ACID-CATALYZED REACTIONS IN POLYIMIDE SYNTHESIS

Alexander A. Kuznetsov*, Anna Yu. Tsegelskaya, Michael Yu. Belov, Vladimir I. Berendyaev, Sergey V. Lavrov, Galina K. Semenova, Anatoly L. Izyumnikov, Nina V. Kozlova, Boris V. Kotov

Karpov Institute of Physical Chemistry, 10, Vorontsovo pole, Moscow, 103064, Russia.

Abstract : Melts of aromatic carboxylic acids are found to be excellent reaction media for 1-pot high molecular weight polyimide synthesis from diamines and tetracarboxylic acid dianhydrides. No reversible reaction of polyamic acids (PAA) formation was observed. The effect of the reactivity equalization was observed for low- and high reactive diamines in acid media. The intrinsic acid catalysis of the imidization reaction was shown to take place also in polycyclization of PAA in concentrated solutions in amic solvents. It is found that the dependence of relative imidization rate (% conv./ min) vs. AA/N-MP ratio for model low molecular and oligomeric amic acids (AA) in N-MP at 140-150°C possesses a sharp maximum near the molar ratio 1:1, the imidization rate at the point of the maximum being an order of magnitude higher than that for diluted solutions. A scheme is proposed which includes the opportunity of two reaction channels to occur: a usual one (I) and a catalytic one (II). In diluted solutions and in solid phase experiments with easy evacuation of volatile products, the role of catalytic channel II is low. To the contrary, in high concentrated solutions or in solid phase experiments under the conditions exluding volatile products evacuation, the catalytic channel becomes the key one. It is proposed that the catalytic reaction proceeds via the common acid catalysis mechanism, the solvent and water playing the role of co-catalysts, probably through the

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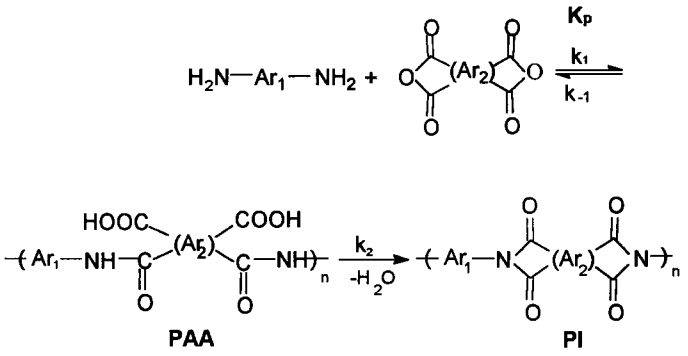
mechanism of ionic dissociation of AA or hydrogen- bound complex AA-solvent. It is shown that the water released in the course of solid phase imidization of phtalamic acid at 140°C under the conditions where vaporization is impossible causes a sharp autocatalytic effect after initial 20%-conversion period to obtain entirely imidizied product.

INTRODUCTION

Aromatic polyimides are known as a typical class of high performance polymers due to the excellent combination of properties such as heat resistance (450°C), excellent mechanical properties in a wide temperature range including cryogenic conditions, nonflammability, superhigh radiation resistance [1,2]. Basically, two methods are used in obtaining aromatic polyimides:

1) The two-step process including polycondensation of aromatic diamines and tetracarboxylic acid dianhydrides in amic solvent at the temperature lower than 60°C and processing soluble polyamic acid (PAA, polyimide precursor) into films and powders followed by solid phase thermal cyclization of PAA.

2) The one-pot solution synthesis [3,4]. In this case polycondensation and cyclodehydratation reactions are carried out without isolation of the precursor at temperatures 140-160°C. The usual solvents are m-cresol and m-dichlorobenzene .



A very specific feature of method 1 is polychronic kinetics of the cyclization reaction in the solid phase. To overcome the kinetic stop, it is necessary to use the treatment at elevated temperatures (up to 300°C). So, this method is used to obtain non- softening polyimides in the form of a film or press-powders. High temperature treatment is expensive and leads to partial destruction of the polymer during the period of precursor transfomation to the final high thermostable product. Method 2 is used basically to obtain soluble and thermoplastic polyimides with the softening temperature< 300°C meant to be processed by injection molding. The disadvantures of method 2 are the long duration of the process (5 hours and more) and the incompleteness of cyclization of PAA fragments .

Demerits of methods 1 and 2 create good stimulus to search for accelerating agents for PAA cyclization. It is known [2] that several chemical compounds or their combinations can accelerate PAA cyclization such as : pyridine-acetic anhydride , organic bases, mineral acids . Organic acids (as additives to amic solvents) were also found to be catalysts of PAA cyclization [5-9]. In the latter case an acceleration effect was found, but it is not very large. We focused our efforts on the investigation the opportunity of using the carboxylic acid catalysis in the one-pot process for obtaining polyimide. The key starting result was our observation that melted carboxylic acids may be excellent solvents for the variety of thermoplastic polyimides. This fact led us to idea to use melted carboxylic acids as the reaction media in the one-pot polyimide synthesis. This idea appeared to be promising enough. In this work, first results obtained by using this approach are presented. Besides, results of studying the cyclization reaction of low molecular model amic acids in concentrated solutions are presented , in the latter case amic acid itself playing the role of acid catalyst.

EXPERIMENTAL PART

m-Phenylenediamine (m-PDA) was distilled under argon before polycondensation. Dianhydride of 2,2-bis[(3,4-dicarboxyphenoxy)phenyl]propane (BPADA (m.p. 188-189°C) was used without additional purification. Benzoic acid (m.p.122-123°C) was distilled under normal pressure.

PAA-I (model compound) with the logarithmic viscosity 0.13 dl/g was obtained by polycondensation of equimol quantities of m-PDA and BPADA in chloroform at 20°C. The total concentration of monomers was 10%-weight. PAA-I precipitated as a fine powder . It was isolated by filtration , dried and stored under argon. Such preparation method allowed to obtain PAA-I containing no residual amic solvent; that is important for interpreting results of PAA-I cyclization kinetics at high concentrations. The data on cyclization kinetics were obtained by comparison of intensities of the bands 620 (imide cycle) and 690 cm^{-1} (reference peak) in IR-spectra (Nicolett Impact 410 FTIR spectrometer). The samples for FTIR were prepared in the form of the CsJ tablets .

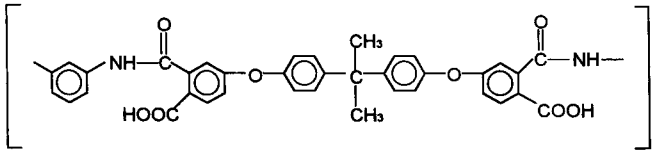
PAA-II with the logarithmic viscosity 0,6 dl/g in N-MP was obtained by polycondensation of 3,4,3',4'-biphenyltetracarboxylic acid dianhydride with 4,4'-oxydianiline (ODA) in N-MP at 20°C. The PAA-II microfiber sample 1,0 mkm in diameter was obtained by means of withdrawing a drop of solution. Monolithic tablets of PAA-II were obtained by treatment of the microfiber material at 500 MPa for 10 min.

PPAA (m.p.170°C) was synthesized from aniline and phtalic anhydride and then purified by crystallization from dry dimethoxyethane. N-MP was dried by storage over P_2O_5 and subsequent distillation. The water content was estimated as 0.02%-w. Kinetic measurements were carried out in argon atmosphere in sealed (closed system) or open (open system) 2.5cm^3 ampoules , placed into the oil heater at 140±0,5°C. In experiments with the addition of solvents, the ampoules with the reaction mixture were preheated previously for 2 min to reach dissolution of PPAA. In reference experiments, it was shown that preheating did not result in changing the PPAA concentration. At the definite moment, the reaction was stopped by placing the ampoule in liquid nitrogen (to avoid any changing in the PPAA concentration in the presence of water released during cyclization). The contents of the ampoule was transferred quantitatively into a glass by subsequent pouring N-MP, MeOH and i-PrOH. The amount of residual PPAA and phtalic acid was determined by means of the potentiometric titration with 0.03N solution of Me_4NOH using automatic titrator T-108. The technique chosen allowed to measure PPAA and PA quantity with the 2% error. In a special control experiment, it was shown that the autocatalytic effect observed in solid state PPAA cyclization was caused just by the presence of water but not small amount of PA (the by- product which appears via hydrolysis of phtalic anhydride formed in the course of PPAA reversible cleavage).

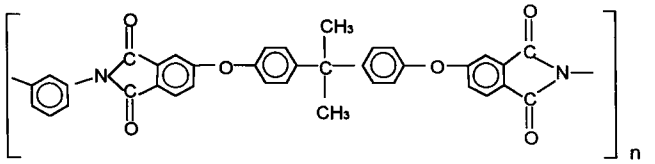
RESULTS AND DISCUSSION

1. CATALYTIC ONE-POT POLYIMIDE SYNTHESIS IN THE MELTS OF AROMATIC CARBOXYLIC ACIDS [10].

The kinetics of the cyclization reaction has been studied for the product of polycondensation of m-PDA with BPADA (PAA-I) at 140°C both in the solid state (as a powder-like substance) and in melted benzoic acid (BA) (as a transparent solution) by means of the FTIR spectroscopy (fig.1).



PAA-I



PEI-I

It can be seen from fig.1 that the imidization rate in benzoic acid is extremely high whereas the reaction rate in the solid state behaves in the usual way. So, benzoic acid was chosen as a medium for the 1-step synthesis of PEI from aromatic diamines and anhydrides.

The kinetics of the intrinsic viscosity build up in the course of polycondensation of m-PDA and BPADA at 140°C in melted benzoic acid is shown in fig.2. The reaction rate is high enough to obtain a high molecular weight polymer in 30-60 minutes. Polymer samples purified by repeated extractions with boiling acetone and dried in vacuo were identified as entirely cyclizied products. They possessed only one glass transition in DSC tests near 218°C . Their IR-spectra were identical to the spectrum of completely cyclizied commercial PEI product Ultem-1000^{R} (General Electric Co.) having the same chemical structure.

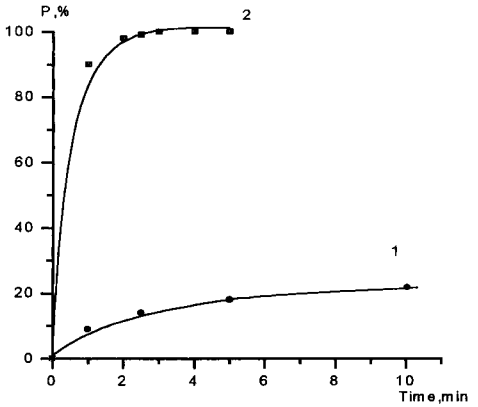


Fig.1. Kinetics of cyclodehydratation of PAA-I: 1) solid state open system; 2) in the melt of benzoic acid.

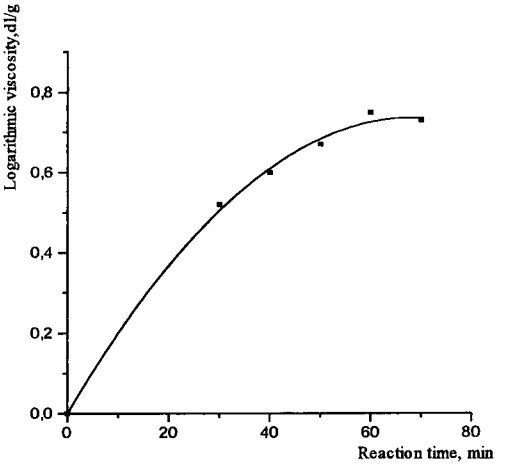


Fig.2. The kinetics of the logarithmic viscosity build in a course of polycondensation of m-PDA and BPADA at 140°C in benzoic acid (monomer concentration 10%).

The level of the logarithmic viscosity of the final product can be controlled by the addition of small amounts of the monofunctional compound - phtalic acid (table 1). Such a behavior is analogous to the usual polycondensation process of diamine and dianhydrides in amic solvents.

Table 1.

Influence of addition of phtalic anhydride on logarithmic viscosity of polyetherimide (140°C , 1.0 hour)

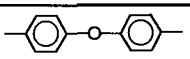
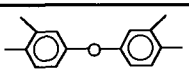
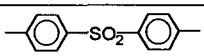
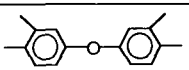
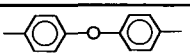
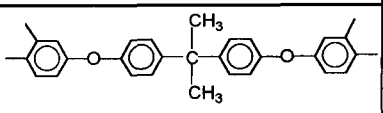
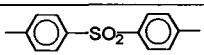
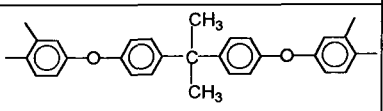
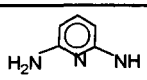
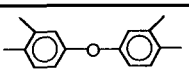
PA/BPADA (mol/mol)	η_{log}, dl/g
3.0	0.35
1.0	0.50
0.5	0.55
0	0.73

It has been established, that melts of aromatic carboxylic acids are efficient catalytic media not only in cyclopolycondensation of diamines and dianhydrides, but also in so-called direct polycondensation of diamines with tetracarboxylic acids. In such systems, the reaction kinetics was found to be slower as compared with the analogous reactions including dianhydride.

Another interesting feature of melted aromatic acids as new reaction media for the polyimide synthesis is effect of the reactivity equalization of low- and high reactive diamines in polycondensation. Experimental data presented at table 2 show that high molecular weight polymers can be obtain in 1 hour from the low reactive (4,4'-diaminodiphenylsulfone) monomer as well as from high reactive (4,4'-diaminodiphenyloxide) one. Probably, this effect can be understood if we take into account the well- known fact of the equalization of basic properties of aliphatic and aromatic amines in acid solvents. Anyway, this effect can be useful for obtaining new polyimides and copolyimides which cannot be obtained by other methods.

Table 2.

Logarithmic viscosity (dl/g) of completely cyclizied polyimide obtained in melt acid media (115°C, 1,5 h)

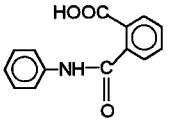
N	Ar_1 in diamine	Ar_2 in dianhydride	η_{log}
1			0.67 (H_2SO_4)
2			0.64 (H_2SO_4)
3			0.6 (N-MP)
4			0.5 (N-MP)
5			0.46 (H_2SO_4)

2.KINETICS OF CYCLIZATION OF MODEL COMPOUNDS IN SOLUTION.

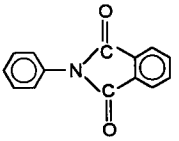
As was shown above, carboxylic acids are powerful catalysts of the PAA cyclization reaction. On the other hand, every carboxyamide fragment of polyamic acids obtained in the polycondensation reaction of diamines and tetracarboxylic acids dianhydrides can be considered as substituted derivative of benzoic acid. So, it was reasonable to suppose that PAA can possess the catalytic activity itself. More probably, such effect could be expected in concentrated solutions of PAA. In this work, we investigated the influence of the concentration of two model amic acids on the kinetics of cyclization in the wide range of concentrations .

The first model compound was oligomeric PAA-1 with logarithmic viscosity 0,13 dl/g, the second one was phenyl phtalamic acid (PPAA) . N-MP , DMAA and nitrobenzene were used as solvents. Both compounds as well as corresponding imidizied products (probably with exception of PPAA-N-MP system in a range of PPAA content higher than 82%-weight) were soluble in amic solvents at the temperature of the experiment

(140°C). So, almost all the measurements in amic solutions seem to be refferred to homogeneous conditions.



PPAA



PPI

Fig.3 shows the typical kinetic curves for PAA-I imidization in N-MP solution. The reduced rate of imidization increases with increase in the content of PAA. The initial part of the kinetic curve can be described in terms of first-order kinetics (as well as the second order one).

Fig.4 shows the dependence of the reduced initial reaction rate on the weight fraction of PAA-I in N-MP solution. In the case of N-MP, the maximum of the rate is observed at 80%-weight of PAA-I. Such a dependence is the evidence of the complicated character of the reaction. Increasing in the reduced initial rate (conversion change per min) with an increase in the starting PAA concentration is the evidence that the order of the reaction in amic acid fragments is higher than 1. This is in the agreement with the data obtained earlier by Kardash [7] and McGrath [9] who found the 2-nd order of the imidization reaction in carboxyamic groups in diluted solution.

It was found that the addition of the equal amount of benzoic acid to the 10% -solution of PAA-I resulted in an increase in the reaction rate up to about the same value, as for the solution with the doubled concentration of PAA-1 in the absence of benzoic acid. So, it can be concluded that PAA-I possesses catalytic effect in cyclization of itself as well as benzoic acid (scheme 2). The reaction scheme can be described in terms of the common acid catalysis which includes protonization of the carbonyl group to obtain the dihydroxy compound which after the elimination of the water molecule, form an acylium cation which reacts with the imide group followed by proton transfer to give the final product. The latter stage probably proceeds with the participation of the amic acid anion which could be a good agent of the proton transfer. The participation of the anion could be proposed on the basis of the fact that weak acids as well as strong acids are good catalysts for the imidization reaction. The analogous scheme was proposed by

Kim and McGrath [9] to explain the second order kinetics of imidization of high molecular ODA-ODDA polyamic acid in diluted solutions. The difference is that in the work by Kim and Mc.Grath [9], the specific acid catalysis was proposed.

It should be noted that in the region of high PAA concentrations the initial rate must increase with increase in the concentration of the solvent, but not of amic acid. Fig.5 shows the dependence of the reduced initial rate of imidization on the molar fraction of PAA-I in N-MP. The same results were obtained in model systems PPAA- N-MP and PPAA-DMAA. In all these cases the maximum of the rate corresponds nearly to 1:1 stoichiometric ratio of amic acid fragments and amic solvent. PPAA-nitrobenzene system is an exception , but it is, apparently, due to the nonhomogenity of the system. At the concentration of PPAA higher than 30% PPAA is insoluble.

It is known that amic acid fragments are able to form strong complexes with amic solvents [17]. The concentration of such a complex must be maximal just in the region of ratios near 1:1. (Similar diagrams for the complex concentration vs. the molar ratio of components are known as Jobb's curves) . If so, it is reasonable to suppose that formation of the complex between amic acid fragment and solvent is a factor influencing the imidization kinetics, for example, via the dissociation process (scheme 3). It could be expected that the concentration of ionic dissociation products (real catalysts) must be maximal at the point of the equivalency. This could explain the appearance of the maximum in the dependence of the initial rate on the content of amic acid fragments.

The preliminary analysis of imidization kinetics of PPAA in N-MP has shown that the effective order of the reaction decreases with increasing PPA content from 2 for 2-5%-w solution to 1 for 12,5% solution and to zero near the rate maximum. This can be explained by changing the rate-determining stage.

From our point of view, the region of the high PAA concentration is close to the solid state. Results presented here, allow to understand better the effect of the acceleration of the solid state cyclization rate in the presence of small amounts of solvents observed by several authors [12-17].

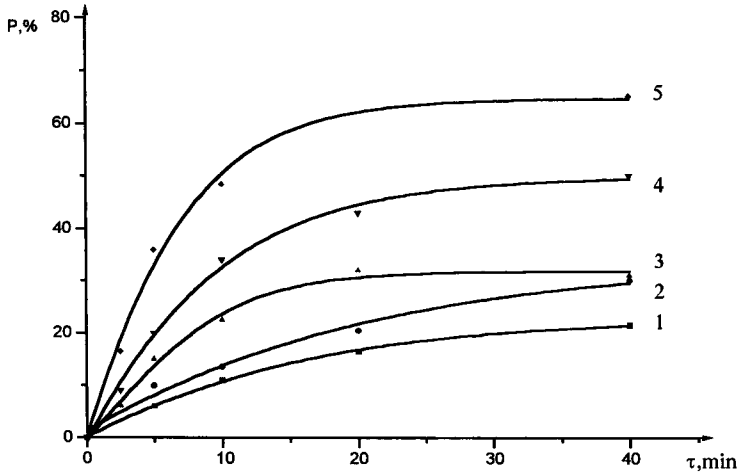


Fig.3. Kinetics of the cyclodehydratation reaction of PAA-I at different PAA-I:N-MP ratios. 1<2<3<4<5.

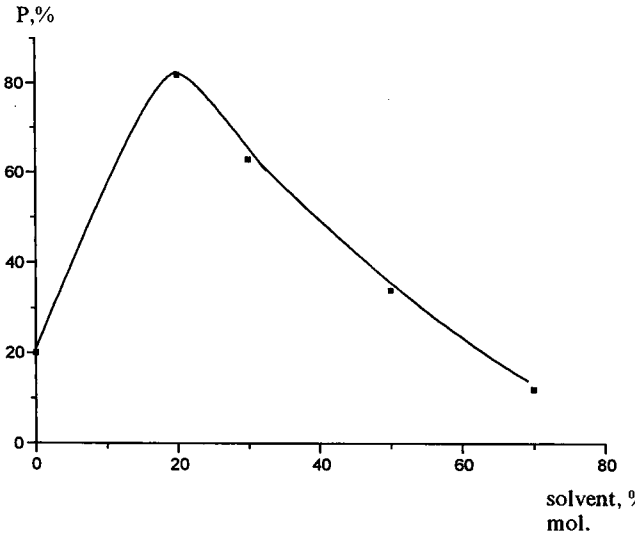
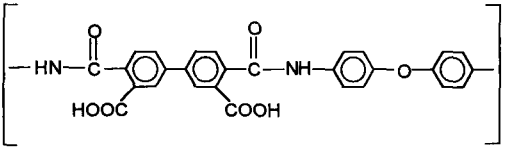
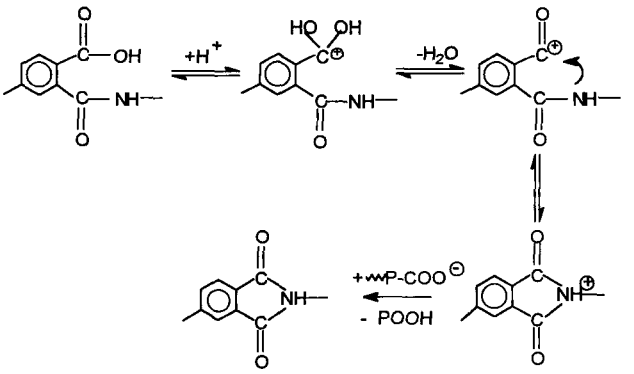


Fig.4. The dependence of the conversion (2min) of the cyclodehydratation reaction of PAA-I in N-MP on N-MP the content.



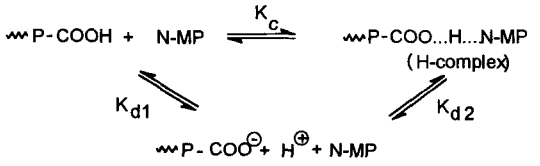
PAA-II

Catalytic channel



Scheme 2

Role of amic solvent



Scheme 3

In this work, special experiments were carried out to study the solid phase-imidization process in PAA-II samples, containing residual (H-bound) N-MP (fig.6). Sample 1 was a microfiber material with a very low density (less than 0,1 g/cm^3) composed of microfibers of 1 micron in diameter. Imidization was carried out by blowing hot air through the microfiber sample. Sample 2 was a monolithic tablet 300 microns thick made of the same starting material which was put between two heated metal plates. The

temperature was 150°C in both experiments. Kinetic measurements were performed using imide peak near 1370 cm^{-1} and reference peak at 1500 cm^{-1} in FTIR spectra. The presence of H-bound N-MP in samples 1 and 2 was confirmed by means of FTIR and the weight loss analysis at heating . It was found that the imidization process in the microfiber sample with good evacuation of volatile products (fig.7 curve 1) has almost usual characteristics which can be expected from literature data. In contrast with this in the case of the monolithic sample with poor evacuation of volatile products, the imidization rate increased dramatically. The initial rate was found to be about 10 times grater than that for sample 1.

Speculations on plastification as the reason of an increase in the polymer chain mobility are often used in the literature to explain the accelerating effect of solvent on the reaction rate in the solid polymer matrix. Indeed, the thermomechanical analysis has shown lowering the glass temperature after the beginning of cyclization in the monolithic tablet(but not in microfiber!). However, when we compare the kinetics in the monolithic sample (fig.7, curve 3) and in dilute solution (fig.7, curve 2) where all the physical and conformation constrains are avoided, it is clear that in the case of the monolithic sample we deal with a new accelerating effect which could not be explained by plastification.

To obtain more data on the influence of the morphological structure of the sample on cyclization kinetics we have studied the kinetics of cyclodehydratation of the crystalline low molecular model compound PPAA in the solid phase at 140°C. The reaction was carried out under conditions of two types: with and without evacuation of the volatile products. The cyclization process in the solid phase with evacuation of water (open system) was found to have the initial rate 0.4% per minute and to reach its upper conversion limit at the conversion about 40% (fig 8, curve 1). To the contrary, in an analogous experiment in a closed system, the sharp acceleration of the reaction has been found after reaching 20% conversion (fig.8,curve 2). In several minutes, the reaction was over to give the 100% cyclizied product. This effect is obviously connected with the autocatalysis of the cyclization reaction with the water evolved at the initial stage of the process. The addition of small amounts of water into closed system results in increasing imidization rate without the induction period (fig.8,curve 3,4). The acceleration effect (not very strong) was also observed in the case of the monolithic tablet made of PAA-I which is an entirely amorphous oligomer product. It can be attributed only to the

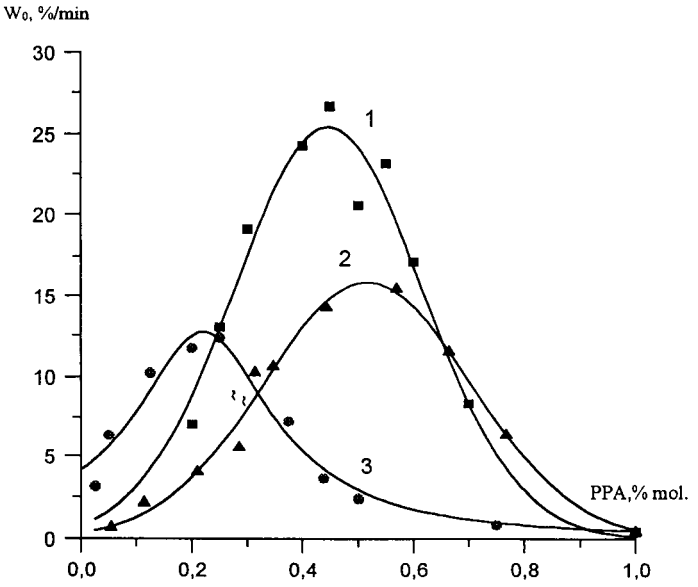
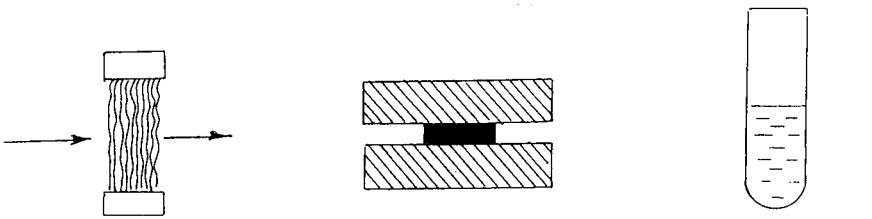


Fig.5. Dependence of reduced initial rate of cyclodehydratation (%/min) on molar fraction of PPA in solution: 1) - DMMA; 2) - N-MP; 3) -Ph-NO_2.



1.Microfiber 2.Monolithic tablet 3. Solution in N-MP (5%)

Fig.6

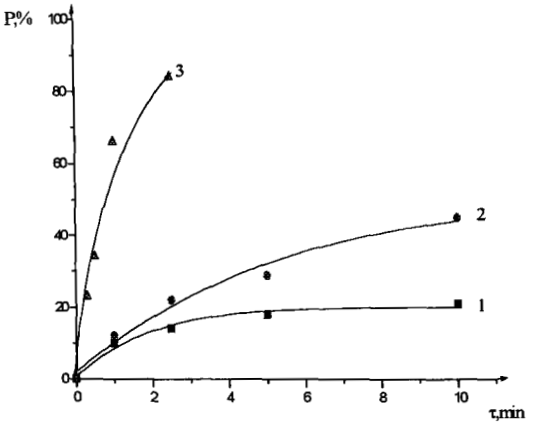


Fig.7. Kinetics of cyclization of PAA-II at 150°C:
1) in solid state (microfiber);
2); in 5%-solution in N-MP; 3) in monolitic tablet

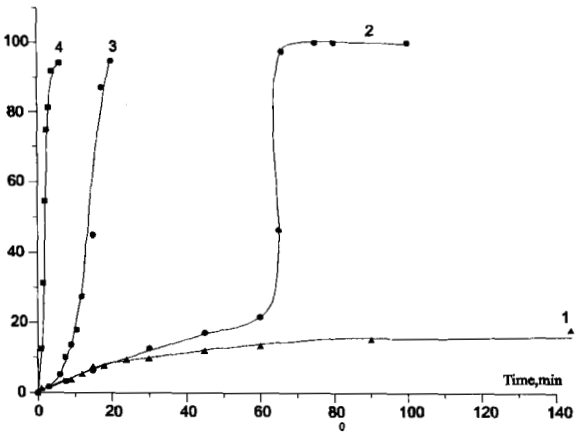


Fig.8 Kinetics of PPA consumption under different conditions (140°C):
1) solid phase (open system); 2) solid phase (closed system);
3) solid phase + H_2O added (2,9%w.) (closed system);
4) solid phase + H_2O added (7,0%w.) (closed system).

autocatalytic action of water released in reaction because this substance doesn't contain any traces of solvent (see the experimental part).

From our point of view, all the data presented above allow to conclude that H-bound amic solvent and the water released during the solid state cyclization reaction under definite conditions (restricted evaporation of volatile products) can lead to the regime of the superfast reaction which proceeds via the mechanism of the common acid catalysis. In our opinion, this effect must be of great importance for the explanation of the large variety of experimental results obtained during the investigation of the imidization reaction in the solid phase in the presence of residual solvents.

CONCLUSION

1. Melts of aromatic carboxylic acids can be used as promising media for the one-step synthesis of polyimides.

2. The cyclization reaction of PAA in concentrated solution at the 1:1 molar ratio can be carried out with an extremely high rate.

3. The mechanism of effect observed is suggested including the common acid catalysis of the reaction with the participation of the anion as a proton transfer agent in the last stage.

4. The catalytic channel can be of great importance also in the solid state PAA cyclization reaction due to the presence of residual solvents and water released. The role of the catalytic channel in the cyclization reaction depends on conditions of evacuation of volatile products (for example, the specific surface of the sample). The better conditions for evaporation, the smaller the role of the catalytic channel.

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