Kinetic laws governing the synthesis of adamantane-containing polyamido acids and polyimides

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INTRODUCTION
Investigations of the kinetics of formation of polyamido acids and model amido acids have been carried out chiefly by IR (refs. 1–9), UV spectrometric (refs. 10 and 11), and calorimetric methods (refs. 12–14).

A comparison of the results of kinetic investigations on the synthesis of a number of aromatic polyamido acids, carried out by methods of IR spectroscopy and calorimetry, showed that the results of the obtained kinetic parameters of the given process differ considerably. Here, the obtained data on the rate constants of polyacylation with dianhydrides of aromatic amines produced calorimetrically have values roughly an order of magnitude higher (refs. 1 and 14). Therefore, to investigate the kinetics of formation of adamantane-containing polyamido acids, we used the calorimetric method.

1. INVESTIGATION OF KINETICS OF SYNTHESIS OF ADAMANTANE-CONTAINING POLYAMIDO ACIDS BY CALORIMETRIC METHOD

A feature of the synthesis of polyamido acids by the reaction of aromatic tetracarboxylic acid dianhydrides and high-basicity diamines (including those containing adamantane) is the occurrence of a secondary reaction of salt formation between the formed carboxylic groups of o-carboxyamido groups and the high-basicity amino groups of the initial diamine (ref. 15). As a result of breakdown of the equimolecular ratio of the initial reactants, it is not possible to produce a polymer of high molecular weight.

In order to study the directions of change in the influence of the secondary reactions on the process of polymer formation, we used kinetic methods to examine the reaction of 3,4,3',4'-tetracarboxydiphenyl oxide (DPO) dianhydride with asymmetrical adamantane-containing diamines: amino-3-(4'-aminophenyl) adamantane (I), 1-aminomethyl-3-(4'-aminophenyl) adamantane (II), 1-aminoethyl-3-(4'-aminophenyl) adamantane (III), 1-aminoethyl-3-aminomethyl adamantane (IV), and 4,4'-diaminodiphenyl oxide (V), for comparison. Also, we used adamantane monoamines as model compounds: 1-(4'-aminophenyl) adamantane (VI), 1-aminoethyl adamantane (VII), and model fragments of polyamido acids (PAAs) of the following structure:
Table 1 gives values of the effective rate constants of PAA formation $k_{\text{eff}}$ for the diamines investigated by the present authors at different temperatures.

On the whole, in the presented series of initial diamines, the values of $k_{\text{eff}}$ differ little. The lowest values of $k_{\text{eff}}$ are observed for diamine I (for example, when the process is carried out in $m$-cresol at 303 K, $k_{\text{eff}} = 0.063 \text{l/mol s}$), for which one of the amino groups is directly linked with the nucleus of adamantane, which creates steric hindrances for its attack by reactants.

Table 2 gives values of the enthalpy of the reaction of DPO dianhydride with asymmetrical adamantane-containing diamines and the pKa of the initial diamines.

An analysis of the data presented in Table 2 makes it possible to note that, when the reaction is carried out in dimethylformamide (DMF), in the case of using diamine IV as the initial compound, a considerably greater heat generation is observed ($-\Delta H = 204.7 \text{kJ/mol}$), 38–44% greater by comparison with the other diamines presented in the given series (with the exception of diamine I). This

### Table 1: Values of effective rate constants of reactions of DPO dianhydride with asymmetrical adamantane-containing diamines

<table>
<thead>
<tr>
<th>Adamantane-containing diamine</th>
<th>$k_{\text{eff}} \times 10^3$, l/mol s*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298 K</td>
</tr>
<tr>
<td>I</td>
<td>50</td>
</tr>
<tr>
<td>II</td>
<td>60</td>
</tr>
<tr>
<td>III</td>
<td>57</td>
</tr>
<tr>
<td>IV</td>
<td>73</td>
</tr>
<tr>
<td>V†</td>
<td>48/86</td>
</tr>
</tbody>
</table>

* Numerators — in $m$-cresol; denominators — in DMF. † For comparison

### Table 2: Values of enthalpy of reaction of DPO anhydride with asymmetrical adamantane-containing diamines and pKa of initial diamines

<table>
<thead>
<tr>
<th>No.</th>
<th>Adamantane-containing diamine</th>
<th>$-\Delta H$, kJ/mol</th>
<th>pKa_1,†</th>
<th>pKa_2,†</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td><img src="image" alt="Diamine I" /></td>
<td>98.4/114.3</td>
<td>15.92</td>
<td>9.17</td>
</tr>
<tr>
<td>II</td>
<td><img src="image" alt="Diamine II" /></td>
<td>116.8/165.4</td>
<td>16.16</td>
<td>9.59</td>
</tr>
<tr>
<td>III</td>
<td><img src="image" alt="Diamine III" /></td>
<td>109.3/159.1</td>
<td>16.73</td>
<td>9.97</td>
</tr>
<tr>
<td>IV</td>
<td><img src="image" alt="Diamine IV" /></td>
<td>126.9/204.7</td>
<td>17.47</td>
<td>16.29</td>
</tr>
<tr>
<td>V†</td>
<td><img src="image" alt="Diamine V" /></td>
<td>141.9/126.6</td>
<td>9.97</td>
<td>8.64</td>
</tr>
</tbody>
</table>

* At 303 K; numerators — in $m$-cresol; denominators — in DMF. † In nitromethane at 25°C. † For comparison, pKa (ref. 18)
is due in all likelihood to the fact that diamine IV contains two highly basic amino groups in its structure (pKa1 = 17.47; pKa2 = 16.29, Table 2) and, along with the process of polymer formation, the secondary reaction of salt formation occurs with the participation of a second highly basic amino group.

When the given process is carried out in m-cresol, the value of −ΔH in the reaction with the participation of diamine IV does not exceed 14% in comparison with the other adamantane-containing diamines presented, which is most likely due to the higher value of pKa1 for diamine IV.

To establish the contribution of salt formation to the overall enthalpy of the process of PAA formation, an investigation was made of a series of model reactions: high-basicity and low-basicity amino groups simultaneously in their structure, salt formation can occur only by the high-basicity amino group.

Comparison of the values of the effective rate constants of the formation of PAA based on DPO dianhydride and diamine V in DMF at 293 K, obtained by the present authors by the calorimetric method (0.086 l/mol s), in comparison with the IR spectrometric method (0.88 l/mol s (ref. 1)), indicates that the values obtained by IR spectrometry are an order of magnitude higher. In our view, such overestimated results may be due to the fact that, when the IR spectrometric method was used, the change in the concentration of reactants was monitored from the change in the optical density of the absorption band of the carbonyl group of the anhydride ring in the 1860 cm⁻¹ region. However, taking into account that the mechanism of PAA formation is fairly complex (ref. 1) and includes a whole series of different transformations, including the formation of a complex with charge transfer between tetracarboxylic acid dianhydride and diamine, opening of the anhydride ring, detachment of the proton from the amino group, its migration and addition to a carboxy anion, etc., it is evident that the stage connected with the breakdown of the anhydride ring, which is monitored by IR spectrometry, is not the limiting stage.

Thus, the calorimetric method is more informative in the given case, since it takes into account the heat generation of the entire process as a whole, and not of an individual part of it.

It must also be pointed out, on the basis of the results of investigating the kinetics of formation of adamantane-containing PAA by the calorimetric method, that, to produce PAA with a high molecular weight, it is necessary to use asymmetrical adamantane-containing diamines in which the two amino groups differ considerably from each other in basicity as the initial compounds.
2. KINETIC INVESTIGATION OF SINGLE-STAGE SYNTHESIS OF ADAMANTANE-CONTAINING POLYIMIDES BY MEANS OF ELECTROMETRY

At present there is, perhaps, only one method for investigating the kinetics of synthesis of polyimides, making it possible under certain conditions to determine simultaneously both the rate constant of PAA formation, \( k_1 \), and the rate constant of polycyclodehydration of PAA to polyimide, \( k_2 \). This is the method of electrometric titration with a Fisher reagent of the forming reaction water under dynamic conditions (ref. 19), which can be used to study the single-stage high-temperature synthesis of polyimides. On the basis of the conducted theoretical analysis of the given process, the authors derived an equation making it possible under certain conditions to obtain linear anamorphoses of the kinetic curves in \( x/ a_0(a_0 - x) - t \) coordinates, where \( x \) is the concentration of the water formed (mol L\(^{-1} \)), \( a_0 \) is the initial concentration of initial components (mol L\(^{-1} \)), and \( t \) is the duration of the reaction (s).

The tangent of the angle cut off by these lines from the ordinate axis is equal to the ratio \( k_1/k_2 \). The rate constant of PAA formation \( (l \text{ mol}^{-1} \text{ s}^{-1}) \) and \( k_2 \) is the rate constant of the polycyclodehydration of PAA \( (s^{-1}) \), in accordance with the transformed kinetic equation of the following form:

\[
\frac{x}{a_0(a_0 - x)} = k_1 t - \frac{k_1}{k_2} \left[ 1 + \frac{1}{a_0 k_1} \left( a_0 k_2 t + 1 \right) \right]
\]

The use of the given method for investigating the kinetics of the single-stage high-temperature synthesis of adamantane-containing polyimides showed (ref. 20) that the reactivity of high-basicity adamantane-containing diamines is two orders of magnitude higher than that of diamines of the adamantane series of asymmetrical structure made it possible under certain conditions to determine simultaneously both the rate constant of PAA formation, \( k_1 \), and the rate constant of polycyclodehydration of PAA to polyimide, \( k_2 \). This is the method of electrometric titration with a Fisher reagent of the forming reaction water under dynamic conditions (ref. 19), which can be used to study the single-stage high-temperature synthesis of polyimides. On the basis of the conducted theoretical analysis of the given process, the authors derived an equation making it possible under certain conditions to obtain linear anamorphoses of the kinetic curves in \( x/ a_0(a_0 - x) - t \) coordinates, where \( x \) is the concentration of the water formed (mol L\(^{-1} \)), \( a_0 \) is the initial concentration of initial components (mol L\(^{-1} \)), and \( t \) is the duration of the reaction (s).

The tangent of the angle cut off by these lines from the ordinate axis is equal to the ratio \( k_1/k_2 \), where \( k_1 \) is the rate constant of PAA formation \( (l \text{ mol}^{-1} \text{ s}^{-1}) \) and \( k_2 \) is the rate constant of the polycyclodehydration of PAA \( (s^{-1}) \), in accordance with the transformed kinetic equation of the following form:

\[
\frac{x}{a_0(a_0 - x)} = k_1 t - \frac{k_1}{k_2} \left[ 1 + \frac{1}{a_0 k_1} \left( a_0 k_2 t + 1 \right) \right]
\]

The use of the given method for investigating the kinetics of the single-stage high-temperature synthesis of adamantane-containing polyimides showed (ref. 20) that the reactivity of high-basicity adamantane-containing diamines is two orders of magnitude higher than that of aromatic diamines.

The use of this method to investigate the kinetics of synthesis of polyimides based on diamines of the adamantane series of asymmetrical structure made it possible, through the presence in such diamines of two amino groups differing considerably in basicity, to establish their different reactivity when the process is carried out in nitrobenzene. Besides the above asymmetrical adamantane-containing diamines I-IV, the following diamines were investigated: 1-aminoethyl-3-aminomethyl-5,7-dimethyladamantane (X) and, for comparison, 1,3-bis(aminomethyl)adamantane (XI), and also DPO dianhydride.

It was shown that, on linear anamorphoses of the kinetic curves (when the process is carried out in nitrobenzene at 200 °C) for adamantylene aromatic diamines (I-III) in the region of 50% conversion, there is a characteristic break indicating a sharp change in the rate constant of the reaction with the participation of the low-basicity aromatic amino group of adamantane-containing diamine.

An analysis of the data presented in Table 3 makes it possible to note that the diamines investigated can be placed in the following order of reduction in reactivity: XI > IV > X > III > II > I. A higher reactivity is characteristic of adamantylene aliphatic diamines XI, IV, and X, and here aminomethyleneadamantane groups are noted for greater reactivity, which is consistent both with their higher basicity and with the reduced dissociation energy of the NH bond, \( D_e \) (ref. 21). Here, as pointed out in ref. 21, a similar (linear) change is observed between \( \ln k_1 \) and pKa of the initial diamines, and also the values of \( D_e \) of the NH bonds of these diamines, with the exception of diamine I, for which one of the amino groups is directly bound with the nucleus of the adamantane. For this diamine, \( D_e \) has the lowest value in the selected series of adamantane-containing diamines (503.8 kJ/mol, Table 3), which seems to be due to the considerable sterical hindrances created by the bulky adamantane fragment for attack on this amino group by the reactant.

A comparison of the rate constants of cyclodehydration of PAA, \( k_2 \), with the values of pKa of adamantane-containing diamines and \( D_e \) of the NH bonds makes it possible to note that there is a certain increase in the reactivity of the diamines of the adamantane series with increase in their pKa and with reduction in \( D_e \), but these

<table>
<thead>
<tr>
<th>Diamine</th>
<th>( k_1 \times 10^2 ) l mol s</th>
<th>( k_{11} \times 10^2 ) l mol s</th>
<th>( k_1 \times 10^3 ) s(^{-1} )</th>
<th>pKaI†</th>
<th>pKa†</th>
<th>( D_e ) kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>8.1</td>
<td>0.82</td>
<td>5.94</td>
<td>15.92</td>
<td>9.17</td>
<td>503.8</td>
</tr>
<tr>
<td>II</td>
<td>29.6</td>
<td>4.86</td>
<td>7.42</td>
<td>16.16</td>
<td>9.59</td>
<td>516.1</td>
</tr>
<tr>
<td>III</td>
<td>36.5</td>
<td>4.92</td>
<td>9.90</td>
<td>16.73</td>
<td>9.97</td>
<td>510.0</td>
</tr>
<tr>
<td>IV</td>
<td>46.2</td>
<td>—</td>
<td>9.84</td>
<td>17.47</td>
<td>16.29</td>
<td>505.6</td>
</tr>
<tr>
<td>X</td>
<td>41.3</td>
<td>—</td>
<td>9.80</td>
<td>17.07</td>
<td>15.91</td>
<td>506.0</td>
</tr>
<tr>
<td>XI</td>
<td>47.3</td>
<td>—</td>
<td>11.00</td>
<td>17.88</td>
<td>16.50</td>
<td>508.0</td>
</tr>
</tbody>
</table>

* \( k_1 \) is rate constant of PAA formation with participation of low-basicity amino group of diamine. † In nitromethane at 25°C.
† \( D_e \) values were calculated in accordance with procedure described in ref. 20.
dependences are not linear in nature. This is possibly connected with the contribution of processes of formation of the optimum conformations of amido acid units of PAA for dehydration.

CONCLUSIONS

Thus, kinetic investigations of the synthesis of adamantane-containing polyamido acids and polyimides have shown that the use of asymmetrical diamines of the adamantane series as the initial compounds makes it possible to control the processes of polymer formation through a reduction in the influence of the secondary reactions (salt formation) and change in the reactivity of the functional groups.

REFERENCES