Investigation of the process of polyimide formation from complexes of the diester of benzophenonetetracarboxylic acid with diamines

6.* Thermal imidization of H-complexes derived from diethyl 3,3',4,4'-benzophenonetetracarboxylate

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The kinetics of thermal imidization of the H-complexes derived from the diethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (EBZP) and various diamines have been studied. A comparison of kinetic parameters obtained for the imidization of H-complexes based on ethyl or methyl esters of this acid has disclosed the differences in the behavior of each of the two H-bonds and the contribution of each bond to the mechanism of polyimide formation from the respective H-complexes.

Key words: H-complexes; polyimide; 3,3',4,4'-benzophenonetetracarboxylic acid, diethyl ester; kinetics.

In the previous communication[1] the mechanism of the formation of polyimides on thermal cyclization of the H-complexes of aromatic dialkyl tetracarboxylates with various diamines was proposed. This mechanism, suggested as a result of the study of thermal cyclization of H-complexes based on the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (MBZP), involves the formation and transformation of a cyclic H-complex having two hydrogen bonds, namely, a bond between the carboxyl OH group and the N atom of the amino group, and another bond between the ester carbonyl and the H atom of the amino group. This communication describes the kinetics of thermal cyclization of the H-complexes formed by MBZP or by the respective diethyl ester (EBZP) with various diamines. The comparison of the respective kinetic parameters should reveal the difference in the behavior of the two H-bonds, and such information could make it possible to estimate the contribution of each of the two bonds to the mechanism of polyimide formation.

Experimental

H-complexes of EBZP with 1,6-hexamethylene diamine (EBZP · HMDA), 4,4'-diaminodiphenylmethane (EBZP · DADPM), 2,6-diaminopyridine (EBZP · DAP), and with a mixture of these three diamines in the molar ratio of 2 : 5 : 3 (EBZP · HMDA · DADPM · DAP) have been chosen as the objects of study. The properties of the starting compounds were reported in the previous communication.[1]

The EBZP was synthesized by refluxing the anhydride of the parent acid (BZP-anhydride) with 96 % ethanol. The H-complexes were prepared by adding the above diamines to a solution of EBZP in EtOH at 20°C.

The study of thermal imidization of the H-complexes was accomplished by the methods used before: IR spectroscopy (IRS)[2] for EBZP · HMDA, EBZP · DADPM, and EBZP · DAP, gas chromatography (GC)[3] for EBZP · DADPM, and the dielectric method[4] for EBZP · HMDA · DADPM · DAP. Kinetics of the thermal imidization of the H-complexes have been studied under the conditions of isothermic heating at 125°C, 150°C, 180°C, and 220°C.

The activation energies were calculated by the Arrhenius equation.

Results and Discussion

Kinetic and thermodynamic parameters calculated from kinetic curves are given in Table 1. It should be noted that the results obtained independently by two methods (IRS and GC) are in a satisfactory agreement. For the complexes studied in this work, as well as for those derived from MBZP,[2,3] a very slight dependence of all the calculated values on the basicity of the starting diamines was observed (see Table 1).

Comparison of kinetic and thermodynamic parameters obtained for the thermal cyclization of the EBZP-derived H-complexes with those obtained for the respective H-complexes based on MBZP (see refs.[2,3]) makes it possible to formulate the following inequalities for rate

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* For part 5, see ref.[1]

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Table 1. Kinetic and thermodynamic characteristics of thermal imidization of the EBZP-derived H-complexes with various diamines

Composition of the H-complex (Investigation method)	Diamine pK_a	Temperature of imidization (°C)	k, s^{-1}	E_a, kJ mol^{-1}	k_0, s^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, kJ (mol deg)$^{-1}$	$\Delta G^{\neq}$, kJ mol^{-1}
EBZP · HMDA (IRS)	10.0	125	$3.510 \cdot 10^{-6}$	92	$1.22 \cdot 10^{7}$	88	-483	280.7
		150	$9.890 \cdot 10^{-5}$					292.6
		180	$4.340 \cdot 10^{-4}$					306.8
		220	$1.223 \cdot 10^{-3}$					325.8
EBZP · DADPM (IRS)	4.7	125	$1.050 \cdot 10^{-5}$	60	$1.90 \cdot 10^{3}$	56	-563	280.4
		150	$1.325 \cdot 10^{-4}$					294.5
		180	$2.735 \cdot 10^{-4}$					311.4
		220	$6.132 \cdot 10^{-4}$					339.9
		300	$4.130 \cdot 10^{-3}$					379.0
EBZP · DADPM (GC)	4.7	150	$6.50 \cdot 10^{-4}$	54	$3.83 \cdot 10^{3}$	50	-575	294.1
		180	$2.74 \cdot 10^{-3}$					311.1
		220	$5.60 \cdot 10^{-3}$					334.0
EBZP · DAP (IRS)	7.0	125	$3.227 \cdot 10^{-5}$	66	$1.11 \cdot 10^{4}$	63	-544	279.1
		150	$1.100 \cdot 10^{-4}$					292.7
		180	$1.840 \cdot 10^{-4}$					309.0
		220	$0.830 \cdot 10^{-3}$					330.8

constants (k), activation energies (E_a), activation enthalpies ($\Delta H^{\neq}$), and activation entropies ($\Delta S^{\neq}$):

$$k_{Me} > k_{Et}, \quad (1)$$

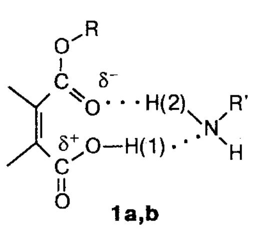
$$E_{aMe} > E_{aEt}, \quad (2)$$

$$\Delta H^{\neq}_{Me} > \Delta H^{\neq}_{Et}, \quad (3)$$

$$\Delta S^{\neq}_{Me} < \Delta S^{\neq}_{Et}, \quad (4)$$

where the subscripts Me and Et indicate that the value in question corresponds to the H-complex based on MBZP and EBZP, respectively.

These inequalities make it possible to apprise the role of each of the two H-bonds in the cyclic H-complex (**1**).



1a,b

R = Et(**a**), Me(**b**)

Let us consider the effect of substituting the ethyl radical for methyl in the carboxylate group on the stability of both H-bonds in the H-complexes **1**. Assuming that the COOMe group exerts a weaker C-effect than the COOEt group[5] one can write the following inequalities:

$$\delta^{+}_{Me} < \delta^{+}_{Et}, \quad (5)$$

$$\delta^{-}_{Me} > \delta^{-}_{Et}, \quad (6)$$

where δ^{+} and δ^{-} are partial charges on the carboxyl carbon and on the carboxylate oxygen atoms in complexes **1 a,b**, respectively.

Hence it follows that in type **1** complexes the H-bonds involving the carboxyl group, i.e., H(1)···N, are stronger in the case of EBZP than for MBZP. On the other hand, the H-bonds involving the carboxylate group, O···H(2), would be weaker for EBZP than for MBZP. This can be expressed by the corresponding relationships:

$$E(\text{—OH} \cdots \text{N})_{Me} < E(\text{—OH} \cdots \text{N})_{Et}, \quad (7)$$

$$E(\text{=O} \cdots \text{HN})_{Me} > E(\text{=O} \cdots \text{HN})_{Et}, \quad (8)$$

where E is the energy of the respective H-bonds.

The inequalities (7) and (8) imply that the strengths of these H-bonds exert opposite effects on the reaction parameters. Thus, on the basis of experimental data one can recognize the bond which determines the rate of reaction. The inequalities (1)—(4) hold in the case when the conversion of the H-complex to the imide begins with the H-bonding of the carboxylate group,[6] O···H(2). This conclusion is in good agreement with the reaction mechanism which stipulates the nucleophilic attack of the amino group on the C atom of the carboxylate group at the beginning of the process.[1]

Earlier,[1] in the case of MBZP complexes, the value of the preexponential factor k_0 was found to be too small for a first-order reaction. This was explained by large

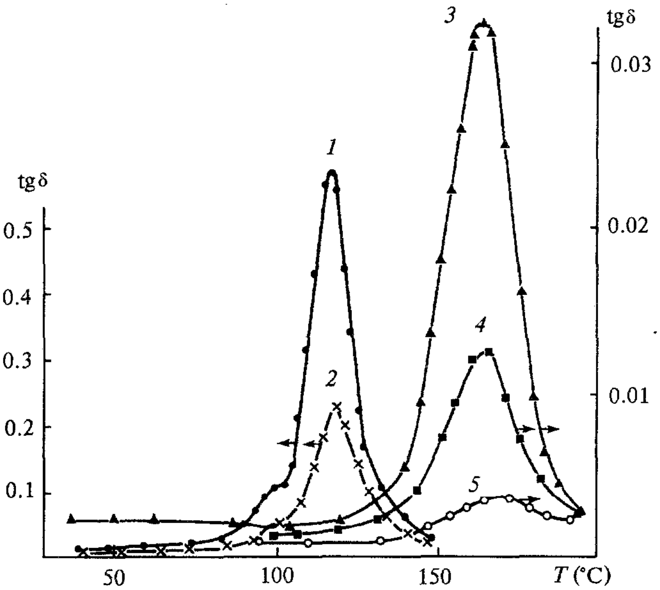
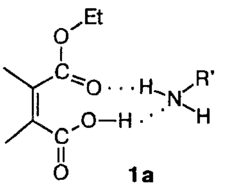


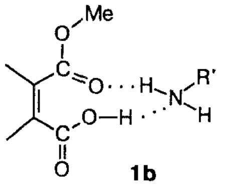
Fig. 1. The tgδ vs. temperature dependence for the H-complex EBZP · DADPM · DAP · HMDA (1 : 0.5 : 0.3 : 0.2 molar ratios): (*1,2*) the initial sample (the left scale); (*3—5*) the pre-heated (145°C) sample (the right scale). Frequencies, in kHz: 100 (*1,5*); 300 (*2*); 0.1 (*3*); 1 (*4*).

negative values of $\Delta S^{\neq}$. As Table 1 shows, the negative values of $\Delta S^{\neq}$ are even greater in the case of complexes of EBZP, and the preexponential factor is consequently even lower. This may be associated with the stereometry of the initial and activated H-complexes.

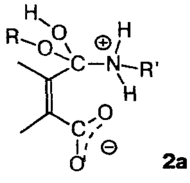
Below are shown the tentative structures of the initial H-complexes based on EBZP (**1a**) and MBZP (**1b**), as well as the possible spatial structure of the activated complex (**2a,b**), the formation of which has been postulated earlier.[1] One can see that the stereochemistry of the initial EBZP-derived H-complex **1a** can differ considerably from that of the activated complex **2a**. Obviously, these differences are substantially greater than in the case of the MBZP-derived H-complex **1b**. This is a consequence of the relations (5)—(8).



1a



1b



2a,b

R = Et(**a**), Me(**b**)

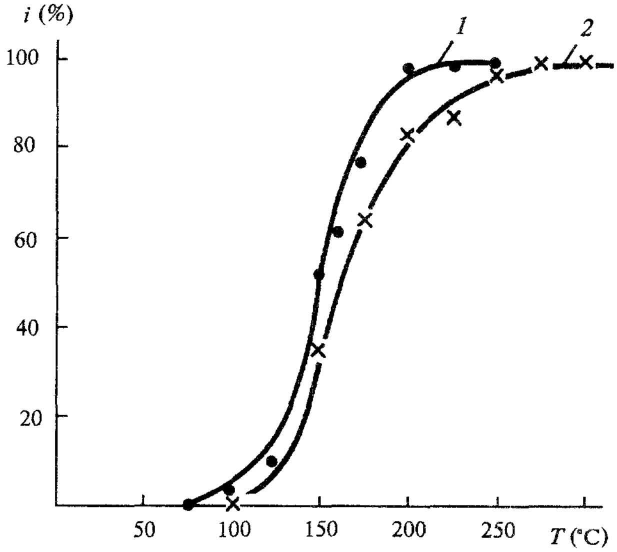


Fig. 2. Temperature dependence of the degree of imidization (*i*) for the H-complexes EBZP · HMDA · DADPM · DAP (*1*) and MBZP · HMDA · DADPM · DAP (*2*).

In practice, for example, in the synthesis of polyimide foams,[7] the H-complexes obtained using a mixture of three diamines rather than an individual diamine are preferable. Therefore, we also studied the thermal imidization of the H-complex EBZP · HMDA · DADPM · DAP using the dielectric method.[4]

Fig.1 shows the temperature dependence of the dielectric loss tangent (tgδ) for the starting EBZP · HMDA · DADPM · DAP (1:0.5:0.3:0.2) complex (curves *1,2*) and for the preliminarily heated (140°C) complex (curves *3—5*).

In the case of the starting H-complex there are two tgδ peaks, at 100°C and 118°C (curves *1,2*). By analogy with the data obtained earlier for H-complexes of MBZP with the same diamines,[4] one can assume that these peaks result from a sharp increase in the mobility in the system owing to melting of the H-complexes. This facilitates the thermal imidization of the H-complexes, the onset of which can be recognized by the appearance of two peaks close to each other (~10°C apart).[8] The process of imidization, in its turn, decreases the mobility of the kinetic units in the system. It is this fact that accounts for the descending part of the tgδ peak at 100—120°C.

In the case of H-complexes pre-heated to 140°C, the temperature dependence of tgδ has a peak at 165°C (curves *3—5*) which is caused by imidization in a system of higher viscosity than the starting sample. On the other hand, the imidization peak for the MBZP-derived H-complex[4] was observed at 150°C. The displacement of the imidization peak to higher temperatures can be explained by two interrelated factors: (i) lower mobility of the low-molecular products formed in the course of imidization and (ii) higher viscosity of the system based on EBZP. Changes in the viscosity of the system occuring upon imidization are to be considered in more detail.

It is the increase in the system viscosity, connected with the progress of imidization, that causes the above-mentioned decrease in the mobility of the kinetic units. It seems natural that the higher the degree of imidization, the higher the system viscosity. Fig.2 presents the data for the increase in the degree of imidization (*i*) of the H-complex MBZP • HMDA • DADPM • DAP on its gradual heating from ~20°C to 300°C, as described earlier.[2] These data were calculated from the absorption band of the imide ring (ν 1725 cm^{-1}) in the IR spectra. Fig. 2 indicates that the thermal cyclization of the EBZP-derived H-complex proceeds at lower temperatures then in the H-complex obtained from MBZP. This is consistent with the lower activation energy required for the transformation of the former complex to the polyimide (see inequality (2)). A lower activation energy suggests that at equal temperatures the degree of imidization of the EBZP-derived H-complex should be higher than that of the H-complex based on MBZP. This assumption is supported by the data given in Fig. 2. As a consequence, the system viscosity should be higher as well.

It is noteworthy that the values of tgδ found both for the starting and pre-heated samples of the EBZP-derived H-complex are nearly an order of magnitude lower than those obtained earlier[4] for the respective H-complex of MBZP. This can be explained by the fact that ethanol which is liberated during imidization has a lower dielectric permeability (ε_{Et} = 25.1) than methanol (ε_{Me} = 33.6).

Thus, by investigating the thermal cyclization of the EBZP H-complexes with various diamines we obtained additional information confirming that the initial transformation of H-complexes involves the rupture of the weaker H-bond between the amino group of the diamine and one of the ester carbonyls in the diester of benzophenonetetracarboxylic acid.

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