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The Physical Chemistry of the Intramolecular Cyclodehydration Reactions of Prepolymers

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The experimental data on the thermodynamics of the intramolecular cyclodehydration reactions of prepolymers in the solid phase are examined and treated systematically. The changes in the thermodynamic functions of the above processes have been analysed in detail over a wide temperature range. The temperature ranges corresponding to the formation of polyheteroarylenes which are "defect-free" to the maximum extent have been estimated.
The bibliography includes 65 references.

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I. INTRODUCTION

Among the numerous thermostable polymers, the heterocyclochain polymers containing different heterocyclic fragments in the main macromolecular chain are of special importance.

The principal methods of synthesising such polymers involve the polycondensation reactions of di- or tetracarboxylic acids and their derivatives with polyfunctional amines. Polymer macromolecules can then be formed both in one and in several stages.
The diphenyl or dimethyl esters of the corresponding acids and polyamides or their derivatives are usually employed as the initial compounds in polycondensation in the melt; as a result, a heterocyclochain polymer (a polyheteroarylene) is formed in one stage. When the synthesis is carried out in solution, polyamines and free carboxylic acids are as a rule used to obtain polyheteroarylenes in one stage and the solvent is normally polyphosphoric acid.

In the two-stage method of synthesis of polyheteroarylenes, intermediate products, the so-called prepolymers, are obtained in the first stage by the polycondensation of amines or their derivatives with the di-anhydrides (halides) of tetra- or di-carboxylic acids in an amide solvent. The prepolymers are converted in the second stage (thermal cyclisation at 400–650 K at a reduced pressure) into the final product—the heterocyclochain polymers. This polycondensation method is superior to the first two mentioned above. The majority of polyheteroarylenes are insoluble and infusible polymers, because they have a fairly rigid structure; however, in two-stage polycondensation articles can be made from the prepolymer and their heat treatment can impart to them the properties of the final polymer.

This is the explanation of the increasing interest in the thermal cyclodehydration reactions of prepolymers, demonstrated by the large number of publications both in the Soviet Union and abroad. This applies primarily to the study of the kinetics of the solid-phase cyclisation reactions of polyamidoacids.[1-11] The relevant data have been published[12-16] for reactions involving the synthesis of polybenzoxazoles via the intramolecular cyclodehydration of poly(*o*-hydroxyamides). The cyclisation reactions of polyhydrazides in the solid phase have been investigated.[17-22] The quantitative kinetic results and the mechanism of the formation of polybenzimidazoles and polybenzoylenebenzimidazoles have been described by Dawans and Marvel, Izyneer, and Korshak and co-workers[23-29] and by Colson et al, Teleshov et al., Laius et al., and Korshak et al.,[30-33] respectively. In the list quoted above we did not include studies whose results have been discussed in the monographs by Adrova et al.,[34] and Korshak and Vinogradova[35] and also studies devoted to general questions of the synthesis of polyheteroarylenes which have been described in detail in other reviews.[36-39]

In the study of the kinetics of the cyclisation of prepolymers, the vast majority of investigators have used infrared (IR) spectroscopy which makes it possible to follow the process from the change in the intensities of the characteristic absorption bands. Different versions of the same method have been used also to determine the degrees of cyclisation of the final polymers. Information about the IR spectra of various cyclic and heterocyclic molecules can be found in Bellamy's monograph.[40] In the case of polyimides one may employ the book of Adrova et al.,[34] while the paper of Rusanov et al.[41] deals with poly-1,3,4-oxadiazoles; the IR spectra of polybenzoxales have been described by Korshak et al.[42] The IR spectra of other polyheteroarylenes have been described in the original papers dealing with their synthesis.[34,36-39]

Systematic treatment of the available experimental literature data permits the conclusion that the cyclodehydration reactions of prepolymers are intramolecular and in the general case are described by a first-order kinetic equation. They have a number of general kinetic characteristics: (1) the effective rate constants for the cyclisation reactions of prepolymers diminish when the latter are converted into the final polyheteroarylenes and the degree of cyclisation–time isotherms show clearly the instant when the process comes to a stop;[43] (2) with increase of the degree of cyclisation, the activation energies for the above processes increase significantly;[44] (3) with increase of temperature, the limiting degree of cyclisation of the polyheteroarylene also increases.

A number of factors, from which it is possible to interpret the above features of the intramolecular cyclodehydration reactions of prepolymers in the solid phase, have been described in the literature. We shall only note that the majority of investigators attribute the increase of the

activation energy and the decrease of the rate constants for the cyclodehydration process to the increasing rigidity of the polymer chains in this process or, in other words, to the decrease of the number of groups in the polymer unit which are capable of hindered rotation. Here the idea has been put forward that, for kinetic reasons, the reaction involving the synthesis of polyheteroarylenes proceeds at an appreciable rate only in the region of the highly elastic state of the polymer.[25-29]

At the same time, one should note the complete absence of literature data for the thermodynamics of the cyclisation reactions of prepolymers in the solid phase. The authors of this review applied for the first time the classical calorimetric methods to the analysis of these reactions. All this made it possible to determine the enthalpies, entropies, Gibbs free energies, and equilibrium constants for the thermal cyclisation reactions of prepolymers. From our point of view, the results obtained are of undoubted theoretical and applied interest, because they make it possible to predict the average degree of polycondensation and the number-average molecular weight of the polyheteroarylene formed. We therefore believe it essential to survey and treat systematically the experimental data obtained previously for the thermodynamics of the intramolecular cyclodehydration reactions of a number of prepolymers.

II. THERMODYNAMICS OF THE INTRAMOLECULAR CYCLODEHYDRATION REACTIONS OF PREPOLYMERS

This Section deals with the results obtained in the study of the thermodynamics of the synthesis of a series of polyheteroarylenes via the intramolecular cyclodehydration of the corresponding prepolymers.

The general approach to the solution of the problem was as follows. A study was made of the heat capacity C_p^0 of the prepolymers and the corresponding polyheteroarylenes in the temperature range 60–650 K. For this purpose, use was made of the adiabatic calorimeters described in detail by Lebedev and Lityagov.[45] The accuracy of the heat capacities of the polymers obtained was to within 0.2–0.3% in the temperature range 60–300 K, to within 0.7–1.0% in the range 300–500 K, and 1.5% at higher temperatures. Extrapolation of the experimental curves for the heat capacities of the prepolymers from 60 to 0 K was carried out in terms of the two-parameter Tarasov equation:[46,47]

$$C_p^0(1,3) = K\left\{D_1\left(\frac{\Theta_1}{T}\right) - \left(\frac{\Theta_3}{\Theta_1}\right)\left[D_1\left(\frac{\Theta_3}{T}\right) - D_3\left(\frac{\Theta_3}{T}\right)\right]\right\}, \quad (1)$$

where Θ_1 and Θ_3 are the characteristic temperatures, D_1 and D_3 the Debye functions of the heat capacities of the one-dimensional and three-dimensional continua, and K is a constant coefficient for the given polymer.

The Kelley–Parks–Huffman extrapolation method was employed for the polyheteroarylenes:[48]

$$C_p^0 = (a + bT) \cdot C_p^0\,(\mathrm{PP}),$$

where C_p^0 is the heat capacity of the given polyheteroarylene, C_p^0 (PP) the heat capacity of the corresponding prepolymer at the same temperatures, and a and b are empirically selected constants.

The coefficients and characteristic temperatures were chosen such that the heat capacities calculated from the corresponding equation do not differ from the experimental values of C_p^0 in the range 60–80 K by more than 0.3%. The thermodynamic functions of the polymers were calculated from the equations

$$H^0(T) - H^0(0) = \int_0^T C_p^0\,\mathrm{d}T;\ S^0(T) - S^0(0) = \int_0^T C_p^0\,\mathrm{d}\ln T;$$
$$G^0(T) - H^0(0) = [H^0(T) - H^0(0)] - T\,[S^0(T) - S^0(0)]\ . \quad (2)$$

The integrals were calculated by Simpson's method[49] or with the aid of a computer. As mentioned above, the reactions leading to the synthesis of polyheteroarylenes by intramolecular cyclodehydration of the prepolymer are carried out in the solid phase and are accompanied by a considerable increase of the rigidity of the macromolecular chain. They hardly ever go to completion and the polyheteroarylene formed is a heterounit polymer containing the structural fragments of the prepolymer in its composition. This factor leads to the necessity for the determination of the degree of cyclisation of the prepolymer (the extent to which the polyheteroarylenes have a heterounit structure). The method employed for this purpose[50,51] is based on the additivity of the enthalpies of combustion of the statistical copolymers relative to the corresponding homopolymers:[52]

$$M_2'\Delta h_c^0(298,\mathrm{PHA}) = N_2\Delta H_c^0(298,\mathrm{PHA}) + (1 - N_2)\,\Delta H_c^0(298,\mathrm{PP}), \quad (3)$$

where $M_2' = N_2M_2 + (1 - N_2)M_1$ is the average molecular weight of the repeat unit of the real polyheteroarylene specimen, N_2 the mole fraction of the heterocycles in the polyheteroarylene specimen investigated, and M_1 and M_2 are the molecular weights of the prepolymer units and the polyheteroarylene respectively; ΔH_C^0 (298, PP) and ΔH_C^0 (298, PHA) are the standard enthalpies of combustion of the prepolymer and the ideal 100% polyheteroarylene at 298.15 K respectively and Δh_C^0 (298, PHA) is the standard specific enthalpy of combustion of the real polyheteroarylene specimen at 298.15 K. Eqn.(3) can be written in the following form

$$[N_2M_2 + (1 - N_2)M_1]\,\Delta h_c^0(298,\mathrm{PHA}) = N_2\Delta H_c^0(298,\mathrm{PHA}) + (1 - N_2)\,\Delta H_c^0(298,\mathrm{PP}).$$

Bearing in mind that ΔH_C^0 (298, PP) − ΔH_C^0 (298, PHA) = ΔH_r^0 (298) is the enthalpy of cyclisation of the prepolymer at 298.15 K, we obtain

$$N_2 = [\Delta H_c^0(298,\mathrm{PP}) - M_1\Delta h_c^0(298,\mathrm{PHA})]/[\Delta h_c^0(298,\mathrm{PHA})(M_2 - M_1) + \Delta H_r^0(298)]\ . \quad (4)$$

The quantity Δh_C^0 (298, PHA) was determined experimentally in an isothermal bomb calorimeter at 298.15 K under standardised combustion conditions. A V-08 calorimeter[53] was used for this purpose; twice the standard deviation of the quantities obtained did not exceed 0.1%.

The ΔH_C^0 (298, PP) were calculated from the experimental enthalpy of formation of the prepolymer in solution taking into account the enthalpies of solution of the starting materials and the polymer as well as the standard enthalpies of combustion of the monomers. Compared with the method based on the direct combustion of the prepolymer, this procedure for the determination of ΔH_C^0 (298, PP) can eliminate the influence of the possible presence of the solvent in the polymer on the enthalpy of combustion of the prepolymer being determined.

The equilibrium water vapour pressure over the prepolymer in the course of its cyclisation reaction was used to determine the enthalpy of cyclodehydration. The tensimetric version of the static method was selected.[54] The absolute values of the measured water vapour pressure in duplicate experiments differed by not more than (1–2) × 10^{-1} kPa, which led to an error in the determination of the enthalpies of cyclodehydration of the prepolymers not exceeding ±2.0 kJ mol^{-1}.

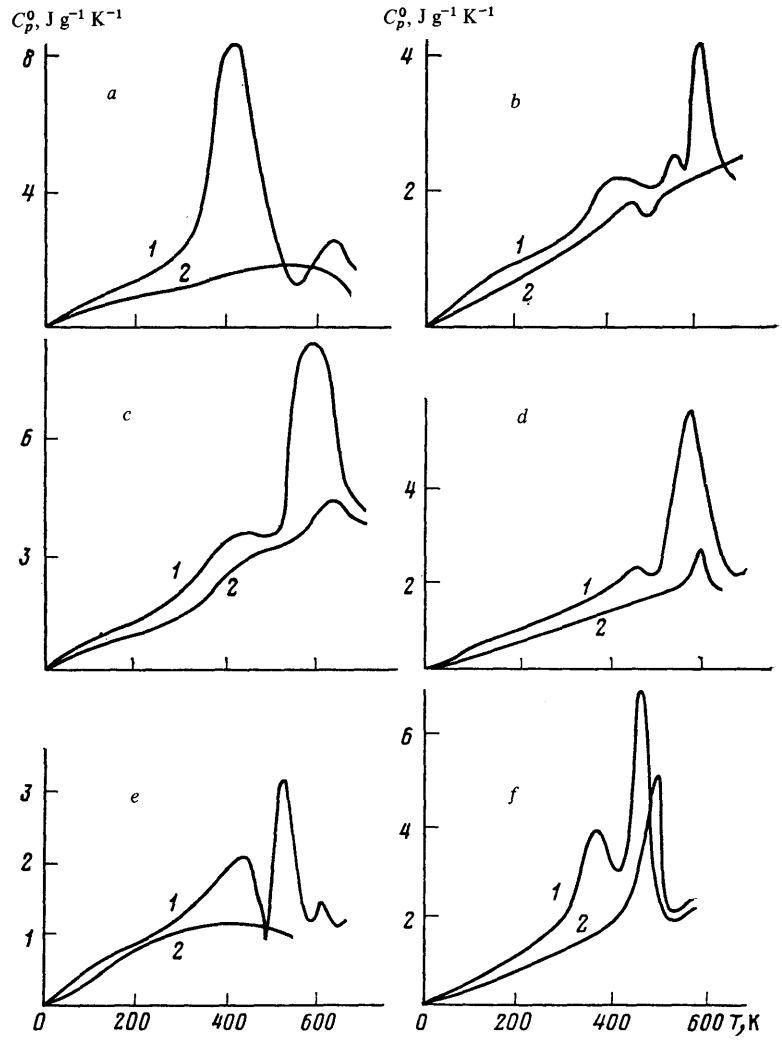


Figure 1. Temperature variation of the specific heats: *a*) of the polyamidoacid (PAA, curve *1*) and poly(*pp'*-diphenyl oxide)pyromellitimide (PI, curve *2*);[55] *b*) of poly(*o*-amido)-1,2,4-triazole (PATA, curve *1*) and polytriazoloquinazoline (PTAQ, curve *2*);[56] *c*) of poly(*o*-aminophenyl)benzimidazole (PBA, curve *1*) and polybenzimidazoloquinazoline (PBIQ, curve *2*);[62] *d*) of poly(*pp'*-diphenylphthalide)hydrazide (PH-P, curve *1*) and poly(*pp'*-diphenylphthalide)-1,3,4-oxadiazole (POD-P, curve *2*);[57] *e*) of poly(*pp'*-diphenyl oxide)hydrazide (PH-O, curve *1*) and poly(*pp'*diphenyl oxide)-1,3,4-oxadiazole (POD-O, curve *2*);[58] f) of poly(4,4'-dihydroxy-3,3'-isophthalamidodiphenylmethane) (POA, curve *1*) and poly[2,2'-(*m*-phenylene)-5,5'-dibenzoxazolymethane (PBO, curve *2*).[59]

→αβωε [6~]

In most cases the vapour phase was analysed chromatographically to determine the possible content of the corresponding solvent. For the given heterogeneous reaction, the equilibrium constant is determined by the expression $K_p = P^n(H_2O)$, where n is the number of moles of water evolved in the cyclisation of the prepolymer per repeat unit. The equation of the reaction isobar can therefore be expressed as $d \ln P^n/dT = \Delta H_p/RT^2$; when the integration is carried out in terms of the approximation that ΔH_p is independent of T over a narrow temperature range, this expression yields $n \ln P = -\Delta Hp/RT + C$, i.e. a linear relation between $\ln P$ and $1/T$. In view of this, the enthalpy of cyclodehydration $\Delta H_r^0(T)$ at a certain average temperature T in the experimental temperature range was determined from the plot of the linear relation $\ln P = f(T^{-1})$. The same quantity at $T = 298.15$ K was calculated from the Kirchhoff formula taking into account the heat capacities of the polymer and water. (It has been established[55] that the heat capacities of polyheteroarylene specimens with a high degree of cyclisation differ little from the heat capacity of the corresponding 100% polyheteroarylene).

The heat capacities and thermodynamic functions of 100% polyheteroarylenes were calculated from the thermodynamic properties of real polyheteroarylene specimens and the known degree of their heterounit structure assuming additivity. For example, the entropy of 100% polyheteroarylene at the given temperature is defined by the relations

$$M_2'S^0(\text{PHA}) = N_2S_M^0(\text{PHA}) + (1 - N_2)S^0(\text{PP}); \quad (5)$$
$$S_M^0(\text{PHA}) = \{[N_2M_2 + (1 - N_2)M_1]S^0(\text{PHA}) - (1 - N_2)'S^0(\text{PP})\}N_2^{-1},$$

where S^0(PHA) is the specific entropy of the polyheteroarylene investigated at the given temperature, S^0_m(PHA) the molar entropy of the 100% polyheteroarylene, and S^0(PP) the molar entropy of the prepolymer at this temperature.

The entropies of cyclodehydration at each temperature were calculated from the entropies of the reactants. The zero-point entropy of the polymer, which is not taken into account in the given instance, introduce a small error into the determination of the entropy of reaction, because the difference between the zero-point entropies of polyheteroarylene and the corresponding prepolymer is comparatively small.

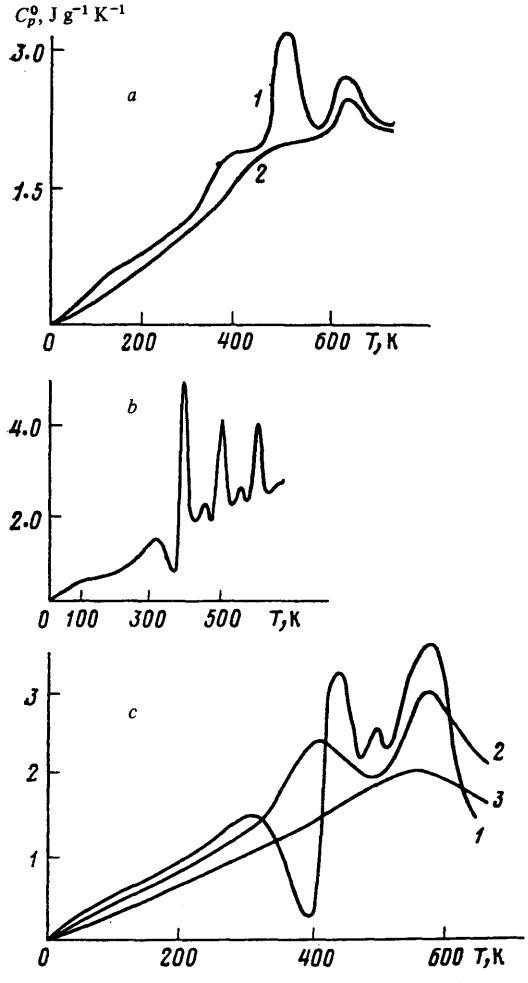


Figure 2. Temperature variation of the specific heats: *a*) of poly[*N*-terephthaloylbis(*N'*-phenyl-*o*-diphenylamine)] (PPDA, curve *1*) and poly[2,2'-(*p*-phenylene)-1,1'-diphenyl-5,5'-dibenzimidazole] (PPDBA, curve *2*);[60] *b*) of polyaminoamidoacid (PAAA);[50] *c*) of poly(*o*-carboxy) benzoylamidrazone (PCBA, curve *1*), polyamidinoimide (PADI, curve *2*), and polybenzoylene-*s*-triazole (PBTA, curve *3*).[63]

The Gibbs free energy of cyclodehydration at each temperature was calculated by the Gibbs–Helmholtz equation from the enthalpies $\Delta H^0_r(T)$ and entropies $\Delta S^0_r(T)$ obtained. The equilibrium constant was calculated from the equation of the reaction isotherm: $\Delta G^0_r(T) = -RT \ln Kp$.

III. THE HEAT CAPACITIES OF PREPOLYMERS AND POLYHETEROARYLENES

In the range 60–300 K the heat capacities of prepolymers and polyheteroarylenes increase monotonically with increase of temperature. As a consequence of the greater rigidity of the macromolecular chain of polyheteroarylenes, their heat capacities are always smaller than the corresponding C^0_p for the prepolymers at the same temperatures. At higher temperatures the curves representing the temperature variation of the heat capacities of the prepolymers investigated exhibit distinct anomalies in the form of endothermic peaks. These anomalies are associated with the intramolecular cyclodehydration reactions of the prepolymers.

In most cases a single peak is observed:[55–63] in the temperature ranges 350–550 K (PAA, Fig.1*a*), 550–650 K (PATA, Fig.1*b*), 550–650 K (PBA, Fig.1*c*), 520–600 K (PH-P, Fig.1*d*), 500–560 K (PH-O, Fig.1*e*), and 450–520 K (POA, Fig.1*f*). The curves for the temperature dependence of the heat capacities of the other prepolymers investigated have two (PPDA, Fig.2*a*) and even three endothermic peaks (PAAA, Fig.2*b*, and PCBA, Fig.2*c*). In many instances, the appearance of the endothermic peak is preceded by a jump in heat capacity due to the devitrification of the initial prepolymer in the temperature ranges 352–420 K (PATA, Fig.1*b*), 380–450 K (PBA, Fig.1*c*), ~510 K (PH-P, Fig.1*d*), 400–450 K (PH-O,Fig.1*e*), 280–350 K (PAAA, Fig.2*b*), and 350–400 K (PPDA, Fig.2*a*).

In view of this, one can assume that the intramolecular cyclodehydration reactions in general actually occur at temperatures above the glass point of the corresponding prepolymer, where there is a sharp increase of the mobility of the polymer segments. Precisely under these conditions, the kinetic energy of the polymer units can exceed the energy of the activation barrier to the reaction and there is a possibility that a transition state may be formed. The occurrence of cyclodehydration in several stages can be accounted for in the same way, i.e. by kinetic causes. For example, in the reaction involving PAAA (Fig.3*b*), two water molecules are split off from the repeat unit of the polymer in the first stage at ~410 K with formation of polyamidoimide (PAI).

It is easy to suppose that the activation energy for the reaction PAA → PAI + $2H_2O$ is appreciably lower than the activation energy for the simultaneous elimination from the polyamidoacid unit of four water molecules with formation of polybenzoylenebenzimidazole (PAAA → PBBA + $4H_2O$). It was more difficult to explain why the elimination of two water molecules from the polyamidoimide unit with its conversion into a polybenzoylenebenzimidazole unit (PAI → PBBA + $2H_2O$) and also the elimination of two water molecules from the polyamidinoamide unit with its conversion into polybenzoylene-*s*-triazole (PADI → PBTA + $2H_2O$) or of two water molecules from the poly[*N*-terephthaloylbis(*N'*-phenyl-*o*-diphenylamine)] via the reaction PPDA → PPDBA + $2H_2O$ proceeds in two stages. We suggest that these are not two different processes or two stages of an overall process but one and the same process occurring partly in one temperature range and partly in another. The point is that, when the cyclodehydration reaction of the prepolymer cannot occur, for kinetic reasons, at a realistic rate at a temperature corresponding to the vitreous state of the polymer, it begins only after the system has been heated above the devitrification temperature. However, having

begun, the process itself leads to an increase of the rigidity of the polymer chain and hence to an increase of the glass point. For this reason, whereas at the beginning of the process, when the system is heated, the devitrification of the polymer due to the increase of temperature predominates over the vitrification process due to the increased fraction of cyclic fragments in the polymer as a consequence of the cyclodehydration reaction, after the attainment of a certain degree of conversion of the prepolymer into the final heterocycle, the relative contributions of the above processes are reversed, which leads to the arrest of cyclisation. However, on further increase of temperature, whereupon the polymer again passes to the highly elastic state, the cyclodehydration process continues. From this standpoint, the difference between the thermodynamic and kinetic parameters of the individual stages of the reaction can be accounted for by the different rigidities of the polymer chains and by the different interchain interaction energies in these stages and also directly by the difference between the temperatures of both ranges where the given processes take place.

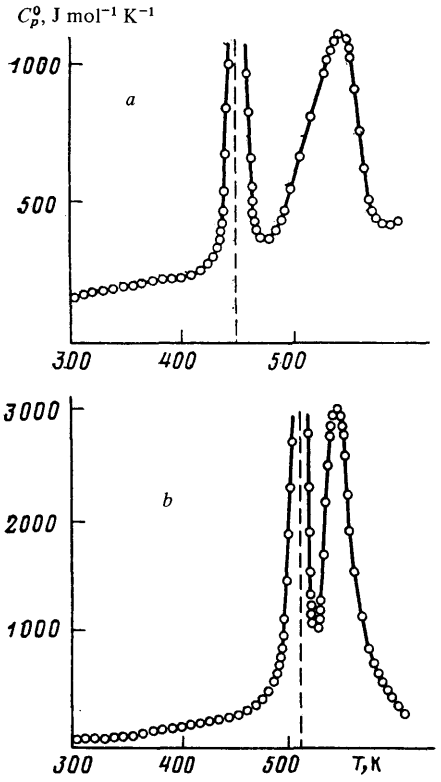
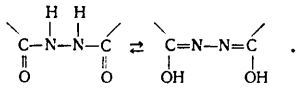
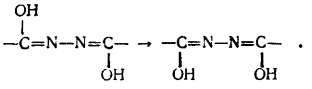


Figure 3. Temperature variation of the heat capacities of the *NN'*-dibenzoylhydrazide of diphenylphthalide-4,4'-dicarboxylic acid (*a*) and the *NN'*-dibenzoylhydrazide of (diphenyl oxide)-4,4'-dicarboxylic acid (*b*).[63]

If the rigidity of the polymer chain plays an important role in prepolymer cyclodehydration processes, their occurrence should depend significantly on the initial structure of the polymer. The authors of this review therefore carried out a comparative study of the cyclodehydration reactions of polyhydrazides and their low-molecular-weight analogues of different structure. It has been suggested[64] that the occurrence of the cyclodehydration of polyhydrazides is associated with the formation of a transition state in the system whose conformation is close to that of the *cis*-form of the hydrazide fragment:



At the same time, analysis of three-dimensional models and conformational calculations for chains of analogous structure[64] have shown that, from the standpoint of the interchain interaction and packing effects in the solid polymer, the *trans*-form of the hydrazide fragment is the most favourable. In view of this, the formation of the transition state is preceded by the rotational isomerisation of the hydrazide group:



Consequently the composition and structure of the initial polyhydrazide should have a significant influence on the tendency of the hydrazide groups towards intramolecular cyclodehydration, because the chemical nature of the fragments determines the initial flexibility of the polyhydrazide chain.

For comparative analysis, Karyakin[63] investigated poly-2,5-(*pp'*-diphenyl oxide hydrazide) (PH-O), poly-2,5-(*pp'*-diphenylphthalyl hydrazide) (PH-P), and their low-molecular-weight analogues: *NN'*-dibenzoylhydrazide of diphenylphthalide 4,4'-dicarboxylic acie (M-P) and *NN'*dibenzoylhydrazide of (diphenyl oxide)-4,4'-dicarboxylic acid (M-O).

It follows from Fig. 3 that the heat capacity of M-P increases monotonically with increase of temperature from 300 to 420 K. At 450 K M-P crystals begin to melt. In the range 460–560 K (the maximum heat capacity is observed at 530 K) a second endothermic peak, associated with the cyclodehydration of M-P and its conversion into the corresponding cyclic compound, appears. An analogous picture is observed also for M-O (Fig.3*b*). The endothermic peak in the range 520 to 580 K (the temperature of the maximum is 530 K), due to the cyclodehydration of M-O, is preceded by the fusion of the polymer at 510 K. Thus one may conclude that the thermal cyclodehydration of the model compounds M-O and M-P with formation of the corresponding 1,3,4-oxadiazoles takes place at an appreciable rate only in the melt of the initial hydrazide. With increase of the rigidity of the molecules of the model compound M-P compared with that of M-O, both the temperature range of the cyclodehydration reaction and the range between the melting point and the temperature of the maximum rate of cyclisation is observed.

Accordingly, the introduction of the bulky phthalide group into the polymer chain, which increases the rigidity of the chain and diminishes thereby the number of groups in the polyhydrazide unit capable of internal rotation, leads, firstly, to an incrase of the glass point of PH-P compared with PH-O (510 and 440 K respectively) and, secondly, increases the cyclodehydration temperature (which is higher by ~50 K for PH-P than for PH-O). An analogous effect is observed also on comparing the temperature variations of the heat capacities of the heterounit PH-P, the degree of cyclisation of which is 0.5, and the uncyclised PH-P. The increase of the rigidity of the system in the former case entails an increase of the glass point and of the temperature of the onset of cyclodehydration.[63]

IV. THE WATER VAPOUR PRESSURES OVER THE PREPOLYMERS IN THE COURSE OF THEIR CYCLODEHYDRATION

In order to calculate the enthalpies of the intramolecular cyclodehydration of the prepolymers, a study was made of the equilibrium vapour pressure of water over the corresponding polymers during their cyclisation.[55-63] The data obtained are fully consistent with the above conclusions concerning the character of the solid-phase cyclisation reactions. As an illustration, Fig. 4 presents such data for a polyaminoamidoacid and poly[*N*-terephthaloylbis(*N'*-phenyl-*o*-diphenylamine)]. The cyclodehydration of the polyaminoamidoacid (Fig. 4*a*) takes place in three stages: the elimination of two water molecules with conversion into PAI (curve *1*) and the subsequent elimination of two water molecules with conversion of the PAI units into PBBA [poly(benzoylene)benzimidazole - Ed. of translation] units. The cyclodehydration of PPDA (Fig. 4*f*) takes place in two stages, in each of which two water molecules are split off from the repeat unit of the initial polymer with formation of PPDBA.

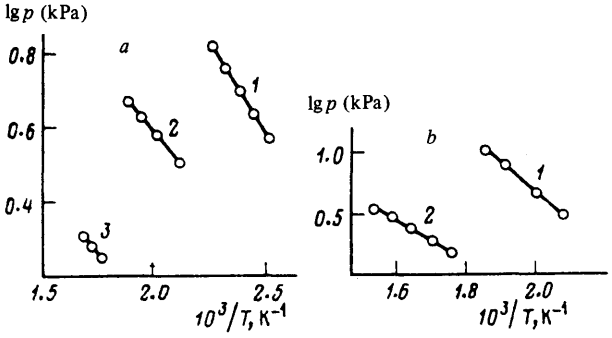


Figure 4. Temperature variation of the water vapour pressures over PAAA[50] (*a*) and PPDA[60] (*b*) in the course of their cyclisation: 1)–3) successive water elimination stages in the reactions.

Table 1 lists the coefficients of the corresponding equations $\lg p = f(T^{-1})$, which describe the experimental water vapour pressures over a series of prepolymers. Table 2 presents the results of the determination of the degrees of cyclisation of various polyheteroarylenes by Eqn. (4). Evidently, the polyheteroarylenes investigated are indeed heterounit polymers whose composition includes also the uncyclised units of the initial prepolymer.

V. ANALYSIS OF THE THERMODYNAMIC CHARACTERISTICS

The data on the thermodynamic properties of the prepolymers and the corresponding polyheteroarylenes described above have been used to calculate the standard enthalpies, entropies, and Gibbs free energies (Table 3). Analysis of the results permits a conventional subdivision of all the prepolymers investigated into two groups (Table 4). $\Delta H_r^0(T) < 0$ is observed at temperatures in the range 100–300 K for the group I prepolymers (PAAA, PCBA, PAA, PAI, PADI, and POA), while $\Delta H_r^0(T) > 0$ occurs at the same temperature for the group II prepolymers (PH-P, PBA, PATA, and PPDA). Above 373 K, the enthalpies of cyclodehydration are positive for polymers of both groups which is caused mainly by the elimination of water in the vapour state. Under these conditions, $\Delta H_r^0(400)$ for the group I prepolymers is lower than for those in group II (Table 4).

Table 1. The coefficients of the equations $\lg p = A - B/T$ (the pressures p are expressed in kPa).

Prepolymer	*T*, K	*A*	*B*	Refs.
PAA	380—440	5.000±0.045	1668±20	[55]
PAAA	400—440	3.301±0.004	1097±40	
	470—530	1.909±0.007	655±20	[50, 63]
	570—590	1.055±0.003	444±15	
PCBA	365—423	2.416±0.075	668±30	
	450—480	2.605±0.008	904±10	[63]
	485—548	5.121±0.344	2012±40	
POA	460—515	5.524±0.016	1945±5	[59]
PH-P	430—490	6.862±0.018	3237±8	[57]
PH-O	470—550	7.082±0.334	3205±30	[58]
PPDA	480—540	6.614±0.055	2959±28	[60]
	570—650	3.701±0.021	2103±3	
PATA	520—580	6.617±0.013	2750±3	[56]
PBA	460—540	5.900±0.240	2650±80	[62]

Table 2. Experimental degrees of cyclisation (N_2) of polyheteroarylenes*.

Prepolymer	Final polymer	$-\Delta H_c^0$ (298, PP) kJ mol^{-1}	$-\Delta h_c^0$ (298, FP) kJ g^{-1}	ΔH_r^0 (298), kJ mol^{-1}	N_2	Refs.
PAA	PI	9619±9	25.05±0.05	—6.5±1.0	0.96	[55]
PAAA	PAI	12940±16	25.38±0.03	—45.0±1.0	0.89	[50]
PAI	PBBA	12895±20	27.00±0.03	—56.0±2.0	0.71	[50]
PCBA	PADI	11072±10	23.37±0.03	—77.5±1.5	0.88	[63]
PADI	PBTA	10995±11	25.15±0.05	—6.0±0.5	0.82	[63]
POA	PBO	10161±14	30.92±0.04	—3.0±1.0	0.88	[59]
PH-P	POD-P	14125±12	28.47±0.03	40.2±1.0	0.97	[57]
PH-O	POD-O	6353±7	26.95±0.02	28.5±2.0	0.97	[58]
PPDA	PPDBA	16134±18	34.75±0.03	22.0±2.0	0.88	[60]
PATA	PTAQ	14862±15	30.31±0.02	34.3±1.0	0.92	[56]
PBA	PBIQ	16387±10	31.03±0.03	31.0±3.0	0.93	[62]

Notation: ΔH_c^0(298, PP) is the enthalpy of combustion of the prepolymer, Δh_c^0(298, FP) the specific enthalpy of combustion of the final polyheteroarylene, and ΔH_r^0(298) the enthalpy of cyclisation of the prepolymer.

In terms of the sign and the absolute order of magnitude, the entropies of cyclodehydration are the same for both groups of prepolymers, because the entropies of the final and intermediate polymers do not differ greatly and the quantity $\Delta S_r^0(T)$ is mainly determined by the entropy of two moles of water.

Table 3. Thermodynamic characteristics of the intramolecular solid-phase cyclodehydration of a series of prepolymers at atmospheric pressure.

T, K	$-\Delta H_r^0(T)$, kJ mol^{-1}	$\Delta S_r^0(T)$, J mol^{-1} K^{-1}	$-\Delta G_r^0(T)$, kJ mol^{-1}	$-\Delta H_r^0(T)$, kJ mol^{-1}	$\Delta S_r^0(T)$, J mol^{-1} K^{-1}	$-\Delta G_r^0(T)$, kJ mol^{-1}
PAAA(s) → PAI(s) + 2H$_2$O(s) (Ref.63)				PAI(s) → PBBA(s) + 2H$_2$O(s) (Ref.63)		
100	52.5	22.0	54.5	85.0	—60.0	79.0
150	53.5	9.0	55.0	85.5	—65.5	75.5
200	54.5	4.0	55.0	88.5	—71.5	74.0
250	56.0	—2.0	55.5	88.5	—81.0	68.0
PAAA(s) → PAI(s) + 2H$_2$O(l)				PAI(s) → PBBA(s) + 2H$_2$O(l)		
298.15	45.0	38.0	56.0	56.0	—39.0	44.4
350	42.0	45.5	58.0	62.5	—42.0	48.0
PAA(s) → PAI(s) + 2H$_2$O(g)				PAI(s) → PBBA(s) + 2H$_2$O(g)		
400	—42.0	270.0	66.0	—21.0	165.5	45.0
PCBA(s) → PADI(s) + 2H$_2$O(s) (Ref.63)				PADI(s) → PBTA(s) + 2H$_2$O(s) (Ref.63)		
100	89.0	—4.00	88.5	—19.0	—4.50	18.5
150	89.5	—9.00	88.0	—19.0	—6.00	18.0
200	90.5	—13.5	88.0	—19.5	—6.50	18.0
250	91.0	—17.0	86.5	—19.5	—6.00	18.0
PCBA(s) → PADI(s) + 2H$_2$O(l)				PADI(s) → PBTA(s) + 2H$_2$O(l)		
298.15	77.5	33.5	87.5	—6.00	42.0	18.5
350	71.5	54.5	90.5	8.50	67.0	15.0
PCBA(s) → PADI(s) + 2H$_2$O(g)				PADI(s) → PBTA(s) + 2H$_2$O(g)		
400	—25.5	307.5	97.5	74.5	230.0	17.5
PAAA(s) → PBBA(s) + 4H$_2$O(s)				PCBA(s) → PBTA(s) + 4H$_2$O(s)		
100	137.5	—38.0	133.5	108.0	—8.50	107.0
150	139.0	—56.5	130.5	108.5	—14.5	106.0
200	143.0	—67.5	129.0	110.0	—20.0	106.0
250	144.5	—83.0	123.5	110.5	—23.0	104.5
PAAA(s) → PBBA(s) + 4H$_2$O(l)				PCBA(s) → PBTA(s) + 4H$_2$O(l)		
298.15	101.0	—1.00	100.5	83.5	75.5	106.0
350	104.5	3.50	106.0	63.0	121.5	105.5
PAAA(s) → PBBA(s) + 4H$_2$O(g)				PCBA(s) → PBTA(s) + 4H$_2$O(g)		
400	—63.0	435.5	111.0	—100.0	538.0	115.0
PAA(s) → PI(s) + 2H$_2$O(s) (Ref.55)				POA(s) → PBO(s) + 2H$_2$O(s) (Ref.59)		
100	—12.0	—8.50	11.0	—8.00	—6.50	7.50
150	—13.5	—20.5	10.5	—11.5	—12.0	9.50
200	—15.0	—31.0	9.00	—12.5	—19.0	8.50
250	—17.0	—39.0	7.00	—14.5	—26.5	8.00
PAA(s) → PI(s) + 2H$_2$O(l)				POA(s) → PBO(s) + 2H$_2$O(l)		
298.15	—6.50	25.0	14.5	—3.00	13.5	7.00
350	—6.50	33.5	18.0	—2.50	12.0	5.50
PAA(s) → PI(s) + 2H$_2$O(g)				POA(s) → PBO(s) + 2H$_2$O(g)		
400	67.0	232.0	26.0	79.0	225.0	11.0
410	64.0	226.0	28.5			
450				78.0	216.5	19.5
490				74.5	210.5	28.5
PH-P(s) → POD-P(s) + 2H$_2$O(s) (Ref.57)				PATA(s) → PTAQ(s) + 2H$_2$O(s) (Ref.56)		
100	23.0	21.5	21.0	19.0	—1.00	19.0
150	23.5	27.5	19.5	19.5	0.00	19.5
200	24.0	31.5	17.5	19.5	1.50	19.0
250	25.0	34.0	16.5	20.5	4.00	19.5
PH-P(s) → POD-P(s) + 2H$_2$O(l)				PATA(s) → PTAQ(s) + 2H$_2$O(l)		
298.15	39.5	94.0	11.5	34.5	58.5	17.0
350	40.5	96.0	7.00	41.0	71.0	16.0
PH-P(s) → POD-P(s) + 2H$_2$O(g)				PATA(s) → PTAQ(s) + 2H$_2$O(g)		
400	124.0	300.0	4.00	122.0	288.5	6.50
450	123.0	300.0	—12.0	118.0	280.5	—8.00
500	122.0	290.0	—23.0	114.0	265.5	—19.0
550	—	—	—	105.5	255.0	—35.0
PBA(s) → PBIQ(s) + 2H$_2$O(s) (Ref.62)				PPDA(s) → PPDBA(s) + 2H$_2$O(s) (Ref.60)		
100	28.5	—3.50	29.0	9.00	—45.0	13.5
150	26.5	—18.0	29.0	8.50	—48.5	16.0
200	24.5	—31.0	30.5	8.00	—51.0	18.0
250	21.5	—45.0	32.5	8.00	—52.0	21.0
PBA(s) → PBIQ(s) + 2H$_2$O(l)				PPDA(s) → PPDBA(s) + 2H$_2$O(l)		
298.15	31.0	—9.00	33.5	22.0	0.50	22.0
350	31.5	—7.75	34.0	25.0	8.50	22.0
PBA(s) → PBIQ(s) + 2H$_2$O(g)				PPDA(s) → PPDBA(s) + 2H$_2$O(g)		
400	111.5	217.5	24.5	102.5	215.5	16.5
450	106.0	206.5	13.0	100.5	209.0	6.50
500	101.5	191.0	6.00	100.5	209.0	—4.00
550	85.5	167.0	—6.50	97.0	201.0	—13.5
600	72.0	144.0	—14.5			

The free energy $\Delta G_r^0(T)$ for the group I prepolymer is negative at all temperatures, because at low temperatures (100–300 K) the cyclodehydration processes are exothermic and their entropies are either small and negative or (usually) positive. At higher temperatures ($T \geq 400$ K) the enthalpies of these reactions are in all cases positive, but they are characterised by large positive entropies (Table 5), so that the role of the entropy factor becomes decisive: $T\Delta S_r^0(T) > \Delta H_r^0(T)$.

Table 4. Standard thermodynamic characteristics of the intramolecular cyclodehydration reactions of the prepolymers at a series of temperatures.[63]

$\Delta H_r^0(T)$, kJ mol^{-1}			$\Delta S_r^0(T)$, J mol^{-1} K^{-1}			$\Delta G_r^0(T)$, kJ mol^{-1}		
100 K	300 K	400 K	100 K	300 K	400 K	100 K	300 K	400 K
Group I prepolymers								
—8.0— —140.0	—2.5— —100.0	20— 100	—60—20	—40—70	170—300	—10— —130	—5— —100	—10— —110
Group II prepolymers								
10.0— 30.0	20.0— 40.0	100— 125	—45—20	—10—100	200—300	15—30	10—35	4.0—25

Table 5. The coefficients of the equations $\Delta G_r^0(T) = A - BT$ for the cyclodehydration reactions of the prepolymers.

Reaction scheme	T, K	A	B	$2\sigma^*$, kJ mol^{-1}
PAA → PI + 2H$_2$O	300—400	24.0	0.125	2.5
PAAA → PAI + 2H$_2$O	300—400	—26.0	0.098	4.0
PAAA → PBBA + 2H$_2$O	300—400	—70.0	0.103	0.5
PCBA → PADI + 2H$_2$O	300—400	—57.5	0.098	2.5
PADI → PBTA + 2H$_2$O	350—500	7.0	0.060	1.0
POA → PBO + 2H$_2$O	400—500	66.5	0.194	1.5
PBA → PBIQ + 2H$_2$O	400—600	102.0	0.195	2.5
PPDA → PPDBA + 2H$_2$O	400—550	97.0	0.201	0.5
PATA → PTAQ + 2H$_2$O	400—550	115.0	0.271	2.5
PH-P → POD-P + 2H$_2$O	400—500	111.5	0.270	3.0

*Twice the average standard error of the calculated Gibbs free energies for the cyclodehydration reaction.

$\Delta G_r^0(T) > 0$ is observed for the group II prepolymers at temperatures from 100 to 400 K, because the corresponding processes are endothermic and their positive entropies do not compensate for the enthalpy of the process: $\Delta H_r^0(T) > T\Delta S_r^0(T)$. At temperatures above 400 K, $\Delta G_r^0 < 0$ for the cyclodehydration reactions of group II prepolymers.

For the majority of the cyclodehydration reactions investigated, the standard Gibbs free energies vary linearly with temperature (Table 5), which make it possible to estimate $\Delta G_r^0(T)$ and the equilibrium constants of these processes at the temperatures used in practice for the heat treatment of the prepolymers. Such data are listed in Table 6 together with the degrees of polycondensation of polyheteroarylenes (P_n) calculated from the Carothers formula[65] and the degrees of conversion X of the initial prepolymer into the final heterocyclochain polymer. Comparison of the data obtained with the results quoted in Table 2 shows that the cyclisation of the corresponding prepolymers in the case of PBIQ, PPDBA, POD-P, and PI at experimental temperatures went to completion, because the values of N_2 and X are equal within the limits of the error of the calculations. The cyclisation reaction of the prepolymers associated with PTAQ, PBO, and, especially, PAI and PADI do not go to completion, because $N_2 < X$ at the experimental temperatures (Tables 2 and 6).

Table 6. The standard Gibbs free energies (ΔG_T^0), the equilibrium constants (Kp), and the degrees (X) of the cyclodehydration reactions of the prepolymers and the degrees of polycondensation ($\bar{P}_n$) of the polyheteroarylenes formed.

Polyheteroarylene	PAI	PADI	PI	PBO	PBIQ	PPDBA	PTAQ	POD-P
T, K	433	443	575	525	643	573	640	603
$-\Delta G_T^0(T)$, kJ mol^{-1}	68.5	101.0	48.0	35.5	23.5	18.0	58.5	51.5
$K_p(T)$	$2.0\cdot10^8$	$8.0\cdot10^{11}$	$2.5\cdot10^4$	$3.5\cdot10^3$	81	44	$6.0\cdot10^4$	$3.0\cdot10^4$
$\bar{P}_n$	$1.5\cdot10^4$	$9\cdot10^5$	152	59	10	8.5	243	195
X	1.000	1.000	0.998	0.983	0.910	0.880	0.996	0.994

The character of the temperature variation of X is significantly different for the cyclodehydration reactions of prepolymers of different groups. For the group II prepolymers (PH-P, PATA, PPDA, and PBA, Fig.5), the values of X are low (0.001–0.354) in the temperature range 300 to 400 K; the degree of reaction then increases sharply with increase in temperature, reaching values virtually equal to unity (100% polyheteroarylene) at 600 K for PH-P, 650 K for PATA, 750 K for PPDA, and 850 K for PP. At these precise temperatures the equilibrium constants of the cyclodehydration reactions become equal to 5×10^3–1×10^4.

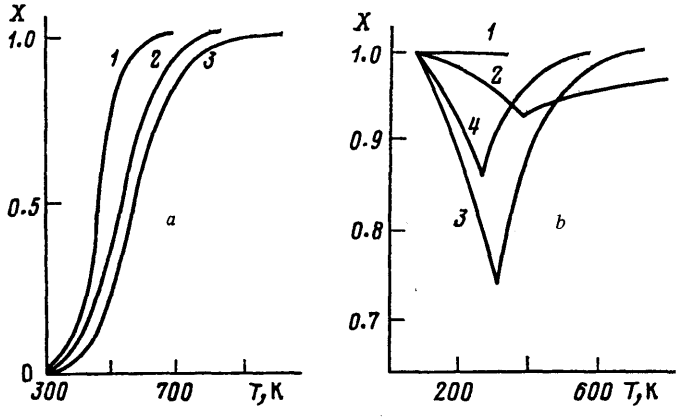


Figure 5. Temperature variation of the degrees of conversion X in the cyclodehydration reactions: *a*) PATA (curve *1*), PPDA (curve *2*), and PBA (curve *3*); *b*) PAAA (curve *1*), PADI (curve *2*), POA (curve *3*), and PAI (curve *4*).[63]

From the thermodynamic standpoint, the preparation of fully cyclised (homounit) polyheteroarylenes from the prepolymers of the first group is possible both at low (100 to 150 K) and relatively high temperatures (500–600 K). The fact that the N_2 for PBO, PAI, PADI, PBBA, and PBTA do not reach limiting values determined by the equilibrium constants of the corresponding cyclodehydration reactions can be accounted for only by kinetic causes. In such cases the rigidity of the heterounit polymer formed is apparently so great that this leads to a virtual inhibition of the cyclisation process at the experimental temperature even for relatively low degrees of cyclisation (N_2 = 0.82 to 0.88).

VI. CONCLUSION

It follows from the data described above that the physical state of the prepolymer is a decisive factor in the practical realisation of solid-phase cyclodehydration reactions. Namely the chemical nature of the substituents and of the atomic groups constituting the polymer chain determines the initial flexibility of the polymer macromolecules and hence the glass point of the polymer on which depends the temperature range of the cyclisation reaction. Together with this, the rigidity of the polymer increases with increasing degree of cyclisation and hence the glass point also rises. As a result, the intramolecular cyclodehydration processes hardly ever go to completion and the polyheteroarylenes formed are always heterounit polymers, i.e. contain a definite number of fragments of the corresponding initial prepolymer. In order to obtain a polyheteroarylene with a high content of cyclic fragments, the cyclisation process is therefore carried out under non-isothermal conditions.

The experimental data also show that the determination of the thermodynamic characteristics of the corresponding polymers and of their reactions constitutes an extremely effective method for the investigation of the solid phase cyclisation reactions. The study of the temperature variation of the heat capacities of the prepolymers and the final polymers and of the water vapour pressure over the prepolymers in the course of their cyclodehydration makes it possible to determine the temperature ranges in which the above reactions take place. Calorimetric study of the enthalpies of combustion of the prepolymers and the final products and of the enthalpies of cyclisation led to the development of a universal method for the determination of the degree of cyclisation of the prepolymers in intramolecular cyclodehydration processes (the method based on the calculation of the extent of the heterounit structure of polyheteroarylenes).

Analysis of the thermodynamic characteristics of the intramolecular cyclodehydration reactions makes it possible to subdivide the prepolymers into two groups differing in the character of the variation of their thermodynamic functions in the solid-phase cyclisation processes. The enthalpies of cyclisation of the group I prepolymers are negative (i.e. the reactions are exothermic) up to 373 K and positive above this temperature, the entropies of cyclisation are positive at T > 100 K, and the standard Gibbs free energies are positive over the entire temperature range. The enthalpies of the cyclisation reactions of group II prepolymers are positive (the reactions are endothermic), the entropies are positive at T > 100 K, and the Gibbs free energies become negative only above 400 K.

The determination of the equilibrium constants of the cyclodehydration reactions makes it possible to calculate the average degrees of polycondensation of the polyheteroarylenes at a specified temperature. These results enable

one in their turn to estimate the temperature ranges in which "defect-free" or homounit polyheteroarylenes can be obtained, which is extremely important for the development of a scientific basis for the synthesis of such polymers and for the preparation of thermostable materials from them.

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