

Reactivity indices of adamantane-containing diamines in the synthesis of polyimides

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The reactivity of adamantane-containing diamines in the reactions with dianhydrides of 3,4,3',4'-tetracarboxydiphenyl oxide was studied as a function of the parameters of their electronic structures. It was found that the reactivity changes in parallel with the charges on the N atoms, the energy of homolytic cleavage of the N—H bond, and the basicity of diamines.

Key words: adamantane, diamines, polyimides, reactivity, basicity, deprotonation, electronic structure, cleavage of the N—H bond.

The reactivities of adamantane-containing diamines in the synthesis of polyimides have been studied in a number of works.^{1–3} In particular, the relationship between the basicity (pK_a) of the initial diamines and the rate constants of their reactions with dianhydrides of aromatic tetracarboxylic acids was established. In some cases, successful development of calculation procedures for studies of electronic structures of compounds allows one to extend a set of reactivity indices.

The aim of this work is to experimentally determine the kinetic parameters of the reactions of adamantane-containing diamines with dianhydride of 3,4,3',4'-tetracarboxydiphenyl oxide under conditions of the one-stage high-temperature synthesis of polyimides in solutions and to reveal the dependence of these kinetic parameters on the calculated and experimental data, which reflect the structures and electronic and energy characteristics of functional groups of the initial diamines.

Experimental

We studied the following diamines of the adamantane series: 1,3-bis(4'-aminophenyl)adamantane (1), 1,3-diaminoadamantane (2), 1,3-bis(aminomethyl)adamantane (3), 1,3-bis(aminoethyl)adamantane (4), 1-amino-3-(4'-aminophenyl)adamantane (5), 1-aminomethyl-3-(4'-aminophenyl)adamantane (6), 1-aminoethyl-3-(4'-aminophenyl)adamantane (7), and 1-aminoethyl-3-aminomethyladamantane (8), as well as dianhydride of 3,4,3',4'-tetracarboxydiphenyl oxide.

Kinetic studies of the one-stage synthesis of polyimides were carried out by electrometric titration of water that was

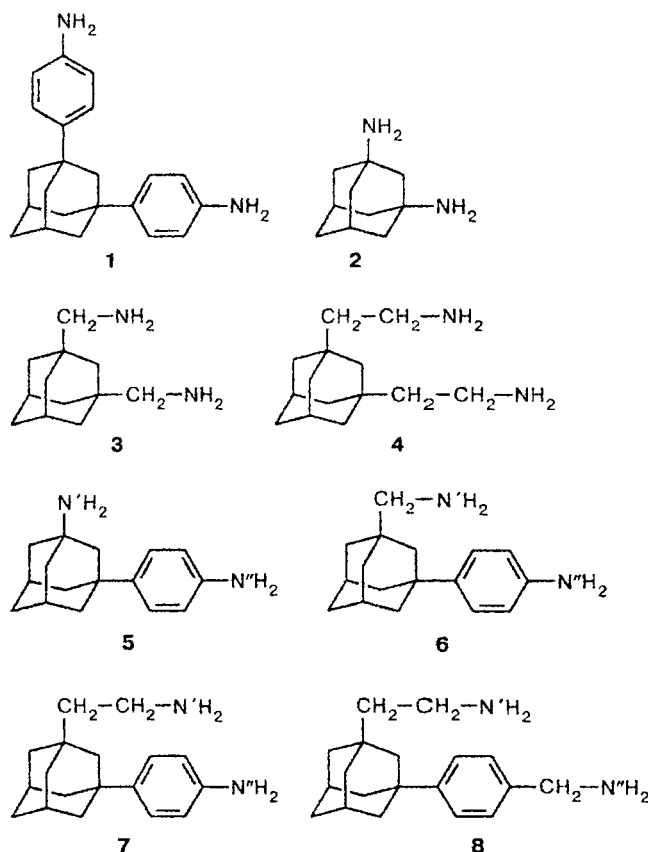


Table 1. Dependences of the reactivities of symmetrical adamantane-containing diamines during the interaction with dianhydride of tetracarboxydiphenyl oxide in the synthesis of polyimides on the charge of the nitrogen atoms (q_N), the basicities (pK_a) of the initial diamine, the energy of deprotonation (ΔE), and the energy of cleavage (D_e) of the NH bond of the initial diamines

Compound	$k_1 \cdot 10^2$ /L mol ⁻¹ s ⁻¹	$k_2 \cdot 10^3$ /s ⁻¹	$-q_N$	pK_{a1}	pK_{a2}	ΔE kJ mol ⁻¹	D_e kJ mol ⁻¹
1	0.5	**	0.325	10.28	9.70	1299.8	538.5
2	6.1	0.9	0.331	16.70	14.32	1458.9	504.4
3	41.3	7.1	0.336	16.67	15.57	1457.3	511.0
4	47.3	10.8	0.337	17.75	16.36	1467.4	508.0

* Under conditions of one-stage high-temperature synthesis in a solution of nitrobenzene at 190 °C: k_1 and k_2 are the rate constants of formation and dehydrocyclization of polyamide acid (PAA), respectively. ** The low reactivity of diamine 1 did not allow us to determine experimentally its k_2 value.

Table 2. Dependences of the reactivities of unsymmetrical adamantane-containing diamines during the interaction with dianhydride of tetracarboxydiphenyl oxide in the synthesis of polyimides on the charge on the nitrogen atoms (q_N), the basicities (pK_a), the energy of deprotonation (ΔE), and the energy of cleavage (D_e) of the NH bonds of the initial diamines

Compound	$k_1 \cdot 10^2$ L mol ⁻¹ s ⁻¹	$k_1^H \cdot 10^2$ L mol ⁻¹ s ⁻¹	$k_2 \cdot 10^3$ /s ⁻¹	$-q_N' / -q_N''$	pK_{a1}	pK_{a2}	$\Delta E' / \Delta E''$ kJ mol ⁻¹	D_e' / D_e'' kJ mol ⁻¹
5	8.1	0.82	5.94	0.330/0.325	15.92	9.17	1455.8/1301.3	503.8/533.0
6	29.6	4.86	7.42	0.336/0.325	16.16	9.59	1461.3/1298.4	516.1/542.1
7	36.5	4.92	9.90	0.337/0.325	16.73	9.97	1470.5/1298.8	510.0/539.4
8	46.2	—	9.84	0.337/0.336	17.47	16.29	1467.5/1460.0	505.6/511.8

* Under conditions of one-stage high-temperature synthesis in a solution of nitrobenzene at 190 °C: k_1 is the rate constant of formation of PAA with respect to the more reactive amino group, k_1^H is the rate constant of formation of PAA with respect to the less reactive amino group, and k_2 is the rate constant of dehydrocyclization with respect to the more reactive amino group.

liberated using K. Fischer's reagent according to a known procedure.^{2,4} The concentrations of the initial reagents were 0.005 mol L⁻¹. Nitrobenzene was used as the solvent. The temperature was 170–200 °C.

The values of pK_a of diamines were determined by potentiometric titration in nitromethane with perchloric acid.⁵

The energies of dissociation of the NH bonds (homolytic cleavage, D_e) were calculated based on the experimental frequencies of stretching and deformation vibrations of NH bonds in the IR spectra of adamantane-containing diamines. The calculations were carried out using the program package reported previously⁶ with the use of variational methods for solving the inverse problem.

The electronic structures of diamines and their anions were calculated with full optimization of geometry by the AM1 method.⁷ The geometry corresponding to the global minimum of the total energy was considered as the optimum structure. The energy of proton abstraction from the nitrogen atom was calculated as the difference between the total energy of the neutral diamine molecule and the sum of energies of the isolated anion and proton.

Results and Discussion

The experimental and calculated parameters, which characterize the reactivities of diamines and their elec-

tronic structures, are given in Tables 1 and 2. The rate constants (k_1 and k_2) characterize the process of formation of polyamide acids (PAA) and cyclodehydration of PAA, respectively.

In the case of symmetrical diamines of the adamantane series (1–4, see Table 1), the reactivity changes in parallel with the charge on the nitrogen atom ($-q_N$). Thus, in going from compound 1 to 4, the value of $-q_N$ increases (in magnitude) from -0.325 to -0.337 . In this case, the values of k_1 and k_2 increase from $0.5 \cdot 10^{-2}$ to $47.3 \cdot 10^{-2}$ L mol⁻¹ s⁻¹ and from $0.9 \cdot 10^{-3}$ to $10.8 \cdot 10^{-3}$ s⁻¹, respectively. The basicity (pK_a) also increases in this series. However, this regularity breaks down for diamine 2. For this diamine (pK_{a1} is 16.70), the values of k_1 and k_2 are relatively small ($6.1 \cdot 10^{-2}$ L mol⁻¹ s⁻¹ and $0.9 \cdot 10^{-3}$ s⁻¹, respectively; see Table 1). Apparently, this is associated with steric hindrances that occur in the case of the attack of the amino group directly bonded to the bulky nucleus of adamantane. The energies of homolytic and heterolytic cleavage (D_e and ΔE) of the N—H bond also change in the series 1 → 4. The value of ΔE changes in parallel with the reactivity, while the value of D_e depends inversely on the reactivity. For diamine

2. the values of D_c and ΔE , like pK_{a1} , do not fit in this series due to steric factors.

We succeeded in determining experimentally the values of k_1 and k_2 for highly reactive aminoalkyl groups and the values of k_1^H (formation of PAA) for poorly reactive aminophenyl groups using adamantane-containing unsymmetrical diamines (5–8, see Table 2) as examples. The values of k_1 are approximately an order of magnitude larger than k_1^H due to the larger strength of the $N''-H$ bonds compared to that of the $N'-H$ bonds. This is also evidenced by the higher energy of cleavage (D_c'') compared to D_c' (see Table 2).

In unsymmetrical diamines 6–8 (except for diamine 5, for which steric hindrances in the reaction can occur because the NH_2 amino groups are directly bonded to the bulky nucleus of the radical) the values of pK_a , the charges on the nitrogen atoms $-q_N$, and the reactivities (k_1 and k_2) increase as the value of D_c decreases. The calculated energies of deprotonation (ΔE), unlike the energies of homolytic cleavage, vary inversely with their reactivities for all compounds 1–8. Apparently, this fact indicates that the deprotonation of amino groups is not a rate-determining step.

Therefore, based on the results obtained it can be concluded that the charges on N atoms, the basicity, and the energy of homolytic cleavage of the $N-H$ bond are the most suitable characteristics for the reactivity

indices of diamines of the adamantane series (in the approximation of isolated reagents).

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