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Effect of Amines in Anionic Polymerization of Caprolactam

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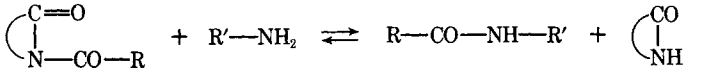
Synopsis

The effect of various amines in anionic polymerization of caprolactam has been investigated. Experiments have been carried out below the polymer melting point. The results are discussed and explained on the basis of imide–amine interaction.

The first patents concerning the cocatalyzed anionic polymerization of caprolactam were issued some ten years ago to Monsanto.[1] In one of them,[2] the influence of various amines on the polymerization is briefly discussed; it is indicated that amines act as regulators of the molecular weight distribution.

Wichterle and Gregor[3] and Sebenda et al.[4,5] have discussed this influence in greater detail by assuming a reaction mechanism involving imide groups with destruction of the cocatalyst [eq. (1)].



(1)

We have tried to examine the influence of several amines on the anionic polymerization of caprolactam (CL) carried out in the solid state (heterogeneous polymerization) with phenyl isocyanate (PICN) and acetyl caprolactam as cocatalyst and sodium hydride as catalyst. Relatively low temperatures were chosen in order to make evident possible differences which may become negligible at higher temperatures due to very high reaction rates.

Preliminary runs were carried out with NaH–PICN in equimolar amounts with the addition of cyclohexylamine at 130°C for 3 hr. This time is sufficient in order to achieve equilibrium between polymer and monomer at that temperature. The concentration of NaH as well as the concentration of amine varied in the range from 2.5×10^{-3} to 2.0×10^{-2} mol/mol CL. The results were examined by means of statistical analysis. The strong inhibitory effect of cyclohexylamine is shown well in Figure 1, where the numbers for each curve refer to the amount of the

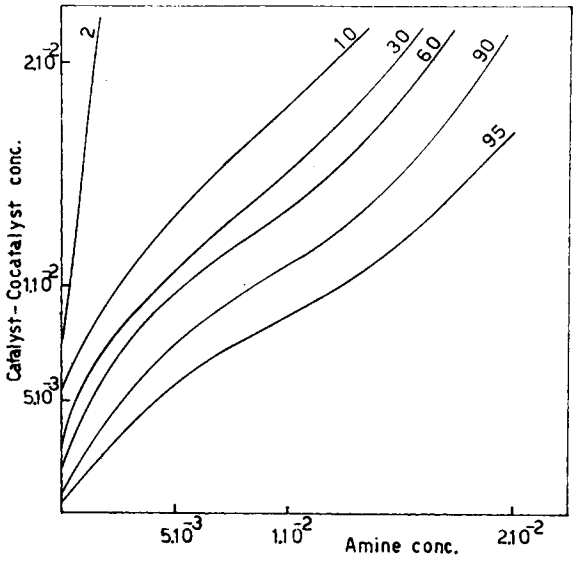


Fig. 1. Polymerizations of caprolactam at 130°C initiated by PICN and NaH in equimolar amounts in the presence of cyclohexylamine. Each line corresponds to the content of residual monomer (methanol-soluble matter), indicated by the figure.

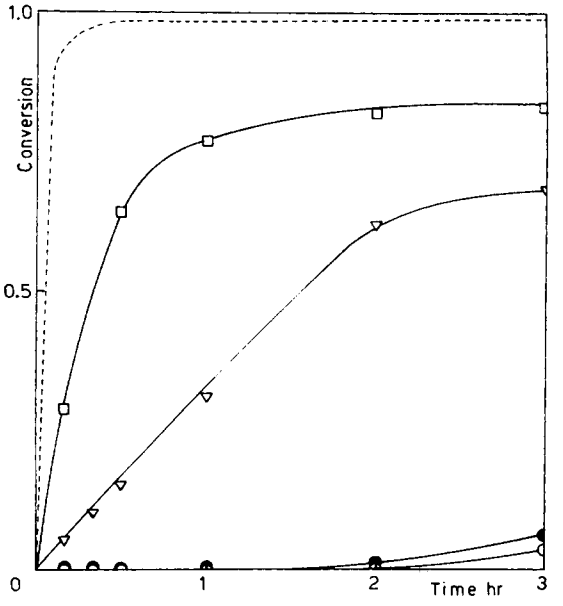


Fig. 2. Polymerization of caprolactam initiated by PICN and NaH in equimolar amounts (0.01 mol/mol CL) at 130°C in the presence of various amines (0.01 mol/mol CL): (▽) *sec*-octylamine; (□) aniline; (●) cyclohexylamine; (○) benzylamine; (- -) polymerization in the absence of amine.

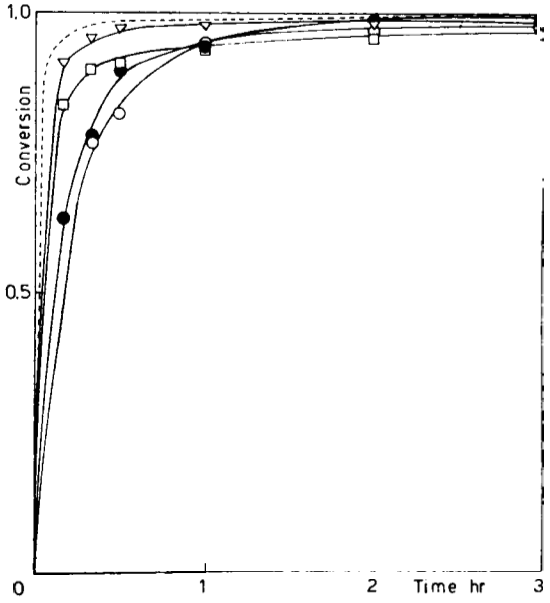


Fig. 3. Polymerization of caprolactam initiated by PICN and NaH in equimolecular amounts (0.01 mol/mol CL) at 175°C in the presence of various amines (0.01 mol/mol CL): (▽) *sec*-octylamine; (□) aniline (●) cyclohexylamine; (○) benzylamine; (- -) polymerization in the absence of amine.

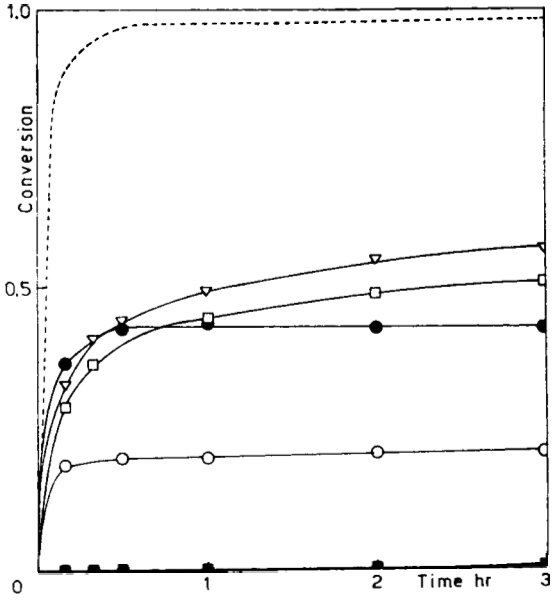


Fig. 4. Polymerization of caprolactam initiated by acetylcaprolactam and NaH in equimolar amounts (0.01 mol/mol CL) at 130°C in the presence of various amines (0.01 mol/mol CL): (▽) *sec*-octylamine; (□) aniline; (●) cyclohexylamine; (○) benzylamine; (■) *n*-heptylamine; (- -) polymerization in the absence of amine.

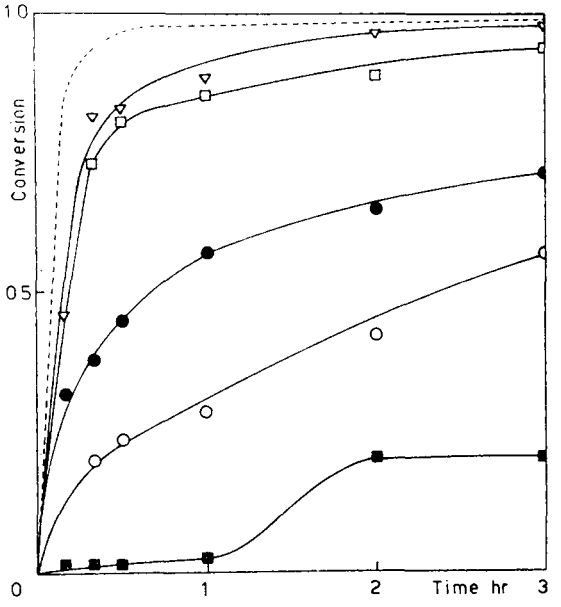
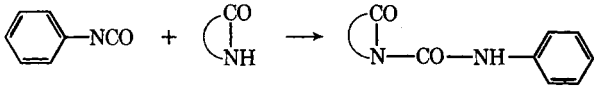


Fig. 5. Polymerization of caprolactam initiated by acetylcaprolactam and NaH in equimolar amounts (0.01 mol/mol CL) at 175°C in the presence of various amines (0.01 mol/mol CL): (▽) *sec*-octylamine; (□) aniline; (●) cyclohexylamine; (○) benzylamine; (■) *n*-heptylamine; (- -) polymerization in the absence of amine.

monomer not converted at the end of reaction. It can be noted that such an inhibition increases with amine concentration and when such a concentration becomes of the same magnitude as that of the catalyst, no more than 10% conversion can be obtained. It is worthy of note that PICN is a powerful cocatalyst and the reaction rates obtained are higher than those with the more classical acyl lactams at moderate polymerization temperatures. We then tried to examine the effect of various primary amines on reaction (1) by considering the effect of their basicity (pK_b) on the equilibrium. The results are shown in Figures 2–5.

In general, a more pronounced inhibitory effect is noted with the initiator acetyl caprolactam, while PICN-catalyzed runs show retardation, except at the lower temperature, where clear inhibition is evident. This can be explained by considering that PICN should react with caprolactam to give the true initiator [eq. (2)].



(2)

However, in the presence of amines it is likely that PICN will react first with the more active hydrogen atom of amines than with those of the amide groups, with formation of disubstituted urea. The latter is stable and hence inactive as cocatalyst at 130°C but decomposes at the higher tem-

perature to the reverse reaction; this was shown in unpublished runs of ours on the cocatalytic activity of diethyl and diphenylureas at various temperatures. On the other hand, the polymerizations initiated by acetyl caprolactam start with a good rate but are followed by a plateau in the conversion–time plot, i.e., the equilibrium of reaction (1) is rapidly shifted to the right. As far as the examined amines are concerned (benzylamine, cyclohexylamine, aniline, *sec*-octylamine, heptylamine), it seems that steric hindrance has a most pronounced effect, in comparison to the basicity of the amine.

The strongly basic *n*-heptylamine ($pK_b = 3.35$) is the most effective inhibitor; on the other hand, the more bulky branched *sec*-octylamine, which should have very similar basicity, has a sensibly weaker effect, it being inferior even to the one of the much more acidic aniline. Cyclohexylamine ($pK_b = 3.36$) should have the same inhibitory effect as heptylamine; however its sensibly lesser efficiency is to be attributed to steric hindrance.

Moreover, benzylamine ($pK_b = 4.63$) is a more powerful inhibitor than cyclohexylamine, in spite of its lower basicity; this could be attributed to higher steric hindrance of the cyclohexylamine molecule compared to benzylamine.

Cyclohexylamine and aniline ($pK_b = 9.3$) clearly show the influence of the basicity, not being very different in steric hindrance.

The results are similar for both temperatures.

Experimental

The details of polymerizations and the determination of conversion are described elsewhere.[6] Relative viscosities were determined by using 1 g of methanol-extracted, dried polymer dissolved in 100 ml of 95.6% H_2SO_4. The measurements were carried out in Ostwald-Fenske viscometers at 20 ± 0.1°C.

Benzylamine, cyclohexylamine, and aniline were R.P. products (C. Erba, Milan) and were rectified prior to use.

The *sec*-octylamine was a B.D.H. product and was used as received. *n*-Heptylamine was synthetized by Hoffman degradation of the amide of octanoic acid (bp, 49°C/20 mm Hg; n_{20}^{D}, 1.4248).

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