

## Effect of Acid Acceptor Concentration on the Interfacial Polycondensation of Nylon 610

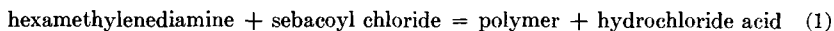
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### Synopsis

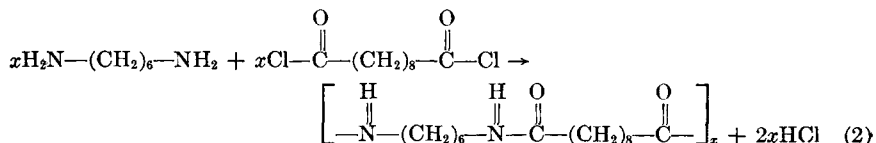
The effect of acid acceptor level (sodium hydroxide) in the interfacial polycondensation of nylon 610 has been studied. It was found that increased acceptor levels shifted the curves of intrinsic viscosity versus sebacoyl chloride concentration to the right. It was also found that peak intrinsic viscosity values first decreased and then increased with increasing acid acceptor levels. The experimental results were shown to relate to balance of reactants and character of polycondensation zone.

Interfacial polycondensations have aroused a considerable amount of research interest during the past six years because they represent rapid low-temperature processes for making condensation polymers at atmospheric pressure. Usually these processes involve contacting two immiscible phases. One is generally water plus a diamine or diol and a base, which is used for neutralizing 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.

A typical reaction system is that for nylon 610. A phase containing water, hexamethylenediamine, and a base (usually sodium hydroxide) makes contact with a phase made up of sebacoyl chloride and carbon tetrachloride. The reaction is:



or, symbolically,



A number of variables will affect interfacial polycondensations, including temperature, reaction time, interfacial area, reactant concentrations,

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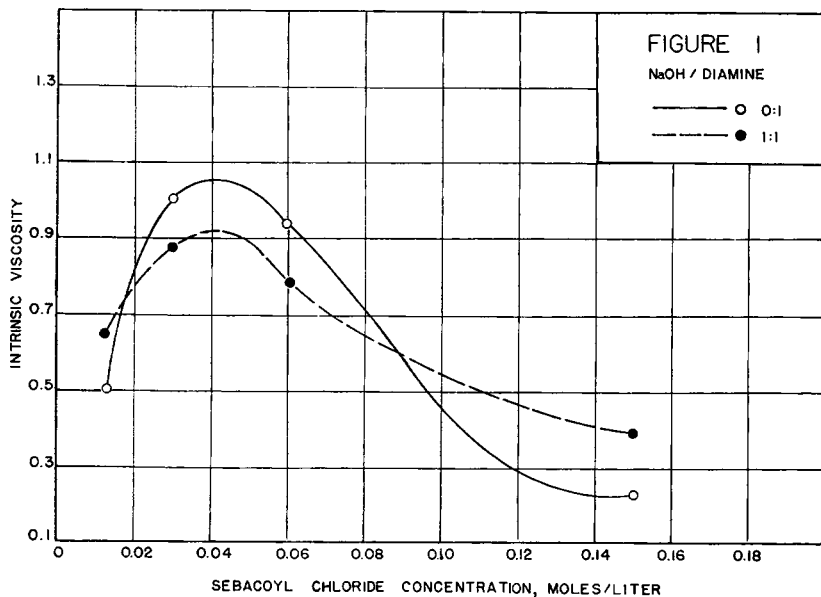


Fig. 1. Intrinsic viscosity versus sebacyl chloride concentration (no acceptor and 1:1 level).

organic solvent, type and degree of stirring, and rate of polymer removal. Morgan and Kwolek<sup>1-3</sup> have summarized much of the research involving these variables. Other investigators in the field have been Akutin and Rodivilova,<sup>4</sup> Alexandru and Dascalu,<sup>5</sup> and Hodnett and Holmer.<sup>6</sup>

None of the above, however, considered to any extent the effect of amount of acid acceptor on the polycondensation reaction. The only work found in the literature relating to this subject was that of Korshak and his collaborators.<sup>7</sup> These investigators considered acid acceptor effects in the polycondensation of nylon 6-6.

The present work was undertaken to determine the effect of varying the acid acceptor level on the interfacial polycondensation of nylon 610. Experiments were carried out in unstirred batch reactors at room temperature. The diamine concentration was kept constant for all runs. The sebacyl chloride concentration was varied for each acid acceptor level studied. Intrinsic viscosities were determined for polymer produced at each sebacyl chloride concentration. The data are shown in Figures 1, 2, and 3.

TABLE I

Peak intrinsic viscosity	Acid acceptor to diamine
1.08	0:1
0.91	1:1
0.93	2:1
1.13	4:1

The effect of changing the acid acceptor level (that is, increasing the sodium hydroxide) is seen to shift the intrinsic viscosity–sebacoyl chloride curves to the right. In addition, the peak intrinsic viscosity values for

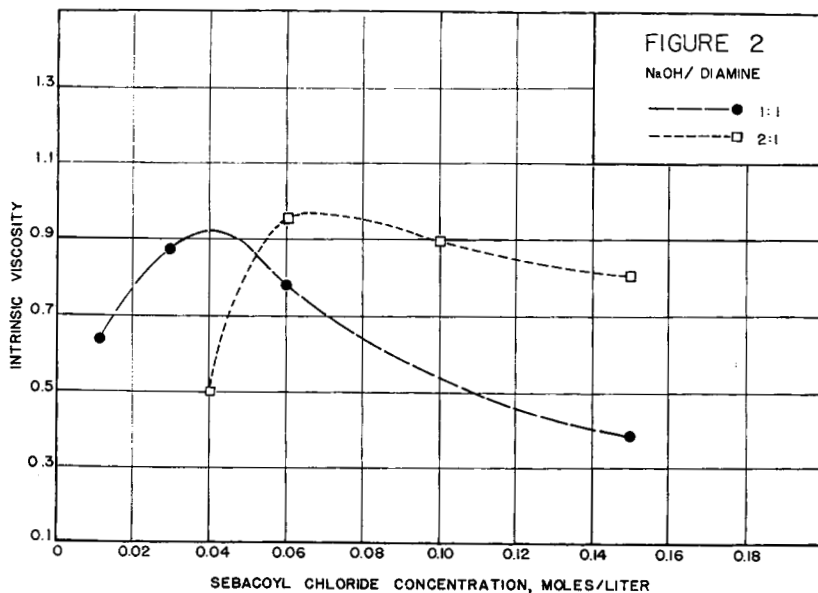


Fig. 2. Intrinsic viscosity versus sebacoyl chloride concentration (1:1 level and 2:1 level).

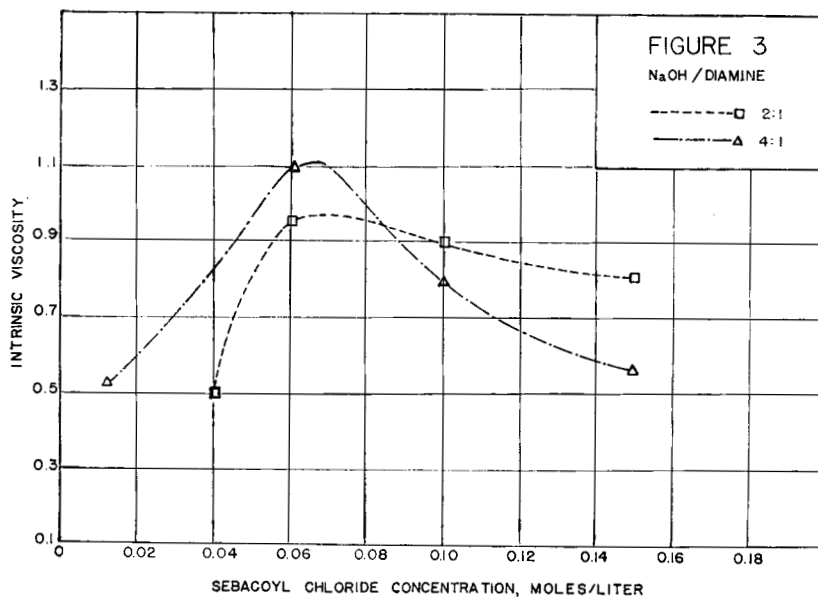


Fig. 3. Intrinsic viscosity versus sebacoyl chloride concentration (2:1 level and 4:1 level).

the curves seem to be affected by changing the acceptor. The peak values are first depressed and then increased with increasing acceptor level (Table I). This behavior is corroborated by the work of Korshak et al.,<sup>7</sup> who found that increasing acid acceptor (pyridine in their case) first depressed and then increased the peak intrinsic viscosity values for nylon 6-6 formed by interfacial polycondensation.

Before considering the possible explanations of the behavior observed in the present work it is helpful to consider certain points concerning interfacial polycondensation and the role of acid acceptor. Mass-transfer rates are generally the limiting factor in interfacial polycondensations because of the rapidity of the chemical reactions involved.<sup>2,3</sup> Hence, for a high intrinsic viscosity it is necessary for the mass-transfer rate to be such that a balance is attained in the polymerization zone (which is in the organic phase<sup>2</sup>), while the growing chains are mobile. For sebacoyl chloride concentrations below the value needed for balance a less compact polymer network is formed. For sebacoyl chloride concentrations higher than the balance point the formation of the polycondensation zone is restricted.

The purpose of the acid acceptor in a polycondensation system is to take up the acid by-product formed in the reaction (in this work, hydrochloric acid). If little or no acceptor is present, the hexamethylenediamine itself will act as an acceptor. The result is to decrease the effective diamine concentration. Increasing the amount of acceptor will in effect increase the amount of diamine available for the reaction. The increased amount of diamine causes an imbalance of reactants, which must be resolved by increasing the sebacoyl chloride concentration. This results in the shift of the intrinsic viscosity-sebacoyl chloride curves to the right, as shown in the figures.

The fall and rise of the peak intrinsic viscosity values (see Table I) is not so easily explained. It has been noted elsewhere<sup>1-3</sup> that, the more compact the polymer network in the polycondensation zone, the less the likelihood of long chains. At zero acceptor level the diamine itself acts as an acceptor. The diamine, however, neutralizes the acid in the polycondensation zone itself. This means that the zone will be diluted by the products of the neutralization reaction and hence have a less compact polymer network. This in turn results in the formation of long chains. Now, if sodium hydroxide is added, the amount of diamine used in neutralizing the acid by-products decreases. Further, since the sodium hydroxide neutralization takes place in the diamine phase rather than in the polycondensation zone, there is now a more compact polymer, resulting in shorter polymer chains. Such a result would account for the drop in peak intrinsic viscosity value for the 1:1 acceptor level from that found for no sodium hydroxide.

This would also explain why the peak value for the 2:1 acceptor level is lower than that for the zero acceptor level. It remains to be explained, however, why the peak value for the 2:1 level is higher than that for the 1:1 level and also why that for the 4:1 level is still higher (higher even than the zero level).

A reason for the upturn in peak viscosity values may be that the increased available diamine so increases the propensity of the diamine to diffuse that a larger polycondensation zone is formed. The formation of such a zone would also make for a less compact polymer network and in turn bring about longer chains and higher peak intrinsic viscosity values.

### References

1. P. W. Morgan, *Advan. Chem. Ser.*, **34**, 191 (1962).
2. P. W. Morgan and S. L. Kwolek, *J. Polymer Sci.*, **40**, 299 (1959).
3. P. W. Morgan and S. L. Kwolek, *J. Polymer Sci.*, **62**, 33 (1962).
4. M. S. Akutin and L. A. Rodivilova, *J. Polymer Sci.*, **52**, 287 (1961).
5. L. Alexandru and L. Dascalu, *J. Polymer Sci.*, **52**, 331 (1961).
6. E. M. Hodnett and D. A. Holmer, *J. Polymer Sci.*, **58**, 1415 (1962).
7. V. M. Korshak, T. M. Frunze, V. V. Kurashev, and K. L. Serova, *Vysokomolekul. Soedin.*, **3**, 2 (1961).

### Résumé

L'effet de la teneur en accepteur d'acide (hydroxyde de sodium) dans la polycondensation interfaciale du nylon 610 a été étudié. On a trouvé que des teneurs en accepteur croissantes déplaçaient les courbes de viscosité intrinsèque en fonction de la concentration en chlorure de sébacoyl vers la droite. On a également trouvé que les valeurs des maxima de viscosité intrinsèque décroissaient tout d'abord et croissaient ensuite avec l'augmentation des teneurs en accepteur d'acide. Les résultats expérimentaux sont liés à un équilibre entre les réactifs et au caractère de la zone de polycondensation.

### Zusammenfassung

Der Einfluss der Säureacceptor-Menge (Natriumhydroxyd) bei der Grenzflächenpolykondensation von 610-Nylon wurde untersucht. Es zeigte sich, dass zunehmende Acceptor-Mengen die Viskositätszahl-Sebacoylchlorid-Konzentrationskurven nach rechts verschieben. Ebenso wurde gefunden, dass die Spitzenwerte der Viskositätszahl mit steigenden Säureacceptor-Mengen zuerst ab- und dann zunahmen. Die experimentellen Ergebnisse zeigten, dass das Gleichgewicht der Reaktanten und die Natur der polykondensationszone miteinander in Beziehung stehen.

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