Poly(2,2′-(1,4-phenylene)-5,5′-bibenzimidazole) from 3,3′,4,4′-Tetraaminobiphenyl and 1,4-Diacetylbenzene

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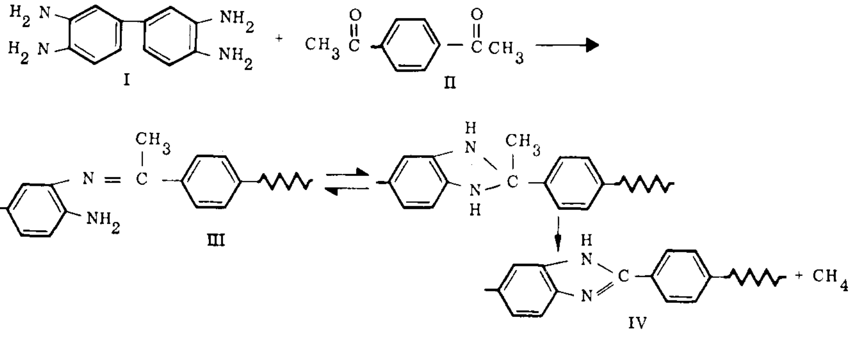
ABSTRACT: The reaction of 3,3′,4,4′-tetraaminobiphenyl and 1,4-diacetylbenzene to give a polybenzimidazole involves two distinct steps: first, the formation of a high molecular weight Schiff base, and second, conversion of this polymer to a polybenzimidazole. The Schiff base intermediate, prepared by melt condensation polymerization, is converted to the polybenzimidazole by thermal aromatization of the intermediate polybenzimidazoline with evolution of methane. Studies of a model compound system, *o*-phenylenediamine and acetophenone, show that the elimination of methyl over phenyl is preferred during thermal aromatization. This synthetic route to polybenzimidazoles does not require a high-temperature dehydration for complete aromatization.

Aromatic polybenzimidazoles (PBI) were first described by Marvel and Vogel[2] in 1961. These polymers are characterized by high thermal resistance and retention of physical properties at elevated temperatures. The polymerization mechanism of the 3,3′,4,4′-tetraaminobiphenyl and diphenyl isophthalate comonomer system has been described.[3] The mechanism as proposed by these workers was supported by kinetic data obtained from melt polymerizations carried out under autogenous pressure in sealed tubes. Gray, Shulman, and Conley[4] have shown that this mechanism is not consistent with the experimental evidence obtained during the melt polymerization of the same monomers at atmospheric or reduced pressures. Mass spectometric thermal analysis of the polymerizing monomers, thermogravimetric and elemental analysis of the polymer, and investigations relating to the synthesis of a model compound, 2,2′-diphenyl-5,5′-bibenzimidazole, all show that the elimination of water is the final step in aromatization of the benzimidazole ring. The dehydration is not complete below 400°.



This mechanistic sequence is in accord with the findings of Korshak and coworkers.[5]

Benzimidazoles have been prepared by a variety of synthetic methods; however, few of them are adaptable to the preparation of high polymers because of low yields.[6] It is well known that the formation of Schiff bases from aromatic aldehydes and amines occurs in high yields and this reaction has been utilized as a synthetic route to Schiff base types of polymers.[7–9]

The reactions of aralkyl ketones with aniline have been studied by Elderfield and coworkers.[10,11] In these papers, the nature of the intermediate and the mode of conversion of this intermediate to the benzimidazole *via* hydrocarbon elimination are discussed. The reaction of phenylenediamine with an aralkyl ketone can yield either a Schiff base or a 2,2-disubstituted benzimidazoline. The isolation of the simple condensation product of acetophenone and *o*-phenylenediamine has not been reported, although Ladenburg and Ruegheimer[12] have reported the formation of 2-phenyl-5(6)-methylbenzimidazole from 3,4-diaminotoluene and acetophenone.

A new synthetic route to polybenzimidazole was investigated involving the reaction of a diketone and an *ortho*-disposed tetraamine. The monomers chosen for this study were 3,3′,4,4′-tetraaminobiphenyl (I) and 1,4-diacetylbenzene (II) since these would yield a polymer identical with those studied by Marvel and

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(1) To whom all correspondence should be addressed at Owens-Illinois Technical Center, Toledo, Ohio 43601.

(2) (a) H. Vogel and C. S. Marvel, *J. Polym. Sci.*, **50**, 511 (1961); (b) C. S. Marvel and H. A. Vogel, U. S. Patent 3,174,947,023 (March 1965).

(3) W. Wrasidlo and H. H. Levine, *J. Polym. Sci., Part A*, **2**, 4795 (1967).

(4) D. N. Gray, G. P. Shulman, and R. T. Conley, *J. Macromol. Sci., Part A*, **1**, 395 (1967).

(5) V. V. Korshak, T. M. Frunze, V. V. Kurashev, and A. A. Izyneev, *Dokl. Akad. Nauk SSR*, **149**, 104 (1963); *Chem Abstr.*, **59**, 6527 (1963).

(6) J. B. Wright, *Chem. Rev.*, **48**, 394 (1951).

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(8) C. S. Marvel and N. Tarkoy, *ibid.*, **80**, 832 (1958).

(9) H. N. Kovacs, A. D. Delman, and B. B. Simms, *J. Polym. Sci., Part A-1*, **4**, 1081 (1966).

(10) R. C. Elderfield and J. R. McCarthy, *J. Amer. Chem. Soc.*, 73, 975 (1951).

(11) R. C. Elderfield and U. S. Meyer, *ibid.*, **76**, 1883 (1954).

(12) A. Ladenburg and L. Ruegheimer, *Ber.*, **11**, 1656 (1954).

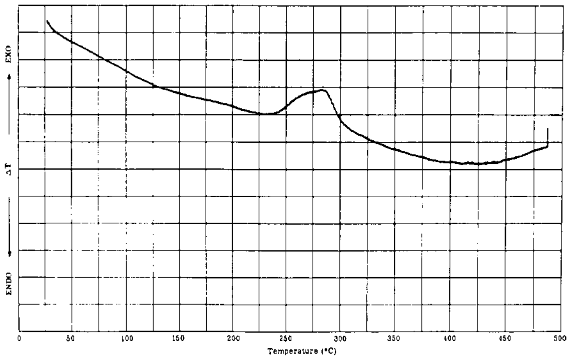


Figure 1. Differential thermal analysis of the conversion of poly(2,2′ - dimethyl - 2,2′ - (1,4 - phenylene) - 5,5′ - bibenzimidazoline) to 2,2′-(1,4-phenylene)-5,5′-bibenzimidazole (20°/min in helium).

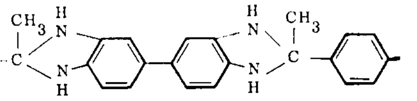
others.[2-5] The polymerization proceeds *via* formation of an intermediate Schiff base (III), followed by ring closure and aromatization, with the elimination of methane, to yield the polybenzimidazole (IV).

In order to confirm that benzimidazole formation involved elimination of methane rather than benzene, model compound studies were undertaken by use of *o*-phenylenediamine and acetophenone. These studies were necessary since in a polymerization reaction involving diacetylbenzene and 3,3′,4,4′-tetraaminobiphenyl, the elimination of the aryl group (*i.e.*, *p*-phenylene) rather than methyl in the intermediate benzimidazoline polymer would be both a chain-breaking and a chain-terminating step.

Experimental Section

Monomers. The 3,3′,4,4′-tetraaminobiphenyl comonomer was purified by multiple recrystallization from distilled water followed by drying *in vacuo*. The purified material was slightly off-white and microcrystalline. The melting point (Fisher-Johns) was 179° (lit.[2a] mp 179–180°). The 1,4-diacetylbenzene, mp 116° (Eastman), was recrystallized from methanol, and showed only one peak with vpc analysis (2-ft LAC-446 column, 210°).

Polymerization. The Schiff base polymers were prepared by melt polymerization. The 1,4-diacetylbenzene (16.2 g, 0.1 mol) and 3,3′,4,4′-tetraaminobiphenyl (21.4 g, 0.1 mol) were thoroughly mixed by grinding in a mortar, then placed in a polymerization tube similar to that described by Foster and Marvel.[13] The system was purged with nitrogen and quickly placed in a liquid metal bath kept at 250°. The mass melted immediately and started to evolve water. As the viscosity of the polymer increased, the material rose in the polymer tube due to the entrapment of water bubbles. Sublimation of diacetylbenzene was noted during the reaction. This could be minimized by good mixing and rapid melting of the comonomers. The reaction temperature was maintained at 250° for 15 min. The resulting product was cooled in an inert atmosphere (N_2), crushed, and removed from the polymer tube. The analytical results are given in Table I. It is seen that the analyses are generally in agreement with the proposed structure (V) which is a poly(2,2′-dimethyl-2,2′-(1,4-phenylene)-5,5′-bibenzimidazoline).



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[13] R. T. Foster and C. S. Marvel, *J. Polym. Sci., Part A*, 3, 417 (1965).

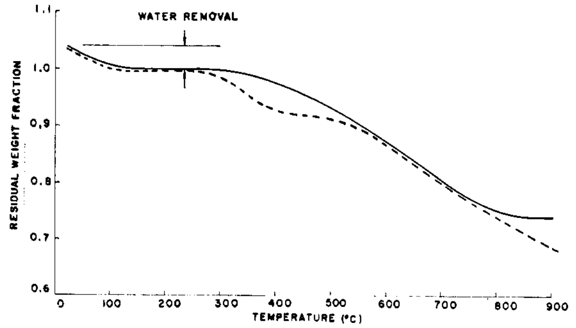

Figure 2. ———, thermogravimetric analysis of polybenzimidazole prepared from 3,3′,4,4′-tetraaminobiphenyl and 1,4-diacetylbenzene (3.3°/min in argon); – – – –, thermogravimetric analysis of polybenzimidazole prepared from 3,3′,4,4′-tetraaminobiphenyl and diphenyl terephthalate (3.3°/min in argon).

Table I
Analytical Results for Tetraaminobiphenyldiacetylbenzene Condensation Polymer

	Anal., %			
	C	H	N	Total
$C_{22}H_{20}N_4$ (calcd)	77.62	5.92	16.46	100.00
$C_{22}H_{20}N_4$ (found)	77.87	5.60	16.22	99.69
Duplicate runs	77.78	5.40	16.31	99.40
Found average	77.82	5.50	16.26	99.58

The polybenzimidazoline was converted to the polybenzimidazole by heating the material to 300°. The powdered polymer was placed in a polymer tube and evacuated to about 0.1 torr. The polymer tube was then placed in a liquid metal bath at 300°. The powdered polymer melted, then outgassed, and foamed in the tube, while turning from a reddish brown to golden yellow. The material was allowed to cool under vacuum. The material had an inherent viscosity of 0.60 (0.2 g/100 ml) in DMSO. *Anal.* Calcd for $(C_{20}H_{12}N_4)_n$: C, 77.92; H, 3.90; N, 18.18. Found: C, 76.95; H, 4.02; N, 18.05.

Preparation of Poly(2,2′-(1,4-phenylene)-5,5′-bibenzimidazole) *via* the Marvel Synthesis. This polymer was prepared by the Marvel technique[2a] for comparison with the polymer prepared above. Tetraaminobiphenyl (2.14 g, 0.01 mol) and diphenyl terephthalate (3.18 g, 0.01 mol) were melt condensed under nitrogen for 10 min at 250°, then evacuated and kept at 250° for 30 min. The foamed product was then crushed, powdered and evacuated and kept at 400° for 4.5 hr.

Differential Thermal Analysis. DTA analysis (Du Pont Model 900; 20°/min in helium) of the Schiff base obtained from the reaction of 1,4-diacetylbenzene and 3,3′,4,4′-tetraaminobiphenyl showed a single exotherm peaking at 275° (Figure 1).

Thermogravimetric Analysis. The TGA apparatus based on a Cahn electrobalance was used at a heating rate of 3.3°/min with argon or oxygen atmospheres. The TGA poly(2,2′-(1,4-phenylene)-5,5′-bibenzimidazole) prepared *via* the Schiff base route and the same polymer prepared by the Marvel synthesis are shown in Figure 2.

The polymer showed the usual weight loss below 100° due to residual water of hydration, yielding the typical PBI thermogram with a stabilized residue of 74%. When the polymer was tested in air, the weight loss started at about 350°, rapidly increased after 400° and no residue remained at 650°.

Infrared Analysis. The spectra of the polymer prepared from 3,3′,4,4′-tetraaminobiphenyl and 1,4-diacetylbenzene

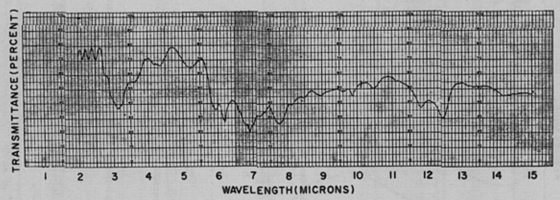

Figure 3. Infrared spectrum of free-standing polybenzimidazole film prepared from 3,3′,4,4′-tetraaminobiphenyl and 1,4-diacetylbenzene.

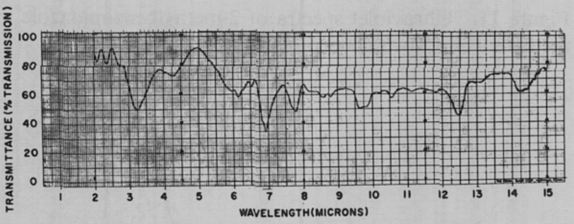

Figure 4. Infrared spectrum of free-standing polybenzimidazole film prepared from 3,3′,4,4′-tetraaminobiphenyl and diphenyl isophthalate.

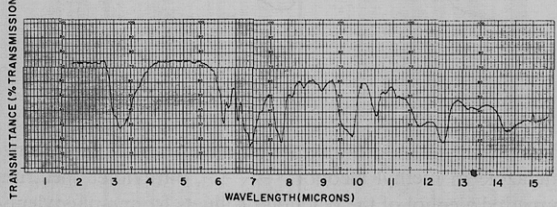

Figure 5. Infrared spectrum of polybenzimidazole film (on salt plate) prepared from 3,3′,4,4′-tetraaminobiphenyl and 1,4-diacetylbenzene.

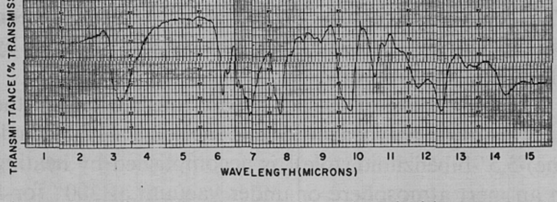

Figure 6. Infrared spectrum of polybenzimidazole film (on salt plate) prepared from 3,3′,4,4′-tetraaminobiphenyl and diphenyl terephthalate.

were obtained on a free film and from a supported film on a salt plate. DMSO was the solvent used in both film preparations.

Figure 3 shows the spectrum obtained from a free film approximately 0.3 mil thick. The spectrum has the same general features as the spectrum of the free film of poly-(2,2′-(1,3-phenylene)-5,5′-bibenzimidazole) (Figure 4). Unfortunately, the 1,4 isomer could not be prepared in sufficiently high molecular weight by the Marvel technique to case a free film.

Direct comparison of polybenzimidazoles prepared by the Schiff base route and the classical route[2a] was made by comparing the spectra of the two polymer films deposited on salt plates. These spectra (Figures 5 and 6) are nearly identical throughout the spectrum.

Ultraviolet Spectroscopy. Ultraviolet spectra were obtained in sulfuric acid for poly(2,2′-dimethyl-2,2′-(1,4-phenylene)-5,5′-bibenzimidazoline) and for poly(2,2′-(1,4-phenylene)-5,5′-bibenzimidazole) prepared *via* the Schiff base route and the Marvel route. The benzimidazoline intermediate was not completely soluble in sulfuric acid hence specific absorptivities could not be obtained.

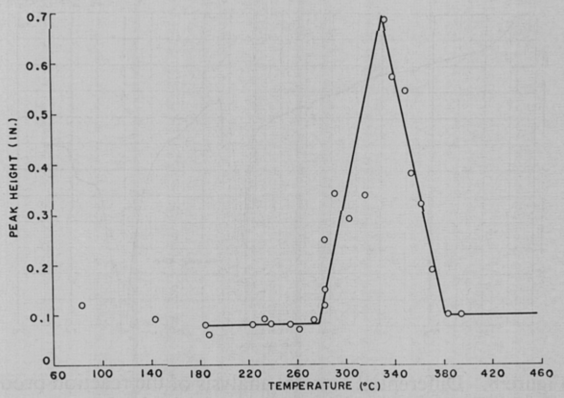

Figure 7. Mass spectrometric thermal analysis of the conversion of poly(2,2′-dimethyl-2,2′-(1,4-phenylene)-5,5′-bibenzimidazoline) to poly(2,2′-(1,4-phenylene)-5,5′-bibenzimidazole).

TABLE II

ULTRAVIOLET SPECTRAL DATA

	$\lambda_{\max}$, mμ	$E^{1\%}_{1\ \mathrm{cm}}$
Poly(2,2′-dimethyl-2,2′-(1,4-phenylene)-5,5′-bibenzimidazoline) (V)	252 (0.56)[a] 330 (9.48)	
Poly(2,2′-(*p*-phenylene)-5,5′-bibenzimidazole) *via* Schiff	256 376	727 1260
via Marvel synthesis	256 375	640 1200

[a] Peak height.

Viscosity Measurements. The inherent viscosities of the polymers were determined as follows. The polymer was dissolved in dimethyl sulfoxide at slightly elevated temperatures. In all cases, 0.2 g of polymer/100 ml of solvent was used. Solution viscosities were run at 30° with a Cannon–Fenske Series 100 viscometer.

Mass Spectrometric Thermal Analysis (MTA). The benzimidazoline prepolymer was subjected to mass spectrometric thermal analysis[14] to determine temperature, the threshold for, and extent of methane evolution during the aromatization. A sample of poly(2,2′-dimethyl-2,2′-(1,4-phenylene)-5,5′-bibenzimidazoline) was placed in the Knudsen cell inlet system of the Bendix time-of-flight mass spectrometer and heated at a rate of 9°/min, while the spectra were recorded at frequent intervals, to a maximum temperature of 450°. As shown in Figure 7, the methane evolution (mass 15 peak) reaches a maximum at 330° after an initial appearance of methane at 280°. No higher mass fragments which could be attributed to phenyl, phenylene, or substituted phenyl were observed.

Model Compound Study. Purification of Starting Materials. The *o*-phenylendiamine was twice recrystallized from benzene to give white plates, mp 103–103.5°. Acetophenone was purified by vacuum distillation and showed only one peak when analyzed by vpc with a LAC-446 column. 2-Methylbenzimidazole (Eastman) and 2-phenylbenzimidazole (Chemicals Procurement), which served as standards, were used as received without purification.

Reaction of *o*-Phenylenediamine with Acetophenone. Equimolar amounts of the reactants were mixed, placed in a small flask equipped with a reflux condenser and the flask

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(14) G. P. Shulman, *J. Polym. Sci., Part B*, 3, 911 (1965).

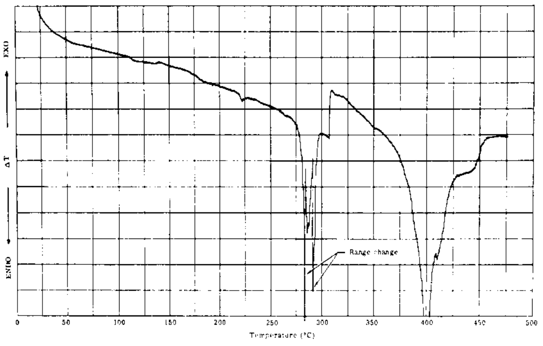


Figure 8. Differential thermal analysis of the reaction product from *o*-phenylenediamine and acetophenone (20°/min in helium).

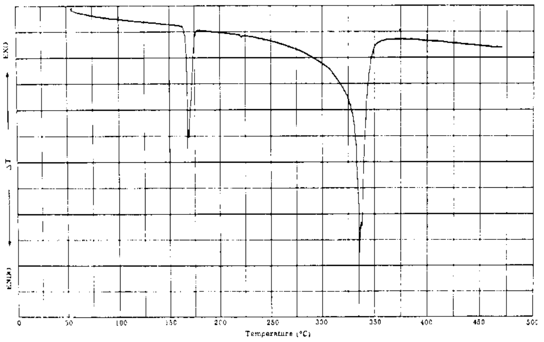


Figure 9. Differential thermal analysis of 2-methylbenzimidazole (20°/min in helium).

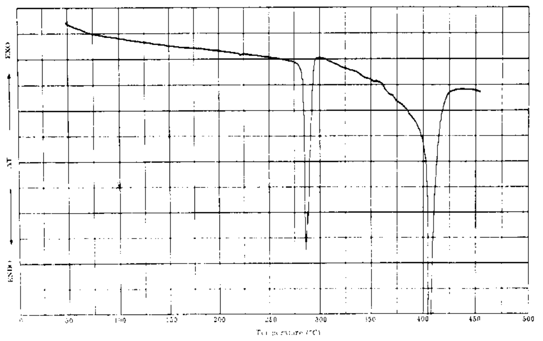


Figure 10. Differential thermal analysis of 2-phenylbenzimidazole (20°/min in helium).

was then heated to 180°. Water was immediately evolved as evidenced by the sputtering of the condensate dropping into the reaction flask. After 18 hr the residue was filtered from the water and dried *in vacuo* at room temperature. No purification was attempted since the composition of the solid residue was of interest. This residue was analyzed by DTA (Figure 8).

The DTA thermograms of 2-methylbenzimidazole and 2-phenylbenzimidazole are shown in Figures 9 and 10 and their ultraviolet spectra, in methanol, are shown in Figures 11 and 12 tabulated in Table III. The ultraviolet spectra of the reaction product from *o*-phenylenediamine and acetophenone is also shown in Figure 12.

Discussion

The reaction of 1,4-diacetylbenzene and 3,3′,4,4′-tetraaminobiphenyl proceeds *via* a polymeric Schiff base intermediate [poly(2,2′-dimethyl-2,2′-(1,4-phenylene)-5,5′-bibenzimidazoline)] to form an aromatic polybenzimidazole. The reaction to form the Schiff base intermediate is carried out as a melt polymerization (15 min at 250° under nitrogen) with the release of water. The chemical structure of the Schiff base has been established by elemental analysis (Table I) and by ultraviolet spectroscopy.

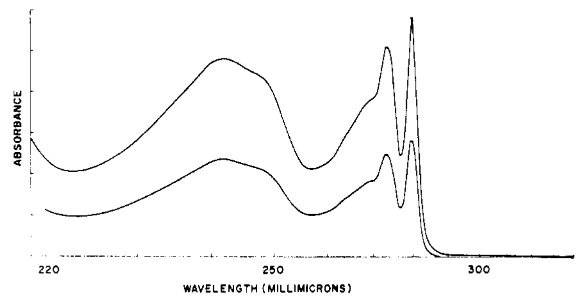


Figure 11. Ultraviolet spectra of 2-methylbenzimidazole in methyl alcohol (two concentrations).

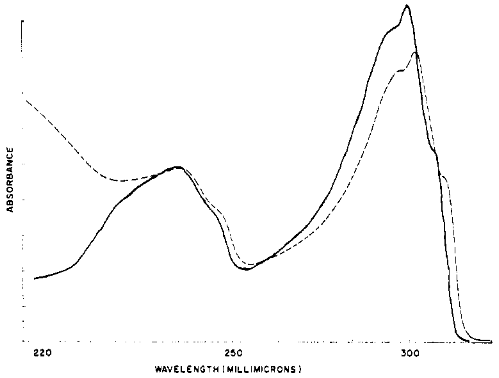


Figure 12. ———, ultraviolet spectrum of 2-phenylbenzimidazole in methyl alcohol; – – – –, ultraviolet spectrum in methyl alcohol of the reaction products from *o*-phenylenediamine and acetophenone.

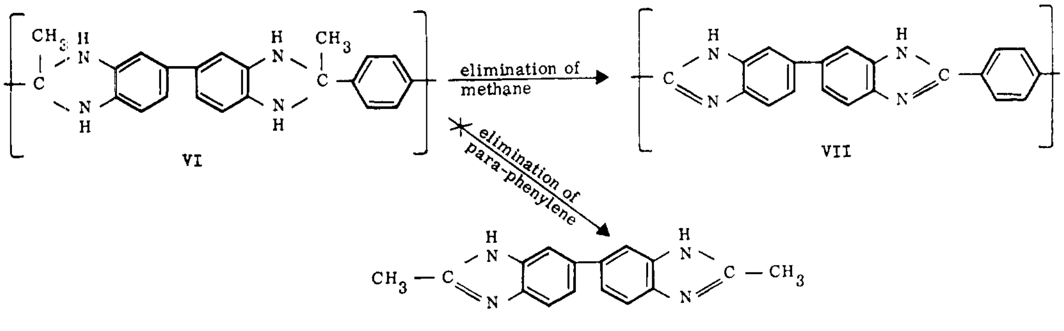
The conversion of the Schiff base intermediate to the fully aromatic polybenzimidazole [poly(2,2′-(1,4-phenylene)-5,5′-bibenzimidazole)] is accomplished by heating in an inert atmosphere or under vacuum at 300° for 1 hr and is accompanied by the release of methane. Mass spectrometric thermal analysis of the conversion step (Figure 7) has substantiated that methane is released in the neighborhood of 300° and, except for water, there are no other volatile products. Differential thermal analysis at a heating rate of 20°/min (Figure 1) shows that the conversion is exothermic and occurs over the range 240–300°. Further evidence of the temperature range of the conversion step was obtained by visibly monitoring the reaction on a Fisher-Johns melting point apparatus and observing softening and

Table III
Ultraviolet Data Model Compound

	λ_{max}, mμ	ϵ_{max}
2-Methylbenzimidazole	242.0	5,000
	273.0	5,250
	278.5	600
2-Phenylbenzimidazole	240.0	13,000
	297.0	Inflection
	300.5	24,500

gas evolution at 280–290°. The conversion of the Schiff base intermediate to the final polyaromatic polymer is irreversible. A differential thermal analysis retest of a sample previously subjected to DTA (to 450°) did not exhibit the exotherm peak at 280° characteristic of the transformation. The ultraviolet spectrum of the intermediate Schiff base shows a 252-mμ absorption band (Table II) of greater intensity that the 330-mμ band. This is expected since the shorter wavelength absorption is the charge-transfer state absorption for the biphenyl chromophore and is present in both the benzimidazole and benzimidazoline polymer. The longer wavelength absorption is due to the benzimidazole and is quite intense in the completely aromatized polymer. In the model compound, 2,2′-diphenyl-5,5′-bibenzimidazole, the biphenyl chromophore absorption is at 254 mμ while the phenylbenzimidazole chromophore absorbs at 327 mμ with less intensity, relative to the lower wavelength absorption, than the polymer.[15] The bathochromic shift noted in going from model compound to polymer (327 to 375 mμ) is due to the extended conjugation in the polymer.

The polybenzimidazole produced from the reaction of 1,4-diacetylbenzene and 3,3′,4,4′-tetraaminobiphenyl *via* the Schiff base route is fully aromatic and equivalent to the polymer produced from diphenyl terephthalate and 3,3′,4,4′-tetraaminobiphenyl by the Marvel procedure. Infrared spectra of the two polymers (Figures 3 and 4) reveal their structural similarity. The differences in the two spectra are noted (1) in the 11.5–13.0-μ region which is characteristic of positional substitution on the benzene nucleus and (2) in the region below 5 μ where the differences in film thickness superimposes the interference fringe pattern on the molecular spectrum at different positions. Further substantiating evidence was obtained by ultraviolet spectroscopy which shows that both polymers absorb at λ_{max} 256 and 376 mμ.

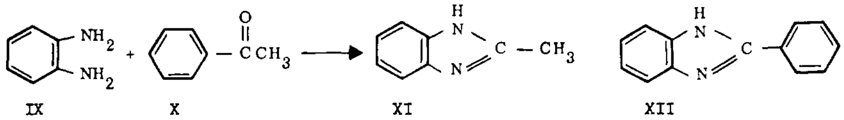


VI VII VIII

The thermal stability of the Schiff base derived polybenzimidazole is very similar to that of the classical (Marvel) polymer. Thermogravimetric analysis for the Schiff base route polymer (Figure 2) shows an early 4% weight loss which is complete at a temperature of 100° and is indicative of physically adsorbed water. Residue weight has stabilized by 900° at a residual weight fraction (neglecting the water loss) of 0.74. By comparison, poly(2,2′-(1,3-phenylene)-5,5′-bibenzimidazole) prepared *via* the Marvel procedure exhibited a 5% water loss (Figure 2) which was not complete until a temperature of 425° was reached; this behavior is therefore indicative of loss of chemically bonded water. This weight loss has been shown to be due to the evolution of water by mass spectrometric thermal analysis.[4] Residual weight fraction at 900° (neglecting water loss) was 0.76; however, the residue weight had not yet stabilized at that temperature.

To gain further insight into the chemistry of the 3,3′,4,4′-tetraaminobiphenyl-1,4-diacetylbenzene reaction, a model reaction (acetophenone and *o*-phenylenediamine) was studied. The latter reaction forms 2-phenyl-2-methylbenzimidazoline as an intermediate. This system thus serves as a model for the polymeric Schiff base. The elimination of the *p*-phenylene moiety instead of methane during the conversion of the polymeric intermediate (VI) would lead to 2,2′-dimethyl-5,5′-bibenzimidazole (VIII)—a nonpolymeric, low melting compound—rather than the aromatic polybenzimidazole (VII) which was obtained. The absence of aryl groups (*i.e.*, the *p*-phenylene moiety) in the effluent gas during the conversion step was shown by mass spectrometric analysis.

The reaction of *o*-phenylenediamine (IX) and acetophenone (X) was carried out at 180° for 18 hr. Theoretically, these compounds could react to form (1) 2-methylbenzimidazole (XI) with the liberation of benzene, (2) 2-phenylbenzimidazole (XII) with the liberation of methane, or (3) a combination of 1 and 2.


IX X XI XII

The solid reaction product from the above reaction was analyzed by differential thermal analysis and ultraviolet spectroscopy. Its thermogram (Figure 8) was distinctly different from that of an authentic 2-methylbenzimidazole sample (Figure 9), but was identical with that of an authentic 2-phenylbenzimidazole sample (Figure 10). The thermograms are similar in that the melting endotherms are followed by a broad vaporization endotherm. It can be seen that neither the melting endotherm at 170° nor the boiling endotherm, peaking at about 300° for 2-methylbenzimidazole, is present

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(15) Y. Iwakura, K. Uno, and Y. Imai, *J. Polym. Sci., Part A*, 2, 2605 (1964).

in the thermogram of the reaction product. However, the product's thermogram is identical with the 2-phenylbenzimidazole thermogram, showing melting at about 275° and boiling at about 410°.

Since benzimidazoles absorb strongly in the ultraviolet region, the electronic spectra of 2-methylbenzimidazole, 2-phenylbenzimidazole, and the reaction product were obtained in methanol. The spectra are shown in Figures 11 and 12. The spectrum of the residue is that of 2-phenylbenzimidazole. However, since the extinction coefficients for 2-methylbenzimidazole are lower than those for 2-phenylbenzimidazole the detection of 2-methylbenzimidazole in 2-phenylbenzimidazole cannot be put on a straightforward mole-to-mole basis. Table III gives the extinctions and absorption maxima for the two benzimidazoles in methanol.

In order to improve the sensitivity of the method, a differential ultraviolet analysis was developed. In this method, synthetic mixtures of 2-methylbenzimidazole in 2-phenylbenzimidazole were made up in methanol. A solution containing 2-phenylbenzimidazole alone at the same molar concentration was used in the reference cell so the absorptions due to 2-phenylbenzimidazole would be subtracted out in the recording of the spectra. It was found that about 0.8% by weight 2-methylbenzimidazole in 2-phenylbenzimidazole could be detected in this fashion. No 2-methylbenzimidazole was detected in the reaction mixture indicating that elimination is predominately, if not entirely, of the methyl group to yield methane and 2-phenylbenzimidazole.

By analogy with the reaction mechanism of this model compound system, it can be concluded that 1,4-diacetylbenzene and 3,3′,4,4′-tetraaminobiphenyl will react preferentially to form the fully aromatic polybenzimidazole with the elimination of methane. This accounts for the high molecular weight, film-forming polymer obtained by this reaction.

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Behavior of the >Al–C_2H_5 Group in the Polymerization by Triethylaluminum–Water Catalyst

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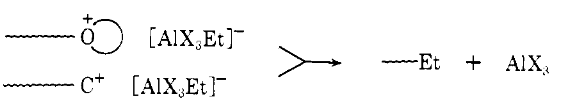
ABSTRACT: In the polymerization of cyclic ethers and vinyl ether by the $AlEt_3$–H_2O system, the change of the amount of the >AlEt group of the catalyst was examined. The amount of the >AlEt group was determined by the volume of ethane gas evolved in the hydrolytic decomposition of the polymerization system with 6 *N* H_2SO_4 at room temperature or with 1 *N* NaOH at reflux temperature. In the polymerization of tetrahydrofuran (THF) by the ternary catalyst system of $AlEt_3$–H_2O–epichlorohydrin (ECH) (2 :1 :0.2), the >AlEt group remained intact during the polymerization. These results agreed with a postulated mechanism of stepwise addition without chain termination. In the THF–ECH (1 :1) copolymerization and the ECH homopolymerization, however, noticeable amounts of the >AlEt group were consumed. These results are in accord with our previous assumption that the reaction of the >AlEt group with ECH gives rise to the formation of an aluminum alkoxide species which in turn induces the coordinate anionic polymerization of ECH. In the cationic polymerization of vinyl ether with the $AlEt_3$–H_2O (1 :1) system, the >AlEt group for the most part remained intact.

During the past few years, the catalytic activity of alkylaluminum compounds has attracted much attention in the fields of polymerizations of aldehyde, cyclic ethers and vinyl compounds. $AlEt_3$ itself is a Lewis acid and is able to induce cationic polymerization.[1,2] The acid strength of $AlEt_3$ is increased by treatment with a controlled amount of water. The $AlEt_3$–H_2O system exhibits a superior catalyst activity in some cases. In polymerizations of alkylene oxide initiated by $AlEt_3$ and the $AlEt_3$–H_2O system, the catalyst species is more complicated; *i.e.*, a part of the >AlEt group is converted into aluminum alkoxide group by the reaction with the alkylene oxide monomer. Introduction of an alkoxyl group to alkylaluminum species decreases the acid strength. Thus $AlEt_3$ and $AlEt_3$–H_2O are transformed into species of decreased acid strengths, which in turn induce the coordinate anionic polymerization of alkylene oxide.

The ethyl group attached to aluminum is nucleophilic. Therefore, the reaction of the propagating species of cationic polymerization with the >AlEt group is possible, which thus constitutes the termination reaction.



The present study was undertaken to examine the behavior of the >AlEt group of the $AlEt_3$–H_2O catalyst during the homopolymerizations of tetrahydrofuran

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[1] T. Saegusa, H. Imai, S. Hirai, and J. Furukawa, *Makromol. Chem.*, **53**, 203 (1962).

[2] T. Saegusa, H. Imai, and J. Furukawa, *ibid.*, **64**, 224 (1963).