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OLIGOMERIZATION OF CAPROLACTAM
WITH AMINOLYSIS REACTIONS

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Using aminolysis of caprolactam by diethylenetriamine, it is shown that the rate constant of this reaction is almost independent of the basicity of the aliphatic amine, but it decreases significantly in going from a melt of a mixture of amine and caprolactam with an almost equimolar ratio of components to dilute solutions of amine in caprolactam or polycaproamide melt. The Monte Carlo calculations suggest that no less than a three-fold molar excess of caprolactam is required for exhaustive conversion of the triamine into oligoamide triamine, and the products formed will be a set of molecules of different structure with a relatively narrow molecular-weight distribution.

Synthesis of oligoamidoamines from caprolactam (CL) and di- and polyamines is of definite practical interest, primarily for obtaining the oligomers used as components of block copolymers for different applications [1-4]. In many cases, it is convenient to use the reaction of aminolysis instead of hydrolytic polymerization of CL in the presence of a large amount of di- and polyamines. In this respect, the question arises concerning the dependence of the kinetic parameters of the reaction on the structure of the amine, on its basicity in particular.

For aliphatic amines, the pKa in water at 293-298 K are within the limits of 7-11 [5]. As a consequence, to answer this question, it is necessary to investigate the reaction of aminolysis of CL with diethylenetriamine (DETA) containing two primary and one secondary amino group in the molecule whose difference in basicity, judging by the pKa of 1,2-ethane- and 1,4-butanediamines [5], is no less than three orders of magnitude.

For this reason, as a function of whether kinetic reactions I-VI which take place in CL melt are different, aminolysis of CL by DETA can, or on the contrary, cannot be described by a simple kinetic equation.

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\begin{align*}
\text{HN} & \text{CH}_2\text{CH}_2\text{NH}_2 + \text{HN} \text{(CH}_2)\text{NH}_2 \text{CH}_2\text{CH}_2\text{NH} \text{(CH}_2)\text{NH}_2 \text{CH}_2\text{CH}_2\text{NH}_2 \\
\leftrightarrow & \text{CH}_2\text{CH}_2\text{NCH} \text{(CH}_2\text{NH}_2 \text{CH}_2\text{CH}_2\text{NH}}\text{H} \text{H}_2 \text{CH}_2\text{CH}_2\text{NCH} \text{(CH}_2\text{NH}_2 \text{CH}_2\text{CH}_2\text{NH}}\text{H}
\end{align*}
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