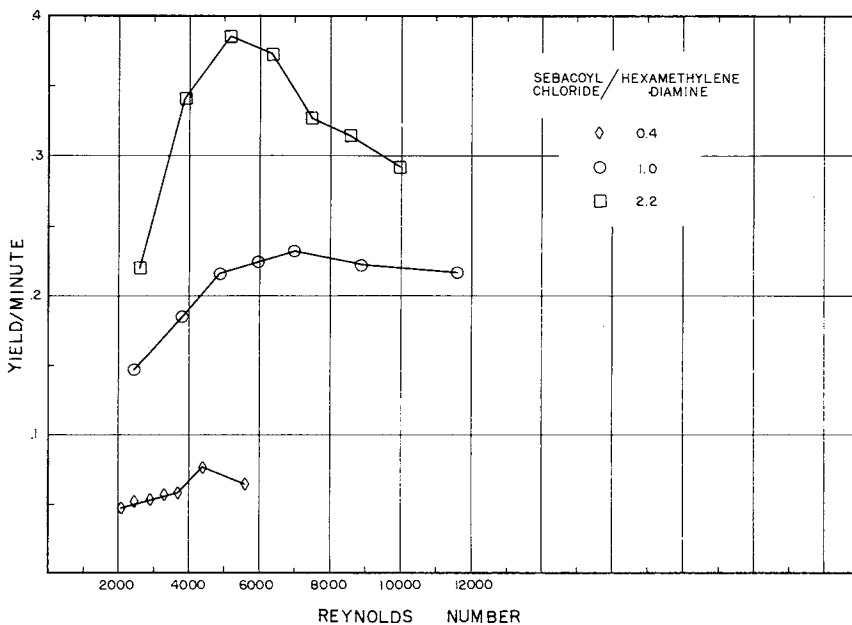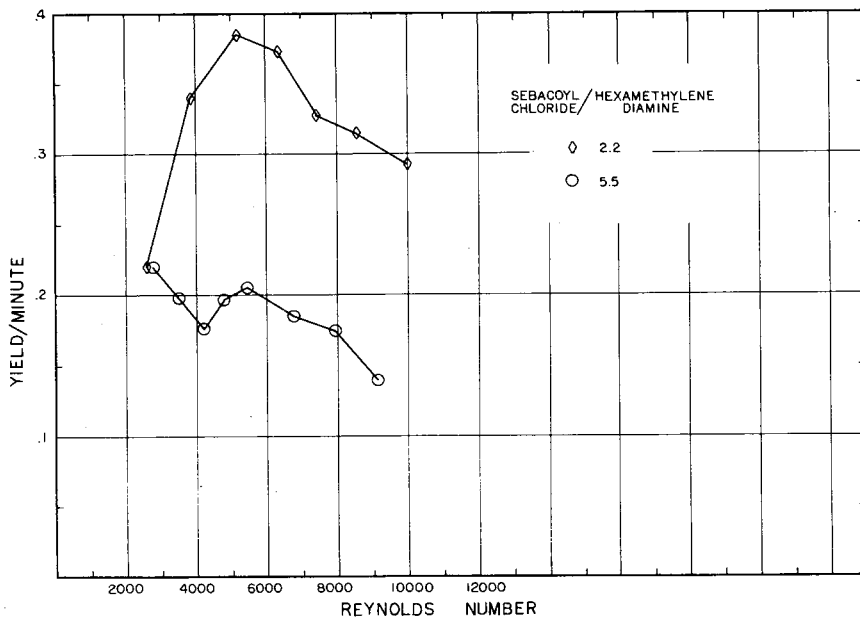

Fig. 3. Yield vs. Reynolds number.
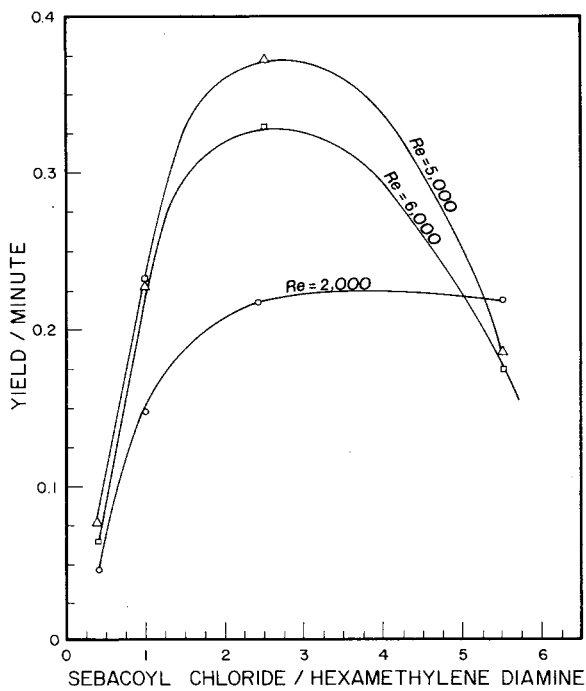
Fig. 4. Yield vs. Reynolds number.

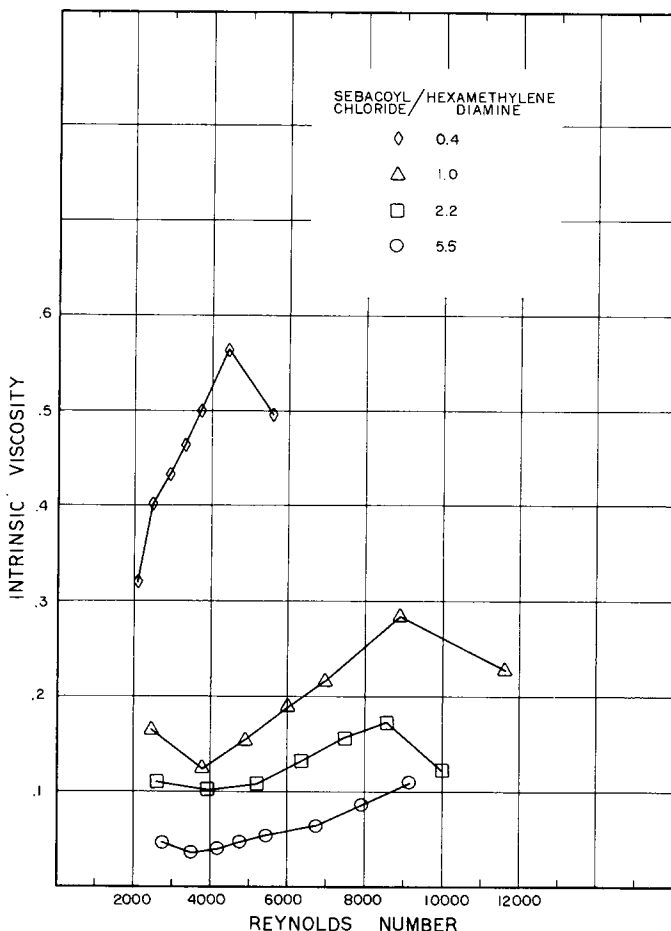Fig. 5. Yield vs. reactant ratio.

Fig. 6. Intrinsic viscosity vs. Reynolds number.

Figures 6 and 7 give the behavior of intrinsic viscosity for nylon 6-10 in a continuous reactor system. In Figure 6, the intrinsic viscosity is plotted as a function of Reynolds number at constant reactant ratio. The intrinsic viscosities tend to increase with increasing Reynolds number, peak, and then decrease. For all the reactant ratios except 0.4, this peak appears to be in the vicinity of a Reynolds number of 9000. Figure 7 shows that intrinsic viscosity is a maximum at low reactant ratio and decreases rapidly and then slowly with increasing reactant ratio.

At this point, let us consider in more detail the behavior of polymer yield and intrinsic viscosity with Reynolds number and reactant ratio. For un-catalyzed liquid–liquid heterogeneous reaction where mass transport can be physically altered,[16] the reaction rate r_b is

$$r_b = \left(\frac{1}{\dfrac{1}{k_b} + \dfrac{\partial_{Bb} \, X_{Bb} \, V_b}{k_{AL} \, A_v}} \right) (\partial_{Aa} \, X_{Aa} \, \partial_{Bb} \, X_{Bb} \, K_A) \qquad (4)$$

where k_b is specific reaction rate in phase b (organic phase); X_{Aa} and X_{Bb} are the mole fractions of diamine (A) in the aqueous phase (a) and sebacoyl
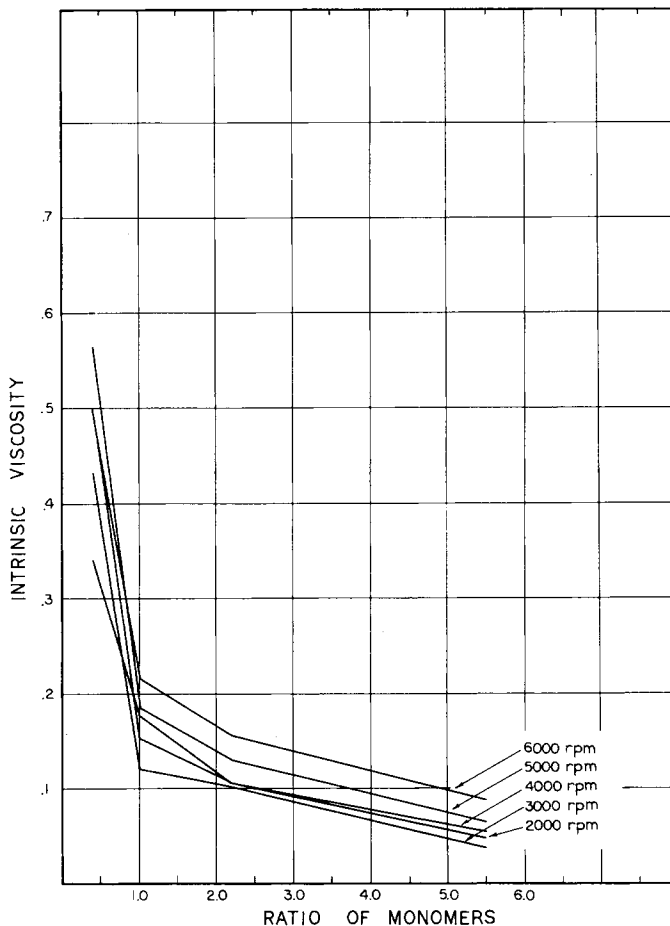
Fig. 7. Intrinsic viscosity vs. reactant ratio.

chloride B in the organic phase, respectively; K_A is the distribution equilib-
rium coefficient of diamine (A); $\eth_{Aa}$ and $\eth_{Bb}$ are the activity coefficients of
the reactants in the two phases; V_b is the volume of phase b (organic phase);
A_v is the interfacial area per unit volume; and k_{AL} is the mass transfer co-
efficient of A (diamine).

Equation (4) can be simplified. First, as noted earlier the values of
specific reaction rate k_b are quite large. Hence, $1/k_b$ will be small and
approach zero. Then

$$r_b = \left(\frac{k_{AL} A_v}{\eth_{Bb} X_{Bb} V_b}\right) (\eth_{Aa} X_{Aa} \eth_{Bb} X_{Bb} K_A) \tag{5}$$

and

$$r_b = \left(\frac{k_{AL} A_v}{V_b}\right) (\eth_{Aa} X_{Aa} K_A). \tag{6}$$

The reaction rate r_b is essentially the yield. Thus, if we use eq. (6), we
should be able to analyze the behavior of yield shown in Figures 3, 4, and 5.
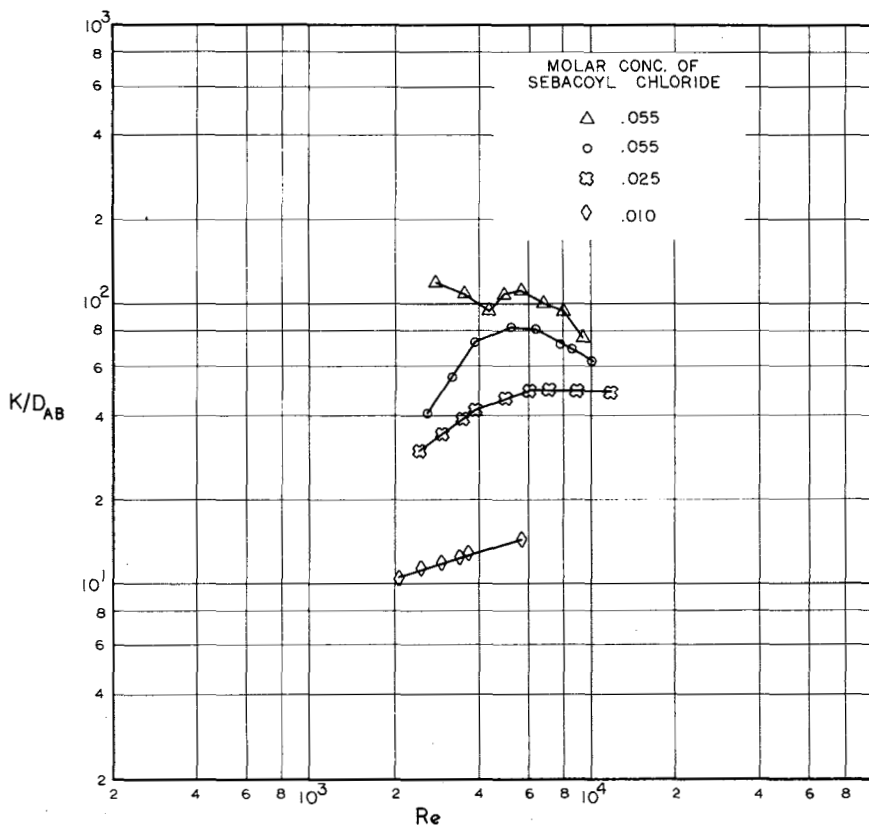In order to do this let us first delineate the mass transfer coefficient behavior.

Fig. 8. Plot of K/D_{AB} versus Reynolds number.

The literature dealing with mass transfer coefficients in liquid–liquid systems is generally not as extensive as that for gas–liquid systems.[17] Furthermore, no such data were found for chemically reacting systems. Mass transfer coefficients were, therefore, estimated using the techniques derived by Handlos and Barton.[18] These investigators studied both heat and mass transfer from drops in liquid–liquid extraction systems.

Figure 8 presents the ratio of the mass transfer coefficient for diamine divided by its diffusivity in the organic phase. As can be seen, four separate plots were obtained, each at constant reactant ratio. No direct comparison could be made with any similar system. However, the values of mass transfer coefficient/diffusivity for the Reynolds number range of Figure 8 are the same order of magnitude as for mass transfer to single spheres[19],[20] or mass transfer in wetted wall columns.[21]

In order to gain more insight into the mass transfer situation, j_D values were also calculated from the data of the present work using the form[18]

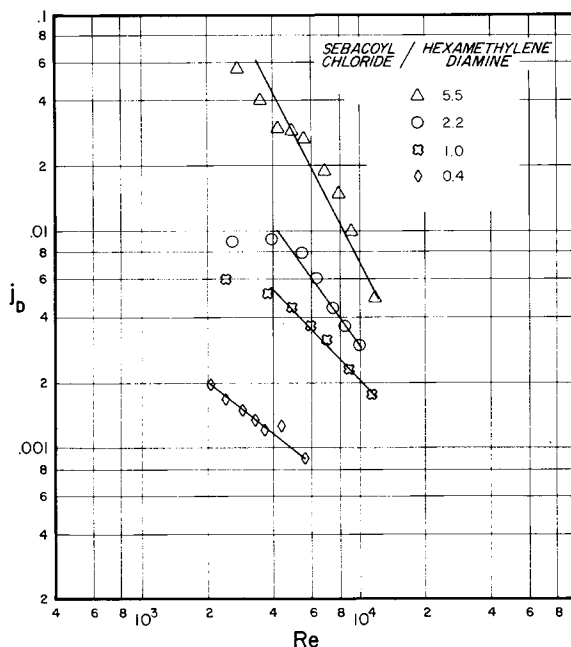$$j_D = \frac{K}{cN} (Sc)^{2/3} \tag{9}$$

Fig. 9. Plot of j_D vs. Reynolds number.

where K is the mass transfer coefficient, c is the diamine concentration, N is the rpm, and Sc is the Schmidt number. Values of j_D are plotted versus Reynolds number in Figure 9. For comparison, curves of j_D versus Reynolds number are given for evaporation from a flat plate,[22] diffusion in a wetted wall column,[21] and rectification in a wetted wall column.[23] In spite of the experimental situations differing from that of the present work, it can be seen that j_D values are of the same order of magnitude (Fig. 10). This tends to reinforce the credibility of the mass transfer coefficient data.

Before leaving this consideration of mass transport, one additional item should be noted. In Figure 11, the j_D values were "normalized" by multiplying these values by the factor necessary to make the reactant ratio unity (for example, all of the data at 0.4 reactant ratio were multiplied by 2.5). As can be seen, the result is a greatly improved correlation of the modified j_D' with Reynolds number. While no strong theoretical basis can be given for this, it is appealing from an empirical viewpoint, especially since it seems to compensate for the chemically reacting nature of the system.

Now let us return to the consideration of the yield data and eq. (6). If we take the data of Figures 3 and 4 at constant reactant ratio together with Figure 8 and eq. (6), we see that the yield behavior with Reynolds number closely parallels the mass transfer coefficient behavior. Therefore, at constant reactant ratio, it would appear that yield behavior is mainly a function of mass transfer coefficient behavior.

Referring next to Figure 5 and the yield behavior with reactant ratio at constant Reynolds number, we find what appears to be an anomaly. This
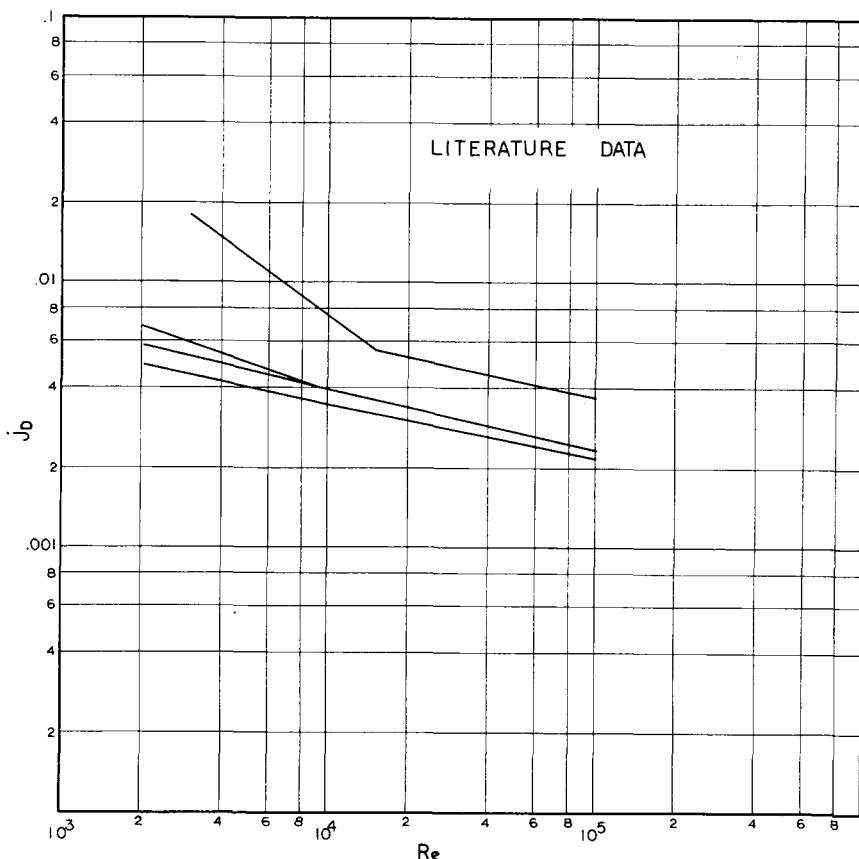
Fig. 10. Plot of j_D vs. Reynolds number (literature values).

seems to result because in Figure 9 mass transfer coefficient at constant Reynolds number *increases* with increasing reactant ratio even up to a value of 5.5. Therefore, if the yield is to decrease at reactant ratios higher than 2.5, some other factor(s) in eq. (6) must decrease. The activity of diamine in the aqueous phase (∂_{Aa}) and the mole fraction of diamine in the aqueous phase (X_{Aa}) would be unaffected by the changing reactant ratio. One factor, however, which would be changed is V_b, the organic phase volume, which would increase with increasing reactant ratio. Such a change would cause r_b to decrease. Apparently, the increase in V_b at values of reactant ratio above 2.5 overwhelms the increase in mass transfer coefficient and causes yield to decrease.

The question of intrinsic viscosity behavior is not as straightforward as the case for the yield. Here, the question is what factors affect the polymer chain length. To better understand this, consider earlier research on batch and continuous cascade systems.

Morgan and Kwolek[3,4] found that in batch reaction systems, a peak intrinsic viscosity was obtained with a balance of reactants. Kispert and Griskey[13] found that such peak intrinsic viscosities for nylon 6-10 occurred
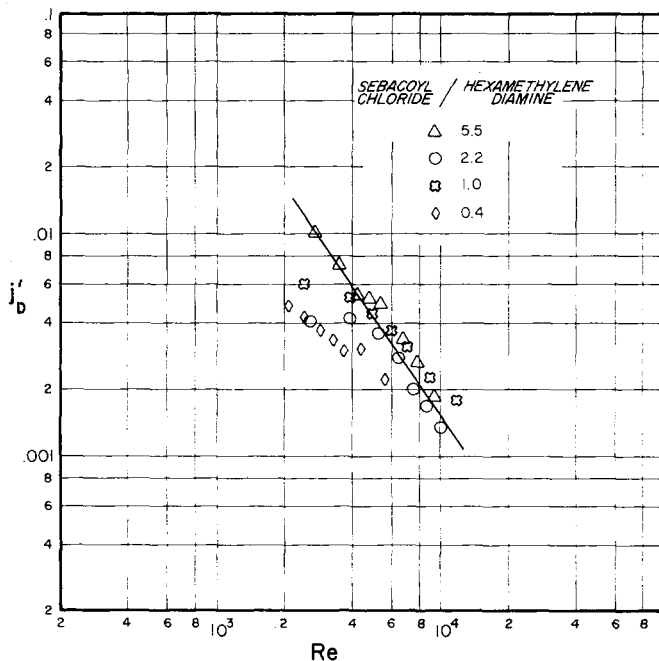
Fig. 11. Plot of j_D' vs. Reynolds number.

at reactant ratio values ranging from 0.1 to 0.25 for both the batch and continuous cascade systems. If we refer to Figure 7, we see that the peak values of intrinsic viscosity will occur between reactant ratios of 0 to 0.4. This checks the behavior found by Kispert and Griskey.[13] The decline in intrinsic viscosity with increasing reactant ratio past the peak value is attributed to a restriction in the formation of the polycondensation zone.[3,4,13]

The effect of Reynolds number on intrinsic viscosity at constant reactant ratio is to first bring about an increase until a peak is reached and then ultimately a decrease (Fig. 6). This ultimate decrease in intrinsic viscosity may be due to the drop in yield at higher Reynolds numbers. The decline in yield does not, however, completely jibe with the behavior in Figure 6 since it commences at Reynolds number of about 4000 or 5000. Something else must be taking place in the region between these values and the peaks of Figure 6. One possibility is that monomer has easier access to the growing polymer chains and increases molecular weight rather than form new polymer chains. This effect is then finally overcome when yields decrease even further.

CONCLUSIONS

The conclusions of this work are:

1. Interfacial polycondensation of nylon 6-10 in a continuous reaction system is mass transfer controlled.

2.   The polymer yield is closely related to the behavior of the mass transfer coefficient of the diffusing species (hexamethylenediamine).

3.   When a large excess of sebacoyl chloride is used, the effect of mass transfer coefficient is altered by an effect of organic phase volume.

4.   Mass transfer coefficients in interfacial polycondensation systems were determined and are of the same order of magnitude as for other systems.

5.   The j_D values in a continuous interfacial polycondensation system can be effectively correlated by normalizing them to reflect reactant ratio.

6.   Peak intrinsic viscosities in a continuous reaction system were found at reactant ratios corresponding to those determined for batch and cascade systems.

7.   Peak intrinsic viscosity behavior was found to be a function of the polycondensation zone.

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