Two-Stage Polybenzimidazole Synthesis via Poly(azomethine) Intermediates

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ABSTRACT: In continuation of an earlier preliminary investigation in this laboratory, a two-stage synthesis of polybenzimidazoles has been elaborated that involves the low-temperature solution polymerization of aromatic bis(*o*-diamines) with aromatic dialdehydes and subsequent conversion of the resulting azomethine-type prepolymers to all-aromatic polybenzimidazoles. The first-stage polycondensation, conducted in dipolar aprotic media at −18 to +25 °C under anaerobic conditions, affords in 80–95% yield linear and soluble prepolymers possessing inherent viscosities of 0.3–1.3 dL g^{-1}. The open-chain poly(azomethine) structure is inferred for these prepolymers from spectroscopic data. The second-stage reaction, performed in dipolar aprotic solvents or other media, proceeds by an oxidative cyclodehydrogenation step under unusually mild conditions; it involves the introduction of air into the prepolymer solution, preferably in the presence of catalytic amounts of certain transition-metal compounds, at temperatures below 100 °C. The polybenzimidazoles so obtained are linear and dissolve in a number of acidic media; most of them, when tested immediately after preparation, are largely or completely soluble also in dipolar aprotic solvents. Inherent viscosities are similar to, or slightly higher than, those measured on the precursor polymers. Polybenzimidazoles synthesized by this two-stage reaction include a number of known structures previously prepared by the more classical direct syntheses such as poly(1,3-phenylene-5,5′(6,6′)-bibenzimidazole-2,2′-diyl) and its 1,4-phenylene-bridged isomeric counterpart. Newly synthesized types include those with 9,10-anthracenediyl, (η^6-tricarbonylchromium)-1,4-phenylene, and 2,3,5,6-tetrachloro-1,4-phenylene bridging segments between bibenzimidazole or benzodiimidazole units. The synthetic approach here described offers a twofold advantage over conventional polybenzimidazole syntheses involving melt and solid-state or poly(phosphoric acid) solution polymerization techniques: first, tractable prepolymers can be isolated and utilized for the ultimate aromatization step, and, second, because of the mild conditions required to accomplish this aromatization, certain groups too labile to survive the drastic high-temperature and/or acidic environments of the conventional processes can be introduced into the ultimate polybenzimidazole structure without detriment to the sensitive constituents.

Introduction

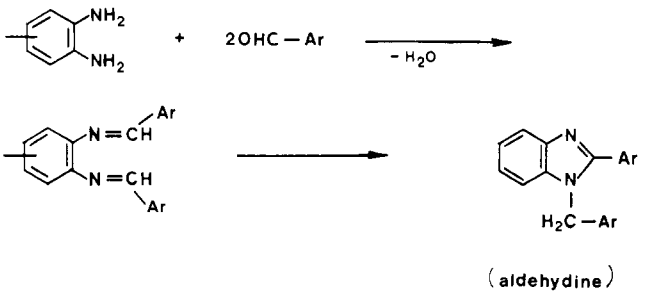
The all-aromatic polybenzimidazoles rank as one of the most promising classes of the heterocyclic polymer family for reasons of outstanding thermal stability, technologically useful fiber and membrane properties, and an excellent potential as hot-melt adhesives for applications at both high and low temperatures.[1] However, severe manufacturing problems, arising from the unavailability of soluble and processible prepolymers, have to this date hampered the large-scale commercialization of polybenzimidazole materials. Several years ago in an effort to provide an inroad into the two-stage prepolymer approach, a preliminary investigation was conducted in this laboratory[2] that comprised the low-temperature solution polymerization of both isophthalaldehyde and terephthalaldehyde with the aromatic bis(*o*-diamines) used in current technology, viz., 3,3′-diaminobenzidine and 3,3′,4,4′-tetraaminodiphenyl ether. These polycondensations, performed in dipolar aprotic solvents, gave rise to the formation of linear and soluble poly(azomethine) intermediates (**1a–c**), which were isolated as structurally well-defined solid materials and could subsequently be transformed into the corresponding polybenzimidazoles (**2a–c**) by dehydrogenation under mild experimental conditions.

While the question of oxidative assistance in the final cyclodehydrogenation step was left open in that study, an investigation of nonpolymer model reactions more recently[3] demonstrated the need for the presence of oxygen in the imidazole-forming step, anaerobic aromatization being an exeedingly slow process. The model reaction study also showed that the dehydrogenation step can be accelerated catalytically, e.g., by iron(III) chloride.

We have since extended and now report herein our studies of the prepolymer approach toward polybenzimidazoles. Specifically, we have reinvestigated some of our earlier work[2] leading to polybenzimidazoles **2a–c** with a view toward optimizing the cyclodehydrogenation conditions; in addition, we have enlarged the scope of applicability of the prepolymer approach by employing other comonomers expected to impart special properties to the ultimate benzimidazole polymer structure.

Results and Discussion

Poly(azomethines). In preliminary experiments employing the monomer pair 3,3′-diaminobenzidine (DAB) and isophthalaldehyde, nitrogen-saturated solutions of the two reactants in dipolar aprotic solvents were simply combined in equimolar concentrations at ice bath temperature, and polycondensation (first step, Scheme I) was allowed to proceed for several hours at ultimately 50 °C. The prepolymer, poly(azomethine) **1a**,[4] was then precipitated with an excess of methanol. However, high instantaneous concentrations of aldehyde resulted in a noticeable extent of additional Schiff base formation involving the available *o*-amino groups and consequent generation of aldehydine units:[5,6]



(aldehydine)

As a result of branch points thus formed, the prepolymers so prepared showed only partial solubility in selected solvents, and the soluble portions tended to undergo cross-linking reactions at an early stage of the subsequent cyclodehydrogenation step. In the next series of polycondensations, therefore, experiments were performed under much more rigorously controlled conditions such that the highly diluted (0.1 M) dialdehyde solution was added dropwise over a 3–4-h period to the 0.5 M tetra-

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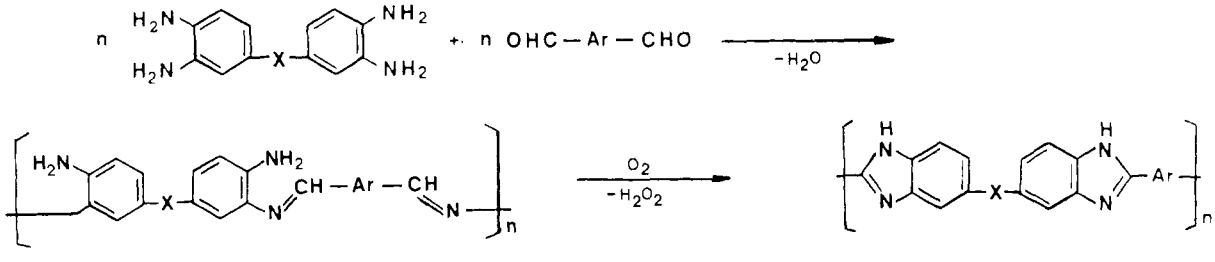
Scheme I
Polycondensation of 3,3'-Diaminobenzidine with Aromatic Dialdehydes



1 2

a, X = direct bond; Ar = 1,3-phenylene
b, X = direct bond; Ar = 1,4-phenylene
c, X = O; Ar = 1,4-phenylene
d, X = O; Ar = 9,10-anthracenediyl
e, X = O; Ar = 4,4'-biphenylene
f, X = O; Ar = 2,6-naphthalenediyl
g, X = direct bond; Ar = (η^6-tricarbonylchromium)-1,4-phenylene
h, X = direct bond; Ar = 2,5-dibromo-1,4-phenylene
i, X = direct bond; Ar = 2,3,5,6-tetrachloro-1,4-phenylene

amine solution, temperatures being kept at the lowest possible level (−15 to −18 °C) short of causing crystallization of the *N,N*-dimethylacetamide (DMA) solvent used in these and all subsequent runs. Oxygen was carefully precluded in an effort to suppress cycloaromatization during this primary polycondensation stage. With these precautions maintained, poly(azomethine) formation was found to proceed smoothly over a period of 15 h at −18 to +25 °C.[7] The formed poly(azomethine) **1a**, precipitated from the reaction mixture as in the preceding series of polycondensations, was collected in 81% yield. The experiment is summarized as the first entry in Table I.

In much the same fashion, polycondensation of DAB with terephthalaldehyde and of 3,3',4,4'-tetraaminodiphenyl ether (TAE) with the same dialdehyde gave rise to the azomethine polymers **1b** and **1c** (entries 2 and 3, Table I). The three types **1a–c** proved to be identical in appearance and solubility behavior with the products of the preliminary study.[2]

With convenient low-temperature solution polymerization conditions thus established for the prototype **1a** and the related poly(azomethines) **1b** and **1c**, similar experimental conditions were employed in the next series of polycondensations, in which the following reactant pairs were used: TAE and 9,10-diformylanthracene, TAE and 4,4'-diformylbiphenyl, TAE and 2,6-diformylnaphthalene, DAB and (η^6-tricarbonylchromium)terephthalaldehyde, DAB and 2,5-dibromoterephthalaldehyde, and DAB and 2,3,5,6-tetrachloroterephthalaldehyde (entries 4–9, Table I). The last-named three dialdehydes were chosen with the aim of demonstrating the practicability of incorporating bridging units too thermolabile to survive the demanding conditions of the classical polybenzimidazole synthesis by melt and solid-state polymerization.[8,10] In the last series of polycondensation runs (Scheme II), 1,2,4,5-tetraaminobenzene (TAB) was used as the bis(*o*-diamine) (entries 10–12, Table I); in order to avoid degradation of the extremely air-sensitive free base, the compound was employed as its stable tetrahydrochloride salt, with pyridine added to the reaction mixture as a proton acceptor. Most of the product polymers remained entirely or predominantly in solution and were separated by precipitation with methanol as before. The more rigid polymer types derived from TAB, however, were only sparingly soluble in the medium and settled out as fine precipitates during the condensation experiments.

Poly(azomethine) **1i**, containing the perchlorinated phenylene group in the repeat unit, deserves a particular comment. The bis-Schiff base **5a**, formed smoothly by anaerobic solution condensation of *o*-phenylenediamine and 2,3,5,6-tetrachloroterephthalaldehyde at temperatures below 50 °C, is readily cleaved at 80–140 °C, in both protic and aprotic solvents under nitrogen, into 1,2,4,5-tetrachlorobenzene and benzimidazole (Scheme III), probably via the tautomeric imidazoline **5b**, fission of the two C–C bonds being brought about by the combined effect of steric crowding at the tetrachlorophenylene center group and the energetic driving force of aromatization of the two N-heterocycles.[11] Not surprisingly, the polycondensation of the same chlorinated dialdehyde with DAB, when conducted at temperatures of 80 °C and higher, was found invariably to proceed with concurrent chain scission of the C–C bonds connecting the tetrachlorophenylene group with the adjacent backbone constituents. Thus, two typical screening experiments performed ultimately at 80 and 100 °C (6 h) gave polymer inherent viscosities of 0.1 and 0.06 dL g^{-1}, respectively, and ultimate heating at 140 °C entailed complete fragmentation, with 1,2,4,5-tetrachlorobenzene isolated by sublimation as one of the major degradation products. Satisfactory polycondensation (η_{inh} = 0.8 dL g^{-1}) did, however, occur under the mild standard conditions employed in the polymerization runs of this study (Table I).[12]

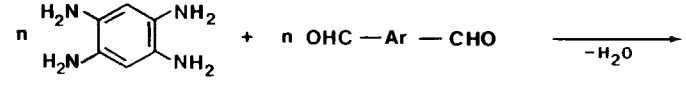
Poly(azomethines) **1a–i** and **3a–c** were yellow-brown, changing to orange-red with increasing extent of conjugation. They were generally infusible up to 300 °C; only the chromium-complexed **1g** underwent partial degradation near 250 °C. Inherent viscosities, determined in DMA or formic acid solutions, were in the range 0.3–1.3 dL g^{-1}. All polymer types derived from DAB and TAE, as well as the TAB-derived **3a** containing the 1,3-phenylene bridging unit, dissolved readily in 98% sulfuric acid and strong organic acids; in addition, when tested shortly after preparation, they showed complete (**1a–c,g**) or predominant (**1d–f,h,i,3a**) solubility in common dipolar aprotic solvents. After several weeks of storage, however, notably when rigorously freed from all solvent traces, the polymers showed somewhat reduced solubility in the aprotic solvents and/or underwent dissolution at a significantly decreased rate. The type **3b** prepared from TAB and terephthalaldehyde, being the most rigid and structurally ordered of all the tabulated poly(azomethines), showed a poorer solubility behavior than the aforementioned types; while soluble in the acidic media, it failed to dissolve to any significant extent in the aprotic solvents. The least satisfactory solubility behavior was shown by **3c**, which dis-

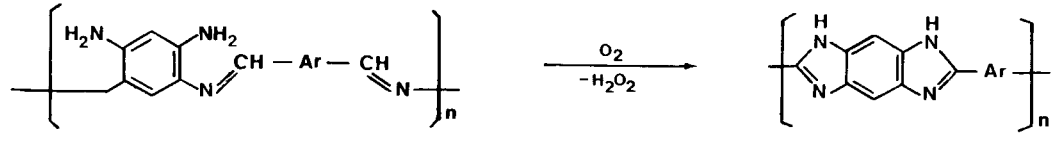
Table I
Synthesis and Some Properties of Poly(azomethines) 1a-i and 3a-c

entry	monomers[a]	poly(azomethine) type	yield, %	η_{inh},[b] dL g^{-1}	anal.	% C	% H	% N	solubility[c] DMA	HCOOH	H_2SO_4
1	DAB + isophthalaldehyde	1a	81	1.3	found	73.01	5.30	15.43	++	++	++
					calcd	76.90	5.16	17.94			
2	DAB + terephthalaldehyde	1b	83	1.1	found	72.45	4.92	15.99	++	++	++
					calcd	76.90	5.16	17.94			
3	TAE + terephthalaldehyde	1c	93	0.6	found	70.06	5.20	15.01	++	++	++
					calcd	73.15	4.91	17.06			
4	TAE + 9,10-diformylanthracene	1d	80	0.3	found	75.96	4.90	11.79	+	++	++
					calcd	78.48	4.71	13.08			
5	TAE + 4,4′-diformylbiphenyl	1e	95	0.5	found	73.60	4.70	12.11	+	++	++
					calcd	77.31	4.96	13.79			
6	TAE + 2,6-diformylnaphthalene	1f	84	0.4	found	72.67	4.89	13.02	+	++	++
					calcd	76.17	4.79	14.81			
7	DAB + (η^6-tricarbonylchromium)terephthalaldehyde	1g	91	0.8	found	62.00	3.20	12.46	+	++	++
					calcd	61.61	3.60	12.50			
8	DAB + 2,5-dibromoterephthalaldehyde	1h	94	0.5	found	48.20	3.11	10.32	+	++	++
					calcd	51.09	3.00	11.92			
9	DAB + 2,3,5,6-tetrachloroterephthalaldehyde	1i	89	0.8	found	52.71	2.59	11.23[d]	+	++	++
					calcd	53.36	2.69	12.45[d]			
10	TAB + isophthaldehyde	3a	96	0.5	found	66.30	4.67	21.93	+	++	++
					calcd	71.17	5.12	23.71			
11	TAB + terephthalaldehyde	3b	95	0.3	found	65.61	4.69	22.00	−	+	++
					calcd	71.17	5.12	23.71			
12	TAB + 2,3,5,6-tetrachloroterephthalaldehyde	3c	91		found	40.07	2.26	13.31	−	−	+
					calcd	44.95	2.16	14.98			

[a] Equimolar quantities of bis(*o*-diamine) and dialdehyde, in DMA; see Experimental Section. Filtration of reaction mixture prior to workup omitted in entries 5 and 8–12. DAB = 3,3′-diaminobenzidine; TAE = 3,3′,4,4′-tetraaminodiphenyl ether; TAB = 1,2,4,5-tetraaminobenzene. [b] Determined at 30 °C in DMA (formic acid in entry 11) (0.1–0.3% w/v) on freshly prepared samples (on soluble portions in entries 4–11). [c] Tested shortly after preparation. Some reduction of solubility in DMA observed after lengthy storage. Soluble (98–100%), ++; partly or predominantly soluble (>50%), +; poorly soluble (<50%) or insoluble, −. [d] Cl found, 29.51; calcd, 31.50%.

Scheme II
Polycondensation of 1,2,4,5-Tetraaminobenzene with Aromatic Dialdehydes

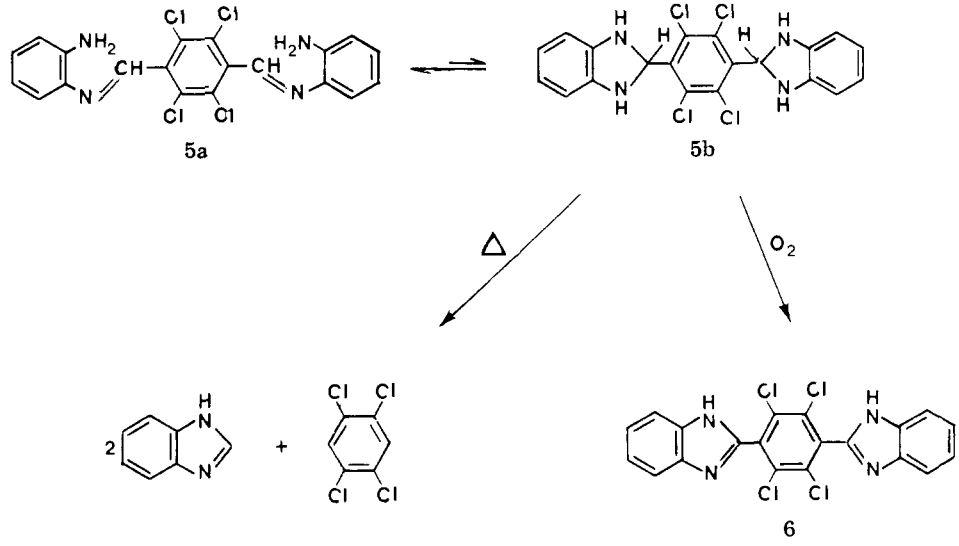




3 4

a, Ar = 1,3-phenylene
b, Ar = 1,4-phenylene
c, Ar = 2,3,5,6-tetrachloro-1,4-phenylene

Scheme III
Thermal Cleavage and Oxidative Imidazolation of 5



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solved only partially in sulfuric acid. All of the poly(azomethines) gave unsatisfactory microanalytical results; especially, the C and N values were consistently found to be several percent low. This behavior, similarly observed with the cycloaromatization products **2a–i** and **4a–c** to be discussed in the subsequent section, is reminiscent of the difficulties in microanalytical characterization reported for other conjugated aromatic or heteroaromatic macromolecules and is a manifestation of an appreciable extent of resistance to combustion.

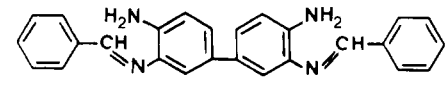
The predominance of the open-chain azomethine structure[13] over the tautomeric imidazoline constitution (cf. Scheme IV), both in the solid state and in solution, was confirmed spectroscopically for all of the poly(azomethines). The solid-state IR spectra (KBr pellets) were dominated by the strong C=N stretching band of the azomethine system in the vicinity of 1620 cm^{-1}, exceeding in intensity the adjacent benzene-aromatic bands at 1590–1600 cm^{-1}. The nonbonded and bonded N–H stretching absorptions of the amino group appeared at about 3450 and 3360 cm^{-1}, and the C–N stretching modes of both the C–N=C and the C–NH_2 groupings gave rise to absorptions near 1280 (s) and 1250 (m) cm^{-1}. In addition, the spectra displayed a strong band at about 1485 cm^{-1} due to an atomatic ring vibration of the anilino and anil groupings, and the out-of-plane C–H bending modes of the various di- and trisubstituted benzene ring systems were manifested in the characteristic absorption patterns at 880–800 cm^{-1}. Spectra of selected poly(azomethines) are reproduced in Figure 1. The collection includes the spectrum of the chromium-containing **1g**, which, like its aromatized counterpart **2g**, is dominated by the typical A_1 and E bands (ν_{CO}) of the tricarbonylchromium system at 1962 and 1900 cm^{-1}.

While the ^1H NMR spectra generally were of limited diagnostic value because of strong line broadening,[14] the electronic absorption spectra (275–500 nm) proved to be highly characteristic and diagnostically useful. The maxima and (base molar) absorption coefficients determined for a number of selected poly(azomethines) are collected in Table II. As can be seen from the tabulation, all polymers examined gave the two strong absorption bands characteristic of the spectra of aromatic bis-Schiff base structures,[3] with maxima in the regions 280–320 and 425–475 nm. The low-energy band is particularly relevant as it vanishes entirely in the cyclodehydrogenation process (to be replaced by the benzimidazole band system in the vicinity of 350 nm; vide infra) and, therefore, can be utilized as a reliable spectroscopic means of monitoring the disappearance of the azomethine structure in the reaction poly(azomethine) → polybenzimidazole (second step, Schemes I and II). On comparing relative band positions, one observes a clear trend of shifts to lower energy with increasing extent of conjugation. This is particularly striking with the high-energy band system associated with a $\pi \rightarrow \pi^*$ transition in the N=CH–Ar–CH=N chromophore. Thus, whereas **1a**, comprising the least conjugating bridging unit (Ar = 1,3-phenylene), gives λ_{max} almost identical with that of the model compound **7**, which ab-

Table II
Electronic Absorption Spectra of Selected Poly(azomethines) and Corresponding Polybenzimidazoles in the 250–500-nm Region

azomethines		imidazoles	
compd	λ_{max},[a] nm	compd	λ_{max},[a] nm
7	285 (2.9),[c] 422 (2.6)	8	336 (3.5), 327[b]
1a	290 sh (1.8),[c] 428 (1.4)	2a	339 (3.0), 336[b]
1b	306 (1.6), 475 (1.7)	2b	383 (4.8), 379[b]
1c	295 (1.3), 454 (1.7)	2c	365 (2.9)
1g	318 (*d*), 460 (*d*)	2g	380 (4.7)
1i	298 (1.3),[e] 442 (0.9)[e]	2i	305 (2.9)[e]
3a	*f*	4a	365 (2.7),[e] 347[b]

[a] In DMA (10^{-5}–10^{-4} M). In parentheses, $\epsilon/10^4$ L mol^{-1} cm^{-1} (ϵ = base molar absorption coefficient). [b] In H_2SO_4; from ref 8. [c] Value unreliable because of interference by solvent edge absorption. [d] Not determined quantitatively. [e] Obtained on portion soluble in DMA; ϵ value adjusted. [f] Not determined.



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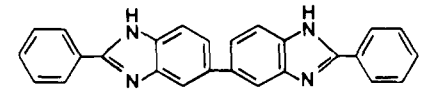

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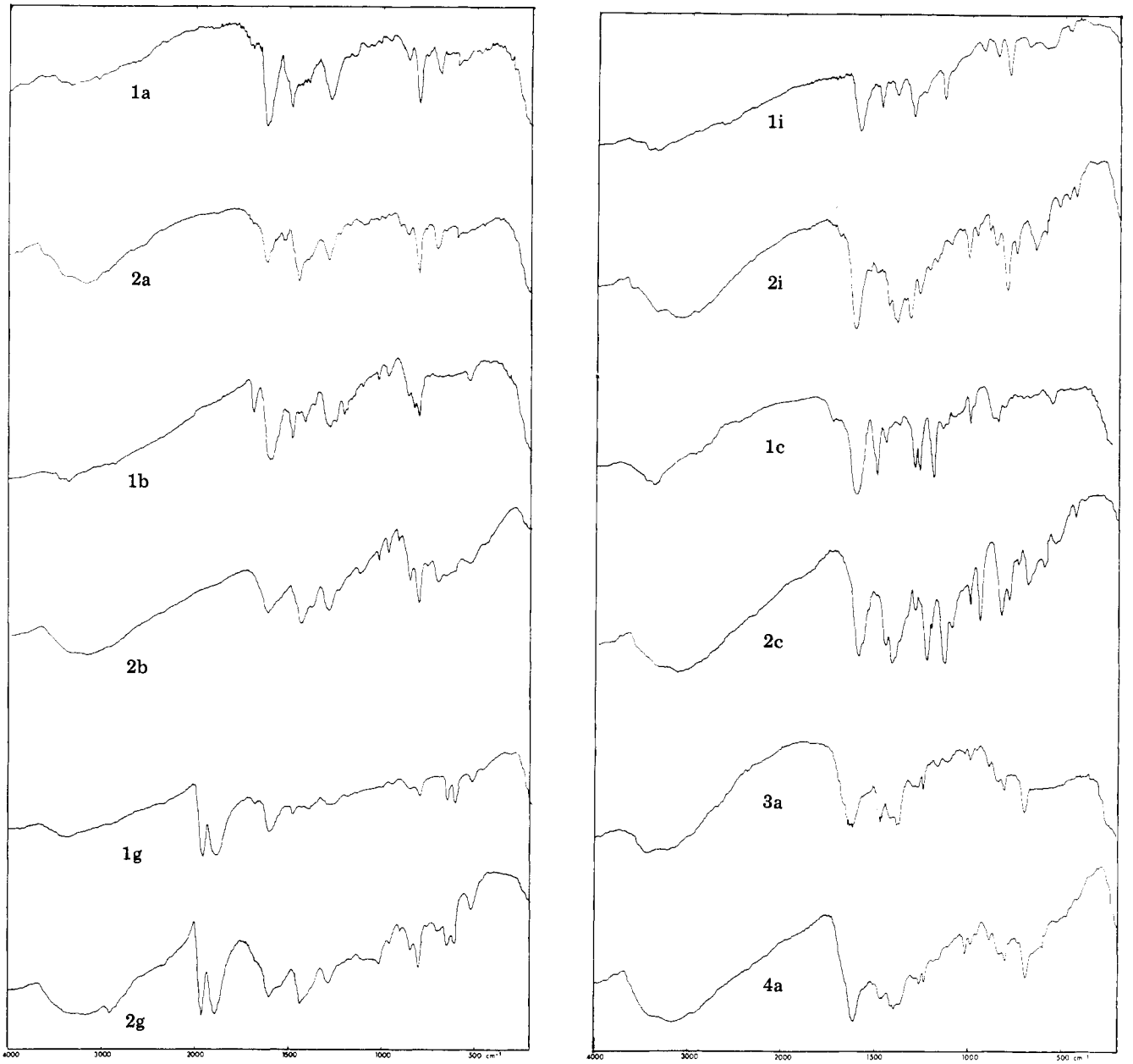


Figure 1. IR spectra (KBr matrix) of selected poly(azomethines) and polybenzimidazoles.

sorbs at 285 nm ($\epsilon = 2.9 \times 10^4$ L mol^{-1} cm^{-1}), the polymer types containing a 1,4-disubstituted phenylene bridge in the recurring unit, including the chromium-complexed polymer **1g**, exhibit maxima at 295–318 nm. The comparatively high transition energy associated with the tetrachlorophenylene-bridged **1i**, as against that of the unchlorinated **1b**, indicates some deviation from planarity within the N=CH–Ar–CH=N segment, which is what one would expect in view of the steric requirements of the four Cl substituents. The similarly low wavelength shown by **1c**, in spite of the presence of the conjugating 1,4-phenylene group, must be ascribed to the interruption of electronic delocalization between the two anil rings brought about by the ether bridge. This suggests that a closer approach toward (sterically enforced) coplanarity and, hence, a higher extent of electronic delocalization across the azomethine link obtain in polymeric Schiff bases than in simple nonpolymeric structures such as benzalaniline, in which the *N*-phenyl ring is appreciably rotated out of the plane of the remaining benzalimino segment[15] as a result of ring π-orbital overlap with the lone pair on N. The sensitivity of the high-energy band position to the extent of conjugation in the N=CH–Ar–CH=N segment would seem to confirm this view.

Polybenzimidazoles. The oxidative cyclodehydrogenation of *o*-amino-substituted aromatic Schiff bases of the general type **9a** (Scheme IV), either presynthesized or formed in situ from aromatic 1,2-diamines and aldehydes, represents a classical method of benzimidazole synthesis.[16] The analogous polycondensation of aromatic bis(*o*-diamines) with dialdehydes, as revealed in a proficiently elaborated patent script,[6] provides a useful synthetic pathway to polymeric benzimidazoles. Cyclodehydrogenation is likely to proceed via the corresponding (less favored[13]) imidazoline ring tautomer **9b**. Although the literature presents conflicting data concerning the question of oxidative assistance in the aromatization of mono-Schiff bases,[17] it is clear from recent studies of bis-Schiff base aromatization (e.g., **5** → **6** and **7** → **8**) that, at least in polynuclear systems, nonoxidative cyclodehydrogenation represents a most inefficient process largely restricted to melt or gas-phase conditions,[3,11] whereas the reaction is smoothly brought about in the presence of air or, better still, of air and catalytic quantities

of iron(III) chloride. The same resistance to nonoxidative cyclodehydrogenation was indeed observed with polymeric azomethines in a series of exploratory experiments in which both **1a** and **1b** were heated in DMA solutions with rigorous exclusion of oxygen; even at teperatures as high as 100–140 °C the dehydrogenation efficiency remained poor. On the other hand, as shown in further screening experiments, both **1a** and **1b** underwent aromatization readily when treated in solution with air[18] at various temperatures, preferably in the presence of a catalyst. The results of these screening experiments can be summed up as follows: (i) all common solvents of the amide type lend themselves as a medium for cyclodehydrogenation; dimethyl sulfoxide, although promoting the oxidative aromatization step significantly, is less useful for the purpose as it is difficult to remove from the polymer after precipitation; (ii) protic, notably acidic solvents, such as poly(phosphoric acid), while not inhibitory to cyclodehydrogenation, tend to enhance side reactions, e.g., hydrolytic chain scission or degradation of sensitive constituents in the recurring unit, and hence offer no particular advantage; (iii) uncatalyzed oxidation by air proceeds smoothly at 50–100 °C, provided that the flow of air introduced into the polymer solution is appreciable ($\simeq$10 L h^{-1}), simple stirring in an air environment being insufficient to bring the cyclodehydrogenation to completion within reasonable periods of time; (iv) the oxidation process can be efficaciously catalyzed (1 mol % based on polymer repeat unit) by readily available, low-cost transition-metal salts and complexes such as nickel bis(acetylacetonate), cobalt naphthenate, or iron(III) chloride, the last-named salt being especially suitable for reasons of solubility and absence of ligands capable of being occluded by the polymeric substrate.

On the basis of these findings, all poly(azomethines) **1a–i** and **3a–c** were converted to the respective polybenzimidazoles **2a–i** and **4a–c** (second step, Schemes I and II)[19] by a standard procedure that involved bubbling air at a rate of 10 L h^{-1} into a stirred 0.15 M solution or suspension in DMA at 60 °C in the presence of iron(III) chloride (1.5 $\times$ 10^{-3} M). Progress of conversion to **2a–i** and **4a–c** was followed in cases of sufficient substrate solubility (**1a–g**, freshly prepared) by monitoring the intensity of the low-energy band in the electronic absorption spectra; the reaction was considered completed when this band had entirely vanished and the benzimidazole band system (vide infra) reached its maximal absorbance.[20] Although this stage was generally attained after 4–6 h, the air treatment was routinely continued for another 1–2 h. The aromatized polymers were precipitated from solution by excess methanol. The less soluble poly(azomethines) **1h,i** and **3a–c** (and also some of the types **1a–g** if used after extended storage) were uniformly, without spectroscopic monitoring, treated with air for a 10-h period; this was considered adequate after IR spectra taken on samples treated for a total of 20 h had proved to be identical with those of the 10-h samples. Polybenzimidazoles **2i** and **4a–c** were largely insoluble in the DMA medium; polymer separation was completed by the addition of excess methanol as before. Overall product yields were 90–95%. The conditions for representative cyclodehydrogenation experiments are summarized in Table III, which also contains analytical and solubility data for the product polymers obtained.

Polybenzimidazoles **2a–i** and **4a–c** were yellow-tan to dark-brown solids; with the exception of **2g**, which underwent partial degradation at 250–280 °C, they were infusible up to 300 °C. Inherent viscosities in DMA or formic acid solution tended to be slightly higher than observed for the precursor azomethines, suggesting a minor extent of chain extension by end group interaction during the cyclodehydrogenation process; accordingly, a weak aldehydic carbonyl stretching band occasionally appearing near 1680 cm^{-1} in the IR spectra of the prepolymers tended to vanish upon conversion to the polybenzimidazoles. The polybenzimidazoles (excepting **4c**) dissolved completely in 98% sulfuric acid and for the most part also in formic acid. Moreover, with the exception of the chlorinated **2i** and the TAB-derived types **4a–c**, they possessed complete or predominant solubility in dipolar aprotic solvents, notably when dissolution was aided by the addition of 3–5% LiCl. Upon extended storage, the more ordered types apparently consolidated to a more closely packed array, and this was reflected in a reduced extent of dissolution in aprotic solvents. Polybenzimidazole **4c** possessed the poorest solubility of all types prepared, being only partly soluble in sulfuric acid and insoluble in other media. All of the polybenzimidazoles were characterized by the same resistance to combustion as shown by the precursor poly(azomethines), the found carbon, nitrogen, and chlorine contents tending to be several percent lower than calculated.

The most notable changes in the solid-state IR spectra (KBr pellets) on going from the polyazomethines to the polybenzimidazoles were found (i) in the N–H stretching region, where the characteristically broad imidazole absorption "hump" at 3600–2800 cm^{-1} due to intermolecularly hydrogen-bonded N–H···N modes[21] replaced the two bands at 3450 and 3360 cm^{-1} of the amino group, (ii) in the vicinity of 1600 cm^{-1}, where C=C and C=N ring stretching absorption of the benzimidazole system appeared as a strong multiplet feature at 1625–1600 cm^{-1} in place of the azomethine C=N stretching band to the low-frequency side, and (iii) in the 1500–1400-cm^{-1} region, in which a strong band group, likely due to aromatic C–H in-plane bending modes, appeared at 1450–1400 cm^{-1} whereas the 1485-cm^{-1} band characteristic of the poly(azomethine) spectra vanished entirely. Furthermore, the C–NH stretching band near 1250 cm^{-1} tended to disappear or be strongly attenuated, and the 1280-cm^{-1} band underwent a considerable enhancement (occasionally paired with a shift to higher frequencies), probably through contributions from C–N= stretching modes of the heterocyclic ring system. Representative spectra are shown in Figure 1. Included are those of the long-known polybenzimidazoles **2a** and **2b**, found to be substantially identical with the ones published in the earlier literature.[8,9]

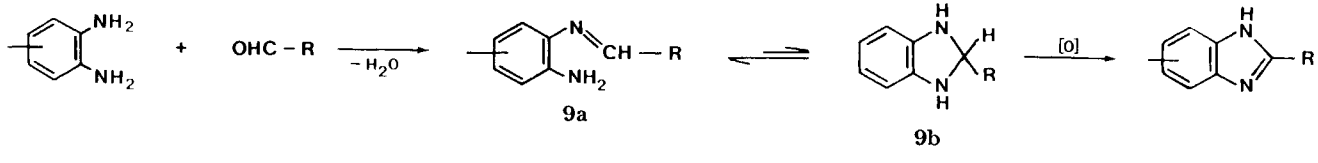
The high-resolution ^{1}H NMR spectra of **2** in Me_2SO-d_6, strongly line-broadened and in most cases difficult to differentiate, showed aromatic proton multiplets in the 7–9 ppm region, and the signals due to the azomethine and amine protons of the precursor polymers were no longer detectable. The most dramatic spectroscopic changes accompanying the poly(azomethine) $\rightarrow$ polybenzimidazole reaction were manifested in the electronic absorption spectra. In place of the two azomethine bands in the vicinity of 300 and 450 nm, a strong, structured band due to $\pi \rightarrow \pi^*$ transitions in the conjugated domain comprising the aromatic bridging group and the benzimidazole unit[22] was observed in the range 310–380 nm. Table II lists pertinent maxima and absorption coefficients determined in DMA solution, with some literature data on the known polymers in sulfuric acid solution given for comparison. The band position, irrespective of the medium used, shows a rough correlation with the extent of conjugation achieved in the polymer backbone. Thus, the *p*-phenylene-bridged

Table III
Polybenzimidazoles 2a-i and 4a-c by Cyclodehydrogenation of Poly(azomethines) 1a-i and 3a-c

entry	poly-(azomethine)[a] prepolymer	reaction time,[b] h	polybenzimidazole[c] type	η_{inh},[d] dL g^{-1}		anal. % C	anal. % H	anal. % N	solubility[e] DMA	solubility[e] HCOOH	solubility[e] H_2SO_4
1	1a	8	2a	1.4	found	73.71	3.40	17.09	++	++	++
					calcd	77.91	3.92	18.17			
2	1b	88	2b	1.2	found	74.23	3.99	16.89	+	++	++
					calcd	77.91	3.92	18.17			
3	1c	8	2c	0.8	found	70.10	3.51	16.17	++	++	++
					calcd	74.06	3.73	17.28			
4	1d	8	2d	0.5	found	73.30	4.01	11.99	+	+	++
					calcd	79.23	3.80	13.20			
5	1e	8	2e	0.5	found	74.79	3.88	12.14	+	+	++
					calcd	78.08	4.01	13.93			
6	1f	8	2f	0.4	found	73.07	3.63	13.16	+	++	++
					calcd	76.99	3.77	14.97			
7	1g	7	2g	0.9	found	62.20	2.93	12.02	+	++	++
					calcd	62.16	2.72	12.61			
8	1h	10	2h	0.6	found	47.02	1.82	11.05	+	++	++
					calcd	51.53	2.16	12.02			
9	1i	10	2i	0.7	found	49.37	1.46	12.16	–	++	++
					calcd	53.85	1.81	12.56[f]			
10	3a	10	4a	0.6	found	65.88	3.09	22.70	–	++	++
					calcd	72.40	3.47	24.13			
11	3b	10	4b	0.3	found	67.56	3.16	22.13	–	+	++
					calcd	72.40	3.47	24.13			
12		10	4c		found	40.30	1.21	13.97	–	–	+
					calcd	45.44	1.09	15.14			

[a] From Table I. [b] Advanced to 2 and 4 at 60 °C in DMA (0.15 M) containing $FeCl_3$ (1.5×10^{-3} M); air flow rate 10 L h^{-1}; see Experimental Section. [c] Obtained in yields of 90–95% throughout. [d] Determined at 30 °C in DMA (entries 1–8) or formic acid (entries 9–11) (0.1–0.3% w/v) on freshly prepared samples (on soluble portions in entries 4–8 and 11). [e] Tested shortly after preparation. Reduced degree of solubility in DMA observed after lengthy storage. Soluble (98–100%), ++; partly or predominantly soluble (>50%), +; poorly soluble (<50%) or insoluble, –. [f] Cl found, 29.66; calcd, 31.79%.

Scheme IV



2b is seen to absorb at higher wavelength than **2a** containing the *m*-phenylene bridge, and a similar shift to higher wavelength is observed for the maximum of **4a**, derived from TAB, relative to that of the corresponding DAB-derived polymer **2a**. In the tetrachlorophenylene-bridged **2i** steric crowding prevents properly planar alignment of both the benzimidazole unit and the bridging segment along the chain; for this polymer, as a result, the maximum appears at the shortest wavelength of the entire series. This blue shift in relation to the other polybenzimidazoles is even more pronounced than in the case of the corresponding poly(azomethine) (**1i**), possibly as a consequence of less efficient relief of steric strain in the all-aromatic benzimidazole polymer than in the more flexible open-chain precursor type. The strikingly high wavelength of the maximum of the chromium-complexed **2g** warrants a comment. Although complexation of a benzene derivative with the $Cr(CO)_3$ group increases the effective positive charge on the arene's σ orbitals, it leaves essentially undiminished both the π-electron density on the ring[23] and the molecule's capability of transmitting resonance effects across the ligand.[24] The spectroscopic data listed for **2g** show that the capacity of the chromium-complexed phenylene group for donating or accepting electronic charge by a mesomeric effect is even greater than that of the free phenylene bridge. The band's high intensity also indicates that the degree of coplanarity of bibenzimidazole and arene bridge is unaffected by the η^6-bonded tricarbonylchromium "handle".

Experimental Section

Instrumental Methods and Analyses. Melting points, uncorrected, were taken to 300 °C. Infrared spectra were recorded on KBr pellets (4000–200 cm^{-1}). Electronic absorption spectra were obtained on DMA solutions ($\sim 10^{-5}$ M; 250–500 nm). Proton nuclear magnetic resonance spectra (60 MHz) were taken on Me_2SO-d_6 solutions (chemical shifts in ppm relative to Me_4Si internal standard). Inherent viscosities, η_{inh}, were measured with a Cannon-Fenske viscosimeter at 30 °C in DMA or formic acid solutions (0.1–0.3% w/v). Microanalyses were performed by Robertson Laboratory, Florham Park, NJ.

Solvents, Reagents, and Monomers. *N,N*-Dimethylacetamide (DMA), predried over molecular sieves (4 Å), was allowed to reflux for 24 h over CaH_2; it was then distilled at reduced pressure from a fresh batch of the hydride and collected under a nitrogen blanket. All other solvents, reagent grade, were used as received. The nitrogen purging gas was deoxygenated by passing it over BASF catalyst R 3-11 at 130 °C and through a suitable (silica gel/soda lime/phosphorus pentoxide) drying train.

3,3′-Diaminobenzidine (DAB), commercially available (Fluka AG), was recrystallized several times from Ar-saturated water containing a pinch of sodium dithionite; mp 172–173 °C (lit.[8] mp 179–180 °C). 1,2,4,5-Tetraaminobenzene (TAB) was obtained commercially (Burdick and Jackson) as the tetrahydrochloride salt. For purification, the free base, liberated as described,[8] was immediately reconverted to the hydrochloride by dissolution in dilute, Ar-saturated aqueous HCl at 60–65 °C and treatment with concentrated aqueous HCl; the salt, which slowly crystallized at 8–10 °C, was collected by filtration, washed thoroughly with dry ether, and dried in vacuo at 70–80 °C. 3,3′,4,4′-Tetraaminodiphenyl ether (TAE; Burdick and Jackson) was purified by Marvel's method;[25] mp 149 °C (lit.[25] mp 149.5–151 °C). Both isophthalaldehyde and terephthalaldehyde (Merck) were recrystallized from ethanol. 9,10-Diformylanthracene,[26] 4,4′-diformylbiphenyl,[27] 2,6-diformylnaphthalene,[28] (η^6-tricarbonylchromium)terephthalaldehyde,[29] and 2,5-dibromoterephthalaldehyde[30] were synthesized by literature procedures. 2,3,5,6-Tetrachloroterephthalaldehyde was prepared by oxidation of 2,3,5,6-tetrachloro-*p*-xylene-α,α'-diol with dimethyl sulfoxide/dicyclohexylcarbodiimide in the presence of pyridinium trifluoroacetate;[11] mp 193–194 °C (ethanol).

Polymerization Reactions. Poly(azomethines) 1a–i and 3a–c. Experiments were generally conducted on a 2.5-mmol scale. The method described below for the preparation of **1a** (first entry, Table I) is representative of the polycondensation involving DAB or TAE as the amine component.

Into a dry, two-necked, round-bottom flask of 50-mL capacity, thoroughly purged with N_2, was placed the solution of 0.535 g (2.5 mmol) of DAB in 5 mL of N_2-saturated DMA. To the magnetically stirred solution was added over a 4-h period in a steady stream of N_2 (gas inlet tube reaching below surface of liquid) an N_2-saturated solution of 0.335 g (2.5 mmol) of isophthaldehyde in 25 mL of DMA. Throughout the addition, the temperature of the reaction mixture was kept at −15 to −18 °C. Stirring under N_2 was continued for 15 h, during which period the temperature was allowed gradually to rise to 20–25 °C. The yellowish solution was filtered, and the residue on the filter was thoroughly extracted with hot DMA under N_2. The combined filtrate and extracts were poured into 200 mL of methanol with vigorous shaking, and the precipitated yellow-brown poly(azomethine) **1a**, after thorough washing with methanol and ether, was dried for 48 h at 65 °C (0.5 torr); yield 0.632 g (81%). For analytical purposes, a sample was postdried overnight at 85 °C (0.1 torr).

The same basic procedure was employed for the synthesis of poly(azomethines) **1b–i** (entries 2–9, Table I). In those experiments that furnished crude products only partially soluble in the medium (entries 5 and 9), the reaction mixture was poured without filtration into excess methanol, and the suspended poly(azomethine) was filtered off, washed, and dried as before.

Reactions employing TAB as the amine comonomer (entries 10–12, Table I) were conducted in a similar fashion, except that the amine was used as the tetrahydrochloride and, hence, required liberation from the salt. To this end, dry, deoxygenated pyridine (5.0 mmol) was injected by syringe into the stirred N_2-saturated suspension of the tetrahydrochloride (2.5 mmol) in the solvent (5 mL). As the liberated tetraamine dissolved, pyridinium chloride precipitated from the solution. The mixture was cooled to the indicated temperature, and the dialdehyde solution was added as described. This was followed by the addition of another 5.0-mmol portion of pyridine. After completion of the reaction at ultimately 25 °C, the mixture was poured into 200 mL of methanol, and the solid product collected by filtration was washed thoroughly with methanol, water, and ether. It was then dried as before.

Oxidative Cyclodehydrogenation Reactions. Polybenzimidazoles 2a–i and 4a–c. General Procedures. Into a pear-shaped two-necked flask of 25-mL capacity, equipped with a gas inlet tube reaching nearly to the bottom of the vessel, was charged the solution or suspension of poly(azomethine), 1.5 mmol (based on polymer repeat unit), in 10 mL of dry DMA containing anhydrous iron(III) chloride, 0.015 mmol. Dry air (10 L h^{-1}) was bubbled into the liquid for the period specified in Table III, while the temperature of the reaction mixture was maintained at 60 ± 3 °C. The solution or suspension was poured into 10 mL of water with vigorous shaking. The precipitated polybenzimidazole, collected by filtration, was washed thoroughly with water, methanol, and ether and was dried for 48 h at 100 °C (0.2 torr). Samples used for microanalysis were additionally dried for 24 h at 180–200 °C (0.1 torr).

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Registry No. **1a**, 56691-11-3; **1b**, 56691-10-2; **1c**, 56691-12-4; **1d**, 83844-71-7; **1e**, 83844-70-6; **1f**, 83844-69-3; **1h**, 83844-67-1; **1i**, 83844-68-2; **2a**, 25734-65-0; **2b**, 28576-59-2; **2c**, 38744-34-2; **2d**, 83802-34-0; **2e**, 83802-35-1; **2f**, 83802-36-2; **2h**, 83802-37-3; **2i**, 83802-38-4; **3a**, 83844-65-9; **3b**, 83844-66-0; **3c**, 83844-64-8; **4a**, 27233-57-4; **4b**, 32075-68-6; **4c**, 32075-70-0; **7**, 83802-39-5; **8**, 15179-41-6; DAB–isophthalaldehyde copolymer, 27288-38-6; DAB–terephthalaldehyde copolymer, 30942-57-5; TAE–terephthalaldehyde copolymer, 56281-15-3; TAE–9,10-diformylanthracene copolymer, 83802-40-8; TAE–4,4′-diformylbiphenyl copolymer, 83802-41-9; TAE–2,6-diformylnaphthalene copolymer, 83802-42-0; DAB–(η^6-tricarbonylchromium)terephthalaldehyde copolymer, 83802-33-9; DAB–2,5-dibromoterephthalaldehyde copolymer, 83802-43-1; DAB–2,3,5,6-tetrachloroterephthal-

aldehyde copolymer, 83802-44-2; TAB–isophthalaldehyde copolymer, 27288-37-5; TAB–terephthalaldehyde copolymer, 31831-59-1; TAB–2,3,5,6-tetrachloroterephthalaldehyde copolymer, 83802-45-3.

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(4) (a) Although represented in the scheme by a single structural formula, the actual structure of **1** doubtlessly is made up of isomeric repeat units comprising tetraamine moieties variously disubstituted at the 3,3′-, 3,4′-, and 4,4′-amino groups. While MO calculations[4b] indicate a slightly higher basicity for the amino substituents at positions 3 (3′) than for those at 4 (4′) in the monomer, the calculated electronic charge difference, as was pointed out before,[3] is too small to warrant the prediction of exclusive or even prevalent C=N bond formation at 3 (3′) as implied in the structural represenation of Scheme I. (b) Bochvar, D. A.; Stankevich, I. V.; Korshak, V. V.; Rusanov, A. L. *Dokl. Akad. Nauk, SSSR* **1969**, *184*, 95.

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(7) Added heating periods of 4–8 h at 50–100 °C, again in the absence of oxygen, did not result in a significant further viscosity increase. On the other hand, we found the poly(azomethines) invariably to undergo some cyclodehydrogenation in the course of such heat treatment. No purpose was seen, therefore, in exceeding the given time/temperature standard conditions.

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(12) The susceptibility to C–C bond cleavage is restricted to structures of type **5**, representing precursor species of benzimidazoles of type **6**. Once the benzimidazole ring system has formed by oxidative dehydrogenation, as in **6** (vide infra), the driving force of aromatization is no longer existent, and steric crowding of the chloro substituents alone is insufficient to achieve C–C bond fission under conditions conducive to the degradation of **5**. Indeed, polybenzimidazole **2i**, unlike its azomethine precursor **1i**, can be heated at 100 °C and higher in DMA solution without undergoing noticeable chain scission.

(13) (a) Aromatic azomethines in which an ortho position of the anil ring system is occupied by an amino group are capable of rearranging to the corresponding closed-ring imidazole tautomer (**9a** → **9b**), Scheme IV), although ring closure is disfavored by the group's high basicity,[13b] and the open-chain Schiff base form is thus predominant. Contrasting with this situation, the more acidic SH group in place of NH_2 enters into cyclization readily; as a result, the corresponding thiazoline tautomers are generally favored over their Schiff base counterparts.[13c] (b) Grellmann, K. H.; Tauer, E. *J. Am. Chem. Soc.* **1973**, *95*, 3104. (c) See, for example: Goetz, F. J. *J. Heterocycl. Chem.* **1968**, *5*, 509.

(14) A reasonably good spectrum, obtained for the 1,4-phenylene-bridged **1b** in Me_2SO-d_6, showed a broad multiplet at δ 6.6–8.5 ppm representing the aromatic protons, from which a broad singlet due to the *p*-phenylene protons emerged at 8.25 ppm. Furthermore, two signals due to the CH=N and NH_2 protons appeared at 8.9 and 5.5 ppm. Area ratios were approximately as expected for the open-chain azomethine structure shown. For comparison, the bis-Schiff base **7** gives azomethine and amino proton signals at 8.6 and 5.2 ppm, respectively.[3]

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(18) The oxygen-assisted cyclodehydrogenation of Schiff bases reportedly[13b] gives rise to the generation of H_2O_2, and not of H_2O, as byproduct. This question has not been examined in the present work.

(19) (a) The structural arrangement shown, in accord with conventional practice,[8,9,19b] comprises 5,5′-bibenzimidazole segments. When dissolved in (neutral) solvents, benzimidazoles undergo rapid 1,3-prototropic exchange,[19c] so that at any instant both tautomers are in existence. Accordingly, the benzimidazole polymers **2**, upon precipitation from solution, may safely be assumed to consist of recurring units containing any one of the three possible dispositions (5,5′, 6,6′, and 5,6′) of the bond interconnecting the two benzimidazole moieties. Structures **2a–i** should hence be viewed as an oversimplified representation of the actual intrachain substitution pattern. The same argument holds for the bibenzimidazole model compound **8** and, mutatis mutandis, for the benzodiimidazole structure in **4a–c**. (b) Gray, D. N.; Shulman, G. P.; Conley, R. T. *J. Macromol. Sci., Chem.* **1967**, *1*, 395. (c) Staab, H. A.; Mannschreck, A. *Tetrahedron Lett.* **1962**, 913.

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