Synthesis and Investigation of Poly(triazoloquinazolines)

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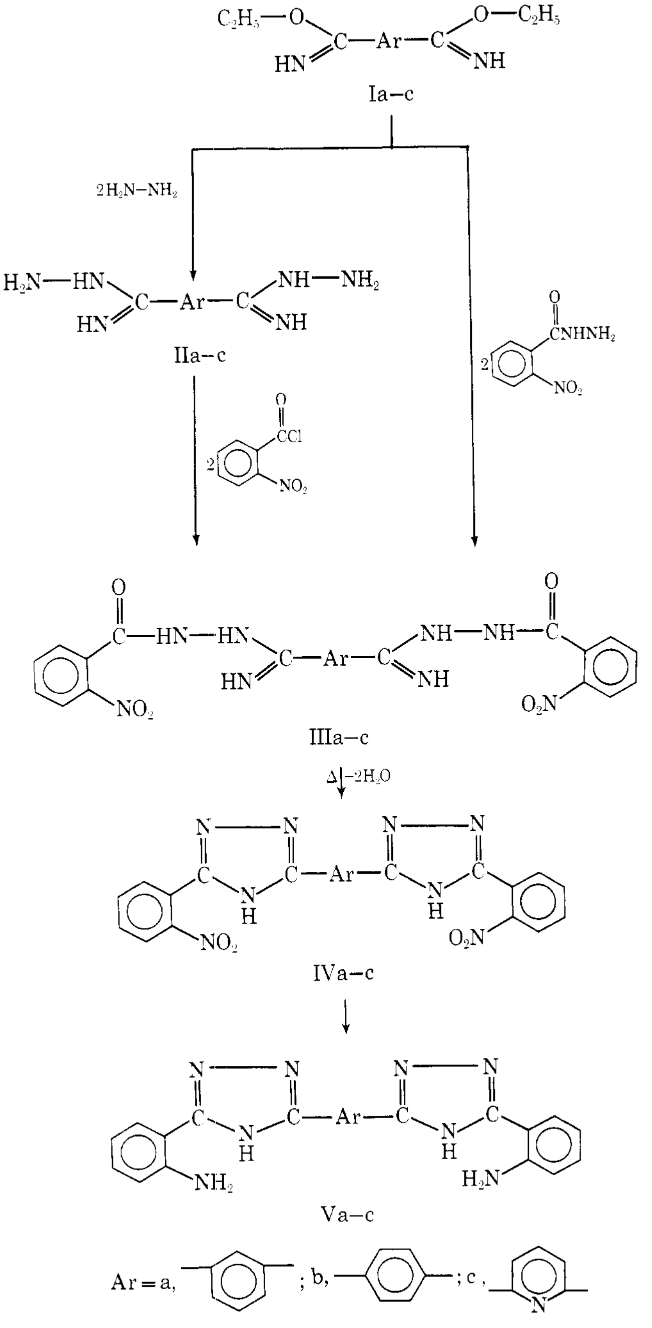
ABSTRACT: A number of polymers containing triazoloquinazoline cycles in the main chains of macromolecules have been prepared by two-stage polycyclocondensation of bis[5-(2-aminophenyl)-1,2,4-triazol-3-yl]arylenes with aromatic dicarboxylic acid dichlorides. The resulting "step-ladder" polymers are completely soluble in trifluoroacetic and sulfuric acids, the reduced viscosities of solutions being 0.3–1 dl/g. The resulting polymers are highly stable to thermooxidative degradation, as shown by dynamic and isothermal thermogravimetric analyses.

Extending the early investigations in the field of new heterocyclic polymers, poly(triazoloquinazolines),[1-4] we have synthesized a number of polymers of this class by interaction of bis[5-(2-aminophenyl)-1,2,4-triazol-3-yl]arylenes with aromatic dicarboxylic acids or with their derivatives. The polymer synthesis was carried out by two-stage polycyclization or one-stage reaction in poly(phosphoric acid), $(P)_n$.

Scheme I

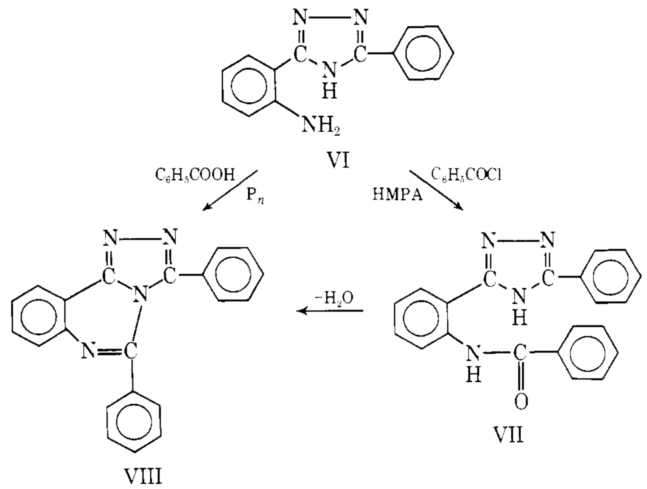


Starting diamines, 1,3-bis[5-(2-aminophenylene)-1,2,4-triazol-3-yl]benzene (Va), 1,4-bis[5-(2-aminophenylene)-1,2,4-triazol-3-yl]benzene (Vb), 2,6-bis[5-(2-aminophenylene)-1,2,4-triazol-3-yl]pyridine (Vc), have been synthesized by two ways (see Scheme I).

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 (VII) and 3,5-diphenyl-*s*-triazolo[4,3-*c*]quinazoline (VIII), have been obtained by interaction of 3-phenyl-5-(2-aminophenylene)-1,2,4-triazole (VI) with benzoyl chloride in hexamethylphosphoramide (HMPA) followed by thermal cyclodehydration or by interaction of VI with benzoic acid in poly(phosphoric acid) (P_n) (see Scheme II).

Scheme II



It should be noted that two isomeric compounds can be produced by cyclodehydration of VII (Scheme III). We succeeded, however, in obtaining only one product of cyclodehydration VII. The structure of this product is presently under investigation; in this paper it is tentatively designated as isomer VIII.

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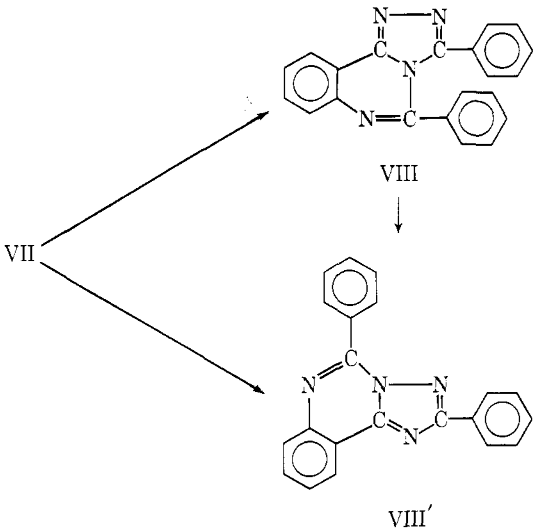
(1) V. V. Korshak, A. L. Rusanov, and Ts. G. Iremashvili, *Avtor. Svidetelstvo SSSR*, in press.

(2) V. V. Korshak, A. L. Rusanov, E. L. Baranov, Ts. G. Iremashvili, and T. B. Bezhuashvili, *Dokl. Akad. Nauk SSSR*, **196**, 1357 (1971).

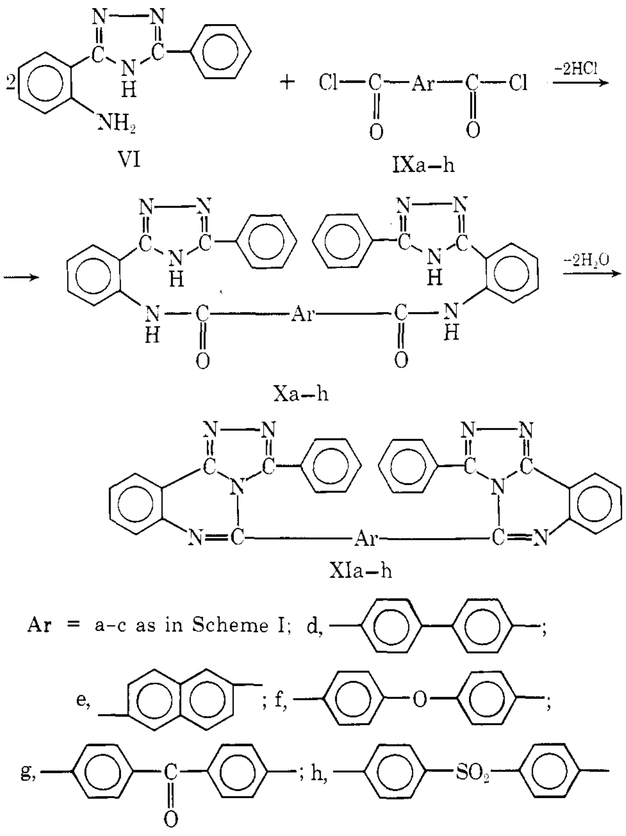
(3) P. M. Hergenrother, *Polym. Prepr. Amer. Chem. Soc., Div. Polym. Chem.*, **12**, 55 (1971).

(4) P. M. Hergenrother, *J. Polym. Sci., Part A*, **9**, 2377 (1971).

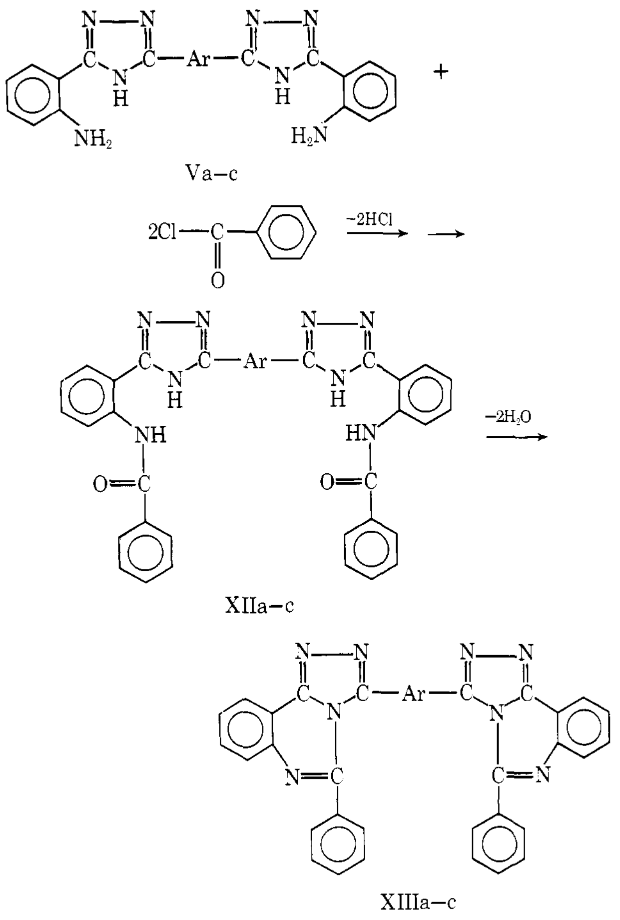
Scheme III



Scheme IV



Scheme V



Ar = a–c as in Scheme I

More complicated model compounds have been obtained by reacting VI with aromatic dicarboxylic acid dichlorides in HMPA followed by thermal cyclodehydration of the reaction products (Scheme IV) as well as by reacting bis[5-(2-aminophenyl-1,2,4-triazol-3-yl]arylenes with benzoyl chloride in HMPA followed by heating of the reaction products (Scheme V).

The structure of all model compounds was confirmed by elemental chemical analysis (Table I) and ir and uv (Table I) spectroscopy. The infrared spectra of all *o*-amido triazoles exhibited the absorption bands at 1640–1670 cm^{-1} which indicated the presence of amide bonds, at 2800–3400 cm^{-1}, which indicated the presence of NH in amide bonds and triazole cycles. In the course of cyclodehydration these bands disappeared, and new bands characteristic of the tertiary nitrogen atom of triazoloquinazoline cycle appeared at 1380 cm^{-1}. As seen from the ultraviolet spectra, the cyclization is accompanied by an increase in intensity, which indicates the formation of a system having a higher degree of conjugation.

Some characteristics of the synthesized model compounds are given in Table I. It should be noted that there are two exothermal processes on the curves obtained from differential thermal analysis of all bis(triazoloquinazolines), which points to a two-stage degradation of these compounds.

The polymers were synthesized according to Scheme VI, where Ar is as in Scheme I and Ar′ is as Ar in Scheme IV.

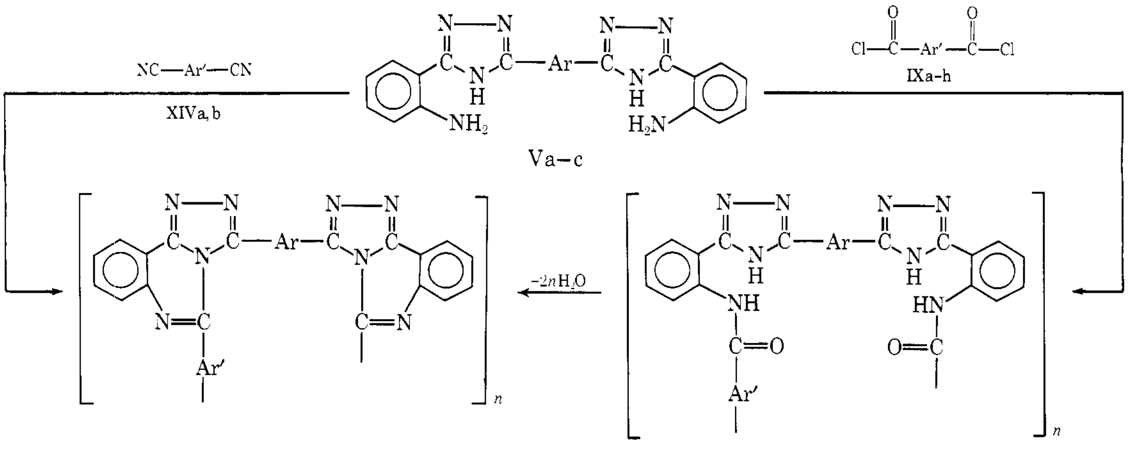
Poly(triazoloquinazoline) synthesis in P_n^{1-4} was realized by interaction of 1,3- and 1,4-bis[5-(2-aminophenylene)-1,2,4-triazol-3-yl]phenylenes (Va and -b) with dinitriles of isophthalic and terephthalic acids. The resulting polymers had viscosities of η_{red} = 0.82–1.2, yet were soluble only in concentrated H_2SO_4, which largely hampers their processing. In this investigation the two-stage method of poly(triazoloquinazoline) synthesis received, therefore, primary emphasis.

The first stage of the two-stage process consisted in the reaction of Va–c with aromatic dicarboxylic acid dichloride under conditions of low-temperature acceptor catalytic polycondensation in HMPA in the presence of LiCl or without it.

On conducting polycondensation in other bipolar aprotic solvents (dimethylacetamide, *N*-methyl-2-pyrrolidone, and so on) polymers with the most rigid chains were isolated from the reaction solution.

The structure of the polymers synthesized was con-

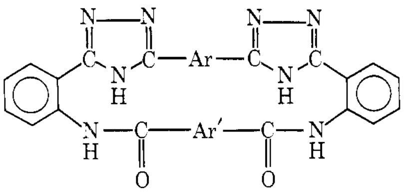
Scheme VI



firmed by elemental chemical analysis, as well as by comparison of their infrared and ultraviolet spectra with those of the model compounds (Table I).

Poly(*o*-amido triazoles) are white to light brown powders soluble in hexamethylphosphoramide, trifluoroacetic, formic, and sulfuric acids depending on thier structure.

Comparatively low viscosity properties of the resulting polymers (η_{red} = 0.28–0.72), indicating a rather low degree of polymerization, can be due both to low nucleophilic reactivity of the diamines used and to possible formation, along with linear macromolecules, of various macrocycles, the simplest of which may be represented as



Due to low viscosities of the polymer solutions, only brittle films were prepared from them.

The X-ray analysis of poly(*o*-amido triazoles) showed that these polymers were partially crystalline, which points to some order of these systems in spite of the asymmetry of their macromolecules.

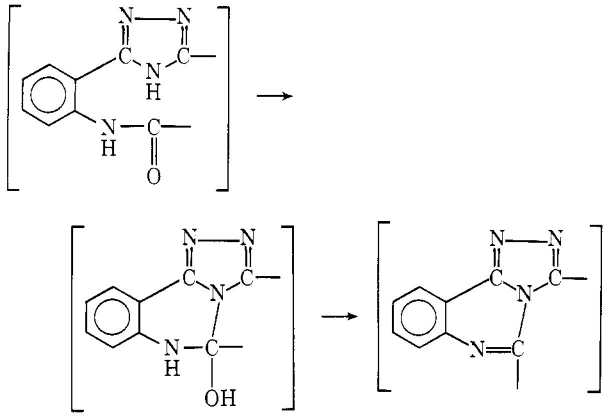
The resulting poly(*o*-amido triazoles) begin to soften in the temperature range of 300–350° as shown by thermomechanical analysis data.

Differential thermal analysis and differential and integral thermogravimetric analysis of poly(*o*-amido triazoles) showed that the weight loss of these polymers occurs in temperature ranges of 60–150°, 300–350°, and at above 475°. The weight loss in the range of 60–150° is apparently brought about by the removal of absorption moisture; that in the range of 300–350° is connected with cyclization of *o*-amido triazole units to triazoloquinazoline ones (Scheme VII), and that at 470° is associated with the degradation process of poly(triazoloquinazolines).

The main properties of poly(*o*-amido triazoles) are given in Table II. The poly(*o*-amido triazoles) synthesized were cyclodehydrated to corresponding poly(triazoloquinazolines) under reduced pressure (0.5 mm) at a maximum temperature of 350–375° for 12 hr. Cyclization conditions for polymers are given in the Experimental Section.

The structure of poly(triazoloquinazolines) was confirmed by the data of elemental chemical analysis, as well as by comparision of the infrared and ultraviolet spectra of polymers with those of the corresponding model compounds (Table III).

Scheme VII



As in the case of model compounds, the cyclization of poly(*o*-amido triazoles) to poly(triazoloquinazolines) is accompanied by the disappearance in the infrared 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 band at 1380 cm^{-1} assigned to the tertiary nitrogen atom. As seen from the ultraviolet spectra, the cyclization is accompanied by the increase in absorption intensity, which is indicative of the formation of a system of a higher degree of conjugation.

The resulting poly(triazoloquinazolines) are brown powders soluble in CF_3COOH and H_2SO_4 (Table III).

As shown by the data of the X-ray analysis, the cyclization gives rise to increasing order in these polymers, that is, all poly(triazoloquinazolines) are crystalline.

As seen from the thermomechanical curves of these polymers, they soften in the range of 400–450°.

Some characteristics of poly(triazoloquinazolines) are given in Table III.

Degradation temperatures of poly(triazoloquinazolines) were determined by dynamic and isothermal thermogravimetric analysis in air. As shown by the dynamic thermogravimetric analysis (circulating air, ΔT = 4.5°/min) the polymers undergo degradation in air (10% weight loss) at 460–545°. Some results of dynamic thermogravimetric analysis are given in Figures 1 and 2 and Table III.

The most thermally stable polymers (for instance, polymer XXIV) reveal practically no weight loss at 425° by isothermal thermogravimetric analysis (in circulating air for 10 hr); at higher temperatures considerable decomposition takes place (Figure 3a). The comparison of polymers XVIc, XXIVc, and XXXIIc prepared from various diamines and terephthaloyl chloride (Figure 3b) showed

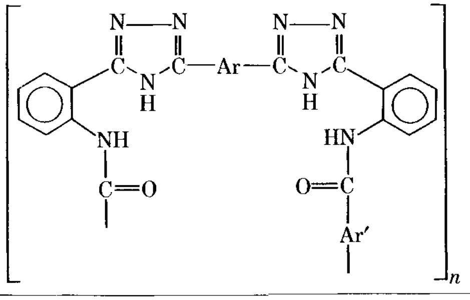
Table I
Some Properties of Model Compounds

Compound 1	Synthesis Condns (°C/hr) 2	Purifcn by Crystzn[b] 3	Yield (%) 4	Mp (°C) 5	General Formula 6	*Anal.*								Dec Temp (°C)		
						Found (%)			Calcd (%)			Uv Spectra[a]		Dec Beginning 15	Max. Dec Temp I 16	Max. Dec Temp II 17
						C 7	H 8	N 9	C 10	H 11	N 12	λ_{max} 13	Log ε 14			
VII		DMF–water (1:1)	79	256	$C_{21}H_{16}N_4O$	73.96	4.59	16.10	74.15	4.69	16.45	280 338	4.70 4.10			
VIII		C_2H_5OH	80	175	$C_{21}H_{14}N_4$	78.34	4.25	17.15	78.25	4.37	17.39	286 341	4.98 4.41			
Xa		DMF–water (2:1)	86.3	328–330	$C_{36}H_{26}N_8O_2$	71.28	4.44	18.09	71.59	4.32	18.6	285 342	4.87 4.13			
Xb		DMF–water (2:1)	83	380–382	$C_{36}H_{26}N_8O_2$	71.16	4.30	18.30	71.59	4.32	18.6	285 348	4.78 4.28			
Xc		DMF	80	355–358	$C_{42}H_{30}N_8O_2$	74.03	4.49	15.90	74.33	4.42	16.52	262 288 370	4.83 4.89 4.6			
Xd		DMF	78.8	391–394	$C_{40}H_{28}N_8O_2$	73.70	4.03	16.99	73.62	4.30	17.17	279 328	4.89 4.75			
Xe		DMF–water (1:2)	81	330	$C_{35}H_{25}N_9O_2$	69.32	4.10	20.58	69.65	4.14	20.90	256	4.83			
Xf		DMF–water (1:1)	75	320	$C_{42}H_{30}N_8O_3$	71.95	4.15	16.02	72.05	4.32	16.16	239 275	4.35 4.75			
Xg		DMF	78	315	$C_{43}H_{30}N_8O_3$	72.84	4.18	15.94	73.08	4.24	15.87	280 340	4.0 4.31			
Xh		DMF–water (1:1)	84	308–310	$C_{42}H_{30}N_8O_4S$	67.58	4.16	15.89	67.92	4.04	16.00	285 340	4.9 4.22			
XIa	375–385/3–4	DMF	75	333–335	$C_{36}H_{22}N_8$	75.93	3.82	19.48	76.32	3.89	19.79	289 345	5.04 4.5	440	490	560
XIb	375–385/3–4	DMA	76	368–370	$C_{36}H_{22}N_8$	76.03	3.75	19.61	76.32	3.89	19.79	289 345	5.02 4.4	440	500	580
XIc	360–375/4	DMF–alcohol (1:1)	80	356–358	$C_{42}H_{26}N_8$	77.33	4.15	17.27	78.5	4.05	17.44	262 288 342	4.87 4.82 4.34	440	500	580
XId	390–395/4	DMA	75	397–400	$C_{40}H_{24}N_8$	77.49	3.44	17.67	77.92	3.88	18.18	278 400	4.75 4.68	460	505	590
XIe	400/4	DMF	82	366–367	$C_{35}H_{21}N_9$	73.44	4.0	22.22	74.02	3.7	22.22	276 370	5.2 4.6	450	500	580
XIf	300–320/4	DMA–alcohol (1:1)	80	310	$C_{42}H_{26}N_8O$	72.15	4.17	16.58	73.56	3.95	17.02	277 400	5.16 4.68	430	510	600
XIg	400/4	DMF	85	330–331	$C_{43}H_{26}N_8O$	76.59	3.18	16.82	77.01	3.88	16.71	294 351	5.01 4.68	430	510	600
XIh	330–334/3–4	DMA	80	345–348	$C_{42}H_{26}N_8O_2S$	70.92	3.52	15.76	71.10	3.68	15.86	289 346	4.94 4.46	460	515	580
XIIa		Alcohol	85	310	$C_{36}H_{26}N_8O_2$	69.83	4.49	18.70	71.59	4.32	18.70	261	4.83			
XIIb		DMF	80	382–383	$C_{36}H_{26}N_8O_2$	71.08	4.38	18.35	71.59	4.32	18.70	254 298	4.7 4.8			
XIIc		DMF	75	321	$C_{35}H_{25}N_9O_2$	70.47	4.16	21.05	70.82	4.96	21.27	257	4.8			

XIIIa	325-330/3	Acetone	76.3	315	$C_{36}H_{22}N_8$	76.85	3.98	19.18	76.07	3.88	19.80	269 283 352	4.73 4.75 4.87	460	530	600
XIIIb	370/4	DMF-H_2O (1:1)	65	368-370	$C_{36}H_{22}N_8$	76.70	3.40	19.74	76.07	3.88	19.80	265 285	4.2 4.3	490	540	610
XIIIc	350/4	DMF-H_2O (1:1)	65	264-264.5[c]	$C_{35}H_{22}N_9$	73.92	3.49	21.98	74.07	3.70	22.22	261 288 340	4.91 5.0 4.4	430	500	580

[a] Ultraviolet spectra are obtained in H_2SO_4, solution concentration being 10^{-5} mol/l. [b] DMF = dimethylformamide; DMA = dimethylacetamide. [c] Mp reported 264-264.5° (see ref 3, 4, and 13).

Table II
Some Properties of Poly(amidotriazoles) of the General Structure



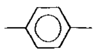
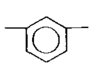
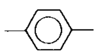
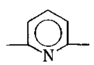
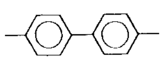
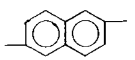
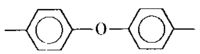
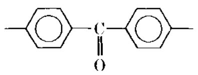
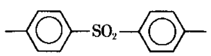
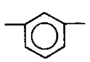
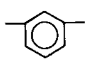
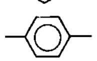
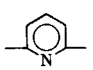
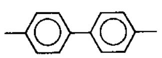
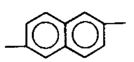
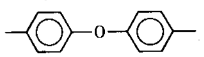
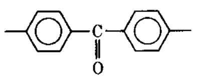
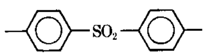
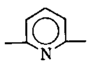
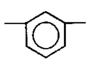
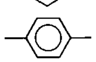
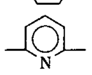
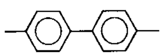
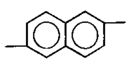
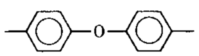
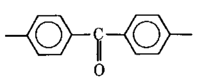
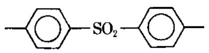
							Anal.						Solubility[c]				Uv Spectra[b]	
							Calcd (%)			Found (%)								
Compound 1	Ar 2	Ar′ 3	Yield (%) 4	η_{red}[a] 5	Color of Polymer 6	General Formula 7	C 8	H 9	N 10	C 11	H 12	N 13	Hexamethylphosphoramide 14	CF_3-COOH 15	HCOOH 16	H_2SO_4 17	λ_{max} 18	Log ε 19
XV			80	0.41	Light brown	$C_{30}H_{20}N_8O_2$	68.72	3.81	21.37	67.79	4.65	19.33	s[d]	s	s	s	236 294	4.35 4.48
XVI			75	0.52	Light brown	$C_{30}H_{20}N_8O_2$	68.72	3.81	21.37	67.74	3.72	19.94	s	s	s	s	248 296	4.45 4.67
XVII			82	0.6	Light yellow	$C_{29}H_{19}N_9O_2$	66.28	3.62	24.0	65.19	4.18	22.55	s	s	s	s	290	4.47
XVIII			80	0.28	Light brown	$C_{36}H_{24}N_8O_2$	72.00	4.0	18.66	69.82	4.55	17.80	ps	s	ps	s	305	4.65
XIX			78	0.55	Light yellow	$C_{34}H_{24}N_8O_2$	70.83	4.17	19.42	69.93	4.03	18.26	ps	s	ins	s	256 289	4.8 4.67
XXX			85	0.33	White	$C_{36}H_{24}N_8O_3$	70.13	3.9	18.18	69.19	3.86	17.63	ps	s	ins	s	236 290	4.73 4.72
XXI			86	0.27	Yellow	$C_{37}H_{24}N_8O_3$	70.8	3.81	17.83	69.39	3.92	16.76	ps	s	ins	s	280	4.55

Table II *(Continued)*

							Anal.						Solubility[c]				Uv Spectra[b]	
							Calcd (%)			Found (%)								
Compound 1	Ar 2	Ar′ 3	Yield (%) 4	η_{red}[a] 5	Color of Polymer 6	General Formula 7	C 8	H 9	N 10	C 11	H 12	N 13	Hexamethylphosphoramide 14	CF_3-COOH 15	HC-OOH 16	H_2SO_4 17	λ_{max} 18	Log ε 19
XXII			75	0.43	Light brown	$C_{36}H_{24}N_8O_4S$	65.06	3.61	16.87	64.80	4.28	17.05	ps	s	ins	s	292	4.55
XXIII			85	0.36	Light brown	$C_{30}H_{20}N_8O_2$	68.72	3.81	21.37	67.82	3.72	20.40	s	s	ps	s	275 352	4.92 4.45
XXIV			90	0.31	Light brown	$C_{30}H_{20}N_8O_2$	68.72	3.81	21.37	66.85	3.91	19.28	s	s	ps	s	282 370	4.96 4.41
XXV			75	0.71	Light yellow	$C_{29}H_{19}N_9O_2$	66.28	3.62	24.0	65.53	4.28	22.83	s	s	ps	s	275 352	4.76 4.4
XXVI			80	0.41	Light brown	$C_{36}H_{24}N_8O_2$	72.00	4.0	18.66	70.82	4.29	17.31	s	s	ps	s	274 390	4.87 4.64
XXVII			75	0.6	White	$C_{34}H_{24}N_8O_2$	70.83	4.17	19.42	69.17	3.83	19.17	s	s	ins	s	273 3.68	4.96 4.85
XXVIII			82	0.32	White	$C_{36}H_{24}N_8O_3$	70.18	3.9	18.18	68.46	4.08	17.59	s	s	ins	s	273 392	4.95 4.36
XXIX			78	0.33	Yellow	$C_{37}H_{24}N_8O_4$	70.80	3.81	17.83	71.04	3.83	16.77	ps	s	ins	s	283 347	4.96 4.65
XXX			80	0.45	Yellow	$C_{36}H_{24}N_9O_1S$	65.06	3.61	16.87	63.87	3.51	16.07	ins	s	ins	s		
XXXI			82	0.42	White	$C_{29}H_{19}N_9O_2$	66.30	3.62	24.00	65.98	3.38	22.94	s	s	s	s	282 346	4.95 4.27
XXXII			84	0.35	White	$C_{29}H_{19}N_{19}O_2$	66.30	3.62	24.00	65.64	3.90	23.07	s	s	s	s	275 355	5.11 4.66
XXXIII			78	0.72	Yellow	$C_{28}H_{18}N_{10}O_2$	63.88	3.42	26.61	62.28	3.50	25.96	s	s	s	s	260 295	4.28 4.18
XXXIV			75	0.4	Yellow	$C_{35}H_{23}N_9O_2$	70.00	3.82	20.96	68.98	3.75	19.48	s	s	ps	s	260 300	4.84 4.80
XXXV			80	0.45	White	$C_{33}H_{23}N_9O_2$	68.63	4.00	21.83	67.84	4.03	21.06	ps	s	ps	s	264 310	4.64 4.47
XXXVI			85	0.52	Yellow	$C_{35}H_{23}N_9O_3$	68.09	3.72	20.42	66.58	3.45	19.17	ps	s	ins	s	273	4.84
XXXVII			78	0.43	Yellow	$C_{36}H_{23}N_9O_3$	68.46	3.64	20	67.09	3.70	18.98	ins	s	ins	s	283 340	4.86 4.34
XXXVIII			80	0.6	Yellow	$C_{35}H_{23}N_9O_4S$	63.16	3.46	19	62.45	3.05	18.20	ins	s	ins	s	272	4.78 4.48

[a] η_{red} of 0.5% CF_3COOH solution at 25°. [b] Ultraviolet spectra obtained in H_2SO_4 with $c = 10^{-5}$ mol/l. [c] Polymer described by Hergenrother.[4] [d] s = soluble; ps = partially soluble; ins = insoluble.

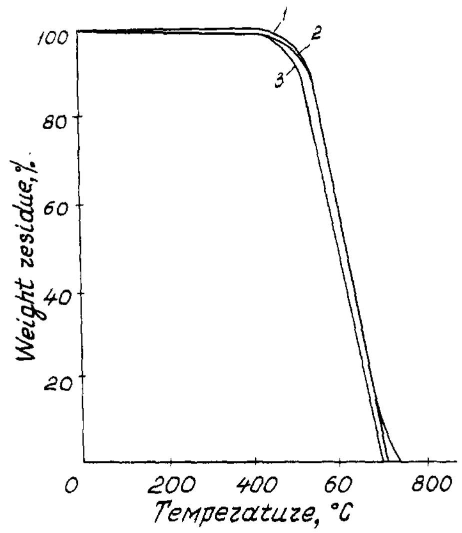


Figure 1. Curves of the dynamic thermogravimetric analysis of poly(triazoloquinazolines) XVIc (1), XXIVc (2), and XXXIIc (3) (in air, ΔT = 4.5°/min)

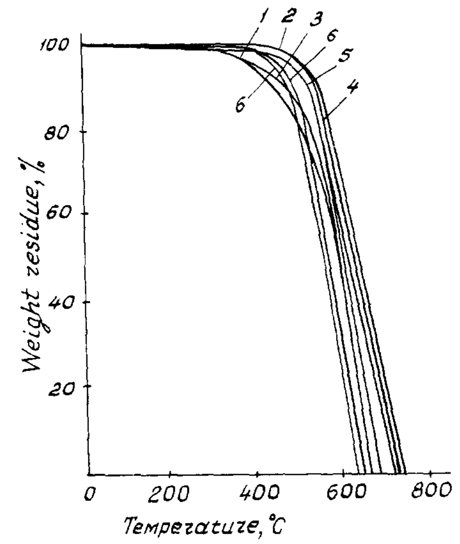
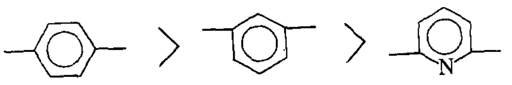


Figure 2. Curves of the dynamic thermogravimetric analysis of poly(triazoloquinazolines) XXIVc (1), XXVIc (2), XXIIIc (3), XXVIIc (4), XXIXc (5), XXVIIIc (6), XXVc (7).

that the thermal stability polymers decreases depending on the diamine residue in Chart I.^{5}

Chart I



The comparison of polymers prepared from 1,3-bis[5(2-aminophenylene)-1,2,4-triazol-3-yl]benzene and dichlorides of various dicarboxylic acids (Figure 3c) showed that the introduction of flexibilizing groups to macromolecules leads to notable lowering of thermal properties of the polymers; this is in agreement with the results obtained previously.^{6} Investigations of the influence of the acid residue on poly(triazoloquinazoline) indicated that thermal stability of polymers decreases according to Chart II.

Brittle films were obtained from solutions of some poly(triazoloquinazolines) in trifluoroacetic acid.

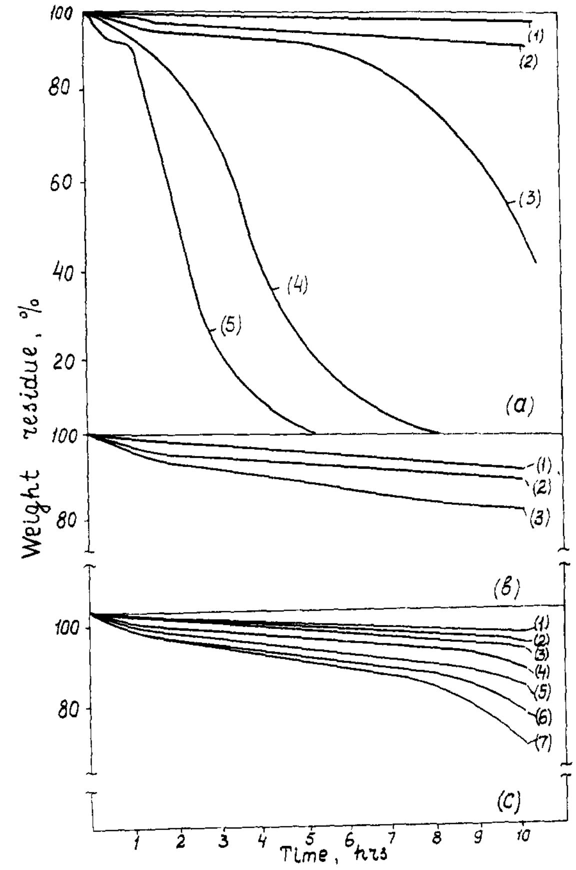
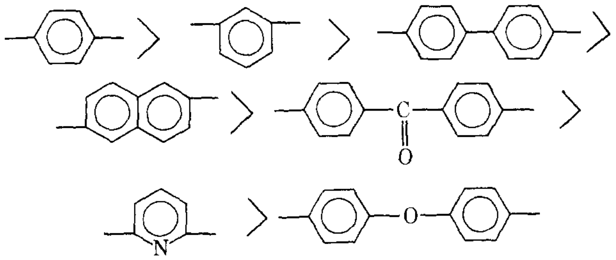


Figure 3. Curves of the isothermal thermogravimetric analysis (in air, for 10 hr). (a) Poly(triazoloquinazoline) XXIVc at 400° (1), 425° (2), 450° (3), 475° (4), 500° (5); (b) poly(triazoloquinazolines) XVIc (1), XXIVc (2), and XXXIIc at 425°; (c) poly(triazoloquinazolines) XXIIIc-XXIXc at 425°: XXIVc (1), XXIIIc (2), XXVIc (3), XXVIIc (4), XXIXc (5), XXVc (6), XXVIIc (7).

Chart II



Experimental Section

The bisiminoethyl ether of isophthalic acid (**1a**) was obtained as described previously^{7} and purified by crystallization from dry ether cooled up to −15 to −20°: mp 71°, lit. mp 71°,^{7} yield 70%.

The bisiminoethyl ether of terephthalic acid (**1a**) was obtained as described previously^{8} and purified by crystallization from dry dioxane: mp 105°, lit. mp 102.5–103.5°,^{8} yield 73%.

The dichlorohydrate of bisiminoethyl ether of pyridine-2,6-dicarboxylic acid was obtained as follows. The dinitrile (12.9 g; 0.1 mol) of pyridine-2,6-dicarboxylic acid was synthesized by the known method,^{9} and 250 ml of dry dioxane and 15 ml of dry ethanol were saturated at 0° with dry HCl for 14–16 hr. The reaction mixture was held for 5 days at 0°, and the residue formed was filtered off, washed with ether, and dried: mp 110°, yield 87%. *Anal.* Calcd for $C_{11}H_{15}N_3O_2\cdot 2HCl$: C, 44.89; H, 5.78; Cl, 24.15; N, 14.29. Found: C, 44.83; H, 5.69; Cl, 24.01; N, 14.25.

The bisiminoethyl ether of pyridine-2,6-dicarboxylic acid (**1a**)

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(5) V. V. Korshak, A. L. Rusanov, and Ts. G. Iremashvili, *Avtor. Svidetelstvo SSSR* 334219, *Bull. 12* (1972).

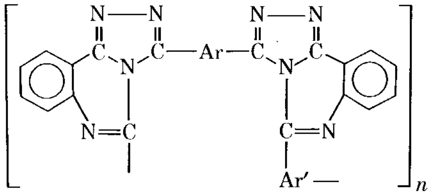
(6) V. V. Korshak, A. L. Rusanov, D. S. Tugushi, and G. M. Cherkasova, *Macromolecules*, **5**, 807.

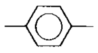
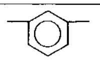
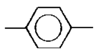
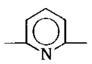
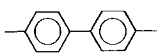
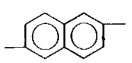
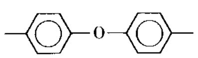
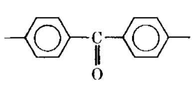
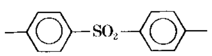
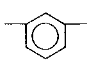
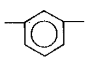
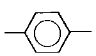
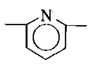
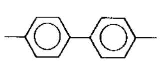
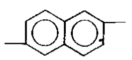
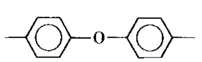
(7) Japan Patent 260 N15991 (1968).

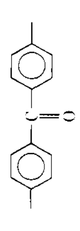
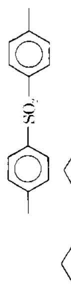
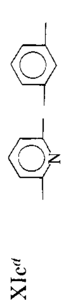
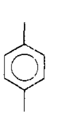
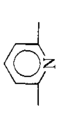
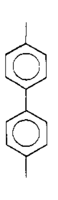
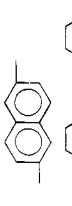
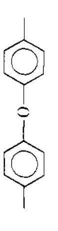
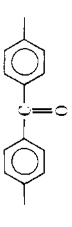
(8) E. L. Zaitseva, A. Ya. Yakubovich, G. I. Braz, and G. P. Basov, *Zh. Org. Khim.*, **34**, 3708 (1964).

(9) P. M. Hergenrother, *J. Polym. Sci., Part A*, **7**, 945 (1969).

Table III
Some Properties of Poly(triazoloquinazolines) of the General Structure



Compound 1	Ar 2	Ar′ 3	Yield (%) 4	General Formula 5	η_{red} CF_3COOH–H_2SO_4 (0.5%), 25° 6	*Anal.*						Solubility			Uv Spectra[b]		Dec Temp[c] (°C) 18
						Calcd (%)			Found (%)								
						C 7	H 8	C 9	C 10	H 11	N 12	CF_3-COOH 13	HC-OOH 14	H_2SO_4 15	λ_{max} 16	Log ε 17	
XVc			70	$C_{30}H_{16}N_8$	0.5–0.45	73.77	3.27	22.95	72.46	3.44	22.11	s	ps	s	293 345	5.04 4.56	540
XVIc			65	$C_{30}H_{16}N_8$	0.48–0.45	73.77	3.27	22.95	70.40	3.19	22.33	s	ps	s	296 355	5.48 4.76	540
XVIIc			73	$C_{29}H_{15}N_9$	0.44–0.2	71.12	3.65	25.76	69.97	3.45	25.59	s	ps	s	290 355	4.96 4.85	500
XCIIIc			80	$C_{36}H_{20}N_8$	0.35–0.3	76.60	3.54	20.0	74.93	3.61	19.20	s	ps	s	289 346	5.04 4.46	540
XIXc			70	$C_{34}H_{20}N_8$	0.53–0.47	75.55	3.70	20.74	75.80	3.92	18.47	s	ins	s	272 368	5.1 4.6	490
XXc			70	$C_{36}H_{20}N_8O$	0.33–0.27	74.48	3.45	19.38	72.99	3.77	18.99	s	ins	s	237 288 404	4.72 5.34 4.35	460
XXIc			75	$C_{37}H_{20}N_8O$	1.0–1.02	74.74	3.36	18.85	73.37	3.72	18.26	ps	ins	s	286 401	4.96 4.33	470
XXIIc			70	$C_{36}H_{20}N_8O_2S$	0.39–0.51	68.79	3.18	19.42	68.94	3.23	17.96	ps	ins	s	292 345	4.95 4.47	510
XXIIIc			75	$C_{30}H_{16}N_8$	0.27–0.25	73.77	3.27	22.95	79.87	3.98	21.90	s	s	s	277 353	4.75 4.28	540
XXIVc			72	$C_{30}H_{16}N_8$	0.4–0.44	73.77	3.27	22.95	72.87	3.26	21.20	s	s	s	277 354	5.0 4.4	540
XXVc			68	$C_{29}H_{15}N_9$	0.72–0.28	71.12	3.65	25.76	69.52	3.81	24.98	s	s	s	282 342 362	5.02 4.4 4.46	465
XXVIc			70	$C_{36}H_{20}N_8$	0.42–0.47	76.60	3.54	20.0	74.86	3.68	18.82	s	ps	s	264 398	4.96 4.76	545
XXVIIc			70	$C_{34}N_{20}N_8$	0.5–0.45	75.55	3.70	20.74	74.77	3.37	20.00	s	ins	s	272 313 354	4.75 4.3 4.0	530
XXVIIIc			65	$C_{36}H_{20}N_8O$	0.54–0.45	74.48	3.45	19.38	72.90	3.46	19.46	s	ins	s	273	5.02	485

XXIXc		70	$C_{37}H_{16}N_8O$	0.4 0.3	74.74	3.36	18.85	74.92	3.38	18.86	s	ins	s	394 285 348	4.54 4.96 4.35	515
XXXc		70	$C_{36}H_{20}N_8O_2S$	0.4–0.2	68.79	3.18	19.42	67.04	3.06	18.84	s	ins	s	285 355	4.3 4.1	480
XXXIc^d		68	$C_{29}H_{15}N_9$	0.38–0.35	71.12	3.07	25.76	69.98	3.15	24.89	s	s	s	275 340	4.46 4.12	495
XXXIIc		70	$C_{29}H_{15}N_9$	0.56–0.45	71.12	3.07	25.76	68.98	3.24	25.15	s	s	s	270 340	4.84 4.38	525
XXXIIIc		60	$C_{28}H_{14}N_{10}$	0.35–0.35	68.57	2.85	28.5	66.83	2.75	27.86	s	ps	s	283 355	4.98 4.25	485
XXXIVc		75	$C_{35}H_{19}N_9$	0.48–0.44	74.34	3.36	22.30	72.98	3.42	21.95	s	ins	s	268 315	5.18 4.68	520
XXXVc		75	$C_{33}H_{19}N_9$	0.55–0.47	73.25	3.15	23.29	72.81	3.60	22.05	s	ins	s	266 310	5.14 4.8	515
XXXVIc		72	$C_{35}H_{19}N_9O$	0.6–0.5	72.30	3.44	21.69	70.85	3.16	20.15	s	ins	s	283 347	5.09 4.47	545
XXXVIIc		65	$C_{36}H_{19}N_9O$	0.45–0.4	72.60	3.25	21.34	71.15	3.02	20.48	s	ins	s	285 350	5.09 4.63	510
XXXVIIIc		65	$C_{36}H_{19}N_9O_2S$	0.45–0.4	70.58	3.02	20.03	68.90	2.96	18.35	s	ins	s	286 356	4.41 4.15	535

[a] See Table II, footnote d. [b] Ultraviolet spectra obtained in H_2SO_4 with $c = 10^{-5}$ mol/l. [c] Decomposition temperature is assumed to be a temperature at which a 1% weight loss occurs with a temperature increase rate of 4.5°/min in air. [d] Polymer first described by Hergenrother.[3,4]

was prepared as follows. The dichlorohydrate of bisiminoethyl ether of pyridine-2,6-dicarboxylic acid was dissolved in distilled water cooled up to 0° and treated with a 30% solution of K_2CO_3 to neutral reaction to receive a free bisiminoethyl ether of pyridine-2,6-dicarboxylic acid. The product was purified by crystallization from dry ether: mp 67°, yield 90%. *Anal.* Calcd for $C_{11}H_{15}N_3O_2$: C, 59.73; H, 6.78; N, 18.99. Found: C, 59.92; H, 6.70; N, 19.00.

The hydrazide of *o*-nitrobenzoic acid was synthesized by the known method[10] and crystallized from ethanol: yield 95%, mp 123°, lit. mp 123°.[10]

The bisamidrazone of isophthalic acid (IIa) was prepared by the known procedure[11] and crystallized from acetonitrile. At 150° the product color changes to orange, and at 280° it becomes colorless, which is in agreement with the published results.[11]

The bisamidrazone of terephthalic acid (IIb) was prepared by the known method;[12] the product has no melting point and changes to an orange color at 180°, being colorless at 300°, which is consistent with the data published.[12]

The bisamidrazone of pyridine-2,6-dicarboxylic acid (IIc) was prepared by the known method[9] and recrystallized from water: mp 231° (in a block preheated to 210°), lit. mp 231° dec.[9]

Bis(2-nitrobenzoyl)amidrazones (IIIa–c) were prepared by two ways: (a) 0.1 mol of bisiminoethyl ether of dicarboxylic acid (IIIa–c) was boiled with 0.2 mol of hydrazide of *o*-nitrobenzoic acid in 300 ml of ethanol. Yellow products precipitated on boiling were filtered off and crystallized.[13]

2-Nitrobenzoic acid chloride (0.02 mol) was dropped at 0° to the stirred mixture of 0.01 mol of bisamidrazone of aromatic dicarboxylic acid (IIa–c), 30 ml of dimethylacetamide, and 2.12 g (0.02 mol) of Na_2CO_3. The reaction mixture was stirred for 3 hr and poured into ice water; the yellow product was precipitated identical with the product synthesized by the above method. The properties of the products IIIa–c are given in Table IV. Bis[5-(2-nitrophenyl)-1,2,4-triazol-3-yl]arylenes (IVa–c) were prepared by heating of IIIa–c under reduced pressure (0.5–1 mm). Synthesis conditions and the general properties of IVa–c are represented in Table IV.

Bis[5-(2-aminophenyl)-1,2,4-triazol-3-yl]arylenes (Va–c) were prepared by reduction of IVa–c with hydrazine hydrate on Raney Ni in boiling ethanol for 4–6 hr. The general properties of the product are given in Table IV.

All aromatic dicarboxylic acid dichlorides were prepared as described previously and had melting points reported in the literature.

3-Phenyl-5-(2-benzamidophenyl)-1,2,4-triazole (VI) was synthesized by the known method[2] and purified by crystallization from the dimethylformamide-water mixture (1:1), mp 256° dec. Compound VIII was prepared as follows: (a) by the known method[2] and crystallization from alcohol (mp 175°); (b) by interaction of 0.01 mol of 3-phenyl-5-(*o*-aminophenyl)-1,2,4-triazole with 0.01 mol of benzoic acid in 15 ml of P_n at 50° for 1 hr, at 100° for 1 hr, at 150° for 1 hr, at 200° for 1 hr, and at 220° for 12 hr. The synthesized product was sublimed at 250–255° (1 mm) and crystallized from alcohol (mp 175°), yield 90%.

Arylenebis[3-phenyl-5-(2-amidophenyl)-1,2,4-triazoles] (Xa–h) were prepared by the known method;[5] the general properties and characterization of the products are given in Table I.

5,5′-Bis[3-phenyl-*s*-triazolo[4,3-*c*]quinazolyl]arylenes (XIa–h) were prepared by thermal cyclodehydration of Xa–h; their general properties and characteristics are given in Table I. Arylene-5,5′-bis[3-(2-benzamidophenyl)]-1,2,4-triazoles (XIIa–c) and 3,3′-bis[5-phenyl-*s*-triazolo[4,3-*c*]quinazolyl]arylenes (XIIIa–c) were synthesized by the known method; their general properties and characteristics are given in Table I.

Synthesis of Polymers. Synthesis of poly(*o*-amido triazoles) (XV–XXXIX) was performed by the following general method. Bis[5-(2-aminophenyl)-1,2,4-triazol-3-yl]arylene (0.01 mol) was placed into a 50-ml four-necked flask fitted with a mechanical stirrer, thermometer, argon inlet, and a funnel to charge aromatic dicarboxylic acid dichloride, 30 ml of hexamethylphosphoramide containing 5% of LiCl was added, and the mixture was stirred to form a solution. To the solution equimolar amounts of corresponding aromatic dicarboxylic acid dichloride were added in solid state during 20 min. The reaction was conducted at room

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Table IV
Basic Properties of Diamines and Some Intermediates

Compound	Cyclizn Condn (°C/hr)	Recrystallization from[a]	Yield (%)	Mp (°C)	General Formula	*Anal.* Found (%)			*Anal.* Calcd (%)		
						C	H	N	C	H	N
IIIa		DMF	90	230 dec	$C_{22}H_{18}N_8O_6$	53.60	3.62	22.54	53.88	3.67	22.83
IIIb		DMF-H_2O (1:1)	92	245 dec	$C_{22}H_{18}N_8O_6$	53.70	3.59	22.48	53.88	3.67	22.83
IIIc		Ethanol	88	199-200 dec	$C_{21}H_{17}N_9O_6$	50.98	3.38	25.63	51.40	3.46	25.66
IVa	260/3	Alcohol-water (1:1)	78.5	246-247	$C_{22}H_{14}N_8O_4$	59.33	2.84	24.33	58.15	3.07	24.67
IVb	260/3	Acetone-water (1:1)	80	313-315	$C_{22}H_{14}N_8O_4$	57.72	2.90	24.65	58.15	3.07	24.67
IVc	210/4	Acetone-water (1:4)	90	315	$C_{21}H_{13}N_9O_4$	55.15	2.40	27.35	55.40	2.42	27.70
Va		Dioxane-water (1:1)	70	318-320	$C_{22}H_{18}N_8$	66.02	4.94	27.90	66.62	4.63	28.35
Vb		DMF-H_2O (1:2)	75	330-331	$C_{22}H_{18}N_8$	66.84	4.52	28.04	66.62	4.63	28.35
Vc		Ethanol	70	338-340[b]	$C_{21}H_{17}N_9$	63.45	3.87	31.63	63.81	4.05	31.90

[a] See Table I, footnote *b*. [b] Lit. mp 338° (see ref 3, 14, and 13).

temperature for 6-8 hr. The resulting solution was poured into distilled water. The polymer was thoroughly washed with water, extracted with ethanol for 45-50 hr, and dried under reduced pressure, to a constant weight at 50-60°. The general properties and characteristics of poly(*o*-amido triazoles) are given in Table II.

Poly(triazoloquinazolines) were prepared by solid-state cyclodehydration of aromatic poly(*o*-amido triazoles) under reduced pressure (0.5-1 mm Hg) at 50, 100, 150, 200, 250, and 300° for 1 hr and at 350-375° for 12 hr.

The basic characteristics of poly(triazoloquinazolines) (XV-XXXIX) are given in Table III.

Synthesis of Polymers in P_n. Bis[5-(2-aminophenyl-1,2,4-triazol-3-yl]arylene (0.01 mol), the dinitrile (0.01 mol) of aromatic dicarboxylic acid, and P_n (20 g) were placed into a three-necked flask. The mixture was stirred at 100, 150, and 200° for 1 hr and at 250° for 3 hr. The resulting polymers are soluble only in H_2SO_4; η_{red} is 0.2-1.2.

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

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

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

Polymerization of 4-Hydroxybenzenesulfonyl Chloride

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ABSTRACT: The conversion of 4-hydroxybenzenesulfonyl chloride (I) to high molecular weight poly(1,4-phenylenesulfonate) by treatment with tertiary amines in polar amide solvents is described. Conditions giving the highest molecular weight polymer are 1.25 equiv of triethylamine in hexamethylphosphoramide at 0°. This crystalline polymer has a glass transition temperature of 119° and a crystalline melting temperature of 276°. Solution polymerization of 3,5-dimethyl-4-hydroxybenzenesulfonyl chloride (II) is also described, along with copolymerization of I and II. Melt polymerization of I produces a polymer containing both sulfonate and hydroxysulfone repeat units.

There has been considerable interest shown in polymers of the general type $(-C_6H_5X-)_n$ throughout the last decade due largely to their high melting points and thermal stability. Several members of this "poly(phenylene) family" have recently become commercial products (X = S, CO_2, CONH). Synthesis of poly(1,4-phenylenesulfonate)($PPSO_3$, X = SO_3) has been prevented by the lack of a suitable monomer (*e.g.*, 4-hydroxybenzenesulfonyl chloride, I). Although a variety of 3,5-disubsituted-4-hydroxybenzenesulfonyl chlorides have been reported,[1-4] the parent compound was only recently isolated.[5,6] We found that I can be prepared by treating sodium 4-hydroxybenzenesulfonate with an excess of thionyl chloride in the presence of a catalytic amount of dimethylformamide at 60°. This study is concerned with the conversion of I into a high molecular weight polymer. Low-temperature solution polymerizations conducted in polar amide solvents in the presence of tertiary amines were found to be quite suitable for this reaction.

Results and Discussion

Polymer Properties. Poly(1,4-phenylenesulfonate) is normally obtained as a white, powdery solid which is insoluble in common organic solvents as well as most polymer solvents [*e.g.*, methylene chloride, tetrahydrofuran (H_4furan), acetone, dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), tetramethylurea (TMU), sulfolane, formic acid, etc.] Polymer of intermediate molecular weight (inherent viscosity, ≤0.5) is soluble in dimeth-

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