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Devoted to 90th anniversary of birth and light memory of dear teacher, great and a kind man, academician of NAS of RK Bulat Akhmetovich ZHUBANOV

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CATALYTIC SYNTHESIS OF ALICYCLIC POLYIMIDES

Abstract. A brief review of the works on one-stage catalytic synthesis of alicyclic polyimides, copolyimides and compositions based on them in phenol and amide solvents in presence of carboxylic acids, tertiary amines, metal salts, etc., is presented.

Key words: alicyclic polyimide, one-stage synthesis, catalyst, phenol solvent, amide solvent, kinetics.

P. T. Anastas and J. C. Warner formulated 12 principles of green chemistry [1], including: where possible, intermediate products should be avoided; catalytic processes should always be preferred.

In Institute of Chemical Sciences (IChS) work on the catalytic method for the synthesis of alicyclic polyimides was initiated by academician of the NAS of RK B. A. Zhubanov in the 70s of last century. The use of catalysts allowed the synthesis of polyimides, consisting of two stages – polyacylation and polycyclisation, in one volume without isolation of the intermediate product (polyamide acid), accelerate the polycondensation process, increase the molecular mass (MM) of the final polyimide, and obtain a soluble polymer in a number of organic solvents. To intensify the process of formation of alicyclic polyimides, various catalysts and catalytic systems of nucleophilic and electrophilic nature were developed: carboxylic and organophosphorous acids, Lewis acids, metal oxides and hydro-xides, tertiary amines, acid amides, azo compounds, etc. Synthesis was carried out

at temperatures of 160–190 °C in protolytic solvents – phenol and its substituted, by the interaction of alicyclic dianhydrides (tricyclodecene tetracarboxylic acid dianhydride – benzene and maleic anhydride adduct (AB), its alkyl, aryl, halogenated derivatives) with aromatic or aliphatic diamines for 4–6 h [2, 3].

As acid catalysts mono-, di- and tetracarboxylic aliphatic and aromatic acids were studied. The experiments showed that in the presence of carboxylic acids, the reaction proceeds much faster than the non-catalytic reaction and ends in 4–5 h in almost 100% alicyclic polyimide formation [3,4]. At the same time in catalytic conditions, the MM of the polymer increases from 55000 in the absence of a catalyst to 150000–330000. In the series of aliphatic acids, the most effective catalyst is acetic, and in the aromatic series– benzoic acid. From a comparison of the catalytic activity of mono- and dicarboxylic acids, it follows that monocarboxylic acids are the more effective catalysts. The use of tri- and tetracarboxylic acids leads to a certain decrease in the MM (viscosity) of polyimides. This is probably due to the fact that polyfunctional acids act as a competing agent for the basic monomer – the dianhydride of the alicyclic tetracarboxylic acid in a condensation reaction with diamine; as a result the monomeric equivalence in the reaction mixture is impaired and the viscosity of the polymer decreases [2, 5].

In addition to carboxylic acids, a wide variety of organophosphorus compounds such as diphenylphosphine, phenylphosphonic, phenylcyclohexylethynylphosphonic, 2,6-dimethyltetrahydrothiopyranol-4-phosphonic, sulfide-2.6diphenyltetrahydrothio-pyranol-4-phosphonic, sulfone-2,6-diphenyltetrahydro-

thiopyranol-4-phosphonic acid, etc was fused. It was been shown

P[€]OH

that a group structurally similar to the carboxyl group has a predominant role in the catalytic action [2, 5].

Analysis of the results obtained with the use of organophosphorus acids showed that the most active catalyst is diphenylphosphine, which facilitates the formation of an alicyclic polyimide with a MM of more than 700 000. Based on the data on the molecular masses of synthesized polyimides, it can be noted that, in comparison with carboxylic acids, the use of organophosphorus acids leads to the production of polymers with higher molecular mass. In some cases, polyimides synthesized in the presence of organophosphorus acids have fire resistance.

To elucidate the peculiarities of the catalytic action of acids of different nature and acidity in the interaction of alicyclic dianhydrides with diamines, the kinetics of the high-temperature polyacylation reaction were studied [2, 5]. On the basis of the carried studies, it was found that with increasing acid strength in proton-containing solvents, there is a tendency to increase the process speed. Carboxylic acids are less effective catalysts for the reaction of polyacylation compared to organophosphorus.



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Based on the results of a study of the mechanism of this process on the model compounds [6–8], it was concluded that the catalytic effect of acid in real polymer systems probably reduces an increase in chain growth rate due to the catalysis of both monomeric and polymeric provides anhydride groups. This is confirmed by the growth of the rate constant of the reaction with addition of carboxylic acids and a significant increase in the MM of the polyimide in the presence of catalysts [2, 5].

The authors of this article paid much attention to the synthesis of polyheterochain polymers in the presence of Lewis acids, some oxygen-containing compounds (oxide, hydroxide, crystalline hydrate), the formation of which is possible as a result of the interaction of Lewis acids with water in phenolic solvents [2, 3, 9-11].

An analysis of the results obtained on the effect of Lewis acids on the reduced viscosity of tricyclodecene tetracarboxylic acid polyimides showed that the introduction of catalysts into the reaction mixture leads to a significant increase in the molecular mass of the polymer over time and is largely determined by the concentration of the catalyst. It was found that for 4–6 h in the presence of Lewis acids, the viscosity of the polyimide reaches a value of 2–3 dL/g. The use of the catalyst reduces the synthesis time by 2–4 h and increases the MM of the polymer from 60,000 in the absence of the catalyst to 160–460 thousand, depending on the catalyst used. By efficiency in the synthesis of polyimides, the catalysts are arranged in a row: SnCl₄ > TiCl₄ > SbCl₅ > Sn(OH)₄ > FeCl₃ > AlCl₃ > FeO > Fe₂O₃ > AlF₃ \approx ZnCl₂ > FeCl₃·6H₂O.

An investigation of the effect of the nature of the dianhydride as well as the diamine component on the MM revealed that replacing the hydrogen atom in the AB molecule with an isopropyl group leads to a decrease in the molecular mass of the polymer. Based on aliphatic diamines, it was not possible to obtain polyimides with a high MM. It is apparently due to the occurrence of a salt formation reaction between the catalyst and the diamine, which leads to a violation of the equivalence of the starting compounds. In the series of aromatic diamines, characterized by lower pK_{α} values in comparison with aliphatic diamines, polyimides with sufficiently high intrinsic viscosity values were synthesized. Polymers with the highest MM were obtained on the basis of AB and diaminodiphenyloxide in a phenol solution [2, 11].

The study of the kinetics of high-temperature one-step synthesis of alicyclic polyimide in phenolic solvents in the presence of chlorine tin was done. Parallel titration of sample of model compounds – aminogroups with conductometric and carboxyl groups by potentiometric methods, allowed the authors to determine the kinetic parameters of both sequentially parallel stages separately [11–13]. It was found that the catalyst accelerates both processes, but to a greater extent its catalytic effect affects the stage of formation of amido acids.

Based on kinetic studies of the formation of polyimides of tricyclodecene tetracarboxylic acids, a general scheme of the mechanism of catalyzing the acylation of diamines with low-active alicyclic dianhydrides and cyclodehydratation of amidoacids in protolytic solvents in the presence of basic catalysts (tertiary amines) was proposed in [2]. As it was established [2, 14, 15], tertiary amines efficiently accelerate both stages of this process. The effect on the catalytic activity of both the basicity and the spatial structure of tertiary amines was shown. It was found that the most effective catalyst is pyridine having the most spatially accessible nitrogen atom, despite its low basicity in comparison with triethylpyridine, in which the basicity is 2 times higher than that of pyridine or N,N-dimethylaniline, which basicity is equal to pyridine.

As is known, most chemical processes, including the preparation of heatresistant polymers, are carried out in amide solvents, and therefore it was of interest to study the possibility of using these solvents in the creation of tricyclodecene tetracarboxylic acid polyimides in a one-stage catalytic process. Synthesis of polyimides was carried out in N,N'-dimethylformamide (DMFA), N,N'-dimethylacetamide (DMAA), N-methyl-2-pyrrolidone (MP) in the presence of triethylamine and pyridine active catalysts for the synthesis of alicyclic polyimides in high boiling solvents, at a temperature of 120–140 °C [2, 15]. As starting materials, 7-fluoro-, 7-chloro-tricyclodecene tetracarboxylic acid dianhydrides – adduct of fluoro-, chlorobenzen – (AFB, AChB, respectively), AB and aromatic, aliphatic diamines were chosen [16, 17]. It was found that under conditions of catalytic polycondensation, the molecular weight of polyimides synthesized on the basis of highly basicity (aliphatic) diamines was first significantly increased; it can be explained by the growth of MM in the first stage of the process – acylation – due to the catalytic action of tertiary amines, as well as more complete interaction of terminal functional groups during the course of the second cycling stage, which is caused by a decrease in the probability of the side processes of salt formation observed in a two-stage synthesis method [16].

The studies carried out on the effect of the nature of the solvent and tertiary amines on the molecular weight of the polyimide showed that the best results were obtained by carrying out the reaction in DMAA in the presence of triethylamine. In order to obtain a polyimide with optimal properties, a smaller amount of triethylamine is needed in comparison with pyridine, in addition, in its presence the process is completed faster [16–18]. The revealed results on the influence of the nature of the tertiary amine on the molecular weight in the DMAA medium differ from those, as mentioned above, in protolytic solvents, which, apparently, is related to the nature of the solvent.

Comparison of the viscosity characteristics of polymers obtained on the basis of the diamines and dianhydrides studied shows that in the DMAA medium in the presence of tertiary amines, better results are obtained in the case of more reactive AFB and diaminodiphenyl ether (DADPhE) [16,17].

Kinetic studies were carried out to determine the catalytic role of tertiary amines in acylation and cyclodehydration reactions in amide solvents [16, 17]. In studying of acylation reaction, the course of the process was controlled by the rate of decrease in the concentration of terminal amino groups [19], the cyclization process was controlled by the rate of imide cycle formation, fixing the changes in the intensity of the 1380 cm⁻¹ band in IR spectra [20]. It was shown that the introduction of tertiary amines into the reaction system leads to some acceleration of the interaction of the above monomers. The rate constants in the case of triethylamine are almost 2 times higher than the reaction rate constant in the presence of pyridine. It confirms the influence of the basicity of amines on their catalytic activity. At the same time, the molecular weight of the polymers increases by a factor of 2-2.5 compared with the non-catalytic process. It was revealed that the reactivity of dianhydrides is increased in the acylation reaction in polar aprotic solvents in a series: AFB>AChB> AB. It coincides with a number of activities established in other media [15, 21]. The mechanism of action of tertiary amines in this case is due to an increase in the nucleophilicity of the nitrogen properties of the amino group of the diamine.

A more significant catalytic effect of tertiary amines was observed in the study of the cyclodehydration reaction proceeding in parallel with acylation. It is shown that the process of cyclodehydration proceeds is faster in the case of polyamide acids (PAA) based on aliphatic diamines, and the dianhydrides form the following series in their activity: AFB>AB>AChB [16,17].

Complex studies were carried out to obtain polyimides based on tricyclodecene tetracarboxylic acid dianhydrides and diamines in amide solvents in a onestep process in the presence of carboxylic acids [16, 17]. As catalysts, acetic, benzoic, phthalic, pyromellitic and pyridinecarboxylic acids were used [22–24]. It was established that carboxylic acids under the conditions of a single-stage synthesis cause the formation to accelerate and increase the molecular mass of polyimides. Their accelerating effect is observed both at the stage of acylation and cyclodehydration. Monocarboxylic aromatic acid (benzoic) is more effective than di- and tetracarboxylic and acetic acids; its presence leads to an increase in the polymer viscosity by 2–3.5 times. The use of an aliphatic acid and an increase in the number of carboxyl groups in the acid leads to a certain decrease in the molecular weight due to their competing interaction with the diamine, accompanied by the formation of an unreactive salt [20, 25].

It is shown that the most high-molecular polymers are formed on the basis of AFB and DADPhE in DMAA, then AB and AChB, respectively. It should be noted that if in a two-stage method, polymers based on the AFB, AChB, AB and aliphatic diamines are formed with an intrinsic viscosity value of 0.24–0.30 dL/g in one-stage synthesis in the presence of carboxylic acids; the viscosity of the polymers was increased in 3–4 times [16,17].

Particular attention was paid to studies of the effect of pyridinedicarboxylic acids on the process. It is connected with the great uniqueness of these compounds, which have two different functional groups in the structure. To determine the catalytic role of isonicotinic acid, a comparative study of the kinetics of the process of polyacylation of DADPhE with AB dianhydride and the imidization of PAA in the presence of isonicotinic, benzoic acids, pyridine and without a catalyst in DMAA was carried out. It is shown that the rate constants for the reaction of polyacylation in the presence of isonicotinic acid are more than 2 times higher than those in its absence. In the presence of benzoic acid and pyridine, taken for the purpose of modeling and differentiating the functional groups of isonicotinic acid, the rate of this reaction is lower in comparison with pyridine carboxylic acid. To a greater extent, isonicotinic acid affects the process of conversion of the polyamide acid into polyimide. In addition, the rate of imidization reaction in its presence is higher in comparison with benzoic acid and pyridine [16, 23].

When carrying out research to improve the physicomechanical properties of alicyclic polyimides using plasticizers – phosphorus-containing compounds (triphenyl- and tricresyl phosphate), it was found that in addition to an extreme change in these properties of polymers, an increase in the intrinsic viscosity occurs. It was found that the viscosity of the polyimide based on AB and DADPhE in the presence of 5 mas. % triphenyl phosphate (TPP) in DMAA reached a value of 1.8 dL/g. The study of the kinetics of the formation of alicyclic polyimide in the presence of TPP revealed that this compound affects both the acylation reaction and the imidization reaction. At the same time, the increase in the rate of cyclodehydration is greater in comparison with the rate of the acylation reaction, and the values of the apparent activation energy of both stages were decreased [16].

The accumulated experience in the one-stage catalytic synthesis of alicyclic polyimides was used in further studies.

A modification of an alicyclic polyimide based on tricyclodecene tetracarboxylic acid dianhydride and 4,4'-diaminodiphenyl ether with polyaniline (PANI), polyaniline, doped nonylnaphthylsulfonic acid (PANI/NNSA), polyaniline composite with TiO₂ and SnO₂ (PANI/TiO₂, PANI/SnO₂) was done. It was found that the presence of polyaniline leads to a change in the basic properties of polyimide films. There is an increase in the ability of the film to metallization. This is due to the formation in the metallization process of metal clusters, in particular of silver, which are larger in size than metal particles in a polyimide film obtained in the absence of polyaniline. Optical and electrical properties of silver-metallised polyimide films undergo more significant changes. The specific volume of resistance for polymer non-metallized compositions with polyaniline is changed by two orders of magnitude [26–30].

When studying the features of synthesis of polyimide in a polar aprotic solvent of amide type (DMAA) in the presence of PANI, and PANI/NNSA, as well as PANI/TiO₂ composite, it has been found that these forms of the electrically conductive polymer have a catalytic effect on the course of the polyimide formation in addition to affecting the basic properties. It is shown that the polymer with higher viscosity characteristics is formed in the presence of PANI/SnO₂. This reduces the duration of the synthesis in comparison with the formation of the polymer in the absence of a modifier for 70 min, a decrease in temperature from 140 to 100 °C [26-30]. The kinetics of single-stage synthesis of alicyclic polyimide in the presence of PANI, PANI/NNSA, and nanocomposites PANI/SnO₂, PANI/TiO₂ in DMAA was studied. It was found that the modifiers have practically no effect on the acylation reaction, their activating action is noticeably manifested at the stage of cyclodehydration. The rate of the imidization reaction in the presence of PANI is lower in comparison with the doped polyaniline, which is due to the influence of the acid groups of the dopant. It was found that PANI/SnO₂ is more active in the polycondensation process.

The optimal method for the preparation of polyimides based on tricyclodecene tetracarboxylic acid dianhydrides and aliphatic diamine is carrying of synthesis in polar aprotic solvents of amide type in the presence of catalytic amounts of isonicotinic acid [16, 23]. Typically, polyimides are formed with an imidization degree of about 80–85 % and an intrinsic viscosity of 0.85–0.92 dl/g (starting solvents for the synthesis are – DMAA and MP).

In order to increase the viscosity characteristics of the polymer, a different amount of polyamidoacids (PAA) of the aromatic structure, based on the pyromellitic, benzophenone and diphenyloxydetracarboxylic acid dianhydrides with DADPhE, was introduced at the completion stage of the synthesis, since it was previously shown that in the presence of acid catalysts, the molecular weight of the alicyclic polyimide significantly increases [2, 16]. Studies have shown that 15–17 % by weight of PAA can be introduced into the polyimide solution as much as possible; it 5–7 % higher compared to aromatic diamine-based polyimides. This can be explained by the greater solubility of prepolymers of the aromatic structure in this polymer system and their better compatibility with polyimides with aliphatic links in the backbone. It was found that by modifying polyimides of PAA based on pyromellitic dianhydride ([η] = 1.34 dL/g) higher

characteristics are achieved. These studies for polyimide based on aliphatic diamine were performed for the first time [31].

In production of polymers for microelectronics, the manufacture of integrated circuits, dielectric coatings, the task is to create materials with enhanced adhesion of the metal layer to the polymer substrate. One way to achieve the necessary adhesion values is the modification of polymers by other highmolecular compounds with higher adhesion properties. To this end, new filmforming polymers were synthesized, which were copolyimides based on alicyclic dianhydrides (AB, AFB, AT) from 3,3',4,4'-benzophenone tetracarboxylic acid (BZPh) and DADPhE in amide solvents (DMFA, DMAA, MP) in the presence of triphenyl phosphate. It was found that polymers with a higher (co)polymers viscosity values are formed at a temperature of 120 °C in DMAA. In the presence of TPP, the viscosity of copolyimides increases from 0.52–0.65 dL/g in its absence to 1.0–1.45 dL/g, depending on the nature of the alicyclic dianhydride; the duration of the synthesis is reduced by 1.5–2.0 h. From BZPh, this method failed to produce a homopolymer with a sufficiently high molecular weight [32].

Earlier it was shown that the realization of a polycondensation process in phenolic type solvents in the presence of certain metal salts led to the production of alicyclic polyimides with high molecular weights [9]. Such studies in polar aprotic solvents of the amide type have not been carried out. Since most chemical processes, including the synthesis of heat-resistant polymers, have been carried out in amide solvents in recent years, it has been of interest to study the effect of metal salts (FeCl₃, CoCl₂, NiCl₂) on the one-step process of obtaining alicyclic polyimides in DMAA. The carried out researches have shown appreciable influence of metals chlorides on a course of polyimide formation. It was found that a more significant effect is achieved for FeCl₃, which has pronounced acid properties [33, 34].

Research on the development of new polymeric metal-containing compositions from the copolyimides of the arylcyclical structure based on 4,4'-diaminodiphenyl ether, tricyclodecene tetracarboxylic dianhydrides and 3,3',4,4'diphenyloxydetetracarboxylic acids (CPI-1), and tricyclodecene tetracarboxylic dianhydrides and 3,3',4,4'-benzophenone tetracarboxylic acids (CPI-2) has been carried out. Metal-containing compositions were obtained by a polycondensation method during one-step synthesis of copolyimides in MP and DMAA in the presence of FeCl₃, CoCl₂, and NiCl₂. It has been found that with higher values of the reduced viscosity (1.56 dL/g), CPI-1 is formed in the MP solution in the presence of 2.0 mas. % iron chloride and the ratio AB: DFO = 90: 10 mas. %. The duration of the process is reduced by 1.5 h in comparison with the process in the absence of FeCl₃. The salts of cobalt and nickel have a less pronounced catalytic effect. Similar results were obtained for CPI-2, for which the maximum value of the reduced viscosity in the presence of an iron salt is 1.32 dL/g.

For practical application of new polymer compositions, such properties as thermal stability, resistance to aggressive agents, high level of dielectric parameters and their stability under the influence of various factors are of great importance. Thermogravimetric analysis of the film samples in air atmosphere revealed that if after complete combustion residue polyimide is 5-7 %, while in case of compositions with metal salts residue increases and reaches 10-12 %, which indicates the content of the metal compounds. The main values of mass loss of samples of metal-containing compositions are fixed at temperatures of 15-20 °C higher than in the unmodified API.

The study of the electrical characteristics of the films showed that, at the above amounts of metal salts, they differ from the properties of the initial PI. The value of the permittivity that is more sensitive to the presence of any impurities by the parameter changes to a greater degree. The tangent of the dielectric loss angle for films with a thickness of 45 ± 5 µm is 0.007–0.012 (at a frequency of 1 kHz), the minimum value of the breakdown voltage is 130–150 kV/mm (the maximum value is 170–180 kV/mm). The dielectric constant increases to 6.3–7.8. For the initial PI, these values are 0.001–0.003, 150–165 kV/mm and 2.8–3.1, respectively. When the content of metal the composition is 3.0–5.0 mas. %, the values of the specific volume and surface resistances also vary from 3.4·10¹⁵ Om·cm and 2.1·10¹⁴ Om to 2.1·10¹³ Om·cm and 0.5·10¹² Om, respectively [33, 34].

To study the effect of copper salts (CuCl, CuCl₂, CuSO₄) on the one-stage process of obtaining alicyclic polyimide and its copolymer with aromatic dianhydrides in MP work was carried out it revealed catalytic effect on the course of polymer formation [35]. Moreover, a more significant effect was noted for CuCl₂ at a temperature of 140 °C. The catalytic effect of copper salts can be explained as by the occurrence under the conditions of synthesis of their partial hydrolysis to the corresponding acid as and copper hydroxide due to the release of water during cyclodehydration of polyamide acid groups. The resulting acid promotes as the course of the polycondensation process by the mechanism of acid catalysis as and the formation of polyimide with higher values of given viscosity compared with the reaction in the absence of copper salts. At the same time, polymer formation is completed faster. Thus, in the presence of 2.5 mas.% CuCl₂, the alicyclic polyimide is formed at a viscosity of 1.35 dL/g in 5.5 hours, while in the absence of a metal salt, these values are 0.70 dL/g and 7.0 h respectively. In the preparation of aryl arylcyclic copolyimide, a polymer with higher viscosity characteristics of 1.50–1.60 dL/g was prepared in the presence of 1.50 mas. % CuCl₂.

It is known using of CuCl and CuSO₄ as catalysts in organic synthesis, however, they were not used in the preparation of polyheterocycles. The authors of this work carried out research on the effect of these salts on the one-stage synthesis of polyimides of the alicyclic structure. It was found that the final polymer with a viscosity value of ~1.2 dL/g is formed in the presence of these salts (1.75 and 2.6 mas. % respectively). The degree of imitation of polyimide, calculated from the main bands of imide cycles of the corresponding IR spectrum, is ≈ 100 %. It is shown that by the introduction of copper-containing compounds in alicyclic polyimide, the volume and surface are resistances decreased. It is one

of the methods for eliminating of the accumulation of excessive static electricity. It has been found that copper-containing film compositions are more resistant to the action of an aggressive acid reagent compared to the initial polyimide [35, 36].

Studies on the production of composite films from alicyclic polyimide and various forms of montmorillonite [natural montmorillonite (Mm), its alkylated form (AMm) and 3-aminopropyl-3-methoxysilane-modified alkyl montmorillonite (AOMm)] have shown that films obtained from polyimide with Mm or AMm, have low values of tensile strength and elasticity; most of the films were fragile.

With the use of AOMm, this could be avoided. To assess the effect of the mineral on the formation of polyimide by a single-step method, course of acylation and cyclodehydration reactions in the absence and presence of AOMm in amide solvents was studied. It is determined that the reaction rate in DMAA is higher than in MP, which corresponds to the previously obtained results. The presence of AOMm does not affect the rate of formation of PAA at the stage of imidization conversion of amido acid groups into imide cycles is accelerated approximately in 2 times. The acceleration of imidization is due to the formation of silicate ions [HSiO₄] formed by hydrolysis of AOMm by the mechanism of acid catalysis [37].

The information given in the present work on the catalytic one-stage synthesis of soluble alicyclic polyimides in phenolic and amide solvents indicates the importance of studies carried out in one of the main fields of polymer chemistry. The developed regularities and features of one-stage synthesis of polyimides of tricyclodecene tetracarboxylic acids are the basis for the development of new high-molecular compounds and materials based on them.

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Резюме

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АЛИЦИКЛДІ ПОЛИИМИДТЕРДІҢ КАТАЛИТИКАЛЫҚ СИНТЕЗІ

Алициклді полиимидтер, сополимидтер сонымен қатар осылардың негізіндегі композицияларды фенолды және амидті еріткіштердегі металл тұздары, үшіншілік аминдер, карбон қышқылдары, т.б. қатысында бір сатылы каталитикалық синтездеу бойынша жұмыстардың қысқаша шолуы берілген.

Түйін сөздер: алициклді полиимид, бір сатылы синтез, катализатор, фенолды еріткіш, амидті еріткіш, кинетика.

Резюме

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КАТАЛИТИЧЕСКИЙ СИНТЕЗ АЛИЦИКЛИЧЕСКИХ ПОЛИИМИДОВ

Приведен краткий обзор работ по одностадийному каталитическому синтезу алициклических полиимидов, сополиимидов и композиций на их основе в фенольных и амидных растворителях в присутствии карбоновых кислот, третичных аминов, солей металлов и др.

Ключевые слова: алициклический полиимид, одностадийный синтез, катализатор, фенольный растворитель, амидный растворитель, кинетика.