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Synthesis and Investigation of Poly(aroylene-*s*-triazoles)

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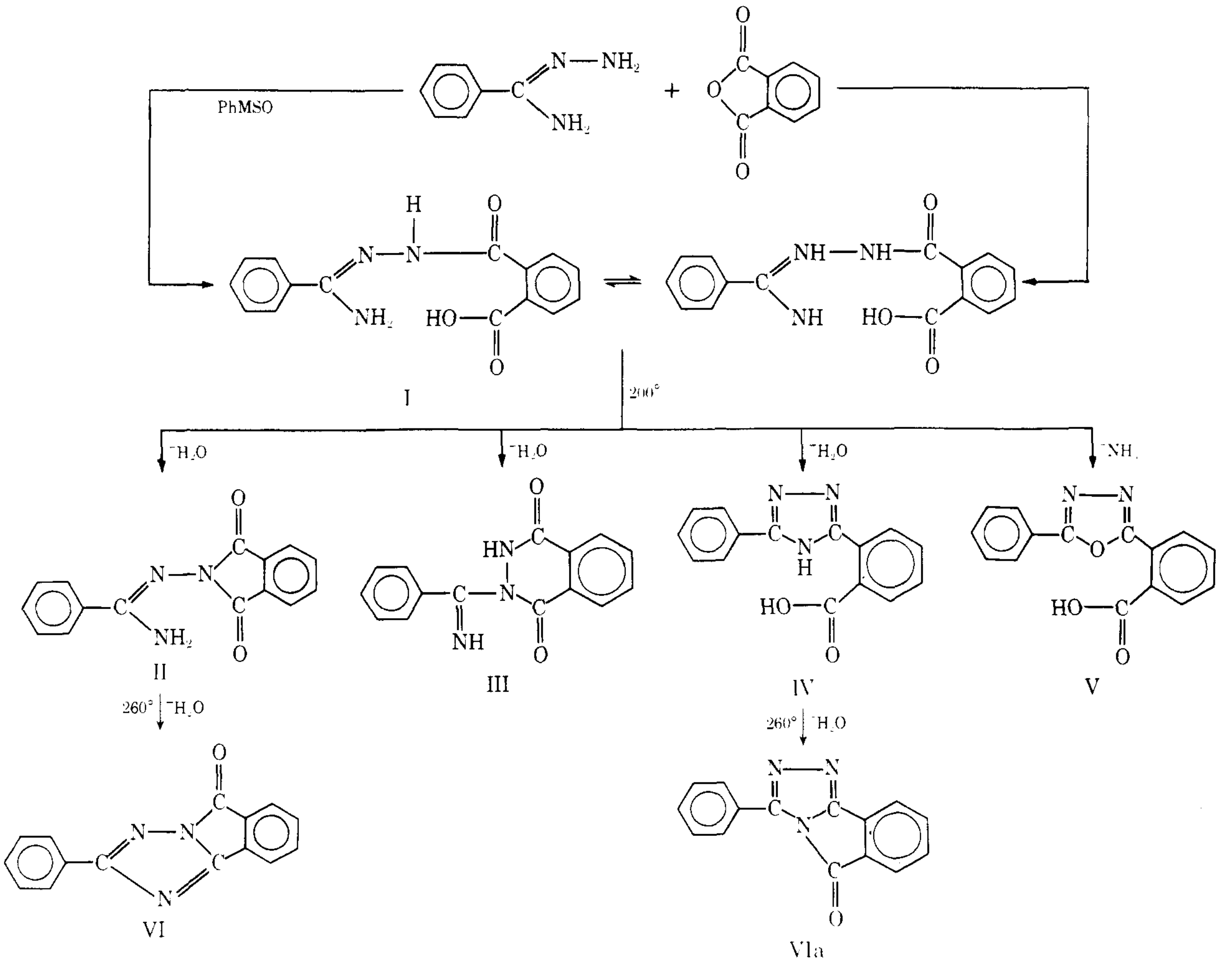
ABSTRACT: Poly(aroylene-*s*-triazoles), thermally stable "step-ladder" polymers, were prepared by the interaction between bisamidrazones and tetracarboxylic acid dianhydrides using the multi-stage procedure and one-stage polycyclocondensation in poly(phosphoric acid) (PPA). The effect of polymer structure on solubility and thermal stability was investigated.

Recent publications on poly(aroylene-*s*-triazoles), poly(benzoylene-*s*-triazoles),[1] and poly(naphthoylene-*s*-triazoles)[2] prompted us to disclose our independent findings on the preparation of these polymers.[3-6] In contrast with the very well-known poly(aroylenebenzimidazoles),[7] these polymers were discovered in 1968,[3] when we found that solid-state polycyclocondensation of poly(*o*-carboxybenzoylamidrazones) led to the formation of poly(aroylene-*s*-triazoles), but not to poly(*o*-carboxyphenyl-*s*-triazoles).[8] Following investigations carried out by several groups resulted in the preparation of the two general types of poly(aroylene-s-triazoles), poly(benzoylene-s-triazoles) [poly-



(1)

Table I
Characterization of Model Compounds

				Elemental analysis						Uv spectra[b]		
				Calcd, %			Found, %					
No.	Yield,[a] %	Mp, °C	Formula	C	H	N	C	H	N	λ_{max}, nm	Log ε	Color
VI	53	172	$C_{15}H_9N_3O$	72.87	3.64	17.01	72.42	3.89	16.99	268	4.6435	Yellow
XI	92	265	$C_{21}H_{13}N_3O$	76.84	3.73	14.15	76.87	3.58	14.09	244	4.4150	
	85[c]									318	4.3424	
										390	4.4624	
										409	4.4314	
XIV + XIVa	49	330–335	$C_{24}H_{12}N_6O_2$	69.23	2.91	20.21	69.13	3.31	20.47	266	4.7634	Orange
XVII +	85	420–425	$C_{30}H_{14}N_6O_2$	73.43	2.86	17.14	73.45	3.05	17.84	239	4.5051	Orange
XVIIa	80[c]									268	4.5563	
										286	4.5315	
										396	4.5315	
XXa	50	420	$C_{18}H_8N_6O_2$	63.53	2.37	24.70	63.39	2.12	25.37	217	4.8513	Yellow
										287	4.2788	
XXb	54	396	$C_{24}H_{12}N_6O_2$	69.23	2.91	20.21	69.80	2.99	20.34	245	4.6435	
										285	4.8573	
XXc	52	350	$C_{24}H_{12}N_6O_2$	69.23	2.91	20.21	69.57	2.93	20.33	242	4.1761	Yellow
										284	3.9031	
XXd	50	392	$C_{23}H_{13}N_7O_2$	65.87	3.10	23.39	65.56	3.13	23.12	244	4.4150	Yellow
										317	4.3617	
XXIIIa	79[c]	500	$C_{26}H_{12}N_6O_2$	70.90	2.73	19.09	70.58	3.14	19.10	240	4.8865	Yellow
										302	4.1461	
										394	4.7243	
										416	4.8062	
XXIIIb	84	450	$C_{32}H_{16}N_6O_2$	74.42	3.10	16.28	73.84	3.07	16.16	224	4.8808	Yellow
	80[c]									250	4.6532	
										273	4.6232	
										380	4.7243	
XXIIIc	82	425	$C_{32}H_{16}N_6O_2$	74.42	3.10	16.28	74.08	3.06	16.51	240	4.2304	Yellow
	80[c]									292	4.3424	
										390	4.7853	
										412	4.7634	
XXIIId	87	440[e]	$C_{31}H_{15}N_7O_2$	71.95	2.91	18.96	71.91	3.04	19.00	228	4.9345	Yellow
	75[c]									304	4.3979	
										394	4.7559	
										416	4.7993	

[a] Yields after two sublimations. [b] Obtained in H_2SO_4 with $c = 10^{-5}$ *M*. [c] Obtained by multistage procedure. [d] Mp reported 360°.[1] [e] Mp reported 410–415°.[2]

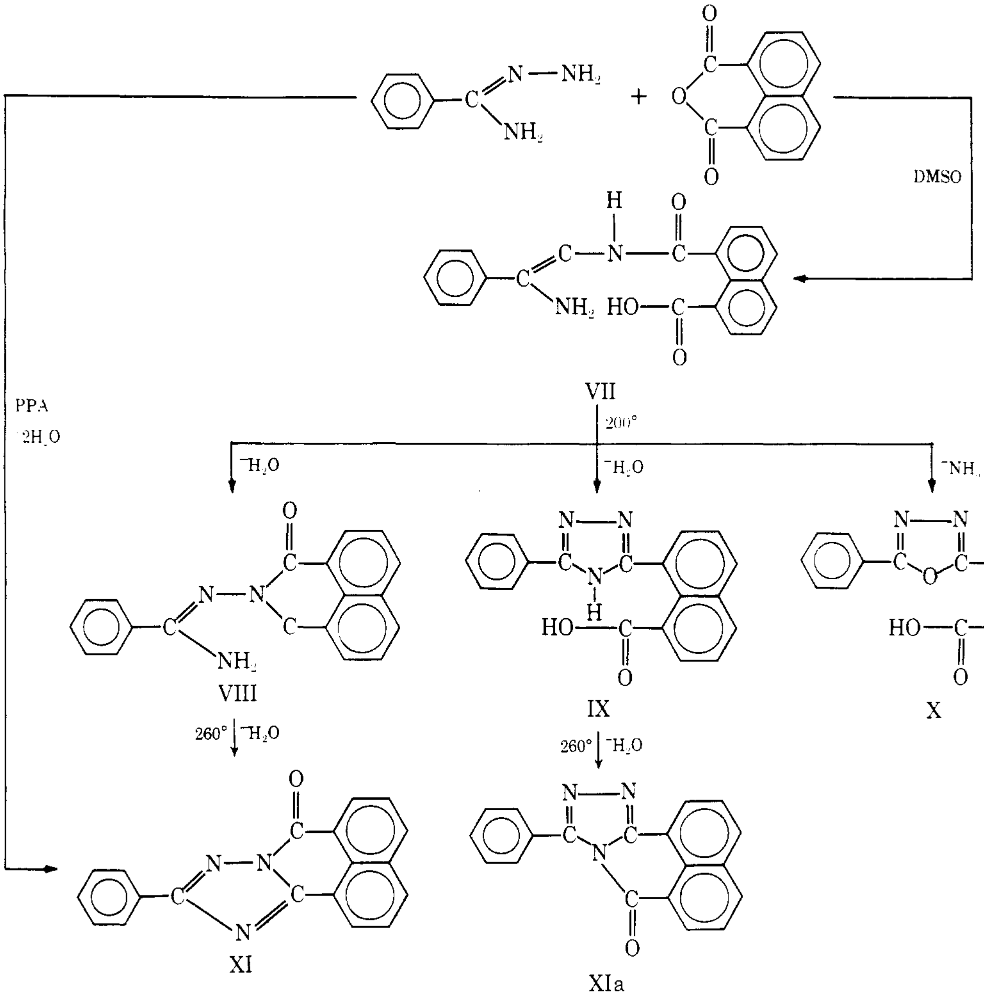
(isoindolotriazolones)],[1] and poly(naphthoylene-*s*-triazoles) (poly[benzobis(*s*-triazolo)phenanthrolines]).[2] It might to be expected that the methods for the preparation of these polymers and their general properties would differ very significally, as it was demonstrated for poly(aroylenebenzimidazoles);[7] however, no experimental data suggesting this point of view were published elsewhere. As a result we have carried out comparative investigations concerning methods for the preparation and general properties of poly(isoindolo-*s*-triazolones) and poly[benzobis(*s*-triazolo)phenanthrolines]. As the general methods for the synthesis of these polymers, the multi-stage procedure and one-stage polycyclocondensation in PPA were used.

Discussion

Model Compounds. Prior to polymer synthesis, a series of model compounds shown in Table I was prepared[9,10] to obtain information on the conditions of polymer formation and to aid in identification. The simplest model compounds, 2-phenylisoindolo[1,2-*b*]-*s*-triazol-5-one and 10-phenyl-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one, were prepared by the reaction of benzamidrazone with phthalic and naphthalic anhydrides.

The one-stage cyclocondensation reaction between benzamidrazone and phthalic anhydride in PPA led to the formation of a mixture of unidentified products. Because of this, the multi-stage process was used for the preparation of 2-phenylisoindolo[1,2-*b*]-*s*-triazol-5-one (eq 1).

The first stage of this process was carried out in dimethyl sulfoxide (DMSO) at 25° and led to the formation of *N*-(*o*-carboxybenzoyl)benzamidrazone (I) in almost quantitative yield. The structure of I was indicated by ir spectra and elemental analysis. On heating, compound I melted and solidified twice indicating that the chemical structure changed due the cyclization reactions. The thermal cyclization of I in the solid state is a very complex process. As may be seen from reaction I, cyclization of I at 200° may lead not only to benzamidino-*N*-phthalimide (*N*-amino(phenylmethylene)aminophthalimide) (II), the main cyclodehydration product, and 3-phenyl-5-(*o*-carboxyphenyl)*s*-triazole (IV), convertable to isoindolotriazolone, but to cyclic hydrazide (III)[11] and 2-phenyl-5-(*o*-carboxyphenyl)-1,3,4-



(2)

oxadiazole (V)[12,13] which may not be converted to isoindolotriazolones. In the model reaction, formation of III and V leads to lower yield of isoindolotriazolone; in polymer forming reactions, formation of structures similar to III and V leads to the presence of imperfections in the macromolecular chains. In addition, the cyclodehydration of II and IV may lead to different isomers of isoindolotriazolones VI and VIa. After heating of the reaction mixture at 360° for 10 hr we have isolated only one product tentatively designated as isomer VI.

Product VI was obtained with the relatively low yield (Table I); it is due not only to the side reactions taking place at the cyclodehydration stage, but also to the cleavage of the isoindolotriazolone ring by nucleophilic reagents as described previously for the 1,2-benzoylenebenzimidazole ring[14,15] and to partial decomposition of VI under severe cyclization conditions (360°).

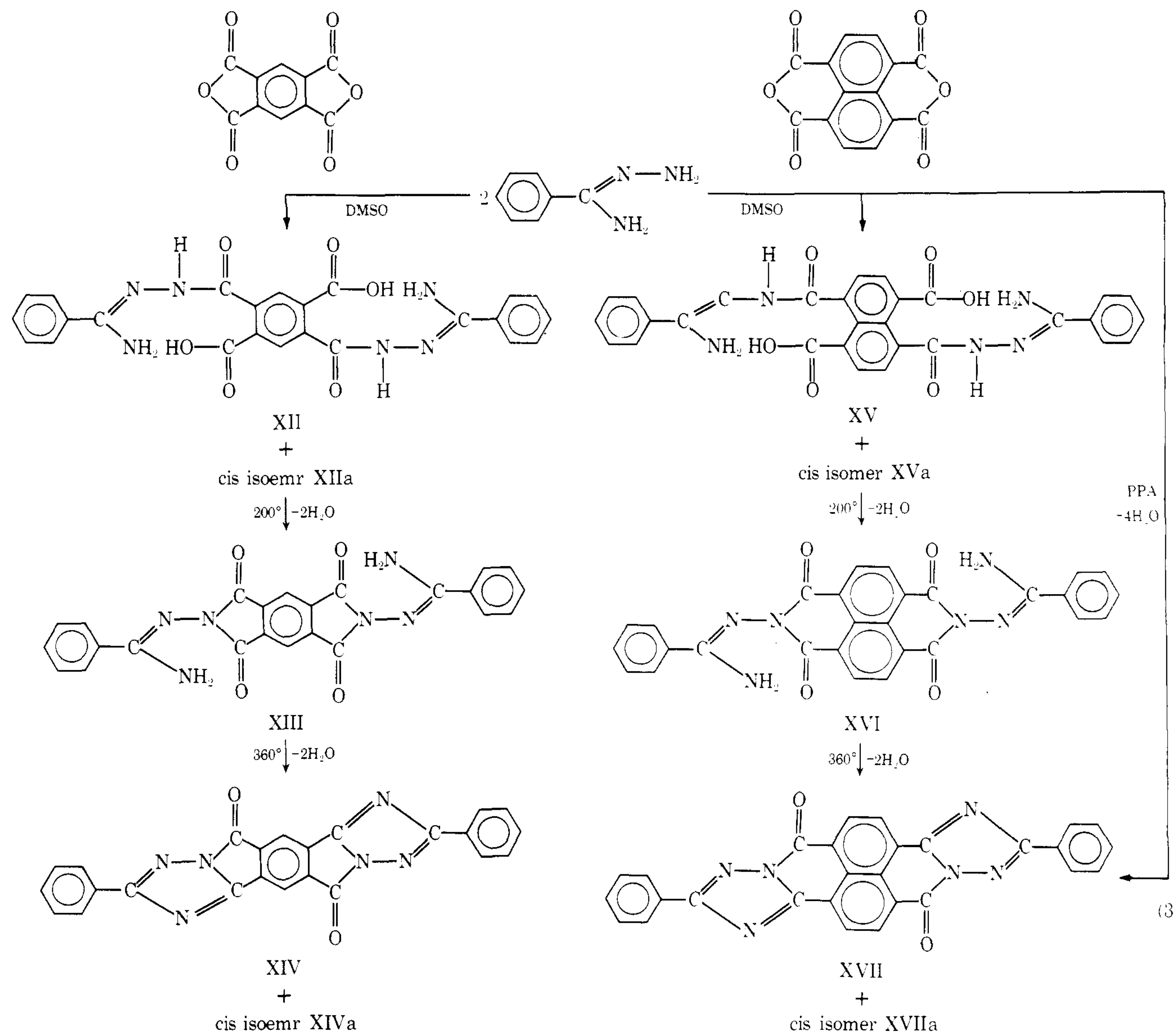
In contrast with VI, 10-phenyl-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one was prepared by both procedures (multi-stage and one-stage in PPA).

It is necessary to note that due to the lower (in comparison with phthalic anhydride) reactivity of naphthalic anhydride the interaction between this compound and benzamidrazone was carried out at 70°. Under these conditions 8-carboxynaphth-1-oylbenzamidrazone (VII) formed was cyclodehydrated, at least partially, to benzamidino-*N*-naphthalimide (VIII). The solid-state thermal dehydration at 200° may lead to complete cyclization and formation of benzamidino-*N*-naphthalimide ([*N*-(aminophenylmethylene)amino]naphthalimide) (VIII), 3-phenyl-5-(8-carboxynaphth-1-yl)-*s*-triazole (IX), convertable to isomeric benzotriazolosoquinolinones (XI and XIa), and to 2-phenyl-5-(8-carboxynaphth-1-yl)-1,3,4-oxadiazole (X), which may not be cyclodehydrated to XI or XIa (eq 2).

The formation of the cyclic hydrazide (a seven-membered ring) is unlikely in the naphthalene series. The driving force to form the six-membered imide in the naphthalene series is far greater than that for the five-membered imide in the phthalic series. As a result, in accordance with ir spectrum data, VIII is almost the only intermediate product. However, the multi-stage cyclodehydration did yield at the last stage small amounts of an unidentified sublimate arising presumably from decomposition of VIII due to the low nucleophility of the amidine NH_2 group and low electrophility of the CO groups in the naphthalimide ring. As a result, the cyclocondensation in PPA was used as a general method for the preparation of XI, Cyclocondensation in PPA may lead to the formation of only two intermediate structures, VIII and X, because cyclization of acylamidrazones in strong acids does not lead to the formation of the *s*-triazole ring.[12,13] X cannot be converted into XI. High yield of 10-phenyl-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one indicates that the reaction proceeds through the formation of VIII only.

The structures of VI and XI were suggested by the ir spectra (Figures 1 and 2), uv spectra, and elemental analysis (Table I).

More complex model compounds were obtained by the interaction reactions between benzamidrazone and dianhydrides of pyromellitic and naphthalene-1,4,5,8-tetracarboxylic acids (eq 3). In accordance with the results obtained during the investigation of the simplest model compounds, the interaction between benzamidrazone and pyromellitic dianhydride was carried out in DMSO and led to the for-



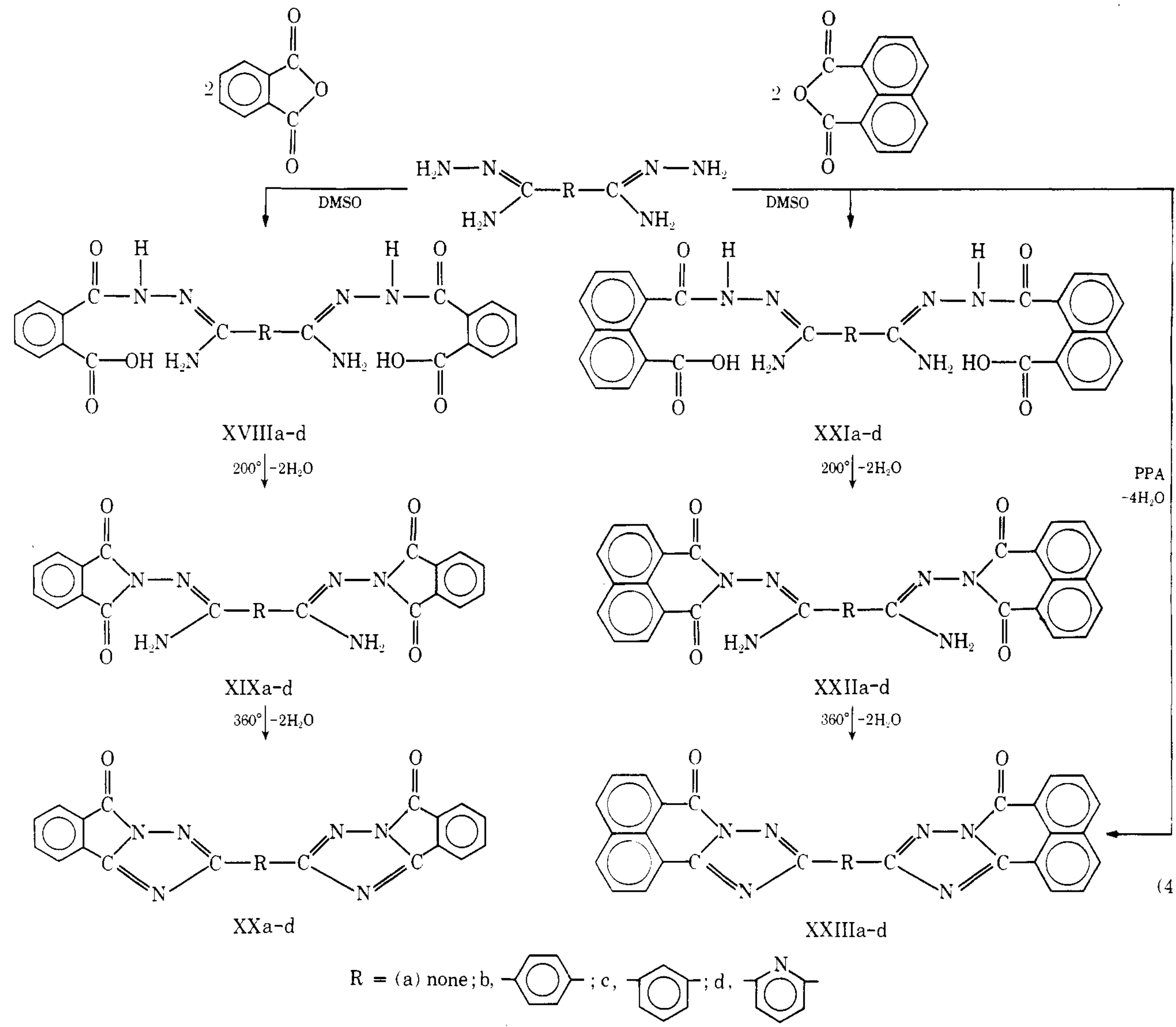
(3)

mation of isomeric [(dicarboxy)tere(iso)phthaloyl]dibenzamidrazones (XII and XIIa) in quantitative yields. Consequent solid-state thermal cyclodehydration at 200° may lead to the products related to II–V; ir spectrum data indicate that the main intermediate product is *N,N′*-di(benzamidino)-*N″,N‴*-pyromellitimide (XIII) (only this product is shown as the intermediate product in eq 3). Cyclodehydration of XIII at 360° led to the formation of *trans*-XIV and *cis*-XIVa isomers of 2,10-diphenyl[benzdi(pyrrolo-*s*-triazolones)].

A mixture of cis and trans isomers was obtained with a low yield (see Table I); low yields of these products are due to the reasons mentioned above for compound VI.

In accordance with the results obtained during the investigation of the simplest model compounds, the interaction between benzamidrazone and naphthalene-1,4,5,8-tetracarboxylic acid dianhydride was carried out by both procedures (multi-stage and one-stage in PPA (eq 3)). The first stage of the multi-stage process was carried out in DMSO at 25° and led to the formation of a mixture of the isomeric (dicarboxy)naphthoylbibenzamidrazones (XV and XVa) in almost quantitative yield. Thermal treatment of these products in the solid state at 200° may lead to the products related to VIII–X; ir spectrum data indicated that the main intermediate product is *N,N′*-di(benzamidino)—1,4,5,8-naphthaldiimide {*N,N′*-bis[aminophenyl(methylen)amino]-1,4,5,8-naphthalenetetracarboxylic-1,4,5,8-diimide} (XVI). (Only this compound is shown as the intermediate product in eq 3.) Cyclodehydration of XVI at 360° led to the formation of the mixture of cis and trans isomers of diphenyl-[benzodi(*s*-triazolo)phenanthrolinediones] (XVII and XVIIa). The exact name of the cis isomer is (in accordance with[2]) 2,11-diphenylbenzo[1*mn*]-*s*-triazolo[5,1-*b*;1′,5′-*j*]-3,8-phenanthrolinedione. A mixture of XVII and XVIIa was obtained in a high yield, but even better results were obtained when the synthesis of this model compound was carried out as a one-stage process in PPA. This reaction led to the formation of the intermediate product XVI and mixture of the final products (XVII + XVIIa) in high yields (Table I). The structures of XIV + XIVa and XVII + XVIIa were suggested by the ir spectra (Figures 1 and 2), uv spectra, and elemental analysis (Table I).

A series of the model compounds was also prepared by the interaction of phthalic and naphthalic anhydrides with the bisamidrazones of oxalic, terephthalic, isophthalic, and pyridine-2,6-dicarboxylic acids. In accordance with the results obtained during the investigation of the simplest model compounds, the interaction between bisamidrazones and phthalic anhydride was carried out as a multi-stage process (eq 4). At the first stage of the reaction the interac-



(4)

tion between bisamidrazones and phthalic anhydride carried out in DMSO at 25° led to *N,N'*-di(*o*-carboxybenzoyl)bisamidrazones (XVIIIa–d) in quantitative yields. Consequent solid-state cyclodehydration of XVIIIa–d at 200° may lead to the products related to II–V. Ir spectrum data indicate that the main intermediate products are *N,N'*-di(phthalimido)diamidines (XIXa–d). (Only these compounds are shown as the intermediate products in eq 4.) Cyclodehydration of XIXa–d at 360° led to the formation of bis(isoindoilo[1,2-*b*]-*s*-triazol-5-on-2-yls) (XXa–d) with relatively low yields (Table I).

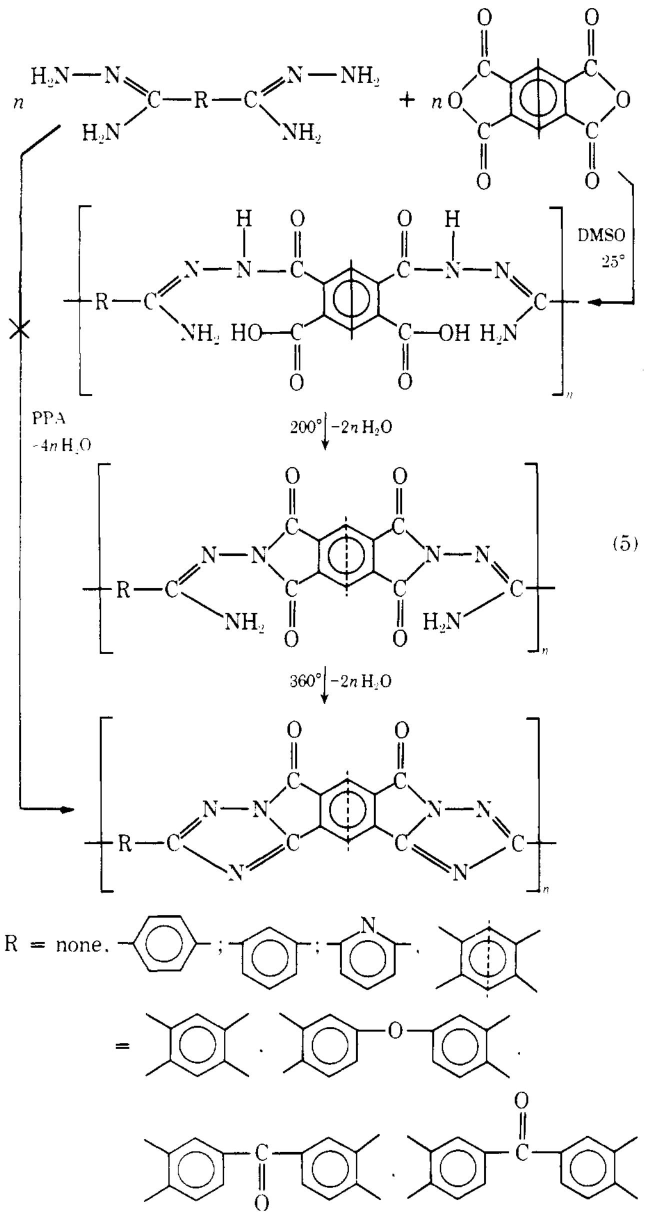
The interaction reactions between bisamidrazones and naphthalic anhydride were carried out by both procedures (multi-stage and one-stage in PPA).

The first stage of the multi-stage process was carried out in DMSO and led to the formation of *N,N'*-di(8-carboxy-1-naphthoyl)bisamidrazones (XXIa–d) in almost quantitative yields. Solid-state cyclodehydration of XXIa–d at 200° led to the formation of *N,N'*-di(naphthoylimido)diamidines {*N,N'*-bis[(aminomethylidyne)nitrilo]dinaphthalimides} (XXIIa–d). Some other intermediates related to IX and X also may be formed, but in accordance with the ir spectrum data just the compounds XXIIa–d are the main intermediate products. Consequent cyclodehydration of XXIIa–d at 360° led to the formation of 10,10'-bis(7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-ons) (XXIIIa–d) in high yields (Table I).

Even better results were obtained when the reaction was carried out as a one-stage process in PPA. The reaction led to the formation of the intermediate products XXII and final heterocycles in high yields (Table I).

The structures of XXa–d and XXIIIa–d were suggested by the ir spectra (Figures 1 and 2), uv spectra, and elemental analysis data (Table I). We did not succeed in synthesizing XXIIIa (where R = none) in PPA which may be explained by decomposition of oxalylbisamidrazone in PPA as previously shown for oxalyldihydrazide.[16,17]

Investigation of model reactions has shown that the synthesis of poly(benzoylene-*s*-triazoles) [poly(isoindolotriazolones)] may be carried out by the multi-stage process, whereas the synthesis of poly(naphthoylene-*s*-triazoles) may be carried out by both the procedures (multi-stage polycyclocondensation and the one-stage procedure in PPA). Furthermore we have found that even the multistage synthesis of the model compounds VI, XIV + XIVa, and XXa–d leads to the formation of pure products with relatively low yields. This result, which is inconsistent with previous results,[1] is a major point, because it indicated that during polymer forming reactions some side processes leading to the formation of imperfect structures can take place.



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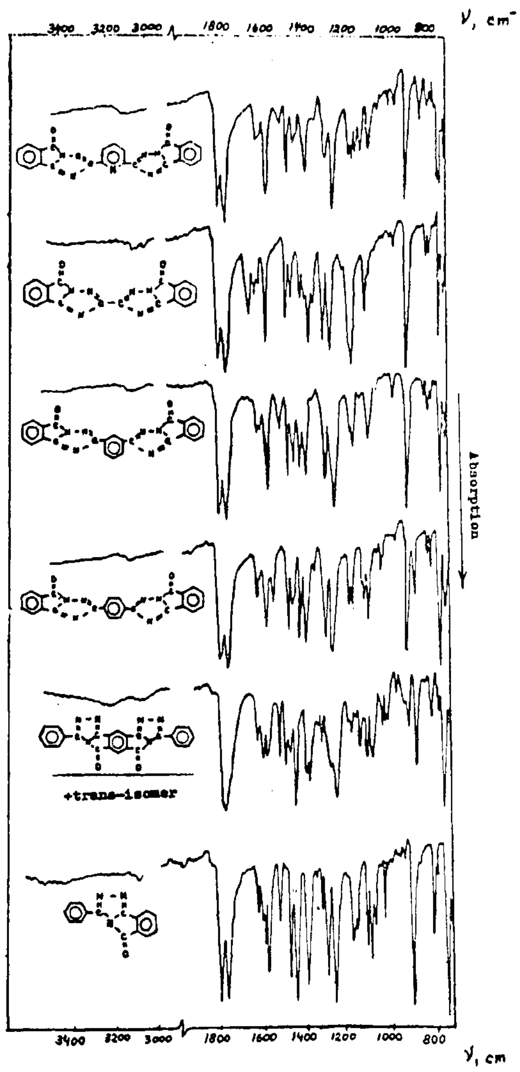


Figure 1. Infrared spectra of model compounds VI, XIV + XIVa, XXa, XXb, XXc, and XXd.

Polymers. The multi-stage synthesis of poly(benzoylene-*s*-triazoles) [poly(isoindolotriazolones)] was carried out by the interaction between bisamidrazones and bis(phthalic anhydrides) in accordance with eq 5.

The first stage of this process, the synthesis of poly(*o*-carboxybenzoylamidrazones), was carried out in polar solvents such as *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAC), hexamethylphosphoramide (HMPA), *N*-methyl-2-pyrrolidone (NMP), and DMSO at 25°. The best results were obtained when the reactions were carried out in DMSO; these results were in accordance with ref 1.

In contrast with unsubstituted bis(*o*-phenylenediamines), the bisamidrazones behave as bifunctional monomers because of the great difference in the nucleophilic reactivities of amide and hydrazine groups of bisamidrazone units;[18] as a result it is possible to add the solid tetracarboxylic acid dianhydride to the solution of the bisamidrazone without any gelation. The only exceptions are the processes using the dianhydride of 3,3′,4,4′-benzophenonetetracarboxylic acid, because benzophenone carbonyl groups may react with bisamidrazone with the formation of the intermolecular Schiff base unit.

The reactions of the poly(*o*-carboxybenzoylamidrazones) synthesis proceed at a high rate due to the high nucleophility of the bisamidrazones hydrazine portions.[19] All reactions are exothermic; for example, the reactions between bisamidrazones and the dianhydride of 3,3′,4,4′-diphenyl ether tetracarboxylic acid in DMSO at 25° are characterized by the following enthalpies: −30.2 kcal/mol for terephthalic bisamidrazone, −27.7 kcal/mol for isophthalic bisamidrazone, −21.1 kcal/mol for oxalic bisamidrazone, indicating that the Gibbs energies in all cases have high negative values (because the enthropies of such reactions are relatively small).[20] The resultant clear yellow viscous solutions of poly(*o*-carboxybenzoylamidrazones) in DMSO were diluted and poured into large excess of dry acetone or were cast onto glass plates as clear yellow films. Similar to poly(*o*-carboxyamides)[21] and poly(*o*-amino-*o*-carboxyamides),[22] poly(*o*-carboxybenzoylamidrazones) are hydrolytically unstable. As a result, their solution viscosities were determined from their reaction solutions without isolating and purification of the polymers. The structures of poly(*o*-carboxybenzoylamidrazones) were suggested by the ir spectra (Figure 3).

Some of poly(*o*-carboxybenzoylamidrazones) whose properties are given in Table II were of sufficiently high molecular weight to form films.

Poly(*o*-carboxybenzoylamidrazones) in the form of films

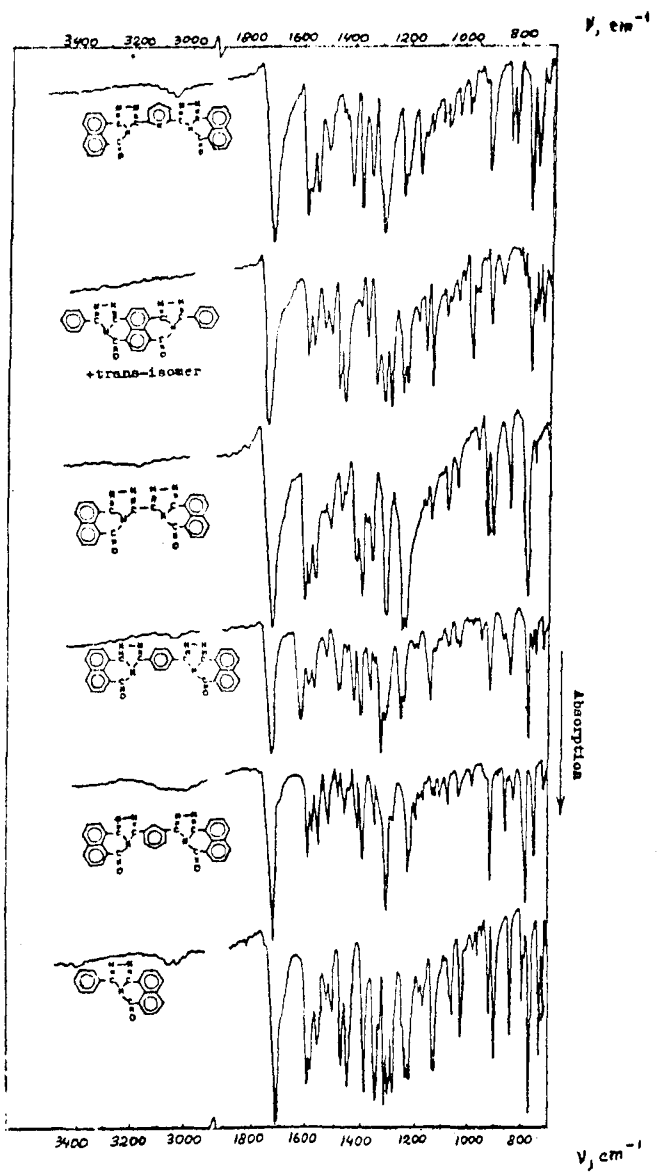


Figure 2. Infrared spectra of model compounds XI, XVII + XVIIa, XXIIIa, XXIIIb, XXIIIc, and XXIIId.

or fibrous precipitates were heated from 25 to 360° for 10 hr, and then at 360° for 10 hr at reduced pressure (10^{-3} mm). Heating to 200° led to the formation of polymers, whose ir spectra indicated a structure of partially cyclized polymers containing repeating units related to model compounds II–V (Figure 3) and mainly amidinoimide structures shown in eq 5. Further heating led to the formation of polymers containing benzoylene-*s*-triazole (isoindolotriazolone) rings along with other structural units (Figure 3).

Powders and films of poly(benzoylene-*s*-triazoles) were reddish-black similar to pyrrone powders and films.[22] Like pyrrone polymers, they were insoluble in all solvents including sulfuric, methanesulfuric, ethanesulfuric acids, PPA, DMSO, HMPA, NMP, DMAC, DMF, etc; it is probable that their insolubility as well as the insolubility of pyrrones[23,24] is due to their cross-linked structure. All polymers failed to soften up to 400° and in accordance with TGA data (ΔT = 4.5°/min) decomposed in air (5% weight loss) at 380–410°. The relatively low thermal stability of poly(benzoylene-*s*-triazoles) is probably due to the imperfections in the polymeric chains and the instability of the fragment of the heterocycle. Some properties of poly(benzoylene-*s*-triazoles) are given in Table III.

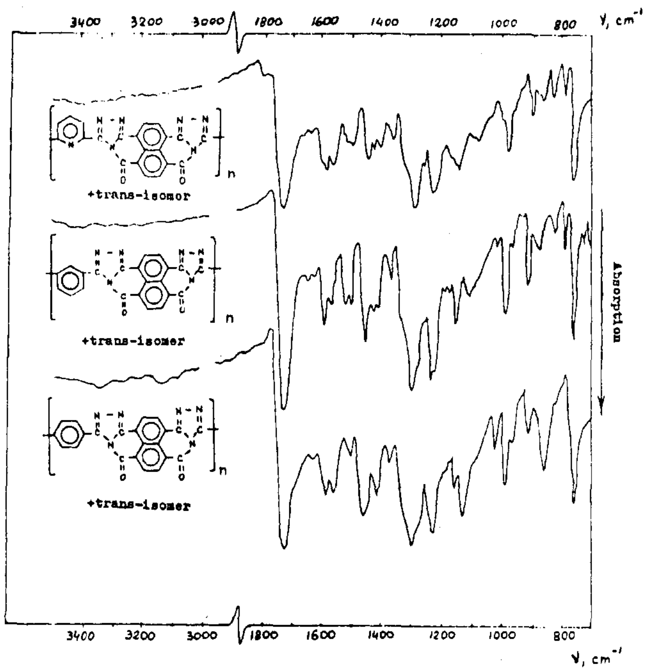
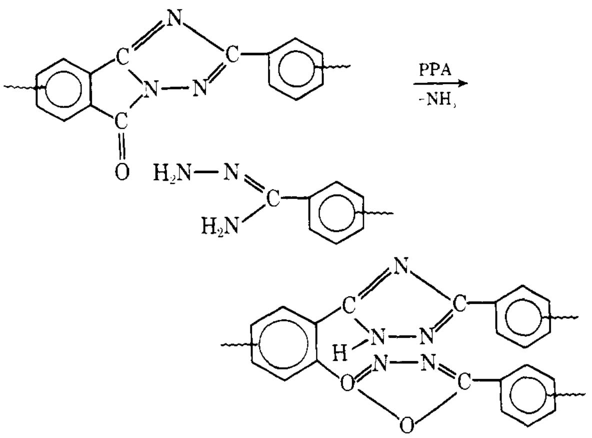


Figure 3. Infrared spectra of polymers P-VI (top); P-VI heated at 200° (10^{-3}) for 10 hr (middle); P-VI heated at 360° (10^{-3} mm) for 10 hr (P-VIC) (bottom).

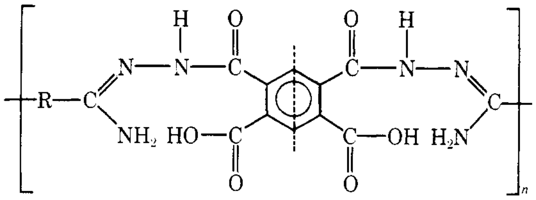
Our attempts to carry out the synthesis of poly(benzoylene-*s*-triazoles) in PPA led to gelation of the reaction solutions; the same results were obtained during direct interaction of bis(*o*-phenylenediamines) with bis(phthalic anhydrides) in PPA.[23,24] Gelation during the synthesis of poly(benzoylene-*s*-triazole) is probably due to the formation of cross-linked structures resulting from cleavage of benzoylene-*s*-triazole (isaindolotriazolone) rings of macromolecules with amidrazone end groups.

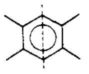
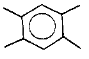
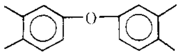
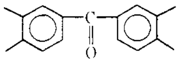
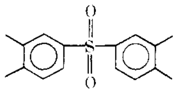
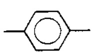
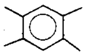
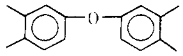
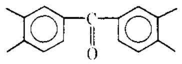
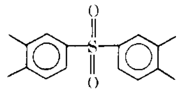
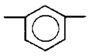
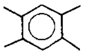
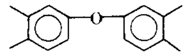
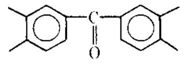
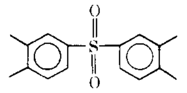
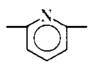
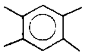
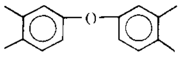
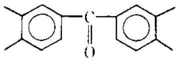
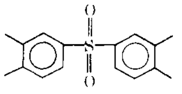


(6)

Poly(naphthoylene-*s*-triazoles) (poly[benzobis(*s*-triazolo)phenanthrolines]) were prepared by the interaction of bisamidrazones with the dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid. In spite of the positive results obtained during the investigation of model reactions, our attempts to synthesize these polymers using a multi-stage process were unsuccessful; during the interaction of bisamidrazones with dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid in polar solvents such as DMF, DMAC, HMPA, NMP, and DMSO, the polymers precipitated from the reaction solutions at early stages of polycondensations. The same results were obtained by Evers.[2]

Table II
Characterization of Poly(*o*-carboxybenzoylamidrazones) of General Formula



No.	R		Formula	η_{red},[a] dl/g	Film-forming properties,
P-I	None		$C_{12}H_{10}N_6O_6$	0.30	No
P-II	None		$C_{18}H_{17}N_6O_7$	0.39	No
P-III	None		$C_{19}H_{17}N_6O_7$	0.39	No
P-IV	None		$C_{18}H_{14}N_6O_8S$	0.43	No
P-V			$C_{18}H_{14}N_6O_6$	0.40	No
P-VI			$C_{24}H_{18}N_6O_7$	0.50	Yes
P-VII			$C_{25}H_{18}N_6O_7$	0.60	Yes
P-VIII			$C_{24}H_{18}N_6O_8S$	0.43	No
P-IX			$C_{18}H_{14}N_6O_6$	0.20	No
P-X			$C_{24}H_{18}N_6O_7$	0.50	Yes
P-XI			$C_{25}H_{18}N_6O_7$	0.45	Yes
P-XII			$C_{24}H_{18}N_6O_8S$	0.32	No
P-XIII			$C_{17}H_{13}N_7O_6$	0.63	No
P-XIV			$C_{23}H_{17}N_7O_7$	0.75	No
P-XV			$C_{24}H_{17}N_7O_7$	0.59	No
P-XVI			$C_{24}H_{17}N_7O_8S$	0.38	No

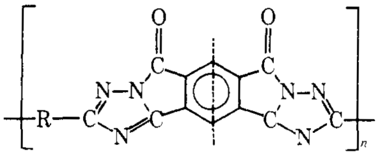
[a] Viscosity of 0.5% solution of polymer in DMSO at 25°.

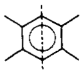
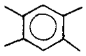
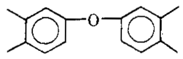
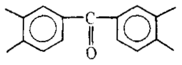
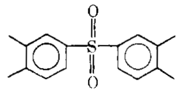
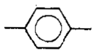
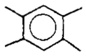
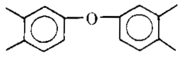
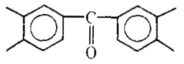
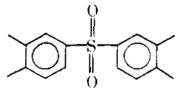
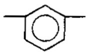
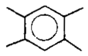
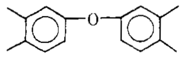
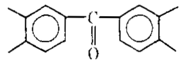
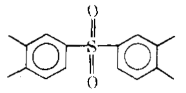
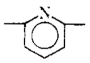
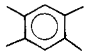
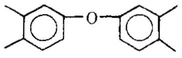
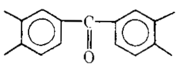
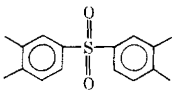
Better results were obtained when the synthesis was carried out in PPA at 180-190° in accordance with Scheme I.

The structures of the polymers thus obtained were indicated by their ir spectra (Figure 4) and uv spectra (Table IV).

The ir spectra of polymers are consistent with the proposed structures and are very similar to the spectra of

Table III
Characterization of Poly(benzoylene-*s*-triazoles) of General Formula



No.	R		*T* dec,[a] °C		Film properties	
			5%	10%	θ, g cm^2	ϵ, %
P-Ic	None		400	440		
P-IIc			390	420		
P-IIIc			390	420		
P-IVc			410	440		
P-Vc			390	420		
P-VIc			380	430	1000	13
P-VIIc			390	420	1350	7
P-VIIIc			380	430		
P-IXc			350	400		
P-Xc			400	430	Brittle	
P-XIc			410	420	Brittle	
P-XIIc			390	420		
P-XIIIc			390	410		
P-XIVc			400	420		
P-XVc			380	420		
P-XVIc			400	420		

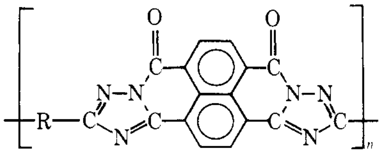
[a] Decomposition temperature is taken to be a temperature at which the polymer reveals a weight loss of 5 and 10% when heated in air, $\Delta T = 4.5°/\mathrm{min}$.

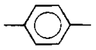
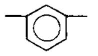
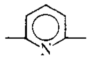
model compounds XI, XVII, and XXIII. Absence in the polymer spectra of absorptions in regions 2800–3400 cm^{-1} indicated a relatively high degree of cyclization. Characteristic of all of the polymers spectra is the presence of the strong absorption in region 1720 cm^{-1} due to the carbonyl group of the benzo-*s*-triazoloisoquinolinone ring.

General properties of the polymers obtained are given in Table IV.

Poly(naphthoylene-*s*-triazoles) (poly[benzobis(*s*-triazolo)phenanthrolines]) are completely soluble in sulfuric and methanesulfuric acids and fail to soften even at 500°. Absence of cross-links in these polymers is probably due to

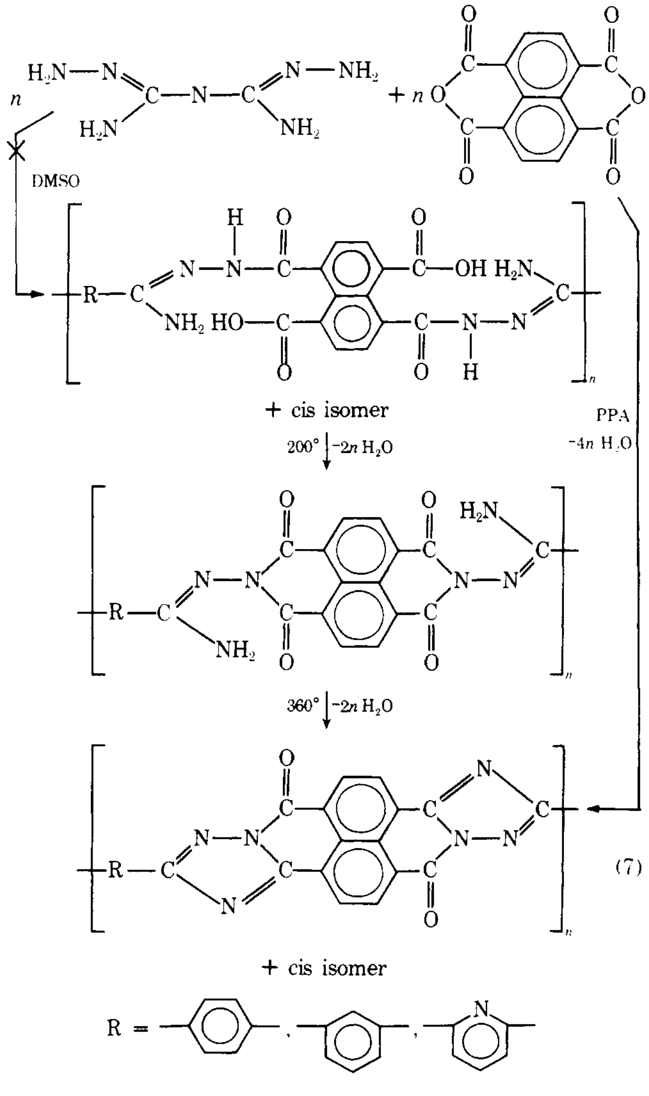
Table IV
Characterization of Poly(naphthoylene-*s*-triazoles) of General Formula



No.	R	R η_{red},[a] dl/g	Uv spectra[b] λ_{max}, nm	Uv spectra[b] Log ϵ	*T* dec, °C 5%	*T* dec, °C 10%
P-XVIIc		1.5	235	4.5563	515	525
			305	4.7993		
			396	4.5911		
P-XVIIIc		0.6	235	4.3222	500	525
			264	4.3424		
			390	4.1761		
P-XIXc		1.1	230	4.7482	505	520
			315	4.2041		
			408	4.4150		
			434	4.3802		

[a] Viscosity of a 0.5% solution of polymer in H_2SO_4 at 25°. [b] Obtained in H_2SO_4 with $c = 10^{-5}$ *M*. [c] Decomposition temperature is taken to be a temperature at which the polymer reveals a weight loss of 5 and 10% when heated in air (ΔT = 4.5°/min).

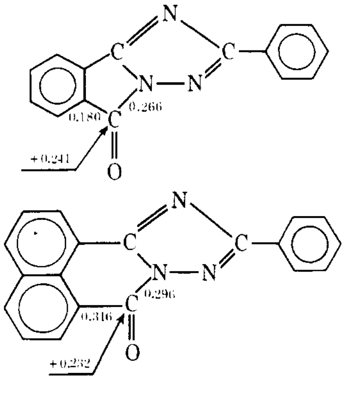
Scheme I



(7)

the lower reactivity of the benzo-*s*-triazoloisoquinolinone ring as compared with the isoindolo-*s*-triazolone ring. This point of view is in good agreement with results obtained from treatment of these heterocycles by the LCAO-MO method with the Hückel approximation.[10]

The analysis of the molecular diagrams has shown that the positive charge on the C atom of the carbonyl group in isoindolo-*s*-triazolone is higher than in the benzo-*s*-triazoloisoquinolinone ring; as a result, isoindolo-*s*-triazolone is more sensitive to nucleophilic attack and hydrolysis than *s*-triazoloisoquinolinone. The analysis of the molecular diagrams has shown also that the orders of the weakest bands are lower in isoindolo-*s*-triazolone than in benzo-*s*-triazoloisoquinolinone indicating that the thermal stability of VI must be lower than the thermal stability of XI.



(8)

Comparative investigation of the thermal stability of the polymers obtained by dynamic TGA (Figure 5) and isothermal aging in air (Figure 6) has demonstrated that poly(naphthoylene-*s*-triazoles) (poly[benzobis(*s*-triazolo)phenanthrolines]) have higher thermal stability due not only to a higher degree of cyclization but also to higher thermal stability of the heterocyclic ring presented in the polymers.

$$-\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}-C\langle \quad \text{and} \quad -\underset{\displaystyle O}{\underset{\|}{C}}-N\langle$$

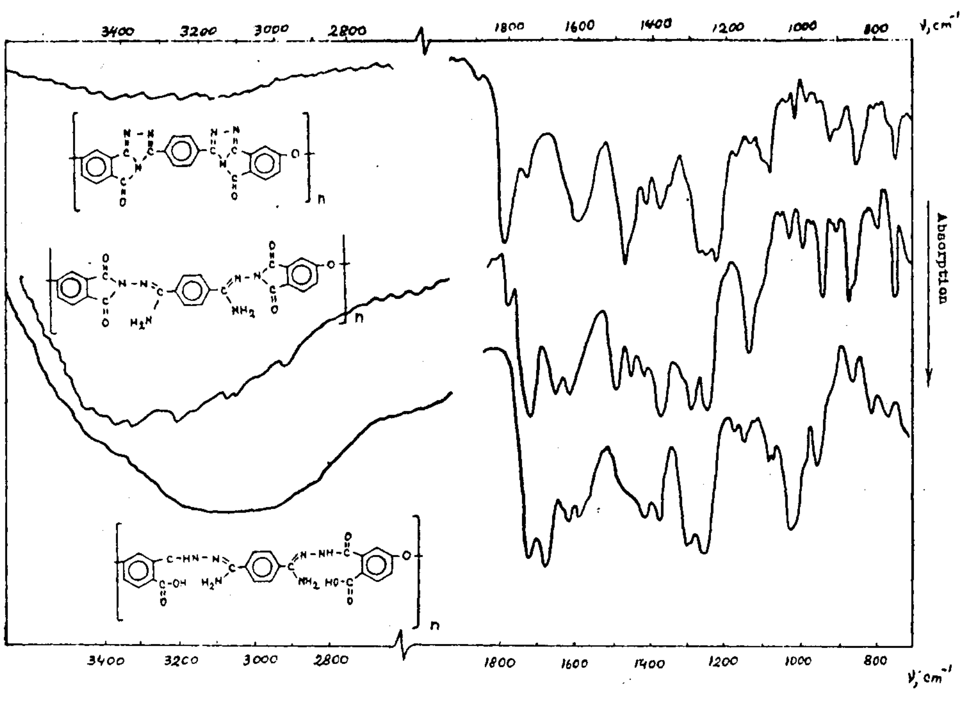


Figure 4. Infrared spectra of polymers P-XVIIc (top), P-XVIIIc (middle), and P-XIXc (bottom).

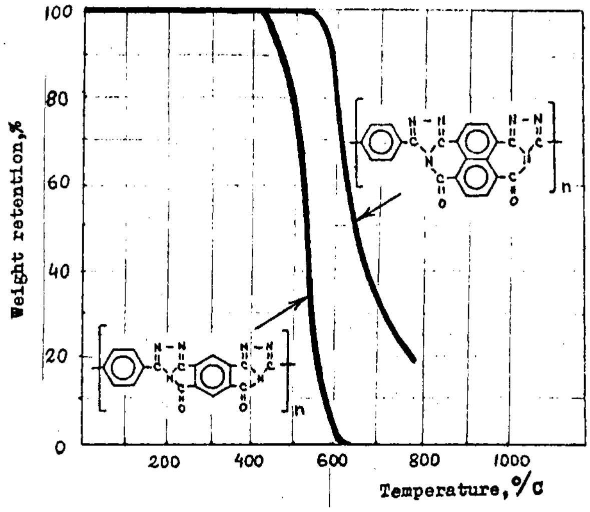


Figure 5. Curves of dynamic TGA of polymers P-Vc and P-XVIIc (in air, ΔT = 4.5°/min).

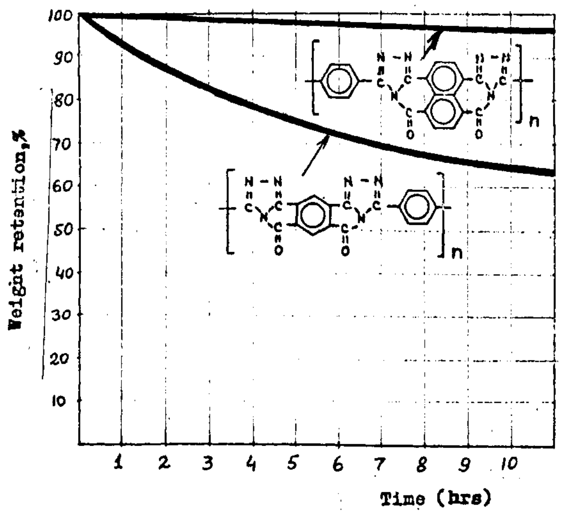


Figure 6. The isothermogravimetric aging curves of polymers P-Vc and P-XVIIc (powders in circulating air, 400°).

From polymer P-XVIIc, pellets were pressed (350°/3500 kg/cm^2) having high ablative stability and fire resistance. High fire resistance of these materials is probably due not only to polymer structure but to the presence of residual amounts of PPA or its salts.

Poly(naphthoylene-*s*-triazoles) from oxalamidrazone were not obtained probably due to the decomposition of oxalyldihydrazide.[16,17]

Experimental Section

Materials. Benzamidrazone was prepared and purified by a known procedure:[25] yield 85%; mp 74.5–76° (lit.[25] mp 75–76°).

Terephthalamidrazone was prepared by a known procedure;[8] yield 70%. Yellow product turned to red at 185° and discolored at 300°.

Isophthalamidrazone was prepared by a known procedure;[26] yield 60%. Yellow product turned to red at 170° and discolored at 350°.

Oxalamidrazone was prepared and purified by a known procedure (treatment of dithiooxamide with hydrazine);[27] yield 70%; mp 179° dec (lit.[28] mp 179–180° dec).

2,6-Pyridinediamidrazone was prepared and purified by a known procedure;[29] yield 71%; mp 230–231° dec (lit.[29] mp 231° dec).

Anhydrides of phthalic and naphthalic acids were purified by recrystallization from benzene and anisole, respectively. Melting points of these products (131 and 274°) are in agreement with the literature data.[30]

Dianhydrides of pyromellitic, 3,3′,4,4′-diphenylethertetracarboxylic, 3,3′,4,4′-benzophenonetetracarboxylic, 3,3′,4,4′-diphenylsulfonetetracarboxylic, and naphthalene-1,4,5,8-tetracarboxylic acids were prepared and purified by the known procedures.[31] Mp of pyromellitic dianhydride is 286° (lit.[30] mp 286°). Mp of 3,3′,4,4′-diphenyl ether tetracarboxylic acid dianhydride is 228–229° (lit.[32] mp 228°). Mp of 3,3′,4,4′-benzophenonetetracarboxylic acid dianhydride is 226–227° (lit.[33] mp 226–227°). Mp of 3,3′,4,4′-diphenylsulfonetetracarboxylic acid dianhydride is 286.5–287.5° (lit.[34] mp 286–287°). Mp of naphthalene-1,4,5,8-tetracarboxylic acid dianhydride is 442° (lit.[35] mp 440°).

Multi-stage Synthesis of the Model Compounds. Syntheses of VI and XI were carried out following the next procedure.

Phthalic (naphthalic) anhydride (0.01 mol) was added to the solution of 0.01 mol of benzamidrazone in DMSO. The reaction solution was stirred overnight at 25–70° and then poured into acetone; the precipitates formed were filtered off, washed with acetone and ether, and dried at 25° (10^{-3} mm). The yields of the products were almost quantitative. The products obtained were treated thermally from 25 to 360° at reduced pressure (10^{-3} mm) for 10 hr and then at 240–360° (10^{-3} mm) for 10 hr. The sublimates formed were collected and sublimed twice more at 240–360° (10^{-3} mm).

The same procedures were employed for the preparation of the model compounds XIV, XVII, XXa–d, and XXIIIa–d.

One-Stage Synthesis of the Model Compounds. Synthesis of XI was carried out following the next procedure. Benzamidrazone (0.01 mol), 0.01 mol of naphthalic anhydride, and 20 cm^3 of 116% PPA were placed in the reaction vessel. The reaction mixture was heated gradually to 180°, stirred at this temperature for 12 hr, and then poured in ice water; the precipitate formed was filtered, washed with sodium bicarbonate solution, and dried. XI was purified by sublimation at 340–360° (10^{-3} mm).

The same procedures were employed for the preparation of the model compounds XVII and XXIIIb–d.

Polymers. Poly(*o*-carboxybenzoylamidrazones) were prepared according to the following general procedure. Solid bis(phthalic anhydride) (0.01 mol) was added portionwise to the stirred solution of 0.01 mol of bisamidrazone in 20 cm^3 of dry DMSO at 25°. The resulting yellow solution became very viscous almost immediately after the addition of anhydride; stirring was continued for 2 hr. The solution of polymer was diluted with DMSO and poured into a large excess of acetone or cast on glass plates. Poly(benzoylene-*s*-triazoles) [poly(isoindolo-*s*-triazolones)] were prepared by heating poly(*o*-carboxybenzoylamidrazones) from 25 to 360° at reduced pressure (10^{-3} mm) for 10 hr and then at 360° (10^{-3} mm) for 10 hr.

Poly(naphthoylene-*s*-triazoles) (poly[benzobis(*s*-triazolo)phenanthrolinediones]) were prepared according to the following general procedure. Naphthalene-1,4,5,8-tetracarboxylic acid (0.01 mol) dianhydride was added to the solution of 0.01 mol of bisamidrazone in 20 cm^3 of 116% PPA. The reaction mixture was heated with stirring up to 180° and this temperature was maintained for 12 hr. The resulting deep-red solution was poured in water, filtered off, washed with water and ethanol, dried, and reprecipitated from sulfuric or methanesulfonic acid in water or ethanol.

Acknowledgment. The authors wish to thank Professor P. M. Hergenrother for the fruitful discussion of the experimental results.

References and Notes

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Kinetic Studies on the Ring-Opening Polymerization of 3-Oxaspiro[3.2]hexane

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ABSTRACT: Kinetics of the cationic polymerization of 3-oxaspiro[3.2]hexane (OSH) has been analyzed by means of the phenoxyl end-capping method. Polymerization proceeded via an S$_N$2 mechanism involving the ring opening of oxetane. The rate constant of propagation (k_p) shows that the spiro cyclopropane ring in OSH does not greatly enhance the polymerization reactivity of OSH. The relatively low $\Delta H^‡$ (favorable) and $\Delta S^‡$ (unfavorable) values were explained by the rigid monomer structure.

In a previous paper we have reported kinetic studies on the cationic ring-opening polymerization of unsubstituted (OX), 3-methyl- (MeOX), and 3,3-dimethyloxetanes (Me$_2$OX) by the phenoxyl end-capping method.[1] Introduction of the methyl group at the 3 position of oxetane ring increased the rate constant of propagation (k_p).[1] In the