

## Interfacial Polycondensation of Nylon 610 in Continuous Cascade Systems

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### Synopsis

The interfacial polycondensation of nylon 610 in unstirred, continuous, cascade systems has been studied. It was found that yields increased with increased reactant flow rates. The increase was shown to result from improved mass transport due to the change from molecular diffusion at low flow rates to eddy diffusion at high flow rates. The effect of improved mass transfer was also shown in the behavior of plots of polymer intrinsic viscosity versus sebacyl chloride concentration.

Interfacial polycondensations have been the subject of a great deal of recent research since they represent a rapid, low temperature technique for producing polymeric material at atmospheric pressure. The process involves bringing in contact two immiscible phases. One of the phases is aqueous and contains a diamine or diol as well as a base which is used to neutralize the acid formed as a by-product of the polymerization reaction. The other phase is organic and contains a diacid halide. Polymerization proceeds near the interface of the phases.

The rapidity of the chemical reaction involved<sup>1-3</sup> makes the rate of mass transfer the controlling factor in interfacial polycondensations. The importance of mass transfer is emphasized in the variables<sup>1-3</sup> which principally affect the process: temperature, time, nature of organic solvent, interfacial area, reactant concentrations, type and degree of stirring, and rate of polymer removal. One particular item which involves several of these variables (interfacial area, type and degree of stirring, rate of polymer removal) is the type of reactor used. Previous investigators had studied interfacial polycondensations in unstirred batch reactors<sup>1-3</sup> stirred batch reactors,<sup>1,3</sup> and continuous stirred reactors such as T-tubes.<sup>1</sup> No studies, however, had been carried out in continuous cascade reactor systems. The present work was undertaken to study such reactor systems.

Interfacial polycondensations of nylon 610 were carried out in a two-stage unit (Fig. 1). This particular system involves an aqueous phase with hexamethylenediamine and sodium hydroxide and an organic phase with

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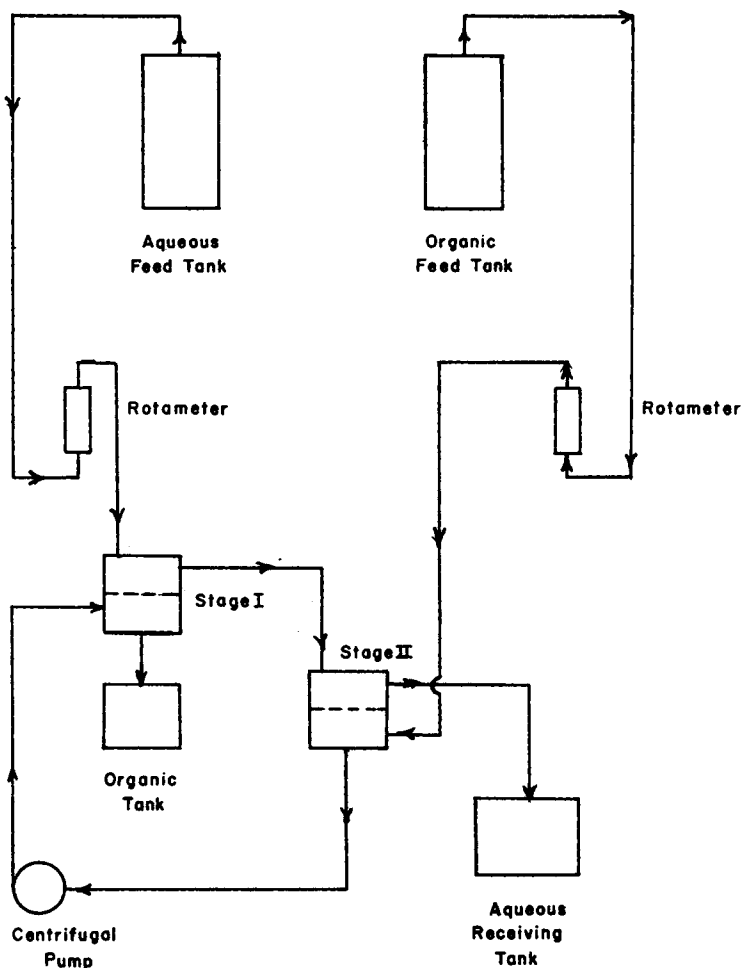
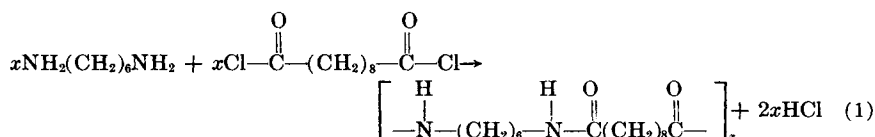


Fig. 1. Experimental apparatus.

carbon tetrachloride and sebacyl chloride. The reaction is hexamethylenediamine + sebacyl chloride  $\rightarrow$  nylon 610 + hydrochloric acid, i.e.,



The reactors were not stirred. All experiments were carried out with a 0.4M diamine concentration and a 2/1 ratio of sodium hydroxide to diamine at 30°C. Results are plotted in Figures 2-5. Figure 2 shows the yield of polymer for various reactant flow rates plotted against the ratio of moles of diamine to diacid chloride for a constant polymer removal rate (about 17 ft./min.). As can be seen, the effect of increasing flow rate at a given mole

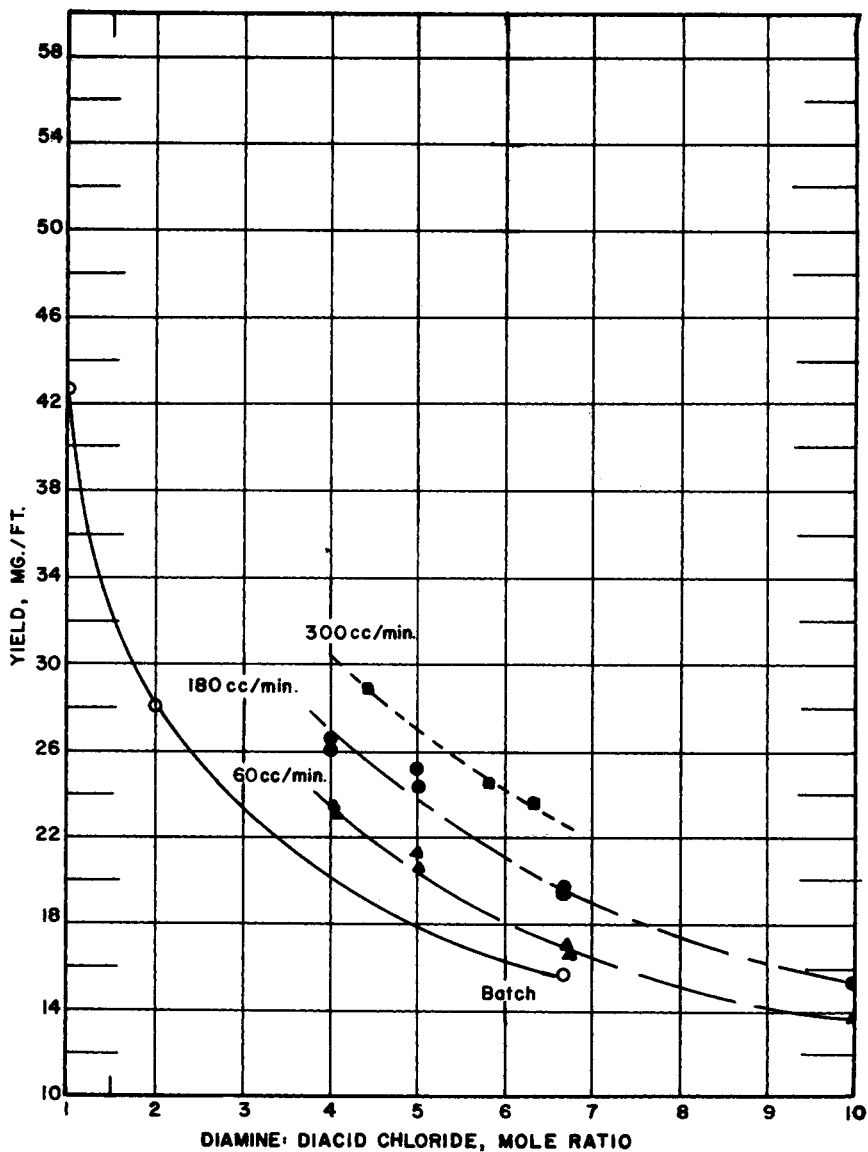


Fig. 2. Yield of polymer vs. diamine/diacid chloride mole ratio.

ratio is to increase the yield of polymer. The result is due to improved mass transport.

The effect of improved mass transport can be demonstrated by considering the treatment of uncatalyzed, liquid-liquid heterogeneous reactions by Hougén and Watson.<sup>4</sup> For systems without stirring or other means of physically altering mass transport the reaction rate  $r_b$  in the organic phase (b) is

$$r_b = k_b(X_{Aa}\gamma_{Aa}X_{Bb}\gamma_{Bb}K_A) \quad (2)$$

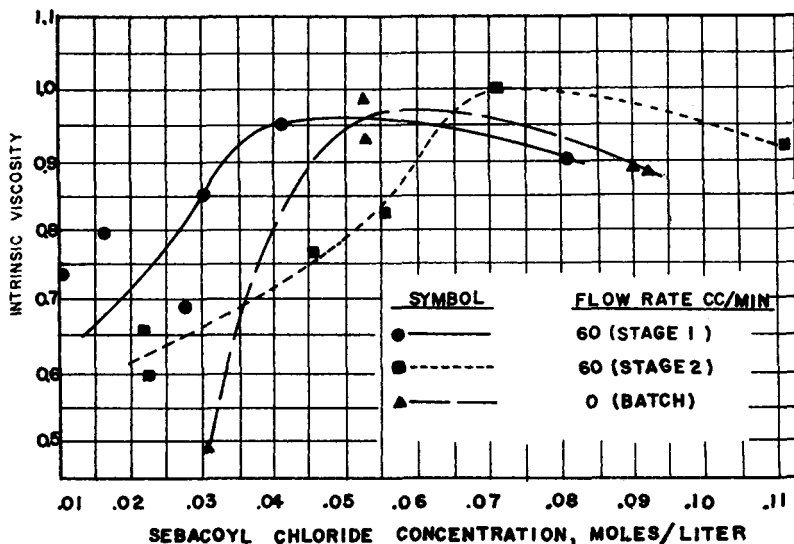


Fig. 3. Intrinsic viscosity vs. sebacyl chloride concentration at 60 cc./min.

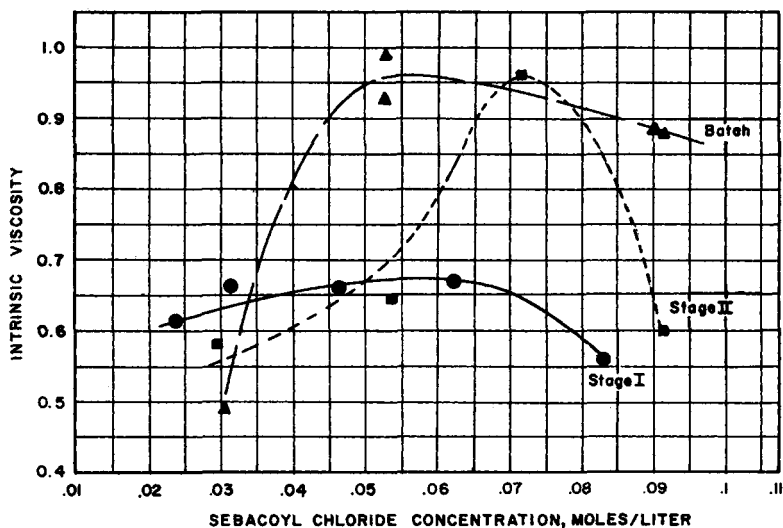


Fig. 4. Intrinsic viscosity vs. sebacyl chloride concentration at 180 cc./min.

where  $k_b$  is the specific reaction rate in phase b (organic phase),  $X_{Aa}$ ,  $X_{Bb}$ , are the mole fractions of diamine (A) in aqueous phase and sebacyl chloride (B) in organic phase, respectively,  $K_A$  is the distribution equilibrium constant of diamine (A), and the  $\gamma_{Aa}$ ,  $\gamma_{Bb}$  are the activity coefficients of the reactants in the two phases. Where there is some means of physically influencing mass transport, we have

$$r_b = \left[ \frac{1}{(1/k_b) + (\gamma_{Bb}X_{Bb}V_b/k_{AL}A_v)} \right] (\gamma_{Aa}X_{Aa}\gamma_{Bb}X_{Bb}K_A) \quad (3)$$

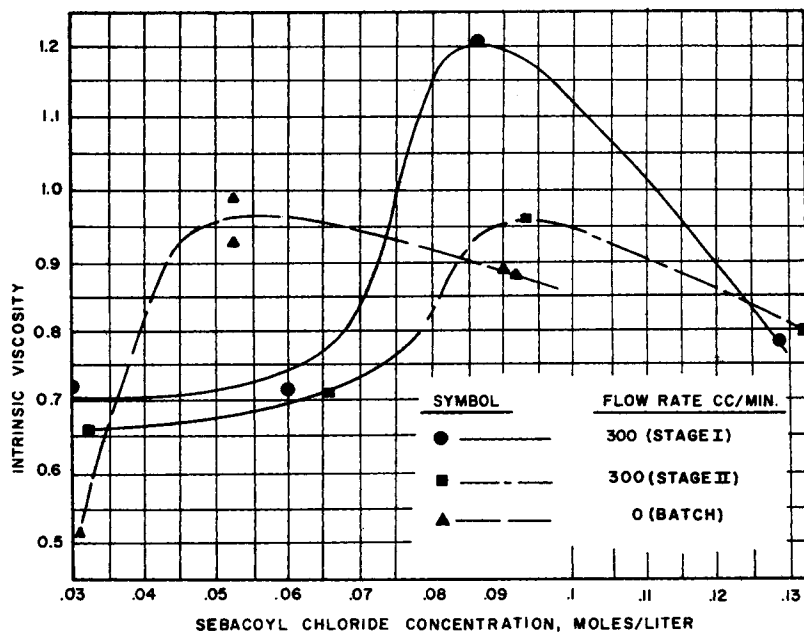


Fig. 5. Intrinsic viscosity vs. sebacyl chloride concentration at 300 cc./min.

where  $V_b$  is the volume of phase b (organic phase),  $A_s$  is the interfacial area per unit volume, and  $k_{AL}$  is the mass transfer coefficient of A (diamine). With increasing velocity the  $k_{AL}A_s$  product increases. This decreases the value of the denominator in the first bracketed term of eq. (3). The net result is an increased value of the first bracketed term which increases the reaction rate and hence the yield.

Some insight into the actual physical situation can be gained by considering Figure 6. This drawing illustrates the behavior found when dye was injected into the cascade system with simulated reaction conditions.

At a flow rate of 60 cc./min., dye injected at the inlet level traveled slowly across the reaction vessel and circulated slowly at the wall. Dye injected just below the interface moved slowly with the pattern shown. Increasing the flow rate to 180 cc./min. caused more rapid transport of dye injected at the inlet and subsequent rapid dissipation of the stream into a uniform color. Much more rapid movement of the dye took place at 180 cc./min. than at 60 cc./min. for interface injection. Finally at 300 cc./min., a solid color was obtained almost instantaneously with both inlet and interface injection.

The results indicate a change from a laminar situation (60 cc./min.) with molecular diffusion predominating to one involving turbulence (300 cc./min.) with eddy diffusion predominating. The 180 cc./min. case falls closer to the 300 cc./min. case and perhaps is indicative of the onset of turbulence.

Figures 3, 4, and 5 are plots of the intrinsic viscosity versus sebacyl chloride concentration. Each plot shows the curves for stages I and II at a particular flow value in comparison to the batch case. Diamine concentration was  $0.4M$  both for the batch case and the diamine feed stream entering stage I for the flow cases.

Somewhat similar behavior was observed for all the flow cases except stage I at  $60$  cc./min., in that all of the curves are to the right of the batch

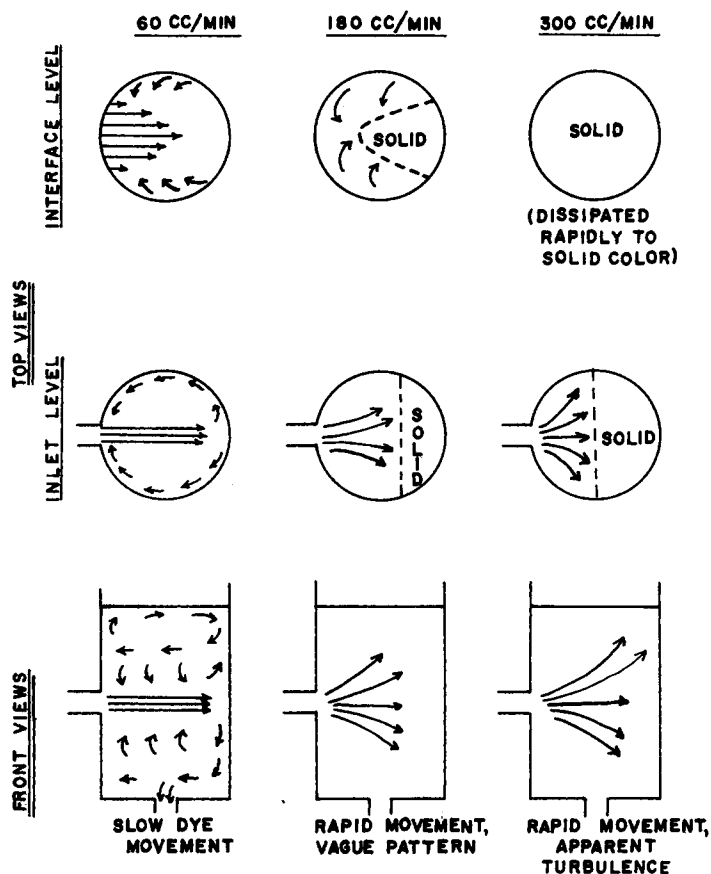


Fig. 6. Flow behavior in cascade system.

case curve. This behavior can be explained by considering the reason for the general curve shape and the conditions of the experiments. It has been stated elsewhere<sup>2,3</sup> that a peak intrinsic viscosity will be obtained when there is a balance of reactants. For sebacyl chloride concentrations below this value needed for balance, a less compact polymer network is formed. For sebacyl chloride concentrations higher than the balance point, the formation of the polycondensation zone is restricted, resulting in lower intrinsic viscosity values.

The flow cases should all have better diamine mass transport than the batch case. The improved diamine transfer causes an imbalance of reactants which must be resolved by increasing the sebacyl chloride concentration. The result is a shift to the right of the intrinsic viscosity-sebacyl chloride concentration curves for the flow cases.

This explanation satisfies the behavior found for the 180 and 300 cc./min. cases as well as the 60 cc./min. stage II case. It does not, however, cover the 60 cc./min. stage I case which shifts to the left rather than the right.

Consideration of the degree of shift of the intrinsic viscosity-sebacyl chloride concentration curves furnished a possible explanation for this anomaly. This shift to the right is slight for the 60 cc./min. stage II case. The shift is also considerably less than for the 180 and 300 cc./min. cases, indicating a much smaller improvement in diamine mass transfer over the batch case for the 60 cc./min. stage II data.

Since the gain in diamine mass transfer is small at 60 cc./min., a slight deleterious change in some other factor affecting mass transfer could shift the intrinsic viscosity-sebacyl chloride concentration curve to the left. This then could account for the position of the stage I curve in Figure 3.

### References

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### Résumé

On a étudié la polycondensation interfaciale du nylon 610 dans les systèmes non-soumis à l'agitation, en continu et en cascade. On a trouvé que les rendements augmentaient lorsqu'on augmentait les vitesses d'écoulement des réactifs. On montre que cette augmentation provient d'une amélioration du transport de masse due au changement depuis la diffusion moléculaire aux faibles vitesses d'écoulement jusqu'à la diffusion turbulente aux vitesses d'écoulement élevées. On montre également l'influence de l'amélioration du transfert de masse en portant en graphique la viscosité intrinsèque du polymère en fonction de la concentration en chlorure de sébacyle.

### Zusammenfassung

Die Grenzflächenpolykondensation von 610 Nylon in ungerührten, kontinuierlichen Kaskadensystemen wurde untersucht. Mit steigender Strömungsgeschwindigkeit der Reaktionsteilnehmer nahm die Ausbeute zu. Diese Zunahme wurde durch einen verbesserten Massentransport durch Übergang von einer Moleküldiffusion bei niedriger Strömungsgeschwindigkeit zu einer Wirbeldiffusion bei hoher Strömungsgeschwindigkeit verursacht. Der Einfluss der verbesserten Massenübertragung zeigte sich auch bei der Auftragung der Viskositätszahl des Polymeren gegen die Sebacylchloridkonzentration.

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