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COMPLEXES OF AMIC ACIDS WITH POLAR APROTIC SOLVENTS

VIII. Nonisothermal kinetics of solid-phase cyclodehydration of polyamic acids

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The nonisothermal kinetics of solid-phase cyclodehydration of poly(4,4'-oxydiphenylene) pyromellitamic acid has been investigated with the aid of mass-spectrometric thermal analysis. It was established that depending on the method of preparation of the samples, the kinetics of cyclization vary from the polychromatic (film) to the monochromatic (fiber) kinetics. The possibility of the catalysis of the process as a result of the formation of complexes between the polymer and imidazole and its substituents is shown.

The process of thermal solid-phase cyclodehydration of polyamic acids has been studied in a great number os papers describing investigations carried out by various methods [1]. The present paper reports the results of the study of this process with the aid of mass-spectroscopic thermal analysis (MTA). It appears that the method has not been applied to this purpose previously. The method consists in the analysis of gaseous products evolved as a result of heating of the sample at a constant rate. The advantage of this method is its high informativeness because it allows easy qualitative and quantitative analysis of the products and the investigation of the kinetics of the reaction based on the dynamics of their evolution.

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Experimental

The samples investigated were films of poly(4,4'-oxydiphenylene) pyromellitamic acid (PAA PM) cast from different solvents, fibres obtained by wet molding and films which are solid PAA PM complexes with organic bases.

Films from the solutions of PAA PM synthesized by a standard method [2] were obtained by casting and drying in air for 1 day at 40°. The film thickness varied from 20 to 100 μm. The films were stored at 0° in order to retard the uncontrolled imidization process.

The PAA PM fibers were obtained from a solution in DMAA by introducing it into a precipitation bath with isopropyl alcohol at a total draw ratio of 6-19. The diameter of the monofilament was 40-60 μm.

The products evolved in the cyclodehydration of PAA PM were analyzed with an M Kh 1320 mass-spectrometer according to a published method [3]. The experiments were carried out at a heating rate of 2 deg/min. The IR spectra were recorded with a Zeiss UR-20 spectrometer. The degree of imidization of the samples was determined by the method described in Ref. [4] according to the equation

$$i = \frac{(D_{1780}/D_{1020})_T}{(D_{1780}/D_{1020})_o}$$

(subscript "T" is the changing optical density and subscript "O" is the optical density of the polymer heated to 300°).

Results and discussion

The MTA of PAA PM films showed (Fig. 1) that during cyclodehydration the solvent is evolved together with water because the film is a solvocomplex which determines to a considerable extent the kinetics of the transformation of PAA PM into polyimide. The temperature of the peak maximum of water evolution, $T_{\max}$ depends on the solvent from which the film was prepared (Fig. 2). Figure 2 shows that not only the chemical nature of the solvent but also the supermolecular organization of the sample affect the kinetics of the process because by varying the film thickness alone it is possible to obtain different values of $T_{\max}$. It should be noted that the amount of the solvent in

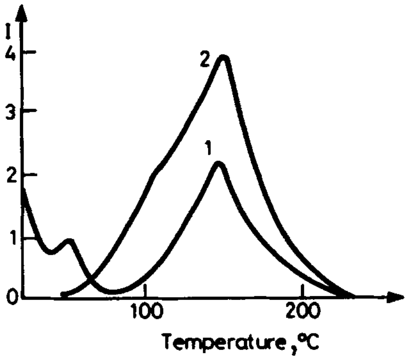

Fig. 1 MTA curves of the solid-phase cyclodehydration of PAA PM film 1) water, 2) DMF

solvates is the same in all cases (2 mol/mol of the polymer) and it is isolated virtually simultaneously with water. Hence, it is not possible to relate the observed effect to the plasticizing action of the solvent.

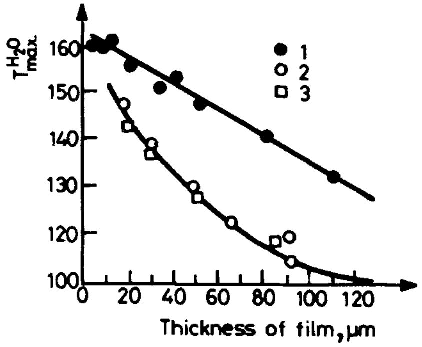

Fig. 2 T_{max} vs. solvent nature and thickness of the PAA PM film obtained from 1) DMF, 2) DMAA and 3) N-methylpirrolidone

The kinetics of solid-phase cyclodehydration of PAA PM is usually investigated under isothermal conditions [1], and the process is described by a first-order equation. The characteristic feature of the reaction is its kinetic termination at an incomplete conversion of PAA PM into polyimide. In order that the process could continue further, it is necessary to increase the temperature or to change the physical state of the system [5]. This phenomenon characteristic of many solid-phase reactions was called polychromatism [6] and is caused by the kinetic inequivalence of assemblies differing in the conformational state of polymer chains, their environment, the steric arrangement of functional groups, the molecular mobility, etc. Under the conditions of non-isothermal heating, the kinetic termination of the reaction is not observed in the explicit form. However, it is impossible to describe the reaction from beginning to end in terms of the first-order kinetic equation with constant parameters, although in all cases the initial part of the kinetic curve (at least up to T_{max})may be described in terms of this equation (Fig. 3). Taking into account this feature of the kinetics, it is possible to evaluate the "monochromatic" fraction of the sample the cyclization of which occurs according to the first-order kinetics with constant values of the activation energy and the pre-exponential factor (with the assumption that up to T_{max} only the units from the "monochromatic" range are cyclized).

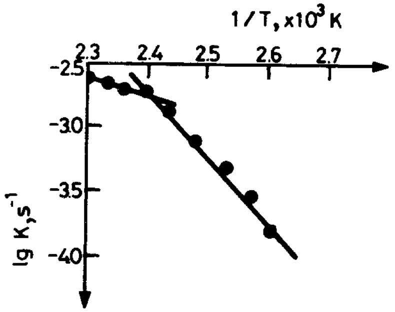

Fig. 3 Dependence of log k on $1/T$ of the cyclization of PAA PM film synthesized in DMF

It has been shown [7] that at points where the reaction rate is maximum (T_{max}) and is one-half of this value ($T_{0.5\ max}$), the concentration ratio of the unreacted units for the first-order reaction is constant and equal to 2.06. Carrying out simple mathematical transformations it is possible to evaluate the kinetic homogeneity of the sample, β, equal to the ratio of the fraction of units characterized by the monochromatic kinetics to the total number of units undergoing cyclization.

$$\beta = \frac{S_1 + 1.94 S_2}{S_o}$$

where S_1, is the area under the curve of water evolution in the range from the beginning to $T_{0.5\ max}$, S_2 is that in the range from $T_{0.5\ max}$ to T_{max} and S_o is that under the entire curve of water evolution from beginning to end.

Table 1 Kinetic and temperature parameters of the solid-phase cyclization of PAA PM samples

Sample	Solvent	Solvent quality	Draw ratio	T^o max	β	$h_{1/2}$	E^* kJ/mol	ΔS^*, J/mol K
Film	DMF	Good, $\alpha = 1.6^{**}$	148	0.8	56	63	–159	
"	DMAA	Good, $\alpha = 1.2^{**}$	139	0.7	34	80	–113	
"	DMAA (15%) + aceto-nitrile (85%)	Bad, near the beginning of precipitation		106	0.5	20	130	+38
			6	120	0.8	33	105	–46
Fiber			11	126	0.95	30	121	+4
			19	160	1.0	14	147	+34

*Calculated at a part up to T_{max}

**The values of the swelling coefficient α are taken from Ref. [8].

It can be seen from Table 1 that the value of β strongly depends on the technology of sample preparation. Since their chemical structure is the same, important differences in the kinetics of their cyclization should be associated with their different supermolecular organization. In other words, the kinetic homogeneity is closely related to the structural homogeneity of the samples, which determines to a considerable extent the operating characteristics of both PAA PM and polyimides based on them.

The solid-phase cyclization of polyamic acid samples differs also in the temperature parameters of the reaction which include T_{max} and the temperature range of the process characterized by the half-width of the peak of water evolution $h_{1/2}$ (Table 1). It should be noted that the cyclization of PAA fibers is characterized by lower values of $h_{1/2}$ than those for films. It is evident that the value of the temperature range of the reaction may be related to the degree of cooperativity of the processes. Since the kinetics of solid-phase cyclization of PAA PM is determined to a considerable extent by structural rearrangements occurring during the transition of carboxyamic groups (CAG) to the imide ring, the simultaneity of transition of different CAG to the imide ring depends on the similiarity of their initial conformations. The spectrum of the CAG states in the fibre formed by extended macromolecules should be narrower than in the film, which is expressed as a decrease in the $h_{1/2}$ value. Hence, the temperature range of the reaction characterizes the structural order of carboxyamic groups. It is noteworthy that the structural order of CAG alone is an indispensable but insufficient condition for the existence of the long-range order in the entire sample. However, in the case of such oriented systems as fibers, these phenomena should be interrelated.

The processing of the results of nonisothermal kinetic studies on solid-phase cyclodehydration of PAA in accordance with the theory of absolute reaction rates made it possible to determine definite correlations between the supermolecular organization of the samples and the kinetic parameters of the reaction (e.g., between the entropy of activation of the process, ΔS^*, and the fibre draw ratio λ (Table 1). By definition, the activation entropy is the difference between the entropy of the activated complex and that of the initial state CAG: $\Delta S^* = S_a - S_i$. Since the stage of structural rearrangements is the limiting stage of solid-phase cyclization of PAA, the value of ΔS^* is also mainly determined by the conformational factors. The conformation of the activated complex should be sufficiently close to that of a rigid imide ring, which is virtually independent of the conformation of the initial state of CAG. Hence, the number of possible states of the activated complex is much smaller than for the initial CAG, and the range of changes in the entropy of the activated complex is much narrower than for the initial state of CAG. Hence, it may be considered that the activation entropy is (to a certain approximation) the function of the initial state of the sample alone, $\Delta S^* = S_a - S_i \approx \text{const} - S_i$, and on the basis of the value of ΔS^* it is possible to estimate the relative order of carboxyamic groups in the sample.

Consequently, it was shown that the directed study of nonisothermal kinetics of solid-phase cyclodehydration of PAA may provide interesting information about the characteristics of the supermolecular organization of polymer samples. The supermolecular organization of PAA samples may be widely varied by changing the system of hydrogen bonds formed by the molecules of polyamic acid and the solvent. These directed changes are possible as a result of the addition to PAA solutions of organic compounds competing with amide solvents and forming a new system of hydrogen bonds.

It was shown that most organic compounds having only one center of interaction with the polymer, being added to the solution of PAA PM are not retained in the film and are removed from the sample in the process of drying. For the compound added to the solution to be retained in the solid film, it should usually have two centres or interaction with the polymer. These centres may be proton donor and proton acceptor groups and aromatic rings. For example, monofunctional aliphatic compounds (such as acids, anhydrides, chloroanhydrides, esters, alcohols, ketones, nitriles, etc.) are not retained in the film and are removed during drying. However, their aromatic analogues as well as bifunctional compounds, e.g. imidazole, form stable complexes with PAA PM which are dissociated only during the cyclization of the prepolymer (Fig. 4).

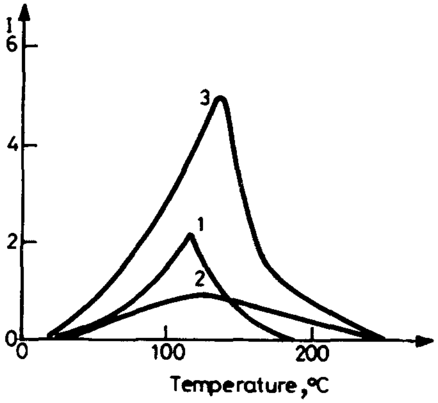

Fig. 4 MTA curves of solid-phase cyclodehydration of the film obtained from the complex of PAA PM with imidazole: 1) water, 2) DMF, 3) imidazole

Among the complexing additives, imidazole is of interest because being added to the PAA solution in a quantity of 2 mole per mole of the polymer it displaces the solvent from the complex almost completely and catalyzes the solid-phase cyclization of PAA PM reducing T_{max} to 118° as compared to 140-150° for a film without additives. It is evident that since it has two active centres (acid hydrogen at atom 1 and basic atom 3), imidazole forms its own stable system of H-bonds with CAG, which determines the characteristics of prepolymer cyclization.

Benzimidazole is a more active catalyst than imidazole. It also forms a complex with PAA PM which is dissociated only during cyclization (Fig. 5). It is the formation of a stable complex that determines the main features of the process in the case of benzimidazole addition since, as is shown below, the highest efficiency of the catalysis is attained at the CAG to benzimidazole ratio close to 1:1.

Quantity of benzimidazole

mole/mole of PAA PM	0	0.5	1.0	1.5	2.0	2.5
T^0 max	148	117	108	100	101	100
ΔS^* J/mol.K	-160	+21	+50	+151	+126	+84

The cyclization of a film containing 2 moles of benzimidazole per mole of the polymer occurs in a narrow temperature range ($h_{1/2}$ = 18°) and is characterized by high values of activation parameters (E_a = 160 kJ/mol, ΔS^* = +126 J/mol.K).

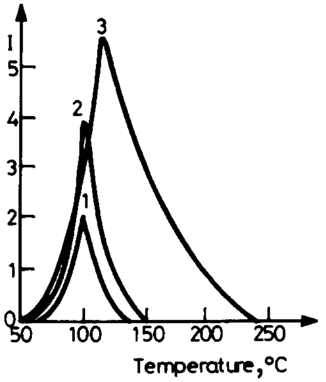

Fig. 5 MTA curves for the solid-phase cyclodehydration of a film obtained from the complex of PAA PM with benzimidazole: 1) water, 2) DMF, 3) benzimidazole

The high value of activation entropy indicates that the complex of carboxyamic groups with benzimidazole exhibits high initial order. The reason for this order may be explained from the standpoint of the established relationships of complexation. Benzimidazole contains three centres capable of bonding CAG : an acid hydrogen, a basic nitrogen and an aromatic ring. Assuming that the bond to CAG is formed on all three centres and taking into account the fact that the π - π complex of aromatic rings exhibits the mutual orienting action, it may be expected that the CAG complex with benzimidazole is a rigid system having few degrees of freedom, in which benzimidazole plays the role of the matrix rigidly fixing the conformation of CAG. The decrease in T_{max} to 100° indicates that the conformation of CAG determined by the structure of the complex is sufficiently favourable for ring closure. As a result, the reaction proceeds virtually without a kinetic stop (Fig. 6).

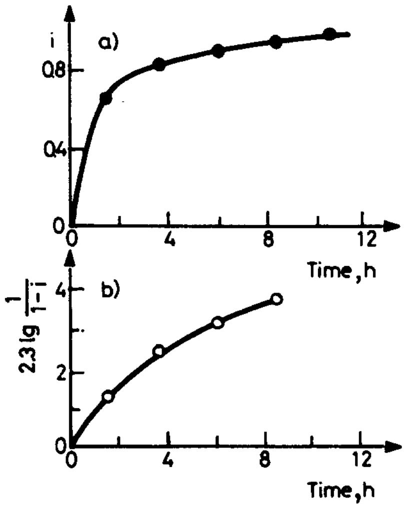

Fig. 6 Dependence of the degree of cyclization i(a) and 2.3 lg (1/(1-i)) (b) *vs.* reaction time under isothermal conditions ($T = 100°C$) obtained by IR spectroscopy for the PAA film with the addition of benzimidazole in an amount of 2 mol/mol of PAA

In spite of the increase in the activation energy of the process, the cyclization of the complex with benzimidazole proceeds more rapidly than in its absence. This is due to the decrease in the free activation energy of the process caused by the entropy factor $T\ \Delta S^*$. In other words, the catalysis of the solid-phase cyclization of PAA PM with benzimidazole is of the entropy nature and in the essence of its driving factors approaches the enzymatic catalysis.

The decrease in the temperature of cyclization of the polymer complex with benzimidazole leads to a considerable decrease in the role of the reaction of intramolecular degradation of PAA PM molecules competing with cyclization. This decrease is reflected in the absence of the so-called, "mechanical hole" (decrease in mechanical strength) in the process of cyclization of the prepolymer. The results obtained for the complex of PAA PM with benzimidazole are in general repeated for complexes with quinoline and other similar compounds.

Hence, the comparative investigation of non-isothermal kinetics of solid-phase cyclodehydration of PAA PM carried out with the aid of MTA broadened the concepts on the main features of solid-phase cyclodehydration of these prepolymers and made possible an attempt to elucidate the catalysis mechanism of this process.

References

1 M. I. Bessonov, M. M. Koton, V. V. Kudriavtsev and L. A. Laius, Polyimidiclass termostoikikh polymerov, Leningrad, 1983.
2 V. E. Smirnova, L. A. Laius, M. I. Bassonov, S. V. Boushin, T. I. Garmonova, M. M. Koton, V. S. Skazka and L. M. Shcherbakova, Vysokomolek. Soed., 17A, (10) (1975) 2210.
3 L. A. Shibaev, Yu. N. Sazanov, N. G. Stepanov, T. M. Boulina, T. I. Zhukova and M. M. Koton, Vysokomolek. Soed., 24A (12) (1982) 2543.
4 M. I. Tsapovetsky, L. A. Laius and M. M. Koton, Doklady AN SSSR, 240 (1978) 132.
5 I. E. Kardash, D. Yu. Likhachev, N. V. Nikitin, A. Ya. Ardashnikov, N. V. Kozlova and A. N. Pravednikov, Vysokomolek. Soed., 27A (8) (1985) 1747.
6 N. M. Emanuel and A. L. Buchachenko, Khimicheskaya physica stareniya i stabilizatsii polymerov, Moscow, 1982.
7 R. A. Khmelnitsky, I. M. Loukashenko and E. S. Brodsky, Pyroliticheskaya mass-spectrometriya vysokomoleculiarnikh soedinenii, Moscow, 1980.
8 M. M. Koton, O. V. Kallistov, V. V. Kudriavtsev, V. P. Sklizkova and I. G. Silinskaya, Vysokomolek. Soed., 21A (3) (1979) 532.

Zusammenfassung — Mittels massenspektrometrischer Thermoanalyse wurde die nichtisotherme Kinetik der Cyclodehydratation von Poly(4,4'-Oxydiphenylen)pyromellithsäure im festen Zustand untersucht. Es wurde festgestellt, daß die Cyclisationskinetik in Abhängigkeit vom Herstellungsverfahren der Proben von polychromatisch (Film) bis monochromatisch (Fiber) variiert. Die Möglichkeit der Katalyse des Vorganges infolge von Komplexbildung zwischen Polymer und Imidazol und seiner Substituenten wird gezeigt.