molecules around the moiety bearing the charge, results in trapping of the electron on one or the other aromatic group. The calculation by Harriman and Maki[9] showed that such a perturbation results in the frequency of transfer greater than 10^8 sec^{-1} when the relevant groups are linked by one CH_2 unit; however, it decreases to about 10^6 sec^{-1}, or less, when the linking bridge consists of a chain of two carbons, *i.e.*, $(CH_2)_2$. Similar calculations by McConnel[8] show that insertion of each additional CH_2 unit to the linking bridge reduces the frequency of the transfer by at least a power of ten.

Our experimental results yield the frequency of transfer due to the *intra*molecular collisions of about 10^8–10^9 sec^{-1} for the $(\alpha\text{-N}.^{-})\text{-}(CH_2)_3\text{-}(\alpha\text{-N})$ system. Hence, the contribution of the direct through-chain transfer to the process observed by us is negligible. Such a contribution, if any, is even less important for $j > 3$.

Let us remark that for $j = 2$ the *intra*molecular collisions are impossible due to steric constraint. In such systems, therefore, the electron transfer may result only from causes discussed above.

In conclusion, it has been shown that a method is available for determining the rate of *intra*molecular collisions between the ends of a polymeric chain, as well as its dependence on the chain's length, temperature, etc. The dependence on the chain's length is particularly interesting for short chains, since the restrictions arising from unfavorable conformations are less understood in such systems than in those involving long chains. The final results of such calculations and their discussion will be published later.

Obviously, much additional work is needed. The effect of large end groups, acting as dampers, should be investigated. Therefore, we intend to study the behavior of chains terminated by smaller as well as by bigger groups. Further extension of these studies calls for the investigation of collisions between end groups linked by other chains as well as collisions in solvents of different viscosity.

Acknowledgment. The financial support of these studies by the National Science Foundation is gratefully acknowledged.

Two-Stage Synthesis of Poly(*N*-phenylbenzimidazoles)

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ABSTRACT: The low-temperature solution condensation of either 1,3-dianilino-4,6-diaminobenzene, 3,3′-diamino-4,4′-dianilinodiphenyl, or 3,3′-diamino-4,4′-dianilinodiphenyl sulfone in combination with various dicarboxylic acid dichlorides leads to high molecular weight poly(*o*-phenylaminoamides). The solid-state polycyclodehydration of poly(*o*-phenylaminoamides) leads to poly(*N*-phenylbenzimidazoles) soluble in organic solvents. The effect of polymer structure on solubility, glass transition, and decomposition temperatures was investigated.

The synthesis of poly(*N*-phenylbenzimidazoles) by melt polycondensation of bis(*N*-phenyl-*o*-phenylenediamines) with dicarboxylic acid diphenyl esters has been reported by several investigators.[1,2] Poly(*N*-phenylbenzimidazoles) exhibit good solubility and thermooxidative stability, but their molecular weights are relatively low. In this investigation we used the two-stage process to synthesize high molecular weight poly(*N*-phenylbenzimidazoles).

Discussion

Model Compounds. Prior to polymer synthesis, a series of model compounds shown in Table I was prepared to obtain information on the conditions of polymer formation and to identify them.[3] The model compounds were prepared by the reaction of benzoyl chloride with *o*-aminodiphenylamine and also with various bis(*N*-phenyl-*o*-phenylenediamines) and by the reaction of *o*-aminodiphenylamine with various aromatic dicarboxylic acid chlorides (eq 1–3).

The intermediates, *N*-phenyl-*N*′-aroylene-*o*-phenylenediamines, were prepared by low-temperature solution condensation in *N*,*N*-dimethylacetamide or *N*-methyl-2-pyrrolidone in quantitative yields. The conversion to 1,2-diphenylbenzimidazoles was effected at elevated temperatures in solid state or in the melt.

The infrared spectra of some model compounds are shown in Figures 1 and 2; the ultraviolet spectral data for the model compounds are given in Table I. In accordance with the dta and tga data, all model compounds degrade in two stages; degradation begins in the temperature range from 340 to 370° and is accompanied by partial sublimation of products.

Polymers. The polymers were synthesized by the reaction of bis(*N*-phenyl-*o*-phenylenediamines) with dicarboxylic acid chlorides followed by cyclization of the resulting poly(*o*-phenylaminoamides) as shown on p 809, column 2 at bottom.

The high molecular weight polymer precursors (η_{red} = 0.2–2.5), poly(*o*-phenylaminoamides), were prepared by low-temperature polycondensation (0–20°) in *N*,*N*-dimethylacetamide or *N*-methyl-2-pyrrolidone. In contrast with unsubstituted bis(*o*-phenylenediamines), the tetramines used in these reactions behave as bifunctional monomers because of the great difference in the nucleophilic reactivities of amino and imino groups doubly joined in positions ortho to each other;[4] as a result it is possible to add the solid dicarboxylic

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(1) H. Vogel and C. S. Marvel, *J. Polym. Sci., Part A*, **1**, 1531 (1963).

(2) V. V. Korshak, G. M. Tseitlin, G. M. Cherkasova, A. L. Rusanov, and N. A. Berezkina, *Vysokomol. Soedin. A*, **11**, 35 (1969).

(3) V. V. Korshak, A. L. Rusanov, D. S. Tugushi, and S. N. Leontjeva, *Chim. Heterocycl. Soedin.*, in press.

(4) V. V. Korshak and A. L. Rusanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 289 (1970); *Polimery(Poland)*, **15**, 400 (1970).

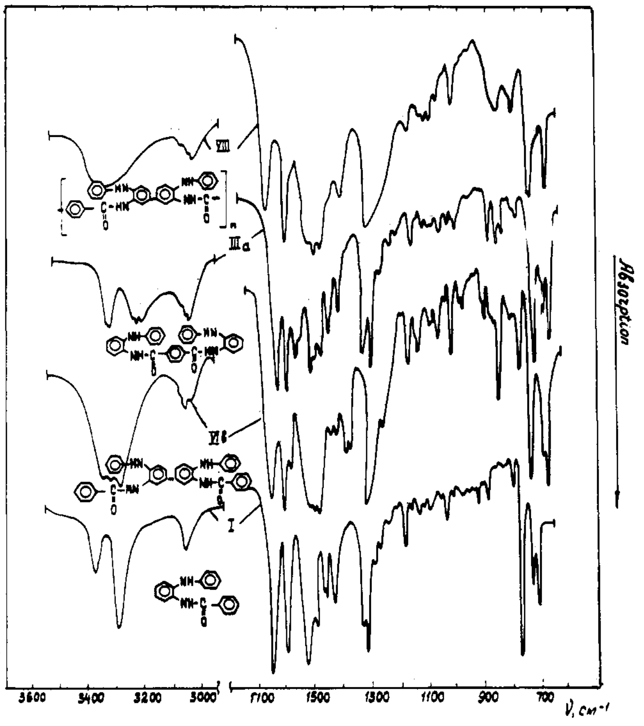


Figure 1. Infrared spectra of model compounds I, IIIa, VIb, and poly(*o*-phenylaminoamide) (VIII).

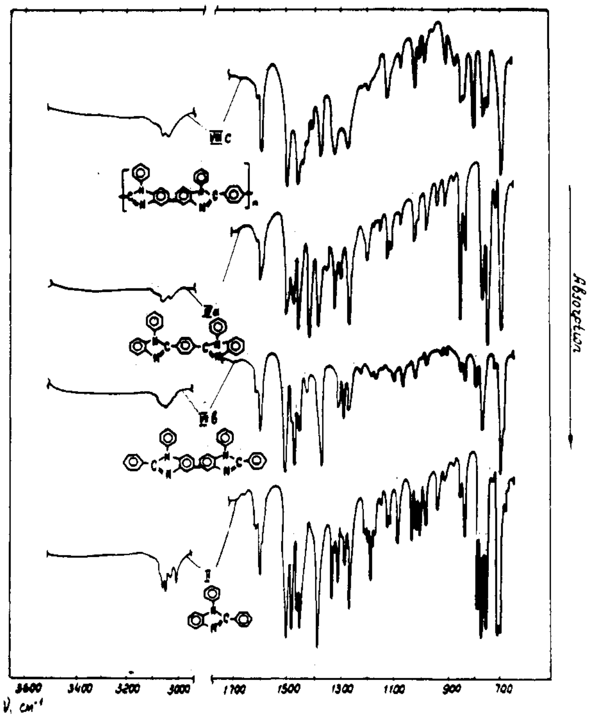
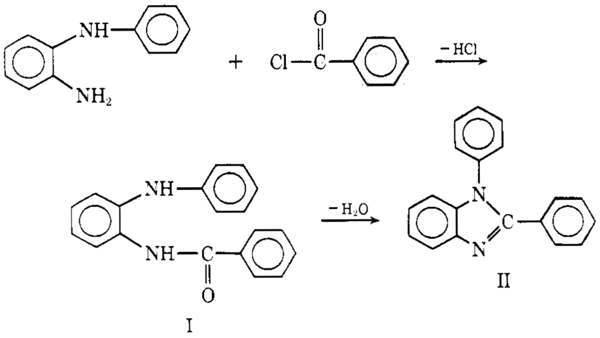


Figure 2. Infrared spectra of model compounds II, IVa, VIIb, and poly(*N*-phenylbenzimidazole) (VIIIc).

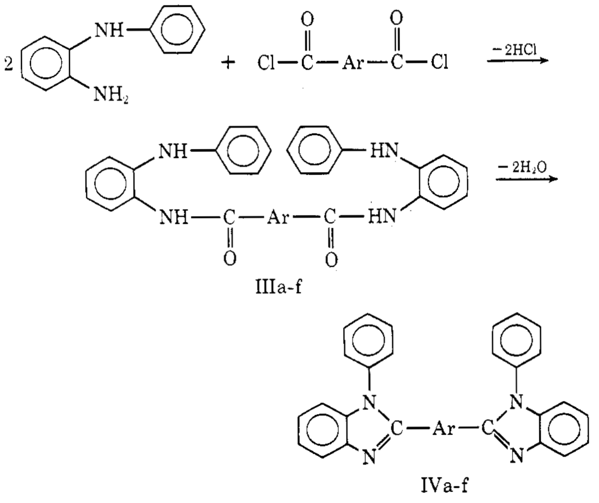
Table I
Characterization of Model Compounds

				Uv spectra (H_2SO_4)[b]		Decomp temp,[c] °C	
No.	Yield,[a] %	Mp, °C	Formula	λ_{max}, mμ	Log ε	Init decomp pt, °C	Max decomp rate, °C
I	95	138 (136)[d]	$C_{19}H_{16}N_2O$	246[f] 295	3.91 4.11		
II	90	111 (111)[d]	$C_{19}H_{14}N_2$				
IIIa	90	238–243[e]	$C_{32}H_{26}N_4O_2$				
IIIb	90	230–235[e]	$C_{32}H_{26}N_4O_2$				
IIIc	92	260–265[e]	$C_{38}H_{30}N_4O_2$				
IIId	90	253–258[e]	$C_{36}H_{28}N_4O_2$				
IIIe	85	202–206[e]	$C_{38}H_{30}N_4O_3$				
IIIf	70	240–244[e]	$C_{38}H_{30}N_4O_4S$				
IVa	80	291–292	$C_{32}H_{22}N_4$	250 326	4.06 4.45	355	470
IVb	80	247–248	$C_{32}H_{22}N_4$	241 298	4.43 4.50	350	460
IVc	75	308–309	$C_{38}H_{26}N_4$	335	4.84	340	510
IVd	75	290–291	$C_{36}H_{24}N_4$	249 284 337	4.81 4.68 4.82	340	480
IVe	65	235–237	$C_{38}H_{26}N_4O$	319	4.96	340	490
IVf	65	267–269	$C_{38}H_{26}N_4O_2S$	315	4.82	340	510
VIa	80	238–242[e]	$C_{32}H_{26}N_4O_2$				
VIb	85	260–265[e]	$C_{38}H_{30}N_4O_2$				
VIc	65	200–204[e]	$C_{38}H_{30}N_4O_4S$				
VIIa	70	283–285	$C_{32}H_{22}N_4$	246 333	4.54 4.81	350	465
VIIb	82	293–295	$C_{38}H_{26}N_4$	255 323	4.81 4.71	360	485
VIIc	65	218–220	$C_{38}H_{26}N_4O_2S$	254 309	4.70 4.70	370	510

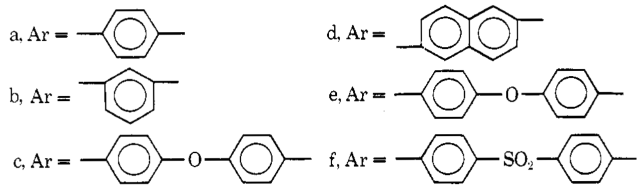
[a] Yield after purification. [b] Obtained in H_2SO_4 with $c = 10^{-5}$ *M*. [c] The decomposition temperature was determined by dta (differential thermal analysis) in air. [d] Melting points reported: H. Wolff, *Justus Liebigs Ann. Chem.*, **394**, 66 (1912). [e] Melting points are distorted by cyclization. [f] Obtained in H_2SO_4 with $c = 10^{-4}$ *M*.

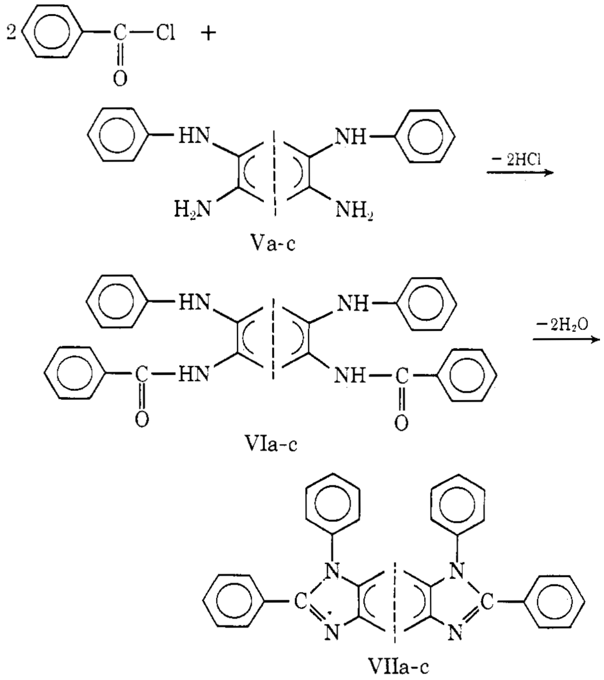


(1)

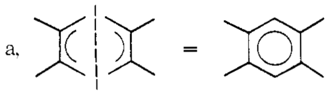


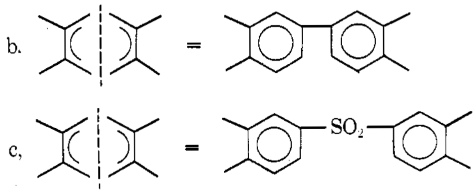
(2)





(3)



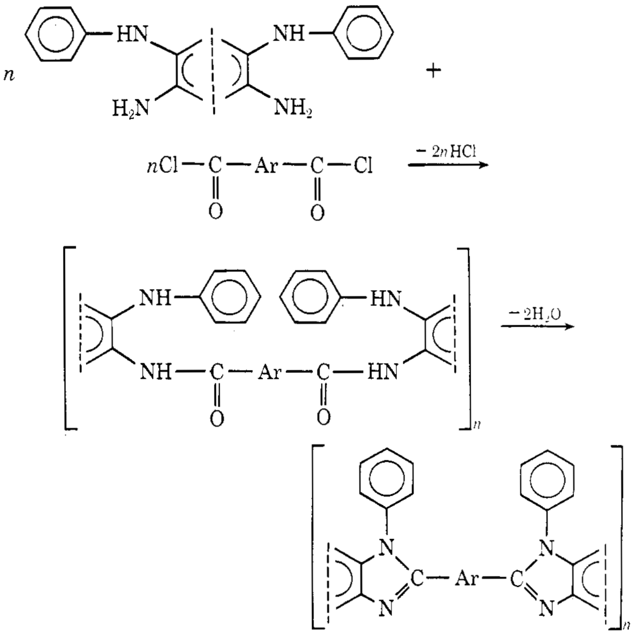


acid dichloride to the solution of bis(*N*-phenyl-*o*-phenylenediamine) without any gelation. The reactions of poly(*o*-phenylaminoamide) synthesis proceed with a high rate; an increase in η_{red} as a function of the reaction time is shown in Figure 3.

The structures of the poly(*o*-phenylaminoamides) were confirmed by their infrared spectra and elemental analysis. A typical infrared spectrum (polymer VIII) is shown in Figure 1.

All poly(*o*-phenylaminoamides) are soluble in highly polar solvents such as *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide, pyridine, dimethyl sulfoxide, *N*-methyl-2-pyrrolidone, and hexamethylphosphoramide, forming solutions of 20–25% concentration. Almost all the poly(*o*-phenylaminoamides) were of sufficiently high molecular weight to form films (Table II). The films were cast from 8–10% solutions in dimethylacetamide at 50–60° and 1–2 mm.

The conversion of the poly(*o*-phenylaminoamides) to the corresponding poly(*N*-phenylbenzimidazoles) was effected by solid-state cyclodehydratation at 250–300°.



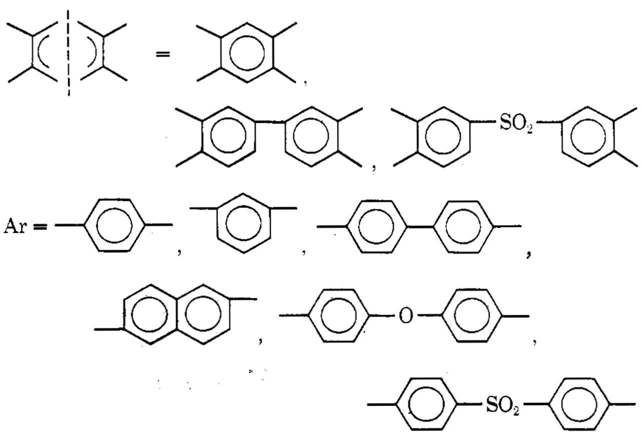
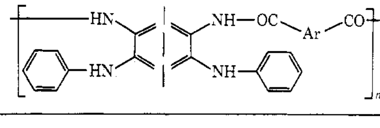
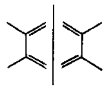
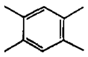
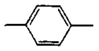
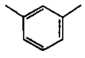
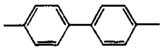
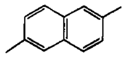
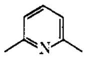
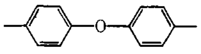
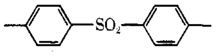
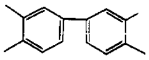
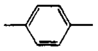
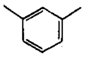
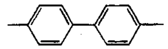
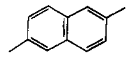
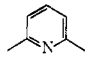
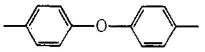
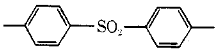
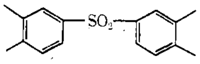
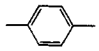
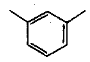
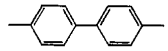
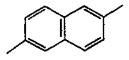
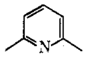
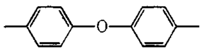
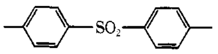


Table II
Characterization of Poly(*o*-phenyliminoamides) of General Formula



No.		Ar	Formula of polymer unit	η_{red},[a] dl/g	σ, kg/cm²	ϵ, %
I			$C_{26}H_{20}N_4O_2$	0.40	650	3–4
II			$C_{26}H_{20}N_4O_2$	2.50	600	8–10
III			$C_{32}H_{24}N_4O_2$	0.38	630	3–4
IV			$C_{30}H_{22}N_4O_2$	0.35	610	2
V			$C_{25}H_{19}N_5O_2$	0.25	520	2–3
VI			$C_{32}H_{24}N_4O_3$	0.33	580	5–7
VII			$C_{32}H_{24}N_4O_4S$	0.28	550	5–7
VIII			$C_{32}H_{24}N_4O_2$	0.40	800	5–8
IX			$C_{32}H_{24}N_4O_2$	1.00	720	10–12
X			$C_{38}H_{28}N_4O_2$	0.40	790	5–6
XI			$C_{36}H_{26}N_4O_2$	0.34	780	5–6
XII			$C_{31}H_{23}N_5O_2$	0.20	550	3–4
XIII			$C_{38}H_{28}N_4O_3$	0.24	580	10–15
XIV			$C_{38}H_{28}N_4O_4S$	0.22	560	10–12
XV			$C_{32}H_{24}N_4O_4S$	0.34	500	1–2
XVI			$C_{32}H_{24}N_4O_4S$	0.30	450	5–8
XVII			$C_{38}H_{28}N_4O_4S$	0.25	480	2–3
XVIII			$C_{36}H_{26}N_4O_4S$	0.25		
XIX			$C_{31}H_{23}N_5O_4S$	0.20		
XX			$C_{38}H_{28}N_4O_5S$	0.22		
XXI			$C_{38}H_{28}N_4O_6S_2$	0.20		

[a] Viscosity of 0.5% solution of polymer in dimethylformamide.

On conducting the cyclization in poly(*o*-phenylaminoamides), some 1–2% dimethylacetamide was left to plasticize the polymers and to facilitate their cyclization. The optimum cyclization conditions are temperatures of 300–310° and reaction periods of 5–6 hr.

The structures of poly(*N*-phenylbenzimidazoles) were confirmed by elemental analysis and absorption spectral data.

The infrared spectra of poly(*N*-phenylbenzimidazoles) were in agreement with the proposed structures. A comparison of the spectral data for polymer VIII with those for model compounds of similar structure (Figure 2) gave good results.

Properties of the polymers are given in Table III. All poly(*N*-phenylbenzimidazoles) are soluble in formic acid and in the tetrachloroethane–phenol mixture (3:1). These polymers were of sufficient molecular weight to form strong films (Table III). The films were cast from 10–12% solutions in a tetrachloroethane–phenol (3:1) mixture at 60° in air.

Good solubility of all poly(*N*-phenylbenzimidazoles) is due to the beneficial effect of the phenyl side-group substitution, as has been illustrated for polyphenylenes[5] and poly-

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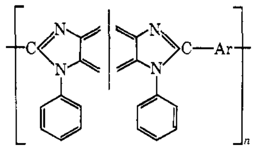
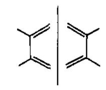
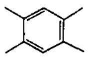
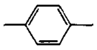
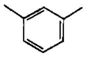
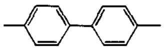
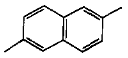
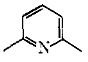
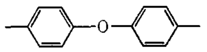
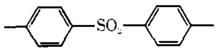
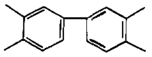
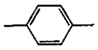
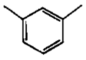
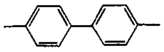
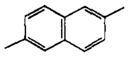
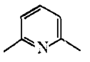
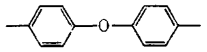
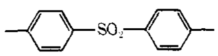
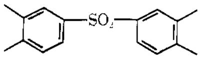
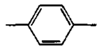
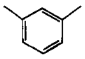
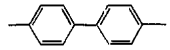
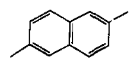
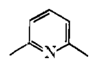
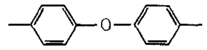
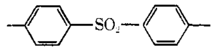
(5) J. K. Stille, F. W. Harris, R. O. Rakutis, and H. Mukamal, *J. Polym. Sci., Part B*, **4**, 791 (1966).

TABLE III
CHARACTERIZATION OF POLY(*N*-PHENYLBENZIMIDAZOLES) OF GENERAL FORMULA



No.		Ar	Formula of polymer unit	Uv spectra $(H_2SO_4)^c$ λ_{max}, mμ	Log ε	η_{red},[a] dl/g	σ, kg/cm²	Softening pt, °C	Decomp pt, °C[b]
Ic			$C_{26}H_{16}N_4$			9.90	1350	380	450
IIc			$C_{26}H_{16}N_4$	241 338	4.66 4.77	7.20	1100	370	490
IIIc			$C_{32}H_{20}N_4$			8.40	1200	345	430
IVc			$C_{30}H_{18}N_4$			5.20	1200	390	480
Vc			$C_{25}H_{15}N_5$			1.00	900	330	420
VIc			$C_{32}H_{20}N_4O$			1.20	950	320	490
VIIc			$C_{32}H_{20}N_4O_2S$	253 342	4.75 4.90	1.10	950	390	430
VIIIc			$C_{32}H_{20}N_4$			8.20	1550	360	490
IXc			$C_{32}H_{20}N_4$	257 360	4.84 4.89	4.60	1400	310	470
Xc			$C_{38}H_{24}N_4$	254 358	4.50 4.86	5.60	1500	385	480
XIc			$C_{36}H_{22}N_4$			1.48	1500	365	450
XIIc			$C_{31}H_{19}N_5$	245 355	4.59 4.44	0.62	1000	290	450
XIIIc			$C_{38}H_{24}N_4O$	253 342	4.89 5.02	0.88	1100	345	470
XIVc			$C_{38}H_{24}N_4O_2S$	255 343	4.71 4.61	0.68	1100	325	465
XVc			$C_{32}H_{20}N_4O_2S$	258 327	4.64 4.67	0.80	700	345	470
XVIc			$C_{32}H_{20}N_4O_2S$			0.68	600	300	500
XVIIc			$C_{38}H_{24}N_4O_2S$			0.75	600	355	455
XVIIIc			$C_{36}H_{22}N_4O_2S$	257 284 342	4.82 4.48 4.73	0.52	620	360	450
XIXc			$C_{31}H_{19}N_5O_2S$	245 310 334	4.77 4.60 4.62	0.44		280	480
XXc			$C_{38}H_{24}N_4O_3S$			0.48		270	440
XXIc			$C_{38}H_{24}N_4O_4S_2$			0.42		275	450

[a] Viscosity of 0.5% solution of polymer in the tetrachloroethane-phenol mixture (3:1) at 25°. [b] Decomposition temperature is taken to be the temperature, at which the polymer reveals a weight loss of 5% when heated in air (ΔT = 4.5°/min(. [c] Obtained in H_2SO_4 with $c = 10^{-4}$ mol/l.

quinoxalines.[6] The thermal stability of the poly(*N*-phenylbenzimidazoles) was determined by dynamic thermogravimetric analysis (tga), differential thermal analysis (dta), and isothermal aging (Figures 4 and 5). The dynamic thermogravimetric analysis data illustrate that the introduction of bridged flexibilizing ether and sulfone groups into the polymer chains does not lower their thermostability (Figure 5). On the other hand, the presence of these electron-donating[7] and electron-withdrawing groups results in a substantial decrease in the thermooxidative stability of these polymers on isothermal aging (Figure 5). Poly(*N*-phenylbenzimidazoles)

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(6) P. M. Hergenrother and H. H. Levine, *J. Polym. Sci., Part A*, **5**, 1453 (1967).

(7) W. Wrasidlo, *ibid.*, **8**, 1107 (1970).

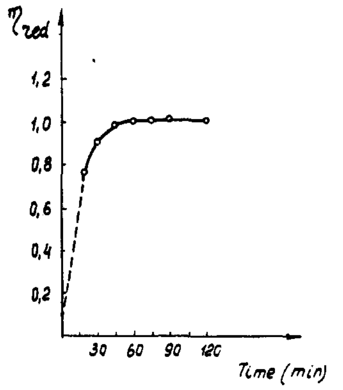


Figure 3. Effect of reaction time on η_{red} of poly(*o*-phenylaminoamide) (VIII).

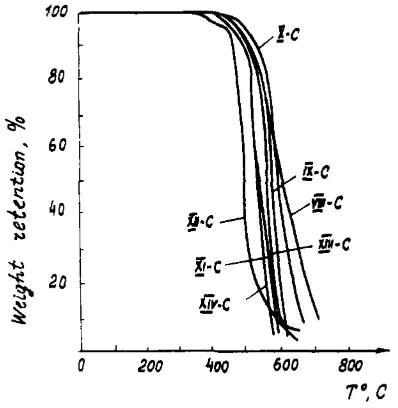


Figure 4. The dynamic thermogravimetric analysis curves of polymers VIII–XIV (powder, in circulating air, ΔT = 4.5°/min).

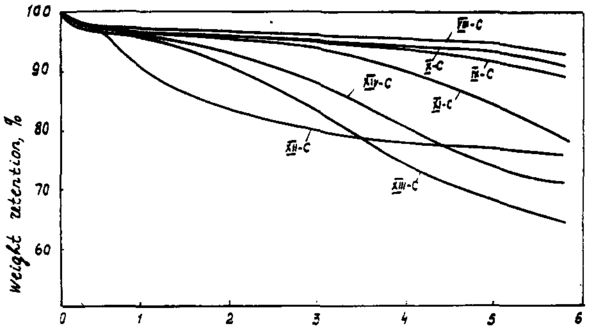
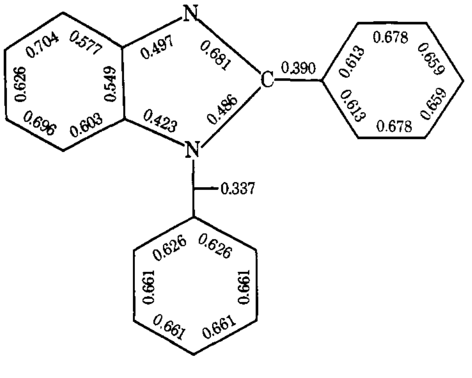


Figure 5. The isothermal aging thermogravimetric curves of polymers VIII–XIV (powder, in circulating air, 400°).

exhibit superior thermooxidative stability, but in an inert atmosphere they are less stable when compared to their nonphenylated analogs.[1] Their degradation begins with the scission of the phenyl side groups,[8] because of the absence of conjugation between the phenyl group in position 1 and the imidazole ring.[9] These results are in good agreement with those obtained from treatment of the 1,2-diphenylbenzimidazole molecule by the LCAO MO method with the Hückel approximation, because the lowest bond order corresponds to the N–C (phenyl) bond; the molecular diagram of this compound is as follows.



Poly(*N*-phenylbenzimidazoles) with similar properties were prepared by cyclization of poly(*o*-phenyliminoamides) in polyphosphoric acid at 170°.

Experimental Section

Materials. 1,3-Diamino-4,6-dianilinobenzene was prepared in 70% yield as described previously.[1] Recrystallization from ethanol gave the polymer grade material, mp 215° (lit.[1] mp 210–211°).

3,3′-Diamino-4,4′-dianilinodiphenyl was prepared in 91% yield as described previously.[10] Recrystallization from ethanol gave the polymer grade material, mp 206–207° (lit.[10] mp 203.5–204°).

3,3′-Diamino-4,4′-dianilino(diphenyl sulfone) was prepared as described previously.[11] Recrystallization from ethanol gave the polymer grade material, mp 186° (lit.[11] mp 186°).

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

Model Compounds. All *o*-phenylaminoamides were prepared in the following manner. Acid chloride (0.01 mol) was added during 15 min to a stirred solution of 0.01 mol of amine in 30 ml of *N,N*-dimethylacetamide. After stirring for 1 hr at ambient temperature, the mixture was poured into 200 ml of distilled water. The precipitated solid *o*-phenylaminoamides were filtered, washed with water, and dried *in vacuo*. The products were recrystallized from a dimethylformamide–water mixture (1:1).

N-Phenylbenzimidazoles were prepared by heating *o*-phenylaminoamides *in vacuo* at 260–270° for 6 hr. All products were purified by vacuum sublimation (1 mm) at 280–300°.

Polymers. All poly(*o*-phenylaminoamides) were prepared in the following manner. Solid acid chloride (0.01 mol) was added in portions during 30 min to a stirred solution of 0.01 mol of tetramine in 15–20 ml of *N,N*-dimethylacetamide at 0–5°. The reaction mixture was then stirred for 10 hr at ambient temperature and the viscous solution was poured into 300 ml of distilled water. The precipitated poly(*o*-phenylaminoamide) was filtered, washed with water and acetone, dried, extracted with ethanol, and dried *in vacuo* at 80–100°.

Poly(*N*-phenylbenzimidazoles) were prepared by solid-state cyclization of poly(*o*-phenylaminoamides) (0.1 mm) at 300–310° for 6 hr. The polymers were reprecipitated from a phenol–tetrachloroethane mixture (3:1) in methanol.

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(8) V. V. Rode, N. M. Kotsoeva, A. L. Rusanov, G. M. Cherkasova, D. S. Tugushi, G. M. Tseitlin, and V. V. Korshak, *Vysokomol. Soedin. A*, **12**, 1854 (1970).

(9) L. N. Pushkina, S. A. Mazalov, and I. Ya. Postovskiy, *Zh. Org. Chim.*, **32**, 2624 (1962).

(10) G. I. Braz, I. E. Kardash, V. V. Kopylov, A. F. Oleinik, G. G. Rosantsev, A. N. Pravednikov, and A. Ya. Yakubovich, *Chim. Heterocycl. Soedin.*, 339 (1968).

(11) F. Ullman and I. Korselt, *Chem. Ber.*, **40**, 645 (1907).