Synthesis and Investigation of New Highly Fused Polyheteroarylenes

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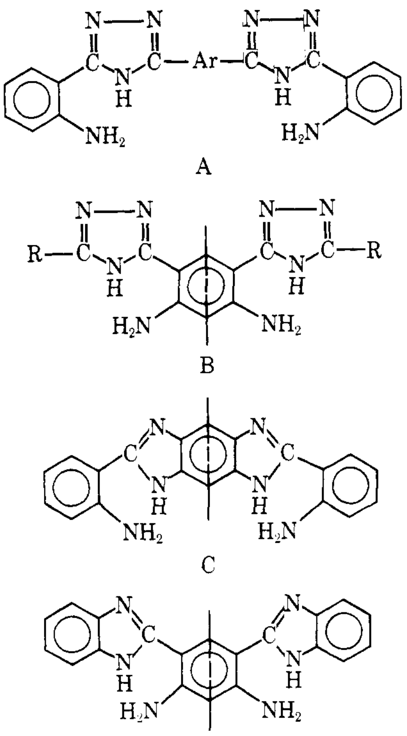
ABSTRACT: Two new aromatic diamines 4,6-diamino-1,3-bis(5-phenyl-1,2,4-triazol-3-yl)benzene and 4,6-diamino-1,3-bis(benzimidazol-2-yl)benzene were prepared from 4,6-dinitroisophthalic acid. Reaction of the diamines with benzoic acid or its derivatives led to the formation of new heterocyclic systems: 3,5,9,11-tetraphenylbenz[1,2-*g*:4,5-*g'*]bis(1,2,4)-triazolo[4,3-*c*]pyrimidine and 2,16-diphenylbenz[1,2-*a*:4,5-*a'*]bis(pyrimido[3,4-*a*]benzimidazole). Interaction between the diamines and aromatic dicarboxylic acid dichlorides followed by solid-state cyclodehydration led to the formation of new highly fused polyheteroarylenes: poly[benzbis(triazolopyrimidines)] and poly[benzbis(pyrimidobenzimidazoles)]. The resulting polymers are highly stable to thermal degradation as shown by dynamic and isothermal thermogravimetric analyses.

Recently[1] we have shown that the interaction between aromatic acids or their derivatives and aromatic diamines containing aromatic heterocycles with reactive hydrogen atoms at the ortho positions to the amino groups may be considered as a general method for the synthesis of highly fused polyheteroarylenes. Further we have shown that as such heterocycles 1,2,4-triazole and benzimidazole may be incorporated in the starting diamines and proposed that four general types of diamines (A–D) may be used as monomers.

Scheme I



In the previous investigations monomers having structures A and C were used by us and other groups for the preparation of new heterocyclic polymers poly(triazoloquinazolines)[1,2–6] and poly(benzimidazoloquinazolines);[1,7–10] much less attention was paid to the syntheses of polyheteroarylenes having structures B and D.[7,11] As a result in the course of this investigation we have tried to synthesize polyheteroarylenes from diamines having general structures B and D.

Results and Discussion

Monomers. We have chosen two diamines: 4,6-diamino-1,3-bis(5-phenyl-1,2,4-triazol-3-yl)benzene and 4,6-diamino(1,3-bis(benzimidazol-2-yl)benzene. These diamines were prepared from 4,6-dinitroisophthalic acid dichloride in accordance with Scheme II.

The structures of compounds II–VII were suggested by elemental chemical analysis and spectral (Table I) data.

Model Compounds. Prior to polymer synthesis, a series of model compounds were prepared as a guide to polymer synthesis and identification.

The simplest model compounds, 3-phenyl-5-(2-benzamidophenylene)-1,2,4-triazole, 3,5-diphenyl-*s*-triazolo[4,3-*c*]quinazoline, 2(2-benzamidophenylene)benzimidazole and 6-phenylbenzimidazolo[1,2-*c*]quinazoline, and the more complicated model compounds, prepared by the interaction between dicarboxylic acids dichlorides and 3-phenyl-5-(2-aminophenylene)-1,2,4-triazole or 2-(2-aminophenylene)-benzimidazole, were described previously. In the course of this investigation attention was paid to products, prepared by the interaction between diamines IV and VII and benzoyl chloride, namely the new heterocyclic systems: 3,5,9,11-tetraphenylbenz[1,2-*g*:4,5-*g'*]bis(1,2,4)-triazolo[4,3-*c*]pyrimidine) (IX) and 2,16-diphenylbenz[1,2-*a*:4,5-*a'*]bis(pyrimido[3,4-*a*]benzimidazole) (XI). The compounds were prepared in accordance with Scheme III.

The structures of compounds VIII–IX were suggested by elemental analysis and ir and uv (Table I) spectroscopy.

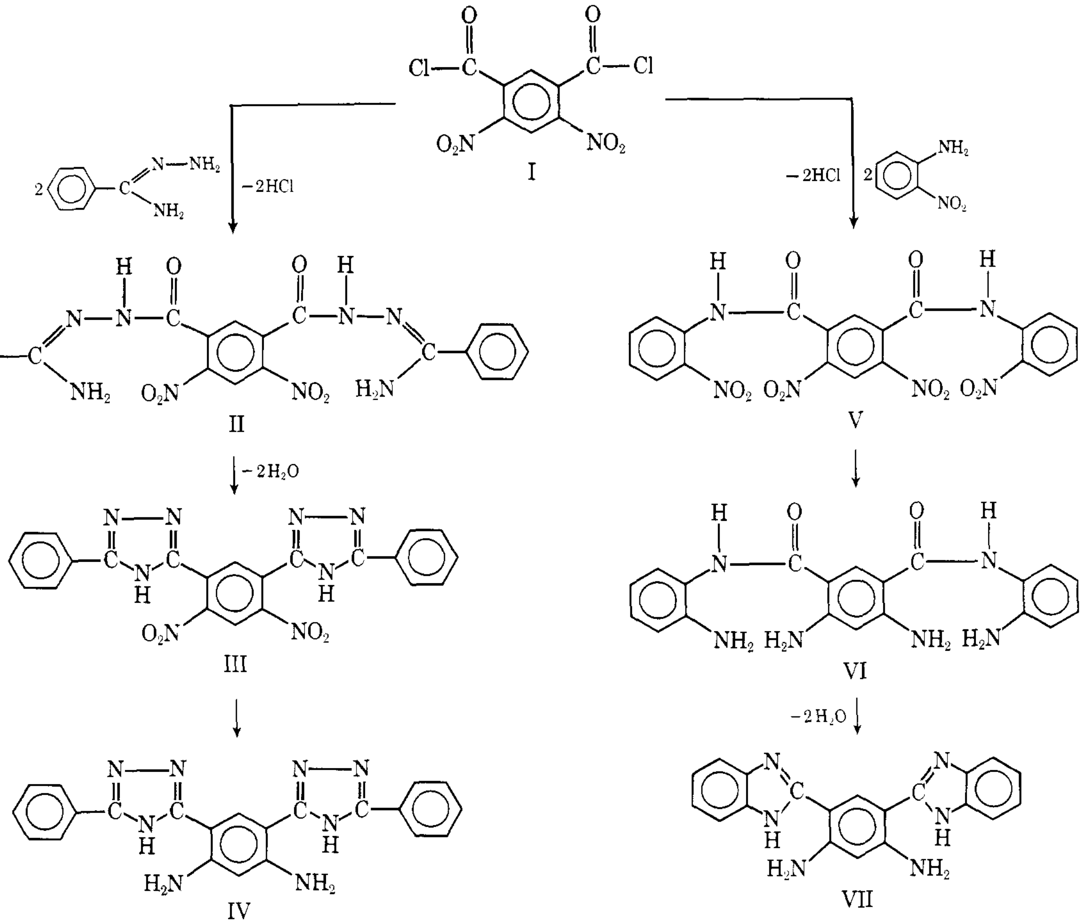
Polymers. The polymers were synthesized according to Scheme IV.

Synthesis of aromatic polyamides containing in ortho positions to amide groups 5-phenyl-1,2,4-triazol-3-yl or benzimidazol-2-yl substituents was carried out in hexamethylphosphoramide (HMPA) in the presence of LiCl or without it. All reactions were homogeneous whereas on conducting polycondensation in other bipolar aprotic solvents (dimethylacetamide (DMAA), *N*-methyl-2-pyrrolidone (N-MP), etc.) polymers with the most rigid chains were isolated from the reaction solutions.

The structure of the polyamides synthesized was indicated by comparison of their ir and uv spectra with those of the model compounds (Table II).

Polyamides containing in the ortho positions to the amide groups 5-phenyl-1,2,4-triazol-3-yl or benzimidazol-2-yl substituents are white to yellow powders completely insoluble, with the exception of polymers XXVIII and XX containing hexafluoroisopropylidene groups, in organic solvents and soluble in trifluoroacetic and sulfuric acids. Low solubility of

Scheme II



the polyamides prepared seems to be rather surprising because it was shown[12] that introduction of benzimidazol-2-yl ortho substituents in rigid-chain polymers leads to improved solubility of the polymers in organic solvents. Probably low solubility of the polyamides containing the above-mentioned ortho substituents is due to intermolecular hydrogen bonding and to regular conformations of the polyamide macromolecules, which may be schematically represented as in Scheme V.

Table I
Some Properties of Monomers and Model Compounds

Compd	Purification	Yield, %	Mp, °C	General formula	Elemental analysis: Found, % C	H	N	Calcd % C	H	N	Uv spectra[b] λ_{max}	log ϵ
II	Crystallization, DMF:water (1:1)[a]	72	338–340	$C_{22}H_{18}N_8O_6$	53.61	3.93	23.00	53.90	3.61	22.80	247	4.6021
III	Crystallization, 2-propanol	62	345–346	$C_{22}H_{14}N_8O_4$	58.15	3.33	24.58	58.12	3.10	24.66	247	4.7324
IV	Crystallization, C_2H_5OH	77	335–336	$C_{22}H_{18}N_8$	66.27	4.78	28.79	66.99	4.54	28.40	275	4.7243
V	Crystallization DMF:water (3:1)	63	256–257	$C_{20}H_{12}N_6O_{10}$	48.49	3.30	16.53	48.39	3.43	16.93	231	4.7505
VI	Extraction, methanol	90	280–282	$C_{20}H_{20}N_6O_2$	61.70	5.39	21.85	63.81	5.36	22.33		
VII	Sublimation, (10^{-4} mm) 360 °C	80	412–413	$C_{20}H_{14}N_6$	70.59	4.92	24.49	70.57	4.74	24.69	305	4.5198
VIII	Crystallization, DMF:water (1:1)	73	367	$C_{36}H_{26}N_8O_2$	69.02	4.93	17.83	71.76	4.32	18.60	263	4.8633
IX	Sublimation, 350–360 °C (0.5 mm)	86	400–402	$C_{36}H_{22}N_8$	75.98	3.99	20.17	76.30	3.91	19.77	260 322	4.7160 4.4150
X	Crystallization, DMF	70	365–366	$C_{34}H_{24}N_6O_2$	74.51	4.41	15.10	74.44	4.41	15.32	265 305	4.6698 4.4983
XI	Sublimation, 300–350 °C (10^{-4} mm) Crystallization, DMF	90	436–440	$C_{34}H_{20}N_6$	78.61	3.99	16.34	79.67	3.93	16.40	235 267 340 427 452	4.4314 4.2041 3.1761 4.5119 4.5250

[a] DMF = dimethylforamide. [b] Uv spectra are obtained in concentrated H_2SO_4 (*c* 10^{-5} M).

Such constitution of the polyamides is supported by their partial crystallinity (x-ray analysis).

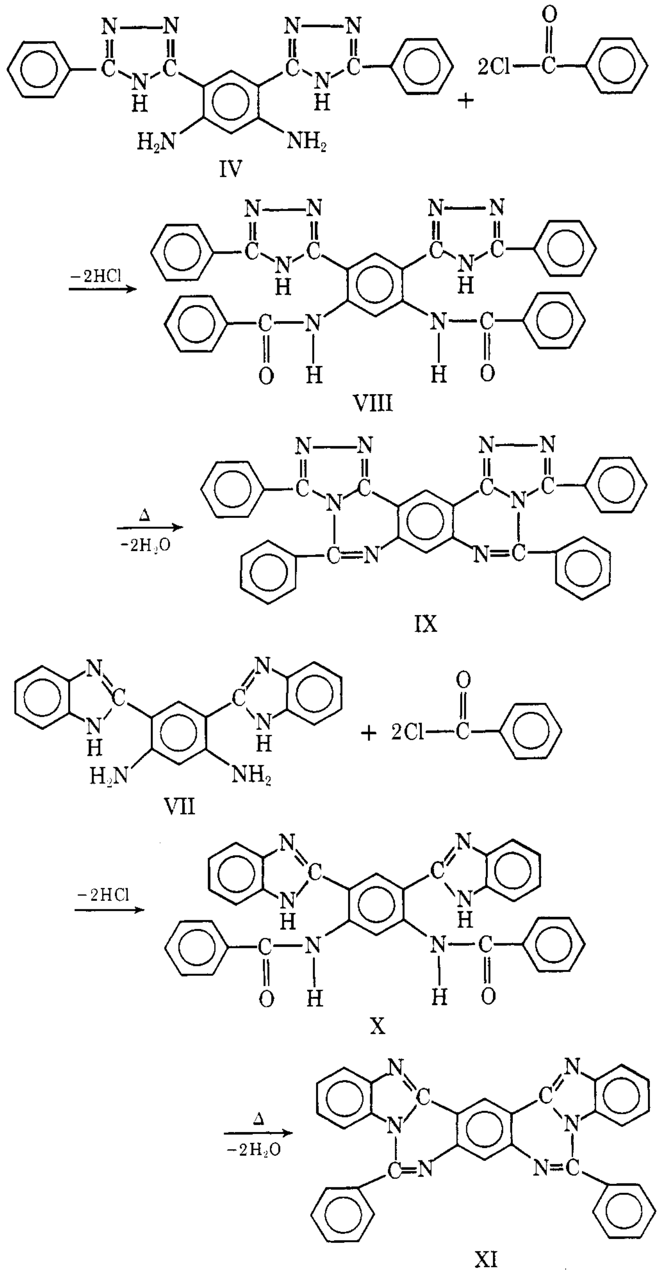
Solution viscosities of the polyamides obtained (η_{red} = 0.1–0.5 dl/g) indicate a rather low degree of polymerization; this can be due to low nucleophilic reactivity of the diamines used (because of the presence of bulky substituents in ortho positions to the amino groups).

To elucidate the range of molecular weight corresponding to η_{red}(obsd), we have measured the molecular weight of the only polyamide with benzimidazol-2-yl ortho substituents soluble in organic solvents, polymer XXVIII. Determination of the molecular weight of this polymer by the light-scattering method in solution in N-MP has demonstrated that η_{red} = 0.21 corresponds to a molecular weight of 16 000.

The resulting polyamides did not soften up to 350 °C, i.e., the cyclization temperature, as shown by thermomechanical analysis data.

Differential thermal analysis and differential and integral thermogravimetric analysis of polyamides showed that the weight loss of these polymers occurs in temperature ranges

Scheme III



Scheme IV

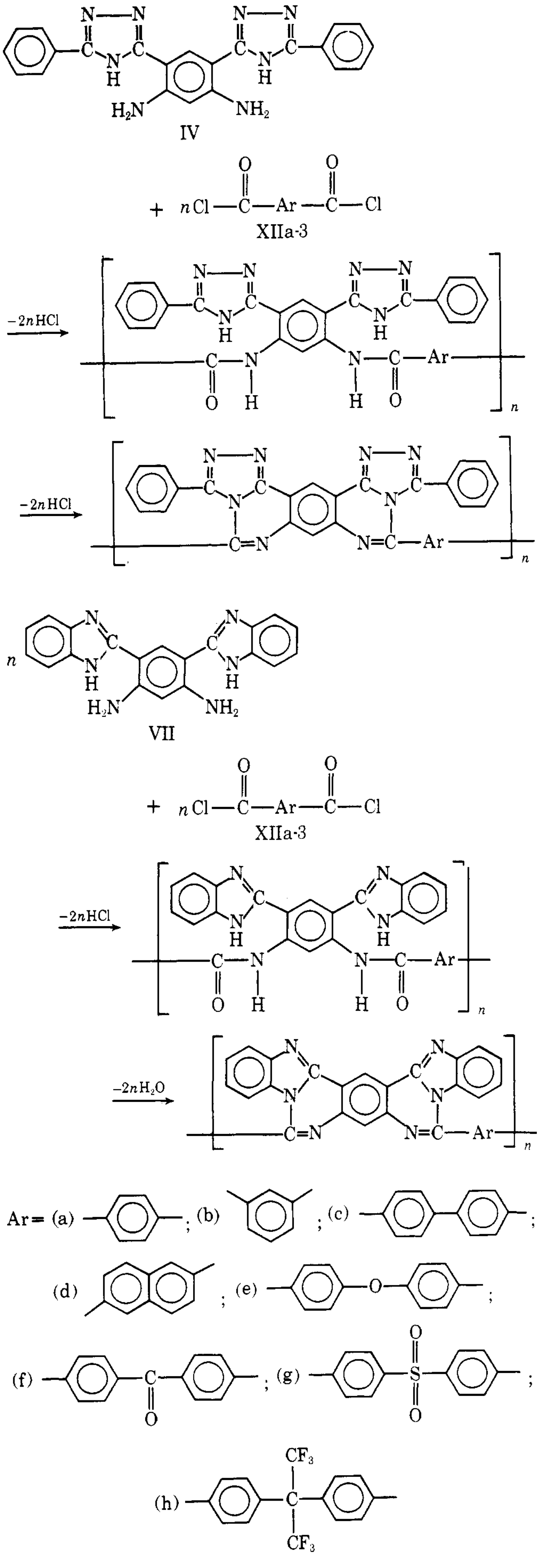
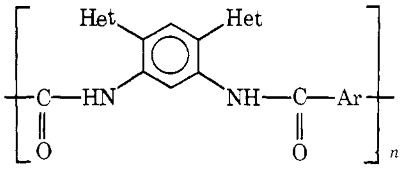
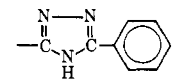
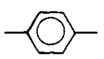
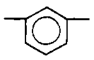
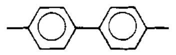
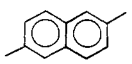
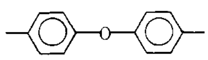
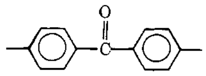
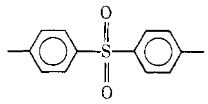
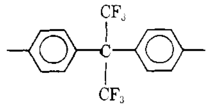
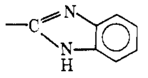
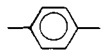
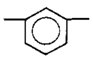
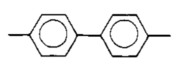
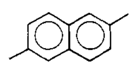
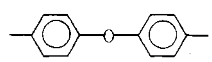
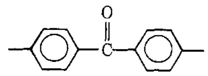
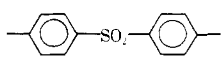
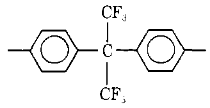


Table II
Some Properties of Polyamides of General Structure



Compd	Het–	–Ar–	η_{red},[a] dl/g	Solubility[b]			Uv spectra	
				H_2SO_4	CF_3-COOH	*N*-Methylpyrrolidone	λ_{max}	log ε
XIII			0.06	s	s	ins	263 327	4.8513 4.7924
XIV			0.06	s	s	ins	250 320	4.6812 4.6812
XV			0.06	s	s	ins	255 280	4.6233 4.6128
XVI			0.05	s	s	ins	252 288	4.6021 4.6335
XVII			0.06	s	s	ins	263 325	4.6902 4.6335
XVIII			0.05	s	s	ins	265 325	4.7076 4.6628
XIX			0.05	s	s	ins	257 275	4.7709 4.6128
XX			0.05	s	s	s	260	4.5798
XXI			0.24	s	s	ins	239 312	4.7404 4.4548
XXII			0.15	s	s	ins	235 305	4.0960 4.4150
XXIII			0.34	s	s	ins	236 330	4.2175 4.6990
XXIV			0.44	s	s	ins	267 331	4.4314 4.6435
XXV			0.30	s	s	ins	228 309	4.4548 4.7482
XXVI			0.25	s	s	ins	238 314	4.5441 4.8195
XXVII			0.20	s	s	ins	240 297	3.9777 4.4843
XXVIII[d]			0.39	s	s	s	236 299	4.4771 4.6857

[a] η_{red} is determined for 0.5% solutions in concentrated H_2SO_4 at 25 °C. [b] s = soluble; ins = insoluble. [c] Uv spectra are obtained in concentrated H_2SO_4 (c 10^{-5} M). [d] Soluble in dimethylformamide.

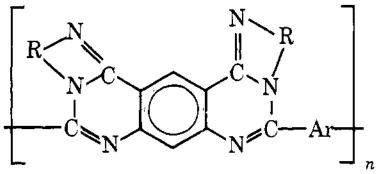
of 280–370 °C and at above 500 °C. The weight loss in the range of 280–370 °C is connected with cyclization of amido-*o*-triazole and amido-*o*-benzimidazole units and that at 500 °C is associated with the degradation process of the final polymers.

The main properties of polyamides are given in Table II.

The polyamides synthesized were cyclodehydrated to corresponding final highly fused polyheteroarylenes under reduced pressure (0.5 mm) at a maximum temperature of 380 °C for 12 h. Cyclization conditions are given in the Experimental Section and in Table III.

The structure of final polyheteroarylenes was indicated by comparison of the ir and uv spectra of polymers with those of the corresponding model compounds (Tables I and III) (Fig-

Table III
Some Properties of Polyheteroarylenes of General Structure



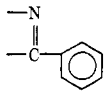
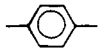
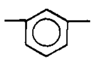
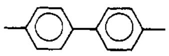
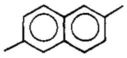
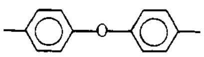
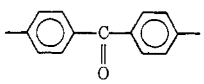
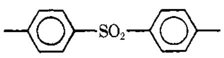
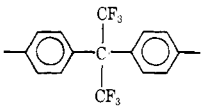
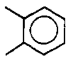
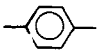
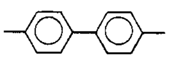
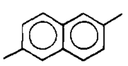
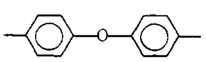
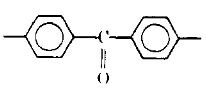
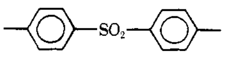
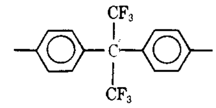
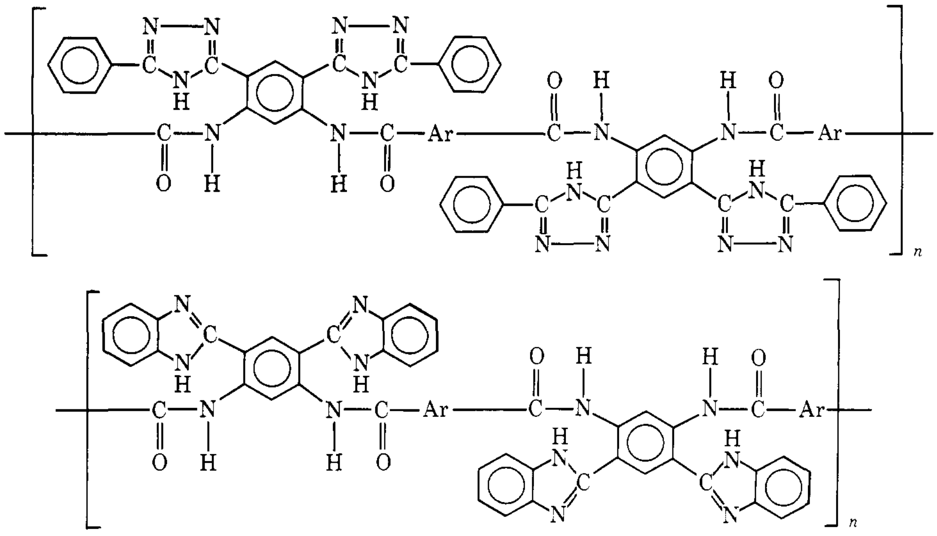
Compd	R<	–Ar–	η_{red},[a] dl/g	Solubility[b] H_2SO_4	Solubility[b] CF_3COOH	*T* dec[c] 5%	*T* dec[c] 10%	Uv spectra λ_{max}	Uv spectra log ε
XIIIc			0.08	s	ps	480	510	263 331	4.7404 4.7404
XIVc			0.11	s	ps	450	510	263 325	4.6628 4.7324
XVc			0.11	s	ps	450	500	260	4.5911
XVIc			0.09	s	ps	475	520	254 290	4.8920 4.5563
XVIIc			0.08	s	ps	450	500	265 327	4.8692 4.7634
XVIIIc			0.09	s	ps	490	520	264 325	4.6021 4.4771
XIXc			0.16	s	ps	430	490	262 322	4.7243 4.8261
XXc			0.09	s	ps	440	480	258 320	4.7160 4.5185
XXIc			0.85	s	ps	600	620	235 264 350 440 464	4.2304 4.2788 4.6902 4.5563 4.5798
XXIIc			0.22	s	ps	545	560	236 265 347 436 456	4.3979 4.4771 4.8388 4.3010 4.2788
XXIIIc			0.20	s	ps	540	560	237 270 347 440 464	4.4472 4.4624 4.7243 4.5563 4.5798
XXIVc			0.20	s	ps	535	560	222 273 351 440 466	4.7559 4.6180 4.8388 4.4065 4.2041
XXVc			0.37	s	ps	550	565	236 264 345 446 470	4.3010 4.3222 4.6128 4.4624 4.5185
XXVIc			0.37	s	ps	550	570	236 267 346 436 454	4.7101 4.8062 5.4786 4.3802 4.3560
XXVIIc			0.16	s	ps	500	530	233 267 345 434 456	4.4314 4.4624 4.7634 4.2304 4.2041

Table III (Continued)

Compd	R<	–Ar–	η_{red},[a] dl/g	Solubility[b] H_2-SO_4	Solubility[b] CF_3-COOH	T dec[c] 5%	T dec[c] 10%	Uv spectra $\lambda_{\max}$	Uv spectra log ε
XXVIIIc			0.20	s	s	510	525	236 265 345 432 454	4.4928 4.6085 4.9956 4.3075 4.2833

[a] η_{red} is determined for 0.5% solutions in concentrated H_2SO_4 at 25 °C. [b] s = soluble; ps = partially soluble. [c] Temperature of weight loss obtained from dynamic TGA curves (air, ΔT = 4.5 °C/min). [d] Uv spectra are obtained in concentrated H_2SO_4 (c 10^{-5} M).

Scheme V



ure 1). The cyclization is accompanied by the disappearance in the ir spectra of absorption bands assigned to amide bonds and NH groups of the amide and triazole cycle (1640–1670 and 2800–3400 cm^{-1}) as well as by the appearance of the absorption of tertiary nitrogen atom (1380 cm^{-1}).

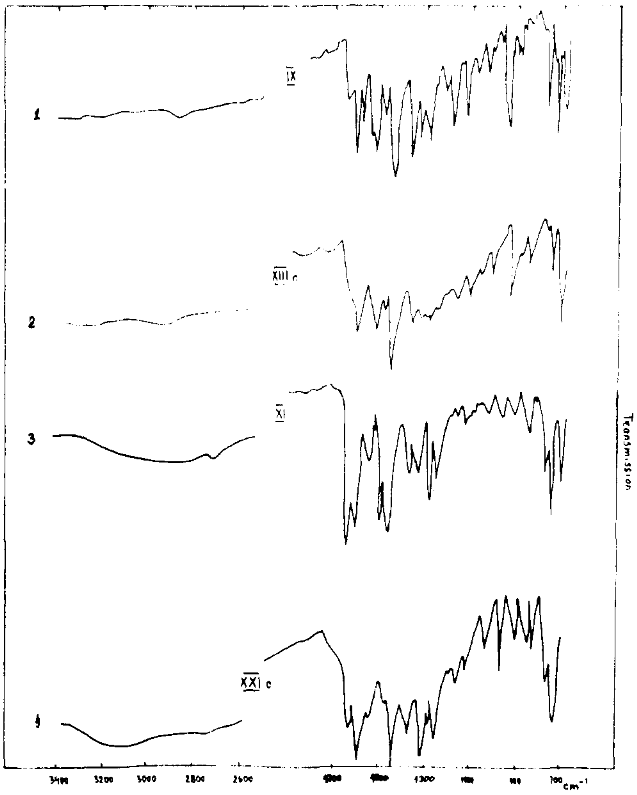


Figure 1. Ir spectra of model compounds IX (1) and XI (3) and polymers XIIIc (2) and XXIc (4).

The resulting polyheteroarylenes are brown to black powders soluble in CF_3COOH and/or H_2SO_4 (Table III).

As seen from thermomechanical curves of these polymers they do not soften even at 450 °C.

Some characteristics of poly[benzbis(triazolopyrimidine's)] and poly[benzbis(pyrimidobenzimidazole's)] are given in Table III.

Degradation temperatures of polyheteroarylenes synthesized were determined by dynamic and isothermal TGA in air. As shown by dynamic thermogravimetric analysis (circulating air, ΔT = 4.5 °C/min) the polymers undergo degradation in air (10% weight loss) at 480–620 °C. It is necessary to note that poly[benzbis(pyrimidobenzimidazole's)] are more thermally stable than the corresponding poly[benzbis(triazolopyrimidines)]; one of them, polymer XXIc prepared from VII and terephthaloyl chloride, has the highest stability. Comparison of dynamic TGA curves of polymer XXIc, graphite, and poly(*N*-phenyl)benzimidazole[13] in air and in argon (Figure 2) has demonstrated that the thermal and thermooxidative stability of polymer XXIc is far greater than those of poly(*N*-phenyl)benzimidazole but lower than graphite. Isothermal TGA of polymers XIIIc and XXIc demonstrated that these polymers exhibit good thermal stability at 400 °C. The same results were obtained by using one-stage cyclodehydration in polyphosphoric acid and in melt.

Experimental Section

Materials. 4,6-Dinitroisophthalic acid dichloride was prepared and purified by a known procedure:[14] mp 104–105 °C; lit. mp, 107 °C;[14] yield 65%.

Benzamidrazone was prepared and purified by a known procedure:[15] mp 74.5–76 °C; lit. mp 75–76 °C;[15] yield 85%.

(4,6-Dinitroisophthaloyl)dibenzamidrazone (II) was prepared by

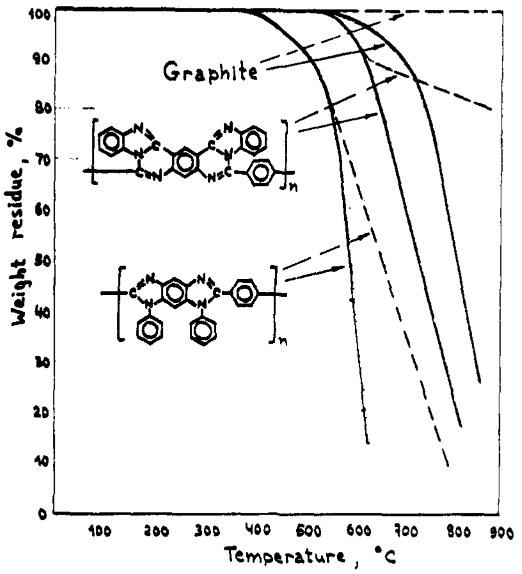


Figure 2. Curves of the dynamic thermogravimetric analysis of poly(*N*-phenyl)benzimidazole, poly[benzdi(pyrimidobenzimidazole)], and graphite in inert atmosphere (- - -) and in air (—); $\Delta T = 4.5$ °C/min.

the following procedure; 2.70 g (0.02 mol) of benzamidrazone was placed in a three-necked 100-ml flask equipped with stirrer, nitrogen inlet and outlet, then 30 ml of dry freshly distilled DMAA and 1.68 g (0.02 mol) of sodium carbonate were added. To the mixture, 2.93 g (0.01 mol) of 4,6-dinitroisophthaloyl dichloride was added. The resulting deep-red solution was stirred at room temperature for 2 h and then poured into 200 ml of distilled water; orange precipitate thus obtained was filtered off, washed with water, dried, and crystallized from a DMF/water mixture: mp 338–340 °C; yield 78%.

4,6-Dinitro-1,3-bis(5-phenyl-1,2,4-triazol-3-yl)benzene (III) was prepared by the heating of II (4.9 g) in a condensation tube at 250–270 °C (1 mm) for 3 h. The color of the product turned from orange to light tan. The product was crystallized from 2-propanol to obtain pure III having mp 345–346 °C and yield 63%.

4,6-Diamino-1,3-bis(5-phenyl-1,2,4-triazol-3-yl)benzene (IV) was prepared by catalytical reduction of III. In a three-necked 500-ml flask equipped with stirrer and reflux condenser 4.54 g (0.01 mol) of III, 300 ml of 2-propanol, 0.5 cm^3 of Raney Ni, and 25 ml of hydrazine hydrate were added and the mixture was refluxed with stirring for 3 h. Raney Ni was filtered off and 200 ml of 2-propanol were evaporated. On cooling of the residue 3.02 g (77%) of IV was obtained. Product crystallized from 2-propanol had mp 335–336 °C.

4,6-Dinitroisophthalbis(*o*-nitroaniline) (V) synthesis was carried out in accordance with the following procedure: In a reaction flask equipped with stirrer, nitrogen inlet, and outlet there were placed 2.76 g (0.82 mol) of *o*-nitroaniline and 25 ml of N-MP. To the solution cooled to 15 °C there was added 2.93 g (0.01 mol) of I. The reaction mixture was stirred at 15 °C for 18 h and then poured into cold water. The orange precipitate formed was filtered off and crystallized from DMF with activated charcoal: yield of V having mp 256–257 °C was 63%.

Reduction of V to 4,6-dinitroisophthalbis(*o*-aminoaniline) (VI) was accomplished by catalytic reduction with hydrogen (initial pressure 150 atm) in DMF at room temperature using as a catalyst Raney Ni. When reduction was complete Raney Ni was filtered off and the solution was poured into distilled water. VI was precipitated, collected, and cyclized by boiling in 4 N HCl overnight. The 4,6-diamino-1,3-bis(benzimidazol-2-yl)benzene dihydrochloride thus obtained was treated with aqueous ammonia and dried; the yield of VII was 55%. The product obtained was purified by sublimation at 340–360 °C (10^{-4} mm) or crystallization from a DMF/water mixture. The melting point of the purified diamine was 412–413 °C.

All aromatic dicarboxylic acid dichlorides were prepared as described previously[16] and had melting points corresponding to those reported in the literature.

Model Compounds. Benzoylation of IV was carried out by the interaction of 3.94 g (0.01 mol) of IV with 2.81 g (0.02 mol) of benzoyl chloride in 60 ml of HMPA at room temperature. The homogeneous solution obtained was poured into water and the white powder thus precipitated was filtered off, washed with water, and purified by crystallization from DMF/water: mp of pure VIII 367 °C (in preheated bath); yield 73%.

VIII (3.01 g; 0.005 mol) was placed in a condensation tube and heated at 370 °C (10^{-3} mm). Cyclization was followed by the sublimation of crude IX. Sublimate was collected and purified by sublimation or crystallization from DMF: yield of IX 86%; mp 400–402 °C.

Benzoylation of VII was carried out in accordance with the following procedure: VII (3.404 g; 0.01 mol) was dissolved in 60 ml of HMPA and to the solution there was added 2.81 g (0.02 mol) of benzoyl chloride. The solution thus obtained was stirred for 2 h at room temperature and poured into distilled water. Yellowish precipitate was filtered off, washed with water, dried, and crystallized from DMF: mp of purified X 365–366 °C (in preheated bath); yield of X quantitative.

VIII (5.48 g; 0.01 mol) was placed in a condensation tube and heated at 300–350 °C (10^{-4} mm). Cyclization was followed by sublimation of product XI. Sublimate was collected and purified by sublimation once more: yield of XI 90%; mp 436–440 °C.

Synthesis of Polymers. Synthesis of all polyamides was performed by the following general method. To the solution of 0.01 mol of diamine in 24 ml of pure HMPA with stirring during 30 min there was added 0.0101 mol of solid dicarboxylic acid dichloride. Solution was stirred for 8 h at room temperature and then poured into distilled water. Polymer was filtered off, washed with water, extracted with methanol, and dried at 80 °C (0.5 mm). Yields of polymers were close to quantitative.

Cyclodehydration of polyamides to corresponding polyheteroarylenes was carried out by solid-state treatment under reduced pressure (0.5 (1 mm)) at 250, 350, and 350–380 °C for 12 h at each temperature.

Investigation of Polymers. The curves of the dynamic thermogravimetric analysis were obtained on the derivatograph of the "Paulik, Paulik and Erdel" type in air. The temperature increase rate is 4.5 °C/min.

The ir spectra of polymers and model compounds were taken with the UR-10 and UR-20 spectrophotemeters by using powders pressed with KBr.

The uv spectra of polymers and model compounds were taken with the "Hitachi" spectrophotometer.

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