Laminar and Turbulent Flow Continuous Interfacial Polycondensations of Nylon 66

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Synopsis

The interfacial polycondensations of nylon 66 in a continuous reaction system have been studied. An experimental stirred flow reactor was used to determine both yield and intrinsic viscosity (molecular weight) as functions of reactant ratio (adipoyl chloride/hexamethylene-diamine), and Reynolds number from laminar to turbulent flow. It was found that mass transfer was the controlling factor in the reaction system. The yield as a function of Reynolds number was found to directly correlate with the behavior of the combination of mass transfer coefficient and interfacial area. Intrinsic viscosity had maximum values in the same reactant ratio range as for batch and continuous cascade systems studied earlier. Intrinsic viscosity behavior was shown to relate to interfacial area behavior.
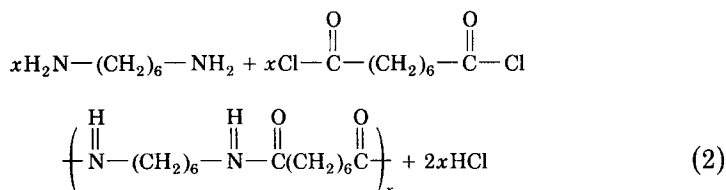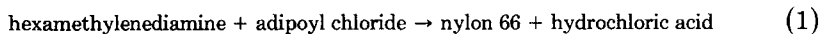
INTRODUCTION

Interfacial polycondensations represent a rapid, low-temperature technique for producing polymeric material at atmospheric pressure. Because of this, they have aroused considerable interest in light of their lower energy requirements. 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 byproduct of the polymerization reactions; 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 co-workers.[14] The most recent study[15] considered the continuous interfacial polycondensation of nylon 6-10.

The preceding Refs. 1–9, 13, and 15 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 10^2–10^6 L/mol s.[1,3-6,8,16]

The present work was undertaken to study in more detail interfacial polycondensation in continuous stirred units and to particularly extend research into the laminar region. 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 for nylon 66.
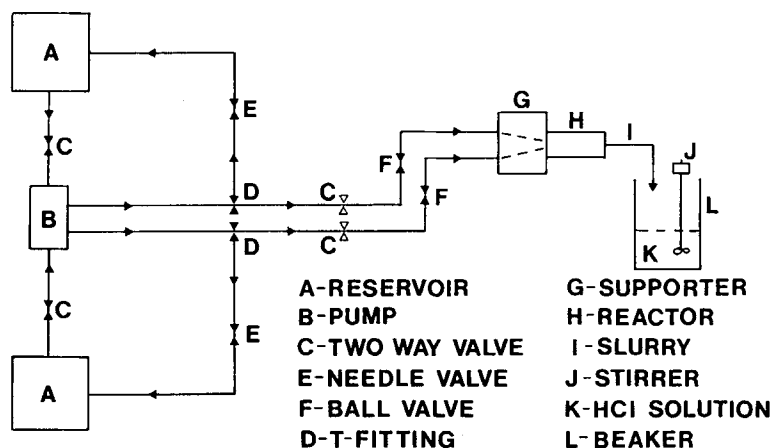
The polycondensation system studied was that for nylon 66. This reaction

$$\text{hexamethylenediamine + adipoyl chloride} \rightarrow \text{nylon 66 + hydrochloric acid} \tag{1}$$

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

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

EXPERIMENTAL

A schematic diagram of the overall experimental apparatus is given in Figure 1. Solutions of reactants (hexamethylenediamine in water and adipoyl chloride in carbon tetrachloride) were stored in constant head reservoirs (A). The reactant streams passed 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 Duralin 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 3/4 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 1/2 in. into the

A-RESERVOIR   G-SUPPORTER
B-PUMP   H-REACTOR
C-TWO WAY VALVE I-SLURRY
E-NEEDLE VALVE   J-STIRRER
F-BALL VALVE   K-HCI SOLUTION
D-T-FITTING   L-BEAKER

FLOW CHART OF THE APPARATUS

Fig. 1. Schematic of apparatus: (A) reservoir; (B) pump; (C) two-way valve; (D) T fitting; (E) needle valve; (F) ball valve; (G) supporter; (H) reactor; (I) slurry; (J) stirrer; (K) HCl solution; (L) beaker.
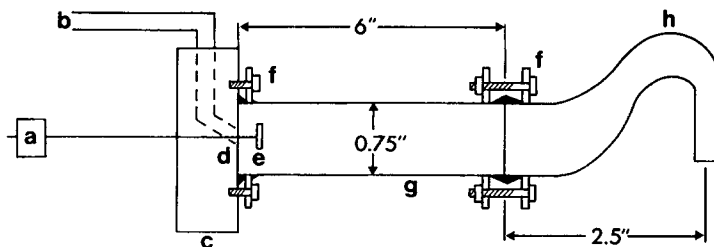
Fig. 2. Reactor.

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 h before the reaction was studied. The reactor was first filled with hexamethylenediamine and the desired rpm was 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-L beaker containing 1 L dilute hydrochloric acid. This solution was stirred to react the acid with unreacted hexamethylenediamine. This stopped further polymerization. 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 h. 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 (formic acid for nylon 66). Efflux times were then measured for various solutions. These data were then used to calculate intrinsic viscosities.

RESULTS AND DISCUSSION

The study gave both yield and intrinsic viscosity data for the polycondensation of 66 nylon.

Figures 3 and 4 present yield (g/min) as a function of stirrer speed constant monomer ratios (adipoyl chloride concentration/hexamethyline diamine concentration). As can be seen, the general pattern is essentially a slight decrease in yield for speeds up to about 3000 rpm followed by an increase and subsequent decrease. Although the overall effect will be explained in more detail, it is worthwhile to point out that the stirrer speed of 3000 rpm (where the curves change shape) corresponds approximately to a Reynolds number of 2100 (laminar-turbulent transition point in fluid mechanics). This number is obtained from

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

where D = stirrer diameter, N = agitator speed in RPM, ρ = slurry density, and μ = slurry viscosity. The Reynolds number, in essence, represents the ratio of inertial to viscous forces in the system.

In order to gain more insight into the behavior for yield, let us consider the case for uncatalyzed liquid–liquid heterogeneous reaction where mass trans-
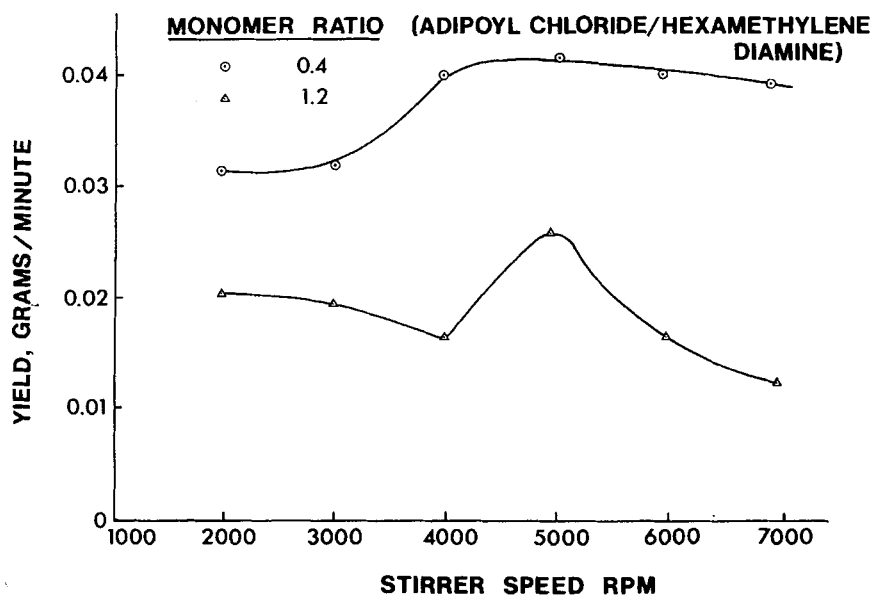
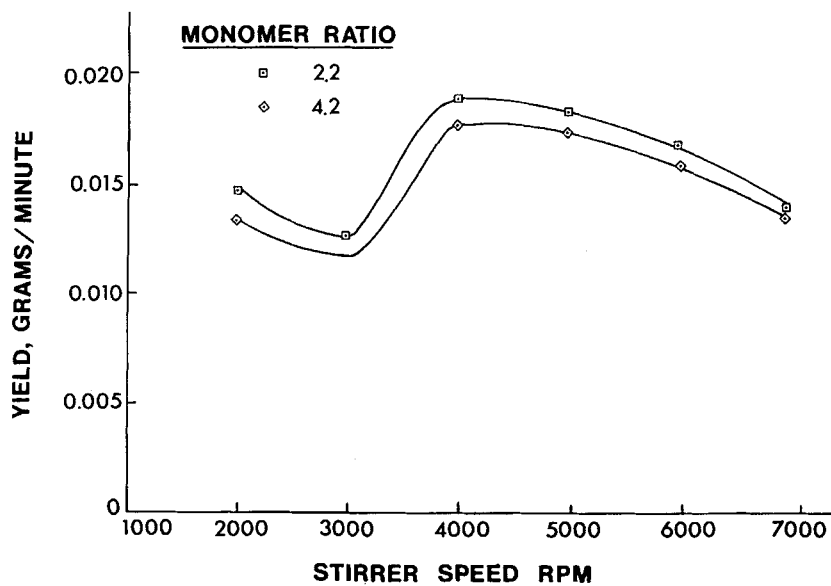Fig. 3. Yield vs. stirrer speed. Monomer (adipoyl chloride/hexamethylene diamine) ratio: (⊙) 0.4; (△) 1.2.

Fig. 4. Yield vs. stirrer speed. Monomer ratio; (□) 2.2; (◇) 4.2.

port can be physically altered.[17] Here, the reaction rate r_b is

$$r_{\mathrm{b}} = \left(\frac{1}{k_{\mathrm{b}}} + \frac{\partial_{\mathrm{Bb}} X_{\mathrm{Bb}} V_{\mathrm{b}}}{k_{AL} A_V} \right)^{-1} (\partial_{\mathrm{Aa}} X_{\mathrm{Aa}} \partial_{\mathrm{Bb}} X_{\mathrm{Bb}} K_A) \qquad (4)$$

where k_{b} is specific reaction rate in phase b (organic phase), X_{Aa}, X_{Bb} are the mole fractions of diamine (A) in the aqueous phase (a) and sebacoyl chloride (B) in the organic phase, respectively, K_A is the distribution equilibrium coefficient of diamine (A), ∂_{Aa}, ∂_{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 coefficient of A (diamine).

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

$$r_{\mathrm{b}} = \frac{k_{AL} A_V}{\partial_{\mathrm{Bb}} X_{\mathrm{Bb}} V_{\mathrm{b}}} (\partial_{\mathrm{Aa}} X_{\mathrm{Aa}} \partial_{\mathrm{Bb}} X_{\mathrm{Bb}} K_A) \qquad (5)$$

and

$$r_{\mathrm{b}} = (k_{AL} A_V) \left(\frac{\partial_{\mathrm{Aa}} X_{\mathrm{Aa}} K_A}{V_{\mathrm{b}}} \right) \qquad (6)$$

In the above, r_{b} is essentially the yield. The terms in the second bracket, namely, the distribution coefficient, volume, activity, and mole fraction of
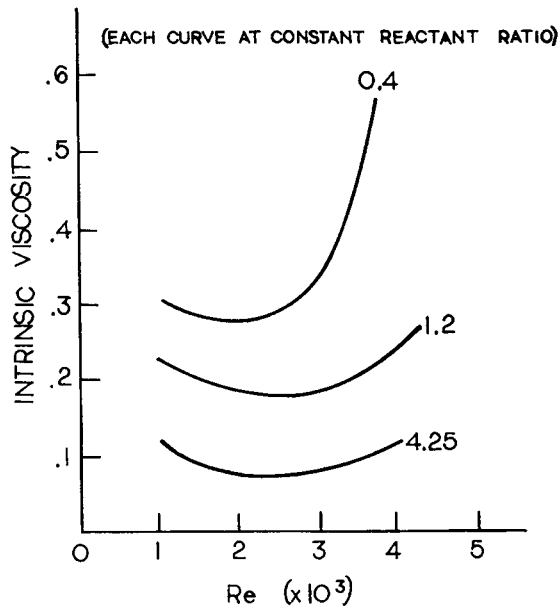

Fig. 5.   Intrinsic viscosity vs. Reynolds number. Each curve is at a constant reactant ratio.

diamine, are either constant or at worst varying slowly. This means that the k_{ALA_V} combination controls (at constant monomer ratio) the behavior of yield.

In terms of Figures 3 and 4, the behavior of k_{ALA_V} with Reynolds number (stirred speed) essentially matches the shape of the curves at constant reactant ratio. Generally in mass transfer situations k_{ALA_V} values change abruptly at the laminar-turbulent transition point. In addition, the low and high stirrer speed portion of the curves in Figures 3 and 4 reflect the separate laminar and turbulent behavior usually found in other mass transfer situations for (k_{ALA_V}). Hence, the yield behavior can be explained on the basis of mass transfer behavior. The intrinsic viscosity behavior shown in Figures 5 and 6, however, cannot be explained as readily as the yield. Nevertheless, there are some insights that can be gained based on prior research.

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 at reactant ratio values ranging from 0.1 to 0.25 for both the bath and continuous cascade systems. If we refer to Figure 6, 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.[2-4]
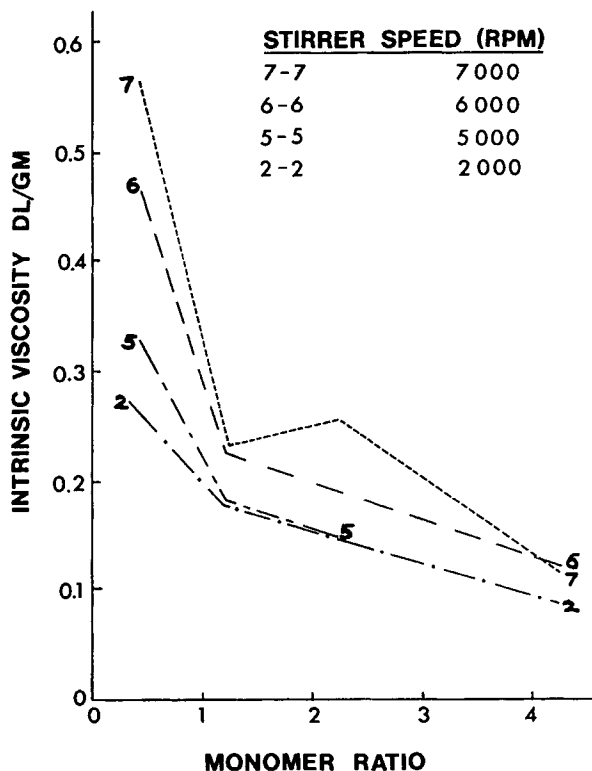

Fig. 6.   Intrinsic viscosity vs. reactant ratio. Stirrer speed (rpm): (2) 2000; (5) 5000; (6) 6000; (7) 7000.

The effect of Reynolds number on intrinsic viscosity at constant reactant ratio is first shown as apparent decrease to about a Reynolds number of 2000; then a gradual increase in intrinsic viscosity with increasing Reynolds numbers. This behavior can be explained in the following way. First, as the system goes from very low Reynolds number values to the range between 1000 and 2000 the reaction zone goes from a relatively uncongested to a more choked condition. Then, transition to turbulent flow significantly increases A_V (the interfacial area per unit volume). The result is a less congested reaction zone which allows polymer chains to grow more rapidly (i.e., an increase in intrinsic viscosity).

The results in the present work dovetail nicely with an earlier study of the continuous interfacial polycondensation of nylon 6-10[15] since it provides laminar region (Reynolds number less than 2100) data not covered in the earlier work.

CONCLUSIONS

1. Interfacial polycondensation of nylon 66 in a continuous reaction system is mass transfer controlled.

2. The polymer yield is closely related to the behavior of the product of the mass transfer coefficient and interfacial area ($k_{AL}A_V$).

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

4. Intrinsic viscosity appears to be a function of the polycondensation zone.

5. The overall behavior observed for nylon 66 polycondensation matches that for nylon 6-10 polycondensation.

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