THE SYNTHESIS OF N,N'-bis-(TRIMELLITIMIDO ACIDS) AND OF POLY(AMIDO IMIDES) FROM THESE*

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POLY (amido imides) (PAI) produced by reactions of trimellitic acid anhydride, or some of its derivatives (the dichloride and imidocarboxylic acids) with diamines have been described before [1–3] The use of bifunctional compounds, containing the imide ring in the molecule, as monomers has a number of advantages, such as the possibility of controlling the complete conversion of amide groups to imide during monomer synthesis, the creation of a regular polymer structure having alternating amide and imide groups, the resistance of the final products to hydrolysis Furthermore, structural alterations in monomers make it possible to modify the polymer properties within a wide range.

This work describes the results of the synthesis of diimidodicarboxylic acids with aliphatic and aromatic fragments, and the polymers produced from them

EXPERIMENTAL

Starting material The trimellitic acid anhydride, 4,4'-diaminodiphenyl ether, mphenylenediamine and benzidine were all purified by vacuum distillation at 10^{-3} mmHg They had the constants given in the literature. The hexamethylenediamine was distilled at 198–199°C in an argon stream; its m.p.=40°C, its neutralization equivalent was 58.3

Dissolve 0.2 moles of trimellitic acid anhydride in *m*-cresol and then add 0.1 mole diamine Heat the mixture 5-6 hr at $160-170^{\circ}$ C while stirring, filter off the precipitating acid, thoroughly wash with alcohol and ether, and dry to constant weight. The acid yield will be 90-93%.

The N,N'-hexamethylen-bis-(trimellitimido acid)had m p 310-311°C, the neutralization equivalent was 232.0 (Theor.=232.0)

Elemental analysis, found, % 62·22, 62·63 C, 4 35, 4 10 H, 5 99, 6 04 N theor., % 62·00, 4·31, 6 03 C₂₄H₂₀N₂O₈ The N,N'-diphenyloxy-bis-(trimellitimido acid) had m p.=369-370°C, and a neutralization equivalent of 273 0 (theor.=274 0).

The dumidodicarboxylic acid dichloride was produced by heating the respective acid with P_2O_5 and adding small amounts of pohsphorus oxychloride. The latter was distilled off after the reaction termination, and the residue was consecutively treated with dry benzene, chloroform and CCl_4 , after which the product was recrystallized from dry toluene

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The hexamethylene-bis-(trimellitimido acid dichloride) (DCH-1) had m.p. = 168-169°C, molecular weight M = 500 (theor = 501.7).

The N,N'-diphenyloxy-bis-(trimellitimido acid dichloride) (DCH-2) had m.p.=236-237° C, M = 590 (theor 585.0).

The respective elemental analyses are given below: (%).

	DCI	H-1: 5	57 18	3, 57.	53 C,	37	1, 3.8	31 H,	52	4, 5.26	N,	14 88,	14·83 Cl
	\mathbf{the}	eor. 5	57.48	3		35	57		5 58	8		14.17	$C_{24}H_{18}N_2O_6Cl_2$.
DCH-2:	61.68,	61.77	С,	2.85,	3 00	H,	5 25,	$5\ 32$	N,	12 06,	120'	7 Cl	
theor :		61 20			2 40			4 ·80			12.13	6 C30H	14N2O7Cl2.

The syntheses of PAI Place 0.02 moles diamine and 0.042 moles triethylamine in a freshly distilled dry solvent into a triple-neck flask fitted with a stirrer, a calcium chloride tube and a capillary for streaming an inert gas (10% reagent solution), add in small portions over 5–10 min 0.02 moles of the diimidodicarboxylic acid dichloride, and react at room temperature for 3 hr. Filter off the triethylamine hydrochloride after the reaction, and precipitate the polymer out of solution with alcohol or acetone, wash it with water and acetone, and finally dry to constant weight.

RESULTS

The PAI synthesis based on the diimidodicarboxylic acid chlorides was carried out by low-temperature polycondensation in solution. This reaction can be schematically illustrated as follows:



The product of this reaction is a linear polymer with strictly alternating imide and amide groups in the main chain.

The selected solvent is of considerable importance in the above process, i.e. its type, its solution capacity of the starting components and the forming polymer, but also its participation capacity in reactions with the components (Table 1).

The lowest polymer yield can be seen to have been obtained in chloroform, also the smallest molecular weight (mol wt). The reason could be the precipitation out of solution of the polymer during the process, which limits chain propagation. Chloroform also easily reacted with the hydrogen chloride acceptor (trimethylamine) to a quaternary ammonium base [4] The polymer yield became larger in acetone and dichloroethane, but the mol.wt. still remained relatively low for the same reason (precipitation) The most suitable from amongst the polar solvents used was N-methylpyrrolidone (MP) and dimethylacetamide (DMA), in which the polymers were soluble Some secondary reactions of the

Diamine	$\mathbf{Solvent}$	Polymer solubility	Yıeld, %	[η], dl/g
I	Chloroform	None	61 0	0 15
II	Chloroform	None	70 0	0 17
III	Chloroform	None	73 0	036
Ι	Acetone	None	87 0	$0\ 22$
II	Acetone	None	80 0	0 20
Ι	Dichloroethane	None	85 0	$0\ 25$
II	Dichloroethane	None	82 0	0 27
II	DMF	No poly-		
		mer produced		—
III	MP	Soluble	85 0	0 60
II	MP	Soluble	90 0	0 56
II	DMA	Soluble	87 0	0 48

TABLE 1. THE PAI SYNTHESIZED FROM DCH-1 AND DIAMINES IN VARIOUS SOLVENTS

acid chloride with the solvent probably take place in dimethylformamide (DMF) as solvent, and the products are incapable of participation in the polycondensation [5, 6].





FIG. 2 The specific viscosities of PAI based on *m*-phenylenediamine and of 1-DCH-1, and 2-DCH-2, as a function of the polycondensation time in MP

^{*} I=hexamethylenediamine, II=m-phenylenediamine, III=4,4'-diaminodiphenyl ether, DMF=dimethylformamide, DMA=dimethylacetamide, MP=N-methylpyrrolidone

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Diamine	Yıeld, %	[ŋ]*, dl/g	Start of decom- position, °C	Dielectric loss factor (at 20° and 10 ³ Hz)	Specific volume capaci- tance $q_v \times 10^{-15}$, ohm \cdot cm	Dynamic elasticity modulus $E \times 10^{-10}$ dyne/cm ² (at 20°)			
Polymers based on DCH-1									
I	80.0	0.18	280	3.4	1.70	21			
II	90·0	0.56	390	3 5	1.46	1.7			
IV	95 5	0.35	420	46	1.16				
III	85 0	0 60	360	3 5	1.32	2.3			
Polymers based on DCH-2									
I	85 0	0 20	300	3 2	0 12	114			
II	87 0	0 55	380	38	1 00	1 81			
\mathbf{v}	89 0	0 15	400	3.7	1 70	$2\ 28$			
III	90 0	0 50	420	33	1 35	2.32			
IV	88 0	0 42	450	33	1.35	2 80			

TABLE 2. THE PROPERTIES OF PAI

* Viscosity determined at 20°C in m-cresol I-III as under Table 1, IV=benzidine, V=p-phenylenediamine

Of considerable influence on the mol. wt. of PAI is the initial concentration of the reacting components. Figure 1 shows the polymers produced from 10%component concentrations to have the largest intrinsic viscosity. The decrease of the latter on increasing the reagent concentrations is due to a substantial increase of the viscosity of reaction solutions and the sedimentation of the polymer The low viscosities at low monomer concentrations are linked with a reduction of the rate of polyamidation in very dilute solutions

Reducing the reaction temperature from 20 to 5°C also reduced the mol.wt While the $[\eta]$ of the PAI produced from DCH-1 and *m*-phenylenediamine was 0.56 dl/g at 20°C, it was only 0.16 dl/g at 5°C The dependence of the reduced viscosity on polycondensation time in MP (Fig 2) indicated that the process time yielding a polymer with a fairly large mol. wt. should be 1.5–3 hr. A longer process time will cause some viscosity decrease, which is probably due to the usual inter-chain exchange reactions

The characteristics of the PAI synthesized in the described low-temperature polycondensation conditions are contained in Table 2. A valuable quality of the majority of the produced polymers was the combination of fairly good heat resistance (from 300 to 450° C in air according to TG) with solubility in a number of easily available solvents (*m*-cresol, DMF, DMA, MP, conc H₂SO₄)

The polymers belong amongst the organic semiconductors as regards their electrical properties and have the same characteristics as the known polyimides. The specific resistance at room temperature was of the order of 10^{15} ohm \cdot cm, and the dielectric permeability from 3.2 to 4.6

The mechanical properties which were characterized from the dynamic elastic-

ity modulus, determined at room temperature by the acoustic method [7], indicate the synthesized polymers to be slightly more rigid than polyamides, but they were as strong as the polypyromellitimides

CONCLUSIONS

(1) N,N'-hexamethylene- and N,N'-diphenyloxy-bis-(trimellitimido acids) were produced and characterized, as well as their acid chlorides

(2) The reactions of the dimidodicarboxylic acid dichlorides with diamines in low-temperature polycondensations in solution yielded regular polyamido imides which were heat-resistant from 300 to 450° C

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THE SORPTION BEHAVIOUR OF CELLULOSE TRIACETATE OVER A WIDE RANGE OF TEMPERATURES*

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SORPTION studies of low molecular weight compounds by polymers, carried out over a wide temperature range, enable one to assess the structural changes which take place in the polymer, and lead to packing density differences of the polymer chains and macromolecular structural elements

The work described here dealt with the study of the cellulose triacetate (CETA) sorption properties in the amorphous and crystalline state in the range 25–200°C.

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