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p-Xylylenediamine and New Polyimides Derived from It

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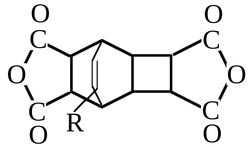
Abstract—*p*-Xylylenediamine was prepared by hydrogenation of terephthalodinitrile; the conditions ensuring high yield of this monomer were found. The influence exerted by the catalyst and solvent on the diamine yield was examined. Single-step polycondensation of *p*-xylylenediamine with tricyclodecenetetracarboxylic dianhydrides in the presence of catalytic amounts of isonicotinic acid gave a series of new polyimides consisting of aliphatic and aromatic fragments.

Polyalkanimides show promise as materials for electrical and radio engineering [1, 2]. The interest in these polymers is not occasional. Occupying an intermediate position between aromatic and aliphatic derivatives, they combine the advantages of both. Introduction of methylene units into the backbone decreases the melting point, enhances the resistance to hydrolysis, and imparts to the polymers other valuable properties allowing their processing with commercially available equipment [2].

A series of polyalkanimides (PAIs) derived from pyromellitic dianhydride and aliphatic diamines (deca- and dodecamethylenediamines, and also their mixtures) have been prepared; these materials shown long service life at temperatures of up to 200°C [2, 3]. At the same time, PAIs can also be prepared from *p*-xylylenediamine (*p*-XDA) and other anhydrides.

In this study, we prepared dianhydrides of cyclodecenetetracarboxylic acids: tricyclo[4.2.2.0^{2,5}]dec-7-ene-3,4,9,10-tetracarboxylic dianhydride (product of photochemical addition of maleic anhydride to benzene, AB) and its 7-fluoro (AFB) and 7-chloro (ACB) derivatives, which are starting compounds for preparing a wide set of heat-resistant polymers, including polyimides [4, 5]:



where R = H (AB), F (AFB), Cl (ACB).

It is known that the prospects for application of polymeric materials are determined by numerous factors, with the availability of the starting monomers being of major importance. We have developed a procedure for preparing *p*-XDA in quantitative yield, which allowed us to begin studies of synthesis of new PAIs derived from *p*-XDA and alicyclic dianhydrides.

Here we report the features of synthesis of *p*-XDA and polyimides derived from it.

EXPERIMENTAL

The starting compounds and solvents were purified by common procedures. The IR spectra were recorded on a Specord IR-25 spectrometer. The monomer samples were prepared as KBr pellets, and the polymer samples, as 3–5-μm films. The reduced viscosities of 0.5% solutions of polyimides were measured with an Ubbelohde viscometer at 25°C in DMSO. The TG and DTA curves were recorded simultaneously on an MOM derivatograph (Hungary) at a heating rate of 8 deg min^{-1}. From the TG curves, we calculated the temperatures of the onset of weight loss and of 5, 10, and 50% weight loss (T_0, T_5, T_{10}, and T_{50}, respectively).

The physicomechanical (tensile strength σ, relative elongation *l*) and dielectric (dielectric loss tangent tan δ, relative dielectric permittivity ε') characteristics were studied under standard conditions by published procedures [6, 7].

p-Xylylenediamine was prepared by catalytic reduction of terephthalodinitrile (TDN)[1] in a high-pressure kinetic unit [8] allowing monitoring of the hydrogen uptake in unit time [9]. As catalysts we used promoted catalytic alloys whose base component was Raney nickel; the catalysts were prepared by leaching of the corresponding alloys with Ni : Al ≈ 1 : 1. A 0.5-l long-necked stainless steel vessel was shaken at a frequency of 600–700 one-side rockings per minute. A 0.5-g portion of the catalyst was loaded under the layer of the solvent (50 ml of methanol preliminarily saturated with ammonia under cooling; nitrile : ammonia ratio 1 : 3). Then 1.43 g of TDN was added. Hydrogenation was performed until the H_2 uptake stopped.

p-XDA was identified by elemental analysis, melting point, and IR spectra.

Found, %: C 70.26, H 8.84, N 19.92.
$C_8H_{12}N_2$.
Calculated, %: C 70.60, H 8.09, N 20.57.

IR spectrum, ν, cm^{-1}: 1500 (benzene ring); 1670, 3420 ($-NH_2$ groups); 2920 (–CH in $-CH_2$ group); mp 34.5–35°C (published data [8]: 35°C).

AB, AFB, and ACB were prepared by published procedures [10, 11] and purified by three- or fourfold 1.5–2.0-h treatment with hot acetone under stirring. The precipitate of the monomers was filtered off and vacuum-dried in an oven to constant weight at 80–90°C.

AB: equivalent weight 68.5 (calculated 68.5), mp 250–252°C; AFB: equivalent weight 73.04 (calculated 73.04), mp 312–314°C; ACB: equivalent weight 77.12 (calculated 77.12), mp 302–304°C. The elemental analyses were consistent; the melting points agreed with published data [10, 11]. The solvents [dimethylformamide, DMF; dimethylacetamide, DMA; *N*-methyl-2-pyrrolidone, MP; dimethyl sulfoxide, DMSO] were dried over 4-Å molecular sieves.

The polyimide derived from AB and *p*-xylylenediamine was prepared as follows. A three-necked flask equipped with a stirrer and an inlet tube for inert gas was charged with 13.71 g (0.05 mol) of AB, 5.20 g (0.05 mol) of *p*-XDA, 0.09 g (5 wt % relative to the sum of the monomers) of isonicotinic acid, and 56.9 ml of DMA. The mixture was heated on an oil bath (50°C) for 15 min with stirring, after which the temperature was raised to 110°C over a period of 20 min, and the mixture was stirred for additional 2 h. After cooling to room temperature, the polyimide was precipitated with chemically pure acetone, and the precipitate was washed with two portions of acetone and vacuum-dried in an oven at 80–90°C to constant weight.

Table 1. Conditions of TDN hydrogenation on Raney nickel catalysts (H_2 pressure 4.0 MPa; 60°C)

Composition of starting alloy before leaching (weight ratio)	τ, min	*p*-XDA yield, wt %
Ni : Al = 50 : 50	140	73–75
Ni : Ti : Al commercial (TU*-59-83–75), prescribed content: Al, 50–53.5; Ni, 44–46.5; Ti, 2.2–2.8	50	90–92
N-5 catalyst		
Ni : M : Al:		
47.5 : 2.5 : 50.0	41	94–95
45.0 : 5.0 : 50.0	32	97–98

* Technical Specifications.

Table 2. Conditions of TDN hydrogenation in various solvents (H_2 pressure 4.0 MPa; 60°C)

Solvent (saturated with NH_3)	Ni–Ti catalyst (~3% Ti)		N-5 catalyst	
	τ, min	*p*-XDA yield, wt %	τ, min	*p*-XDA yield, wt %
Methanol	50	90–92	32	97–98
Ethanol	62	89–91	41	96–97
Propanol	69	90–91	48	96–97
Butanol	71	90–91	53	96–97

The elemental composition of the precipitated polymer corresponds to the theoretical value. Polyimide films were prepared by casting 25% solutions of the polyimides in DMA on glass plates. To remove the solvent, the films were predried by vacuum heating in an oven at 80°C for 0.3 h, after which they were heated to constant weight at 150°C for 1 h.

Polyimides derived from *p*-XDA and halogenated dianhydrides were prepared similarly. Yield 98.5–99.0%, degree of imidization about 100%.

Catalytic hydrogenation of nitriles involves a set of parallel-consecutive reactions [8, 12–14]. The reduction of TDN was performed on the catalysts listed in Table 1. The results are given in Tables 1 and 2.

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[1] Terephthalodinitrile was kindly submitted by P.B. Vorob'ev and L.F. Gabdullina (Bekturov Institute of Chemical Sciences, Ministry of Education and Science of the Republic of Kazakhstan).

Table 1 shows that Ni–Ti and N-5 catalysts are more active, compared to straight Raney nickel. The yield of the target product is 90–92% on Ni–Ti and as high as 97–98% on N-5. Therefore, the subsequent experiments were performed with N-5 catalyst.

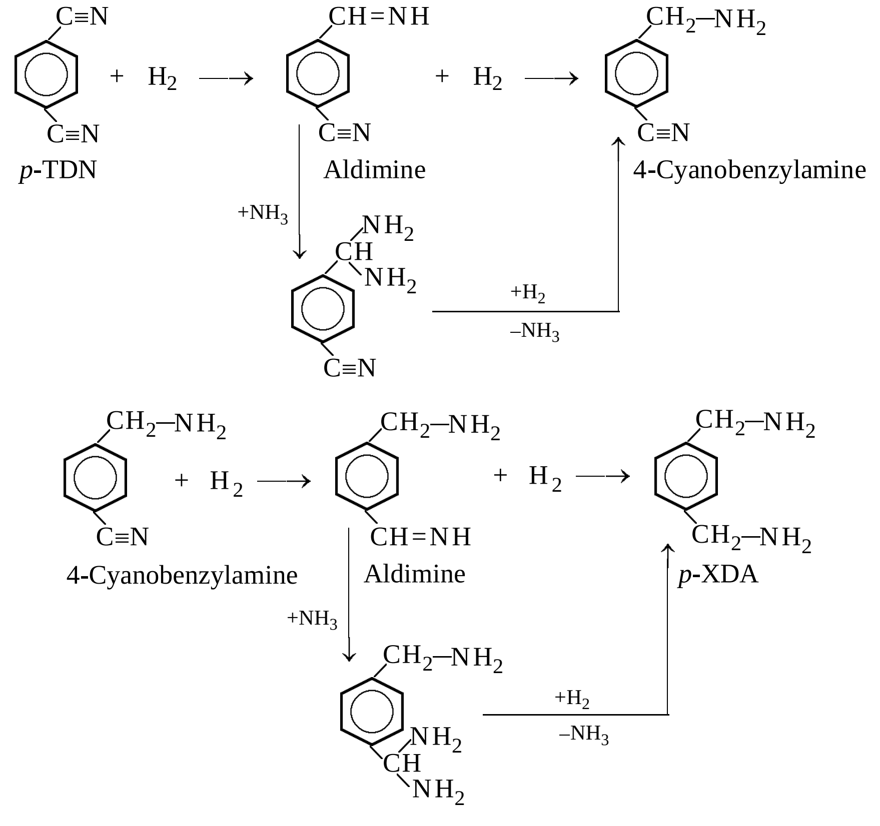
Published data on hydrogenation of aromatic dinitriles demonstrate a significant solvent effect on the process; the best results are attained in alcohols [14].

In this study, we examined the influence exerted by the nature of a solvent on hydrogenation of TDN on N-5 catalyst in the presence of ammonia. The results are listed in Table 2. It is known that the highest rate of formation and highest yield of the product are attained at the stoichiometric ratio of the reactants on the catalyst surface [15]; this fact was taken into account in our experiments.

Table 2 shows that the most favorable ratio of the reactants on the catalyst surface in alcohol is attained at the nitrile : ammonia ratio of 1 : 3.

It is known that the products of hydrogenation of phthalonitriles contain amino nitriles [14, 16, 17]. This fact suggests consecutive reduction of the nitrile groups. The hydrogenation rate on N-5 catalyst decreases with time; the hydrogen uptake corresponds to the reaction stoichiometry [18]. Hydrogenation starts and proceeds at a high rate until 2 mol of H_2 is taken up per mole of the dinitrile; after that, the rate of hydrogen uptake somewhat decreases, and the remaining 2 mol of H_2 is added at a lower rate [17, 18].

Hydrogenation of TDN can be described by the following scheme:



This scheme suggests that, initially, one of the nitrile groups is hydrogenated to give the amino nitrile (cyanobenzylamine), and only after that *p*-XDA is formed.

Bizhanov [19] believes that the growth of activity of Raney nickel catalysts is associated with an increase in the content of the $NiAl_3$ phase relative to the Ni_2Al_3 phase. Thus, the yield of the target product and the reaction rate depend on both the synthesis conditions and the catalyst used. The activity and selectivity of N-5 catalyst may be due to its high enrichment in firmly bound adsorbed hydrogen; its amount is 2–3 times higher than that on straight Raney nickel [19].

Tricyclodecenetetracarboxylic dianhydries are the starting monomers for preparing various heat-resistant

Table 3. Optimal conditions for preparing polyalkanimides

Polymer no.	Dianhydride	c_{mon}, wt %/c_{INA}, wt %	*T*, °C	τ, h	η_r (0.5% solution in DMSO, 25°C), dl g^{-1}
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	20/0	25	2.5	0.32

Table 4. Thermal characteristics of PAI

Polymer no.	T_g, °C	Temperature of weight loss, °C							
		in air				under Ar			
		T_0	T_{15}	T_{10}	T_{50}	T_0	T_{15}	T_{10}	T_{50}
1	270	340	380	420	530	380	440	470	580
2	280	325	350	400	500	360	415	450	545
3	265	335	365	415	510	355	435	460	560

polymers, including polyimides [20, 21]. No data are, however, available on synthesis of high-performance polyimides from *p*-XDA and the above dianhydrides, because of the lack of efficient synthesis procedures. In this study, we developed such procedures. The polyimides were prepared by single-stage polycondensation of the components in polar aprotic solvents (amides) in the presence of catalytic amounts of isonicotinic (pyridine-4-carboxylic, INA) acid, which is known [5] to appreciably intensify polycondensation, like other pyridinecarboxylic acids.

It is known that polyheterocycles prepared in solution are more soluble than the same polymers prepared by solid-phase imidization of polyamido acids. Among the chosen solvents (DMF, DMA, MP, DMSO), the best results were obtained with DMA; the polyimides prepared in this solvent have the highest viscosity. For example, η_r of 0.5% solution of the fluorinated polyimide prepared in various solvents under the optimal conditions is as follows (dl g^{-1}): 0.45 in DMF, 0.53 in MP, 0.75 in DMSO, and 1.23 in DMA. Therefore, all the subsequent syntheses were performed in DMA.

A study of the reactions of *p*-XDA with alicyclic dianhydrides showed that the fluorinated dianhydride (AFB) is more reactive in acylation, which is due to the high electronegativity of the fluorine atom at the endocyclic double bond; as a result, the anhydride groups become more electrophilic. AB and ACB are less reactive [10].

It should be noted that PAIs with fairly good characteristics, derived from an alicyclic dianhydride, were prepared for the first time. The syntheses were performed at 110–120°C for 2.0–2.5 h. All the reactions occurred under homogeneous conditions and gave PAIs in almost quantitative yields, with degrees of imidization of about 100%. The viscosity of the polymers was as high as 0.94–1.23 dl g^{-1}.

The optimal conditions for preparing PAIs are listed in Table 3; for comparison, we also give data for the two-stage synthesis of the polyimide from AFB and *p*-XDA (polymer no. 4). Table 3 shows that the single-stage procedure ensures higher η_r of the polyimide.

The compositions and structures of the polyimides were confirmed by elemental analysis and IR spectroscopy. The IR spectra of the polyimides contain absorption bands at 1775 and 1715 (carbonyl groups of imide rings), 1365–1370 (>N–), and 715–725 cm^{-1} (imide ring); the PAI derived from AFB also exhibits C–F vibration band at 1260–1300 cm^{-1}, and the PAI derived from ACB, a C–Cl band at 860 cm^{-1}. No bands characteristic of uncyclized amido acid fragments were detected.

The structural features of polyimides derived from tricyclodecenetetracarboxylic dianhydrides (presence of the alicyclic structure and, in the case of AFB and ACB, also of halogen atoms) are responsible for some specific properties; for example, the glass transition points T_g decrease somewhat. Comparison of the glass transition points of PAIs, determined by dielectric measurements [22], showed that they are within 265–280°C; T_g of the halogenated polymers is 10–15°C lower, compared to the PAI derived from AB; introduction of Cl decreases T_g to a greater extent, compared to F (Table 4, polymer nos. 1, 2).

We evaluated the heat resistance of the new polymers. As seen from Table 4, decomposition of all the three PAIs in air (onset temperature T_0) starts at 325–340°C, with the nonhalogenated polymer being somewhat less heat-resistant. Decomposition under Ar starts at higher temperatures.

Table 4 shows that, for the polyimides prepared, the interval between T_g and T_0 is 45–70°C, which allows processing of the polymers by pressure molding.

The relatively high viscosity characteristics and good solubility of the polymers in DMA allowed us to prepare films with strength of 70–80 MPa and 30–40% elongation. The modulus of elasticity ranges from 2700 to 3400 MPa depending on the modifying additive (triphenyl phosphate, dimethyl phthalate, dibutyl phthalate, dimethyl terephthalate, etc.).

The dielectric loss tangent at $f = 1$ kHz, $T = 25$°C, and zero moisture content is 0.002–0.004; relative dielectric permittivity, 3.22–3.35. The relative dielectric permittivities of the new PAIs are relatively low, especially of those containing an F atom, which is due to the alicyclic structure of the anhydride ring and to the effect of the electronegative halogen atom. The relative dielectric permittivities of aromatic polyimides containing aliphatic and aromatic fragments are higher.

CONCLUSIONS

(1) Conditions were found for preparing *p*-xylylenediamine in quantitative yield by hydrogenation of terephthalodinitrile in lower aliphatic alcohols in the presence of promoted catalysts containing Raney nickel as base component and obtained by leaching of the corresponding alloys with Ni : Al ≈ 1 : 1. The catalysts used in this study are 3–4 times more active than straight Raney nickel.

(2) A series of new (including fluoro and chloro derivatives) polyimides were prepared by condensation of *p*-xylylenediamine with tricyclodecenetetracarboxylic dianhydrides in polar aprotic solvents (amides). These polymers exhibit high, for this class of materials, physicomechanical and dielectric characteristics and high heat resistance.

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