

p-Xylylenediamine and Its New Polyimides

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Abstract

p-Xylylenediamine was synthesized with high yield through a hydrogenization of dinitrile of terephthalic acid. The effect of catalyst and solvent on the yield of the product was studied. The hydrogenization was carried out on skeletal catalysts based on alloy of Reney nickel Ni:Al (1:1) in aliphatic alcohols (C₁-C₄) at 4.0 MPa and 60°C. New alkanearomatic polyimides were synthesized by one-step polycondensation of *p*-xylylenediamine and dianhydride of tricyclodecentetetracarboxylic acid in the presence of isonicotinic acid as a catalyst in nonpolar amide solvents at 110-120°C. The films based on the synthesized polyalkanimides are stable with 70-80 MPa breaking strength and 30-40% elongation. The glass transition temperature of the polymers is within 265-280°C temperature range, the temperature of decomposition is above 340°C. The tangent of dielectric loss of the films at 1 kHz and 25°C is 0.002-0.004, the dielectric permittivity is about 3.22-3.35.

Introduction

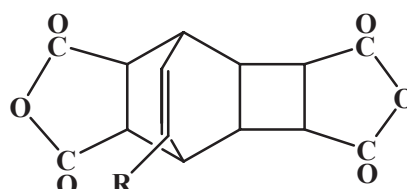
Polyalkanimides (PAIs) is a promising material for electro- and radiotechnic utilization [1,2]. Being between aromatic and aliphatic polymers, PAIs possess properties of both type of polymers, having aromatic polyheterocycles with aliphatic groups. The introduction of a methylene chain to a polymer leads to the decrease of its melting point but promotes an increase in hydrolysis stability. That insures easy production such polymers in industry [2].

There is a number of PAIs on the basis of pyromellite dianhydride and aliphatic diamines – deca-, dodecamethylenediamines and their mixtures. They manifest good performances during long period of their exploitation with high temperature above 200°C [2,3]. However, we consider in this paper the synthesis of PAI based *p*-xylylenediamines (*p*-XDA) with various dianhydrides.

Earlier we have reported the development of the new monomer – dianhydride tricyclodecentetetracarboxylic acid at the Institute of Chemical Sciences (Scheme 1). On the Scheme 1 R: H (Adduct of benzene - AB), F (Adduct of fluorobenzene - AFB), Cl (Adduct of chlorobenzene - ACB), which are initial com-

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pounds for the synthesis of various thermoresistable polymers, including polyimides [4,5].



Scheme 1

Institute of New Chemical Technologies and Materials developed the new procedure for the preparation of *p*-XDA with high yield on Reney nickel catalysts. This paper describing synthesis of polyimides on its basis and some physical properties of materials from the polyimide.

Experimental

Purification of original agents and solvents was carried out according to the standard procedures.

IR-spectra were recorded on Jasco IR-810 as KBr disks for monomers and films for polymers.

Viscosity of 0.5 wt.% polymer solutions was measured with Ubellode capillary viscosimeter at 25°C in DMSO.

Thermogravimetric analysis was performed with

TGA Metler Toledo at 8°C per min and DSC Metler Toledo for T_g analysis. The loss of weight was calculated from TGA data at loss of 0, 5, 10 and 50% of weight (T_0 , T_5 , T_{10} , T_{50}).

Breaking strength σ , relative elongation l , tangent of dielectric loss angle $\text{tg}\delta$, and dielectric permeability ϵ^1) were measured according standard procedures using GP-3 machine [6,7].

p-XDA was synthesized by catalytic reduction of *p*-dinitrile of terephthalic acid (*p*-DTA)^x. The hydrogenization was carried out in the kinetic reactor under high pressure [8] with control of hydrogen supply [9]. An alloy of Reney nickel based on Ni:Al (1:1) was used as a catalyst. The reactor was a cylinder with volume of 0.15 L under shaking with frequency of 600 per min. 50 mL methanol as a solvent saturated by ammonia at cold conditions. The catalyst (0.5 g) was immersed in the reactor under the solvent with following gradual injection of 1.43 g of *p*-DTA. The hydrogenization was carried out until finishing of its absorption from gas phase by the solvent.

The composition and the structure of *p*-XDA were identified by element analysis and IR-spectroscopy.

Measured: $C_8H_{12}N_2$, %: C 70.26; H 8.84; N 19.92.

Calculated: %: C 70.60; H 8.09; N 20.57.

IR-spectra cm^{-1} : 1500 (benzene ring), 1670, 3420 - NH_2 -group, 2920 - CH in $-\text{CH}_2$ -group.

Melting point is 34.5-35°C (ref. 35°C [8]).

Dianhydride of tricyclo-[4,2,2,0]^{2,5}-dec-7-en-3,4,9,10-tetracarboxylic acid (photoadduct of benzene and maleic anhydride - AB), and dianhydrides of 7-fluorotricyclo-[4,2,2,0]^{2,5}-dec-7-en-3,4,9,10-tetracarboxylic acid (AFB) and 7-chlorotricyclo-[4,2,2,0]^{2,5}-dec-7-en-3,4,9,10-tetracarboxylic acid (ACB), synthesized according to our procedure [10,11], were purified 3-4 times washing in hot acetone during 2 hrs. The precipitated monomers were filtered followed drying at 80-90°C.

AB m.p. – 250-252, AFB m.p. – 312-314, and ACB m.p. – 302-304°C.

Composition of monomers is coincided with theoretical calculation, and their melting points are in good agreement with the data reported [10,11]. Solvents – N,N¹-dimethylformamide (DMFA), N,N¹-dimethylacetamide (DMAA), N-methyl-2-pyrrolidone (MP), dimethylsulphoxide (DMSO) were dried before the use.

Synthesis of polyimide based on dianhydride tricyclo-[4,2,2,0]^{2,5}-dec-7-en-3,4,9,10-tetracarboxylic acid and 4,4¹-diaminodophenyl ester: 13.71 g (0.05 mol) AB, 5.20 g (0.05 mol) *p*-XDA, and 0.09 g (5

wt.% of both monomers) isonicotinic acid were mixed in 56.9 mL DMAA in a three-neck flask supplied with an inert gas. The flask was placed in the oil bath at 50°C with 15-min stirring. Then within 20 min the temperature was gradually increased up to 110°C and the flask was kept for another 2 hrs. After cooling down until the room temperature, polyimide was precipitated by acetone and the final precipitate was washed twice and dried at 80-90°C until the constant weight.

The resulting polymer has the composition in accordance with the theoretical calculation. Polyimide films were prepared by casting of their 25 wt.% DMAA solution on a glass followed drying at 80°C within 20 min and final drying during 1 hr at 150°C.

Polyimide based on *p*-XDA and ACB was prepared with a yield 98.5-99.0% and degree of imidization about 100%.

Results and Discussion

The catalytic hydrogenization of nitriles is a complicated process with a number of parallel-sequent reactions [8,13,14]. The reduction of *p*-DTA was carried out in the presence of catalysts, which are summarized in Table 1.

Table 1

Hydrogenization of *p*-DTA on skeletal Ni catalysts

No	Composition of initial alloy before leaching (wt.%)	Duration (min)	<i>p</i> -XDA yield (wt.%)
1	Ni:Al = 50.0:50.0	140	73-75
2	Ni:Ti:Al - industrial Al-50-53.5; Ni-44-46.5; Ti-2.2-2.8	50	90-92
H-5 catalyst			
3	Ni:Me:Al = 47.5:2.5:50.0	41	94-95
4	Ni:Me:Al = 45.0:5.0:50.0	32	97-98

Hydrogen pressure – 4 MPa, temperature 60°C

The data of the hydrogenization of *p*-DTA to *p*-XDA was shown as a reference in Table 1 and 2. Table 1 proves that catalysts Ni-Ti and H-5 are the most active and selective in comparison with Ni-skeletal one. The yield of the product on Ni-Ti is 90-92% and on H-5 is about 97-98%. From this point we carried out the synthesis with H-5 catalyst. It is known that the hydrogenization of aromatic dinitriles is mostly affected by the type of solvent and the best

results were achieved in the presence of methanol [14].

In this paper we studied especially the effect of solvent on the hydrogenization of *p*-DTA on H-5 catalyst in the presence of ammonia. The data are listed in Table 2. It is known that the maximal yield is reached at stoichiometric ratio of components on a catalyst surface [15]. That was taken into account during the synthesis.

The highest yield was obtained at ratio of nitrile: ammonia = 1:3 in alcohol solution.

The presence of aminonitriles among the products of nitrile hydrogenization points out that sequent reduction of nitrile groups occurs [14,16,17]. There is a reducing rate of *p*-DTA hydrogenization on H-5 catalyst accompanied with sorption of the calculated amount of hydrogen [18]. The hydrogenization at appropriate speed occurs until beginning sorption of 2 mol hydrogen per 1 mol of dinitrile. Then the rate decreases and the following hydrogen reacts at lower speed [17,18].

The hydrogenization of *p*-DTA could be schematically described as a hydrogenization of a nitrile group of dinitrile with the formation of aminonitrile (cyanbenzylamine). Then it forms a final *p*-XDA after hydrogenization of the second nitrile group.

The increase of catalyst activity could be achieved by changing of by different ratios of nickel and alumina components from NiAl₃ and Ni₂Al₃ alloys to NiAl₃ one [19]. Thus, the product yield and the reaction rate are strongly dependent on the type of catalyst and synthesis conditions. High activity and selectivity of H-5 catalyst are due to high degree of its hydrogen sorption, which is 2-3 times higher than that of Ni one [19].

Dianhydrides of tricyclodecentetracarboxylic acid are the initial monomers for the preparation of various thermostable polymers, including polyimides

[20,21]. Earlier polyimides based on *p*-XDA and the dianhydride could not be synthesized efficiently due to the absence of any effective synthetic procedures (Scheme 2).

In this work the polyimides were polymerized by one-step polycondensation in polar non-proton solvent of amide type in the presence of isonicotinic acid (pyridine-4-carboxylic acid) as a catalyst. This agent as any pyridinecarboxylic acid speeds up essentially the polycondensation [5]. It is known that the polyheterocycles prepared in liquid medium show an appropriate solubility in comparison with poly-(amide acid)s synthesized in solid phase. Among DMFA, DMSO, MP and DMAA solvents, the last one manifests the highest viscosity of synthesized polyimide solution. For instance, the viscosity of 0.5 wt.% solutions of fluoro-containing polyimide at optimal conditions is: DMFA – 0.45; DMSO – 0.75; MP – 0.53; and DMAA – 1.23 dL per g. The further investigations were carried out using DMAA solvent.

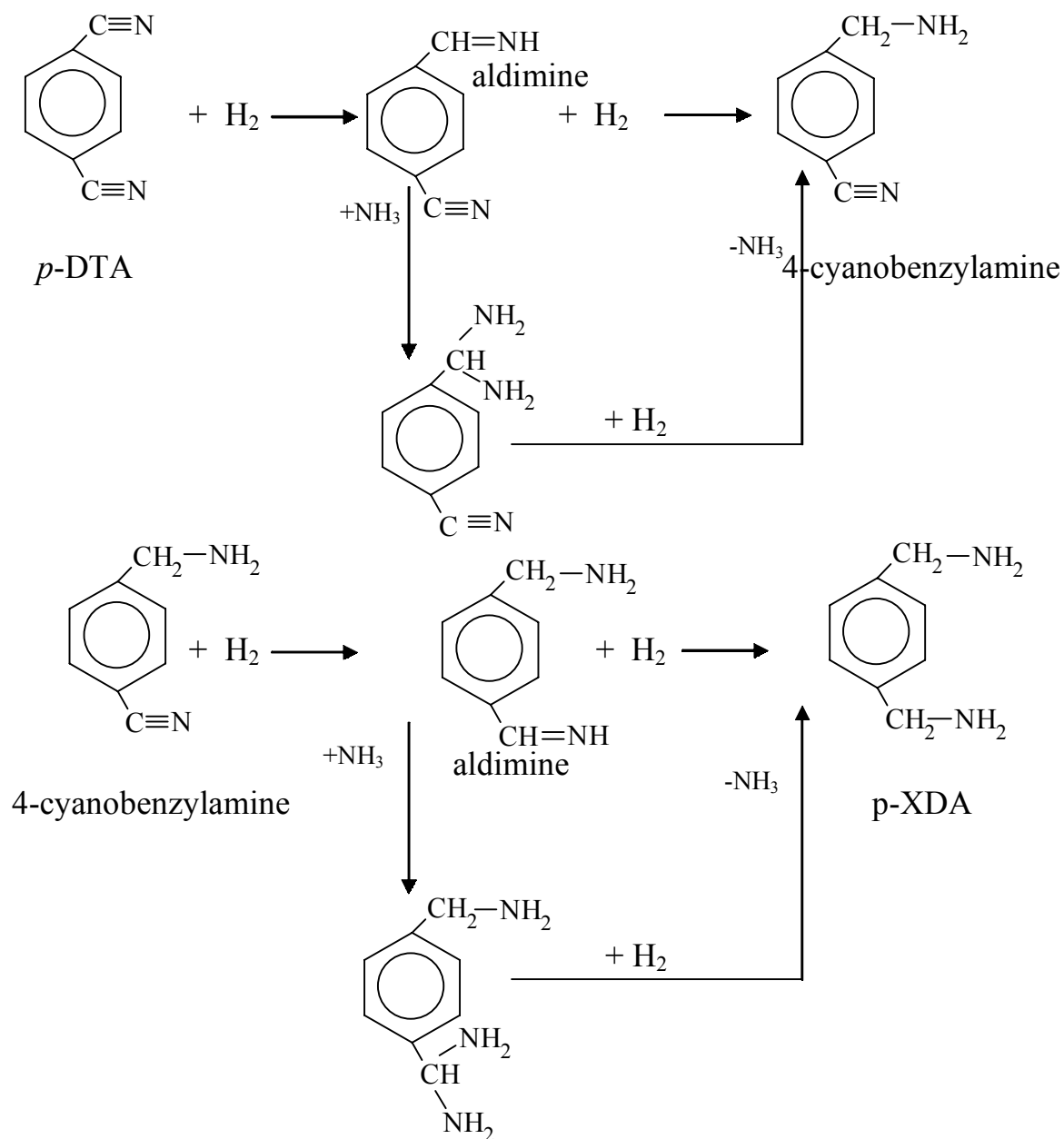
The study of interaction between *p*-XDA and alicyclic dianhydrides shows that the most active dianhydride is AFB. That is due to the presence of fluorine atom at the endoethylene bond. Fluorine having the highest electronegativity is a reason of the increase of electrophilicity of the anhydride groups. The activity is typical for AB and ACB [10]. The polymerization was carried out at 110-120°C within 2-2.5 hrs with 100% imidization. The viscosity of resulting PAIs is 0.94-1.23 dL per g range. The optimal conditions of PAI synthesis are summarized in Table 3 in comparison with the data on two-step synthesized polyimide based on AFB and *p*-XDA (number 4). The one-step polyimides show higher performances of their viscosity than two-step one.

The composition and the structure of PAIs were identified by elemental analysis and IR-spectrometry. There are bands of polyimides in IR-data at 1775

Table 2
Effect of solvent on hydrogenization of *p*-DTA

No	Solvent: alcohol + ammonia	Catalyst Ni-Ti (\approx 3% Ti)		Catalyst H-5	
		Duration (min)	<i>p</i> -XDA yield, (wt.%)	Duration (min)	<i>p</i> -XDA yield, (wt.%)
1	methanol	50	90-92	32	97-98
2	ethanol	62	89-91	41	96-97
3	propanol	69	90-91	48	96-97
4	n-butanol	71	90-91	53	96-97

Hydrogen pressure – 4 MPa, temperature 60°C.

**Scheme 2****Table 3**

Synthesis of PAI by one- and two-step polycondensation

No	Dianhydride	C _{mon} /C _{catalyst}	T, °C	Time, hr	η (0.5%, DMSO, 25°C), dL/g
1	AFB	40/2.0	120	2.2	1.23
2	AB	40/2.5	120	2.5	1.10
3	ACB	40/2.5	110	2.5	0.94
4	AFB 2-step	20/0	25	2.5	0.32

and 1715 (carbonyl of imide cycle), 1365-1370 (tert-N) and 715-725 cm⁻¹ (imide cycle). Fluoro-contain-

ing PAI shows C-F peak at 1260-1300 and chloro-one – C-Cl at 860 cm⁻¹. The absorbance bands of

non-cycled amide acids are not present.

The presence of alicyclic structure as well as fluorine and chlorine atoms in the case of AFB and ACB gives rise to their decreased the glass transition point. The presence of halogen atom decreases the glass transition point of PAI by 10-15°C approximately, besides a decrease by chlorine is more significant than that by fluorine presence (Table 4).

Table 4
Thermal properties of PAI

Poly- mer	T _g , °C	Temperature of weight loss, °C							
		air				argon			
		T ₀	T ₅	T ₁₀	T ₅₀	T ₀	T ₅	T ₁₀	T ₅₀
AB	270	340	380	420	530	380	440	470	580
ACB	280	325	350	400	500	360	415	450	545
AFB	265	335	365	415	510	355	435	460	560

The temperature of PAI decomposition in air is the narrow range within 325-340°C, however halogen-containing polyimides decompose at lower temperature. The thermal stability of PAI in argon is obviously higher. The lag between T₀ and T_g is about 45-70°C that points out the possibility of their processing under pressure.

The synthesized polymers demonstrate a good viscous performance, and an appropriate solubility. That makes able to cast excellent films with breaking strength 70-80 MPa and elongation 30-40%. Module of elasticity in the dependence of modifiers (triphenylphosphate, dimethyl- and dibutylphthalate, dimethylterephthalate et al.) is limited within 2700-3400 MPa

The tangent of dielectric loss angle at 1 kHz, 25°C and zero humidity is 0.002-0.004, and dielectric permittivity is about 3.22-3.35. Low performance of dielectric permittivity is due to the effect of both alicyclic unit and electronegative halogen atom. That shows the better results in the case of aromatic polyimides.

Conclusions

p-XDA with high yield was synthesized by hydrogenation of *p*-DTA in the presence of skeletal catalyst based on Reney nickel from Ni:Al alloys in aliphatic alcohol solvents. A series of new non- and halogen-containing PAI were polymerized by poly-

condensation of *p*-XDA with various dianhydrides of tricyclodecentetracarboxylic acid in polar non-proton solvents of amide type at the presence of isonicotinic acid as a catalyst. These polymers demonstrate good physico-mechanical and dielectric performances as well as a high thermal stability. Due to the high content of functional groups these PAIs could be a good candidate for the preparation of metal-containing polyimide films for application in electronics and aerospace industry.

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