The results of a study, by thermal mass spectrometric analysis and NMR spectroscopy, of the polycondensation of H-complexes are presented from which it is possible to propose a mechanism for the reaction. It is shown that conversion of the H-complexes into polyimides takes place through the formation of intermediate zwitterions with an amino acid bond after initial separation of methanol, following which elimination of water commences in one stage to form an imide ring. The role of the ortho position of the functional groups in the acid ester during the formation of the hydrogen bond is discussed.

**Keywords:** H-complex, polyimide, dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid.

In previous communications we reported the study, by various methods (IR spectroscopy [1], dielectric [2], and gas chromatography [3]), of the kinetics of the polycondensation of H-complexes of acid methyl diesters of 3,3',4,4'-benzophenonetetracarboxylic acid (BTCE) with various diamines: 4,4'-diaminodiphenylmethane (DADPM), 2,6-diaminopyridine (DAP), and 1,6-hexamethylene diamine (HMDA), reactions which lead to foam polyimides [4]. Polycondensation was effected by heat treatment of H-complexes which were previously prepared by mixing BTCE with diamines in alcoholic solvents and isolated in the solid form by evaporation of the solvent at 20°C [5]. On the basis of the kinetic and thermodynamic characteristics of the polycondensation of the H-complexes it was concluded that polycondensation via the intermediate formation of either amino acid (scheme 1, reaction 1) or aminoester (scheme 1, reaction 2) units is almost equally probable. The possibility of the formation of the imide ring in one stage by simultaneous elimination of methanol and water (scheme 1, reaction 3) should also be considered [1]:

**Scheme 1**

```latex
\begin{align*}
1. \text{-CH}_3\text{OH} & \rightarrow \text{CO}-\text{NHR} \\
\text{COOH} & \rightarrow \text{CO} \\
\text{COOCH}_3 & \rightarrow \text{COOCH}_3 \\
2. \text{-H}_2\text{O} & \rightarrow \text{COOH} \\
\text{COOH} & \rightarrow \text{COOH} \\
\text{H}_2\text{NR} & \rightarrow \text{H}_2\text{NR} \\
3. \text{-H}_2\text{O}, \text{-CH}_3\text{OH} & \rightarrow \text{CO} \\
\text{CO} & \rightarrow \text{CO} \\
\text{NHR} & \rightarrow \text{NHR} \\
\text{NR} & \rightarrow \text{NR}
\end{align*}
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In the present communication, we report the results of a study of the polycondensation of H-complexes by mass spectrometric thermal analysis and NMR spectroscopy which has made it possible to be more precise concerning the mechanism and to select unequivocally the route for the conversion of the H-complexes to polyimide.

### EXPERIMENTAL

To prepare the H-complexes, we used 4,4'-benzophenonetetracarboxylic dianhydride (mp 225-226°C), DADPM (mp 90-92°C), DAP (mp 120-122°C), and HMDA (mp 42°C). The mp of the model compounds is given in Table 1.

The H-complexes were prepared by the method of [5]. They were heat-treated at 80°C for 10 min to remove the adsorbed solvent.

Model H-complexes based on 4-aminodiphenyl ether (ADPE) and the model compounds listed in Table 1 were prepared by mixing in solution in 1:0:1 (vol.) methanol—water in equimolar quantities and then evaporating the solvent at 20°C.

Thermal mass spectrometric analysis was carried out on an MX-1320 mass spectrometer by the method of [6], using an ionization energy of 18 eV. The rate of temperature increase was 2.5 deg/min.