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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Gray, D. N. , Shulman, Garson P. and Conley, R. T.(1967) 'The Mechanism of Polybenzimidazole Formation by Condensation of Aromatic Tetramines and Esters and the Structure of the Resulting Polycondensates', *Journal of Macromolecular Science, Part A*, 1: 3, 395 – 411

To link to this Article: DOI: 10.1080/10601326708053979

URL: <http://dx.doi.org/10.1080/10601326708053979>

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The Mechanism of Polybenzimidazole Formation by Condensation of Aromatic Tetramines and Esters and the Structure of the Resulting Polycondensates*

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Summary

The vacuum or inert-atmosphere condensation of diphenyl isophthalate and 2,2',3,3'-tetraaminobiphenyl to poly-2,2'-(*m*-phenylene)-5,5'-bibenzimidazole has been investigated. Evidence from polymer and model compound (diphenylbibenzimidazole) spectral studies, elemental analysis, and analysis of volatile effluent indicates that the prepolymer formed at 260 to 300°C contains both benzimidazole and hydroxybenzimidazoline but is essentially free from phenoxybenzimidazole structures. A mechanism involving loss of phenol initially, followed by evolution of water to give benzimidazole structures, is established from experimental evidence. Polymerization in vacuum to 400°C gives the polybenzimidazole.

The formation of benzimidazole polymers by condensation of aromatic tetramines and bifunctional aromatic acid derivatives

* Paper presented at the 150th Meeting of the American Chemical Society, Atlantic City, N.J., September 1965.

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such as esters (1) and amides (2) has recently received considerable attention. Polymers formed in this way exhibit high thermal stability. Materials produced by this type of condensation are not amenable to the normal characterization procedures usually used for linear polymers; definitive studies concerning the structure of such materials have, therefore, not been forthcoming. The present investigation was undertaken to determine the key structural features that affect the high-temperature molding of polybenzimidazoles. The approach chosen was an investigation of prepolymeric species isolated at various stages of the most common polymerization method [amine-phenyl ester (1)], to characterize their functionality, combined with a determination of the rates of formation of volatile polymerization products at the various stages. The specific system employed was diphenyl isophthalate-tetraaminobiphenyl, which leads to poly-2,2'-(*m*-phenylene)-5,5'-bibenzimidazole. These data were considered necessary for the correlation of physical behavior, particularly molding characteristics, with resin structure.

A combination of techniques was employed. They included mass spectrometric thermal analysis, infrared and ultraviolet spectral examination at the various polymerization stages, elemental analysis, thermogravimetric analysis, and differential thermal analysis, with both polymers and model compounds. This approach provides firm experimental grounds on which to base a mechanism of polybenzimidazole formation and, hopefully, should lead to greater success in developing fabrication techniques for these substances.

Proposals concerning the mechanism of polybenzimidazole formation have been advanced previously (1,2), but no substantiating data are reported. Most of the original studies assumed that the mechanism is similar to that proposed for model systems. An alternate mechanism has recently been suggested by Wrasidlo and Levine (4). Since their experimental procedure differs significantly from those normally used for synthesis of model compounds or for tetramine-diester condensation in vacuum or inert atmosphere, application to the usual procedures without confirmatory data did not appear feasible. Figures 1 and 2 show the two fundamentally different mechanisms.

From the chemistry of model systems (5) it appears that these reactions (Fig. 1) are very similar to ester saponification and the

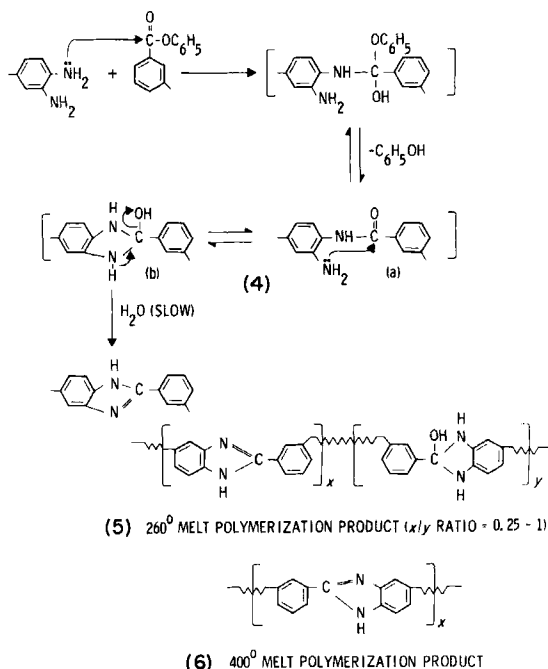


FIG. 1. Mechanism of melt polycondensation forming polybenzimidazoles.

basic hydrolysis of amides. They are accelerated by electron-attracting groups, retarded by electron-withdrawing groups, and necessarily involve acyl-oxygen cleavage, and their kinetics suggest bimolecular rate-determining steps. Thus, the mechanism consistent with existing literature proceeds through an adduct, in which elimination of the phenoxy group should be preferred in the initial reaction sequence. It would be predicted that the most effective leaving group must be only weakly basic (i.e., the conjugate base of a relatively strong acid). Therefore, the mechanism shown in Fig. 1 should be the most realistic for polybenzimidazole formation. As previously noted, such a mechanism has been implicit in the literature (1), but no confirmatory quantitative evidence has been reported.

Figure 2 summarizes the details of the alternative mechanistic proposal (4). The adduct (1) similar to that formed during the aminolysis of esters, dehydrates (in a presumably reversible step) to form a Schiff base type of structure (2). Intermediate (2), together

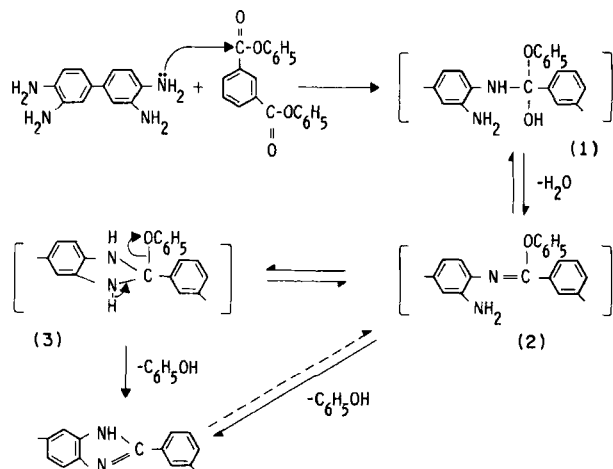


FIG. 2. Proposed mechanism of the formation of polybenzimidazoles (4). Dashed arrow indicates additional equilibrium step.

with its potential stereochemical modifications, was proposed as the key intermediate in benzimidazole ring formation. Cyclization of (2) to the benzimidazoline structure (3), followed by irreversible loss of phenol, formed the benzimidazole unit. The postulated mechanism of melt polymerization was supported by kinetic data for both water and phenol formation. The critical experiments used for determining the rates of formation of these products were carried out at 200 and 265°C in sealed tubes.

It should be pointed out that with the use of Fig. 2 the mechanistic interpretation leading to a proposal concerning the polymer structure at the intermediate stages of polycondensation (i.e., prepolymers) differs significantly from these structures postulated via the route shown in Fig. 1.

EXPERIMENTAL

Synthesis of Poly-2,2'-(*m*-phenylene)-5,5'-bibenzimidazole

The polymer was prepared by the method of Vogel and Marvel (1). Equimolar amounts of 3,3'-diaminobenzidine and diphenyl isophthalate were heated in vacuo to 260°C. Heating was continued

for 30 min. The material was removed and pulverized. A portion of this material was then heated at 400°C in vacuo for 9 hr. Elemental analyses were obtained on both the 260 and 400°C products. The results and theoretical calculations of elementary composition for the $C_{20}H_{12}N_4$ repeat unit, mono- and dihydrate, are shown in Table 1.

TABLE 1
Summary of Elemental Composition Studies of Polybenzimidazole

| | C | H | N | O ^a |
|---------------------------------------|--------------------|-------------------|--------------------|----------------|
| $C_{20}H_{12}N_4$ (calc.) | 77.91 | 3.92 | 18.17 | — |
| $C_{20}H_{12}N_4 \cdot H_2O$ (calc.) | 73.61 | 4.32 | 17.17 | 4.90 |
| $C_{20}H_{12}N_4 \cdot 2H_2O$ (calc.) | 69.76 | 4.69 | 16.27 | 9.29 |
| 260°C polymer (found) | 70.57 | 4.42 | 16.49 | 5.06 |
| 400°C polymer (found) | 78.00 ^b | 4.10 ^b | 18.16 ^b | — |

^a By difference.

^b Ref. (1) reports C 78.06, H 4.39, N 18.05.

Vapor-Phase Chromatography

A mixture of 3.18 g (0.01 mole) of diphenyl isophthalate and 3.14 g (0.01 mole) of 3,3'-diaminobenzidine was heated in a 50-ml round-bottom flask placed in a 260°C Wood's metal bath. The flask was equipped with a wide-bore still head wrapped with heating tape and attached to a spiral condenser positioned downward, leading to receiver traps cooled by a mixture of dry ice and acetone. The entire apparatus was maintained at 15-mm pressure by constant pumping. The distillate from the melt condensation was sampled at various time intervals via a side-arm septum inlet on the trap. The samples withdrawn (2 μ l) were analyzed by gas-liquid chromatography* by means of a Carbowax 1500 on Teflon column. The samples were analyzed for phenol and water content and compared with known mixtures of the two components used for calibration standards. After 30 min the contents of the traps were combined. The weight of material in the second trap was only 0.5% of that in the first trap.

* The instrument used was an F & M Model 720 dual-column thermal-conductivity unit. The analysis conditions were 60 ml of helium per minute at a programmed temperature increase from 125 to 175°C at 5°C/min with an isothermal hold at the upper temperature.

The combined sample was also analyzed for both phenol and water. The composition was found to be 1.71 g (95.6%) of phenol and 0.20 g (52.6%) of water. The analysis of volatiles from such a polymerization, typical of materials formed by this preparation, is recorded in Table 2.

TABLE 2
Phenol-Water Evolution (% Yield) as a Function of Heating Time at 260°C from Melt Condensation

| Time, min | Phenol, % | Water, % |
|-----------|---------------------|---------------------|
| 5 | 37 | 7 |
| 10 | 62 | 17 |
| 20 | 85 | 35 |
| 30 | 96 ± 4 ^a | 53 ± 8 ^a |

^a Yields of both phenol and water fluctuated from a high to a low value within the ranges indicated from run to run.

Thermogravimetric Analysis

The TGA apparatus based on a Cahn electrobalance (6) was used at a heating rate of 3.3°C/min with an argon atmosphere. Typical

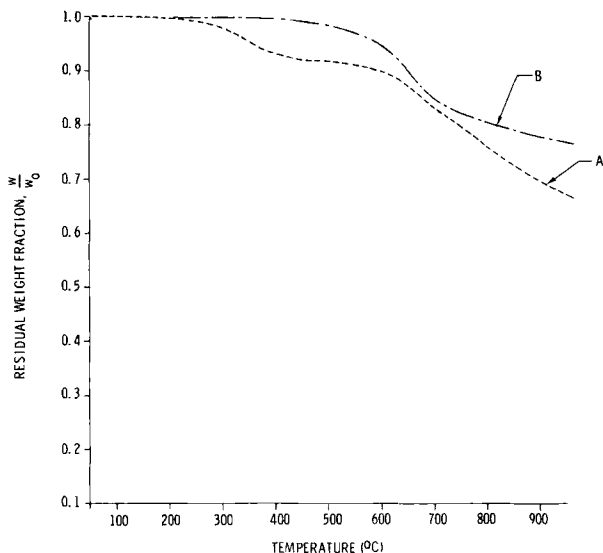


FIG. 3. TGA of poly-2,2'-(*m*-phenylene)-5,5'-bibenzimidazole.

thermograms from two resins are shown in Fig. 3. A sample cured as a powder to 400°C under 1 atm of nitrogen lost 2% of its weight on being heated from 150 to 500°C. A range of weight-loss values from 5 to 8% over the same temperature interval was obtained from polymers cured for 3 hr at 300°C under nitrogen, then for 3 hr at 300°C under vacuum, and then postcured under 2000-psi pressure in a 0.54-in.-diameter cylindrical mold to 400°C for 2 hr.

Mass-Spectrometric Thermal Analysis of Tetraaminobiphenyl-Diphenyl Isophthalate Mixture

An equimolar mixture of diphenyl isophthalate and 3,3',4,4'-tetraaminobiphenyl was placed in the Knudsen Cell inlet of a Bendix Time-of-Flight Mass Spectrometer. The specimen was heated at a rate of 10°C/min to 500°C, while spectra were obtained at 1- to 2-min intervals. The only volatile products observed were water and phenol. Relative yields of each were determined from areas under curves of rate of formation versus time (or temperature) in accordance with the procedures previously described (7); see Fig. 4.

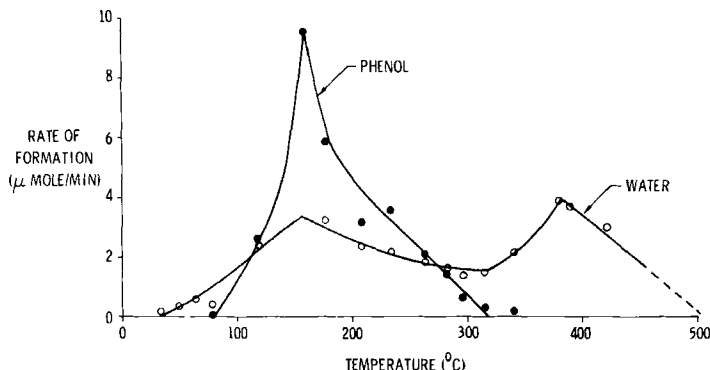


FIG. 4. MTA of diphenyl isophthalate-tetraaminobiphenyl mixture.

Infrared Spectroscopy of Polybenzimidazole

Infrared spectra of a $285 \pm 15^\circ\text{C}$ prepolymer (1% in a potassium bromide pellet) and the 400°C polymer (0.3-mil film cast from dimethyl sulfoxide) were determined with a Perkin-Elmer Model 21 Spectrophotometer (Fig. 5).

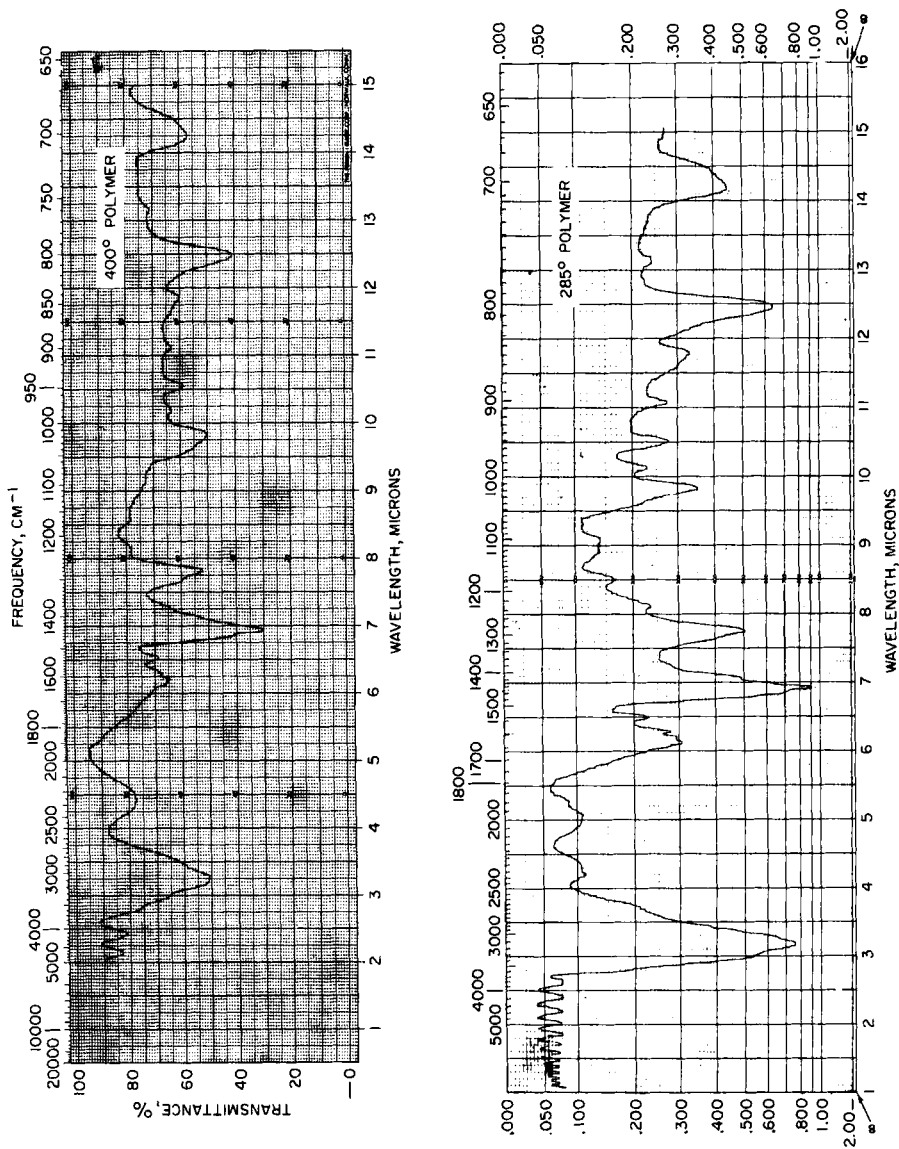


FIG. 5. Infrared spectra of polybenzimidazole and prepolymer.

Synthesis of 2,2'-Diphenyl-5,5'-bibenzimidazole

The procedure of Vogel and Marvel (1) was used with a minor modification. A mixture of 5.35 g of tetraaminobiphenyl and 100 g of phenyl benzoate was heated under nitrogen for 1 hr at 285°C. The crude material was recrystallized from warm (ca. 65°C) glacial acetic acid, to which ether was added, to precipitate the product. After standing overnight in a refrigerator it was filtered and dried under vacuum at room temperature for 4 days. The material did not melt at 360°C. A portion was heated in vacuo at 350°C, giving 2,2'-diphenyl-5,5'-bibenzimidazole, melting point 358°C [lit. 350 to 352°C (1), 332 to 333°C (8)]. Elemental-analysis data are shown in Table 3.

TABLE 3

Summary of Elemental Composition Studies of 2,2'-diphenyl-5,5'-bibenzimidazole

| | C | H | N | O ^a |
|---|-------|------|-------|----------------|
| C ₂₆ H ₁₈ N ₄ (calc.) | 80.81 | 4.69 | 14.50 | — |
| C ₂₆ H ₁₈ N ₄ ·H ₂ O (calc.) | 77.21 | 4.98 | 13.85 | 3.95 |
| C ₂₆ H ₁₈ N ₄ ·2H ₂ O (calc.) | 73.92 | 5.25 | 13.25 | 7.57 |
| 285°C product (found) | 77.90 | 4.81 | 13.39 | 3.90 |
| 350°C product (found) ^b | 80.59 | 4.47 | 14.32 | — |

^a By difference.

^b Reported: C 79.77, H 4.75, N 13.90, after 8 hr in vacuo at 118°C (1).

Differential Thermal Analysis of Model Compounds

A differential thermal analysis was performed on the 285°C product, with a Du Pont Model 900 DTA apparatus at a heating rate of 10°C/min. The curve is shown in Fig. 6. On heating to about 297°C an exotherm is observed, followed by a sharp endothermic dehydration at 396°C. After this dehydration a melting point of 334°C/min is observed [reported: 332 to 333°C (8)]. On heating at a rate of 20°C/min the melting point after an endothermic dehydration at 430°C is 350°C [reported: 350 to 352°C (1)]. The exotherm at 297°C is not noticeable. A sample dehydrated by solution in sulfuric acid showed a melting point of 337°C (10°C/min heating rate), whereas a sample heated at 300°C for 15 min showed only the endothermic dehydration at 400°C on the first heating cycle. X-ray powder diffraction patterns of the materials at 285, 300, and 400°C and

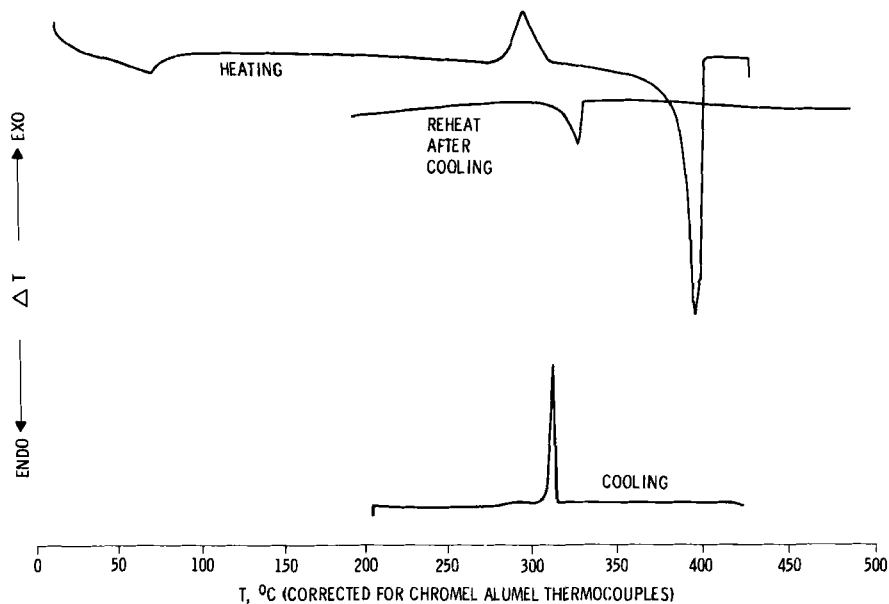


FIG. 6. DTA of 2-hydroxy-2,3-dihydro-2,2-diphenyl-5,5'-bibenzimidazole.

the materials treated with sulfuric acid were obtained using copper K_{α} radiation with a nickel filter. Each pattern was unique. The material treated with sulfuric acid appeared to be amorphous.

Pyrolysis-Gas Chromatography of Model Compounds

Experiments were conducted in the manner described by Jackson and Conley (9). Samples of the 285°C product were heated at 400, 500, 600C, and higher temperatures. Carboxax 1500 on Chromosorb and molecular-sieve columns were used at each temperature. At 400°C no peaks were noted except for oxygen and nitrogen from a small air leak. At 500°C water was the only product observed; at 600°C water amounted to 31% of the total products (integrated area). The chromatogram was otherwise similar to those characteristic of polybenzimidazole decomposition.

Infrared Spectroscopy of Model Compounds

The spectra for the 285°C materials and the materials treated with sulfuric acid (at a 2.5 to 5% level in potassium bromide pellets) are

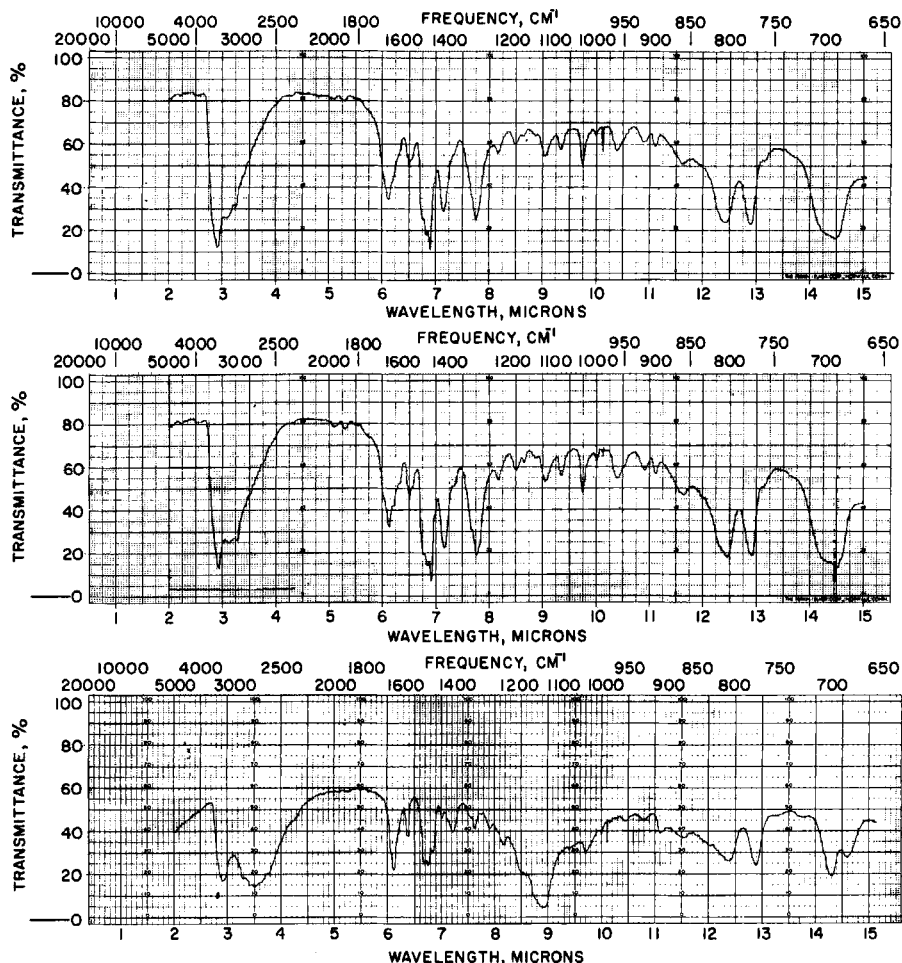


FIG. 7. Infrared spectra of 2-hydroxy-2,3-dihydro-2,2-diphenyl-5,5'-bibenzimidazole. (a) 285° sample. (b) 300° sample. (c) H₂SO₄-treated sample.

shown in Fig. 7. No significant difference between the spectra of the 285°C and the 300°C materials was noted.

Ultraviolet Spectroscopy of Model Compounds

The ultraviolet spectra of the 285°C and 400°C materials and those treated with sulfuric acid were recorded with concentrated sulfuric acid as solvent. Two broad peaks were noted at 254 and 326 μm with $E_{1\%}^{1\text{cm}}$ extinctions of 1150 and 1290, respectively. These

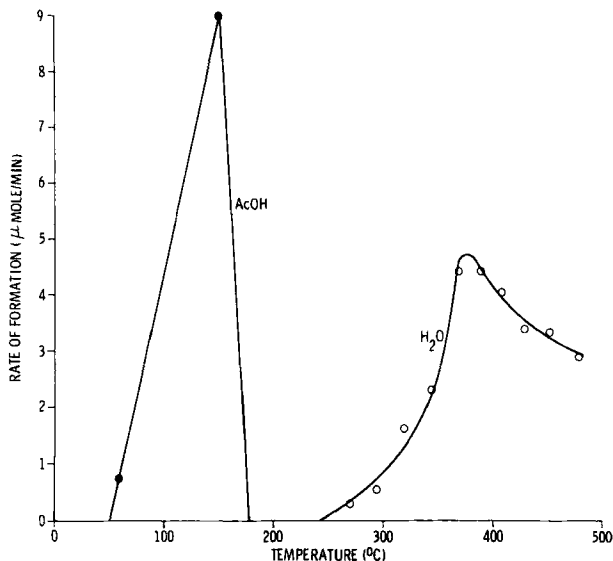


FIG. 8. MTA of 2-hydroxy-2,3-dihydro-2,2-diphenyl-5,5'-bibenzimidazole.

are essentially the same as reported by Vogel and Marvel (1) (254 $m\mu$, $E_{1\text{cm}}^{1\%} = 1100$ and 327 $m\mu$, $E_{1\text{cm}}^{1\%} = 1330$). Since sulfuric acid completely dehydrates the monohydroxy material, the spectrum of the 285°C sample is actually that of the dehydrated material. Ultraviolet spectra taken in glacial acetic acid gave identical absorption maxima.

Mass Spectrometric Thermal Analysis of 2,2'-Diphenyl-2-hydroxy-2,3-dihydro-5,5'-bibenzimidazole

A sample of 285°C material was placed in the Knudsen Cell inlet system of the Time-of-Flight Mass Spectrometer and heated at a rate of 25°C/min, while spectra were recorded at intervals. As shown in Fig. 8, acetic acid (recrystallization solvent) was liberated at 50 to 200°C and then water with a maximal rate of formation at 375°C.

DISCUSSION

Structural Changes during Polymerization

The experimental evidence clearly shows that the 260°C prepolymer differs from the 400°C polymer, not only in degree of

polymerization or extent of crosslinking, but also in molecular structure. The elemental composition of the prepolymer does not correspond to that of the poly(phenylene) bibenzimidazole repeat unit of $C_{20}H_{12}N_4$ but, rather, to a partial hydrate structure [intermediate (4a) or (4b) or both, Fig. 1], as shown in Table 1. The fully cured (400°C) polymer has the correct analysis. This suggests that the intermediate polymer contains a large number of benzimidazoline or amino(poly)amide structures that have not been dehydrated to benzimidazoles. Similar experiments were conducted with the model compound of this polycondensate system (2,2'-diphenyl-5,5'-bibenzimidazole), to determine whether reaction of tetraaminobiphenyl with phenyl benzoate under similar conditions would also give a partially hydrated product. Elemental analysis of a 285°C reaction product (Table 3) indicates that it contains one hydrated ring and one in which dehydration is complete and is presumably 2-hydroxy-2,3-dihydro-2,2'-diphenyl-5,5'-bibenzimidazole. Prolonged heating at 350°C in vacuo converts the hydrated material to 2,2'-diphenyl-5,5'-bibenzimidazole.

Infrared spectral studies (Fig. 5) indicate that the hydroxyimidazoline (4b) is probably the predominant species in the prepolymer. The C=N stretching vibration and N—H bending vibration (6.0 to 6.5 μ) of the benzimidazole ring do not significantly change during the staging of the resin (i.e., heating) from 250 to 400°C. No amide structure is discernible from the spectrum, although it would be expected that the presence of 50% of amino(poly)amide linkages would readily be apparent. In addition, N—H or O—H vibrations are hydrogen-bonded in a complex mass and, therefore, not readily separated as discrete entities. The monosubstituted phenol ring absorption (12 to 16 μ), however, is reasonably free for study. No absorption bands due to the aromatic phenol ring are detectable in the 260-to-300°C product.

The model compound spectral studies, while not conclusive, also suggest that no major structural changes (such as ring closure) occur during staging. On treatment with sulfuric acid absorption bands at 3220, 1538, 1460, 1400, 1070, 960, and 690 cm^{-1} disappeared, and new bands at 1570, 1385, 1125, 700, and 685 cm^{-1} appeared in the spectrum. Generally, changes in these bands may be ascribed to changes in ring structure, except that the 3220- cm^{-1} absorption represents an N—H or O—H frequency, and the 1125- cm^{-1} band is a sulfate absorption. A C=C absorption at about 1590 cm^{-1} is characteristic of the fused benzene ring in benzimidazoles (10). Thus,

appearance of a band at 1570 cm^{-1} may represent dehydration to a conjugated structure.

Perhaps the most convincing evidence that the water is incorporated in the molecule by covalent bonding was obtained for the model system from the differential thermal analysis. Upon heating to about 400°C a sharp endotherm was observed. The melting endotherm or cooling exotherm at the reported melting point (1) was not obtained until after this transformation had occurred. Mass spectrometric thermal analysis indicated that only water is liberated under these conditions. The DTA and MTA behavior is not what would be expected for a hydrogen-bonded hydrate. The temperature required for dehydration is more nearly that required for conversion of alcohol to olefin.

Mechanism of Reaction

The nature of the volatile species involved in the two stages of the curing process is the mechanism-dependent parameter, which can be unequivocally determined. The Wrasidlo and Levine mechanism (4), were it applicable to vacuum or low-pressure inert-atmosphere conditions, would predict formation of water in the low-temperature stage followed by phenol evolution during high-temperature staging. The more commonly accepted mechanism (1,3) calls for evolution of phenol in forming the first stable intermediate (IV), with subsequent water evolution. Temperature-programmed and isothermal heating of the diphenyl isophthalate-tetraaminobiphenyl mixture in high vacuum and at 15 mm pressure, respectively, gave equivalent results.

Mass spectrometric thermal analysis (MTA) indicated that water and phenol are liberated simultaneously; only half the water, however, is eliminated in the early stage of polycondensation ($< 300^\circ\text{C}$), together with almost all the phenol. Figure 4 shows the relative rates of formation of phenol and water as a function of temperature. Because a linear temperature-time program was used, the areas under the curves are proportional to the amount of each product. The rate of phenol production rises sharply well below 200°C , and its formation is nearly complete at 300°C . Water formation reaches a second maximal rate at about 400°C . The gas chromatographic studies gave the same results at 260°C (Table 2); that is, liberation of $96 \pm 4\%$ of the theoretical amount of phenol, but only

$53 \pm 8\%$ of the water in 30 min. In these polymerization procedures water, not phenol, was the predominant product by far at or above 300°C (approximately 99%). MTA of the intermediate (285°C) model compound also shows evolution of water, not phenol, at about 375°C . This conclusion is further supported by thermogravimetric analysis, in which the loss of weight is consistent with a loss of water rather than phenol (10% calculated, based on one water molecule for each potential benzimidazole ring). The actual weight losses (A, Fig. 3) amount to between 5 and 8%, depending on the sample. Thus, approximately 50 to 80% of the rings in the polymer are not dehydrated after melt polymerization at 260°C . A polymer cured to 400°C (B, Fig. 3) has a weight loss of only 2%. This is in good agreement with the MTA and gas chromatographic data.

This kinetic evidence combined with structural studies indicates that the polybenzimidazole ring system has as precursor an intermediate (**4**) capable of undergoing a loss of water. Since (**4a**) and (**4b**) are tautomeric structures of the ring-chain type, (**4b**) should be favored sterically (i.e., the ring form). It must be concluded that phenol elimination cannot be the final stage of polycondensation. The rate at which cyclization [(**4a**) to (**4b**)] occurs depends markedly upon the number of atoms in the ring, not only because the ring forms of five members are particularly stable, but also because reactions forming such rings have high entropies of activation.

From these data it must be concluded that the mechanism reported by Wrasidlo and Levine (*4*) does not apply to the normal procedures utilized for the melt polycondensation. It must further be concluded that the mechanism indicated in Fig. 1 most adequately describes these polycondensation reactions giving polybenzimidazoles. The data indicate that the polymeric material at the prepolymer stage (260°C) has the structure (**5**) with both benzimidazole and hydroxybenzimidazole structures; heating in vacuo to 400°C results in the formation of the polybenzimidazole structure (**6**). It is unusually difficult to complete the dehydration to bibenzimidazoles (as compared to phenylbenzimidazoles). Probably this is a steric effect, although additional work will be required to substantiate this supposition. A further test of the mechanism established in this investigation is its applicability to the mechanism of polybenzimidazole degradation presented in another paper, in which reversal of the final dehydration steps to an amino(poly) amide is required (*11*).

Acknowledgments

The authors are indebted to Mr. Eric Strauss for his helpful discussions and to Messrs. H. W. Lochte, R. Bunting, S. Pevera, and L. Rouch for their assistance in experimental phases of this work.

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Zusammenfassung

Die unter Vacuum oder inerte Atmosphäre erfolgende Kondensation von Diphenylisophthalat und 2,2',3,3'-Tetraaminobiphenyl zu Poly-2,2'-(*m*-phenylen)-5,5'-bibenzimidazol wurde untersucht. Aus spektroskopischen Studien des Polymeren und von Modellschubstanzen (Diphenylbibenzimidazol), der Elementaranalyse und der Analyse der flüchtigen Reaktionsprodukte ergab sich, dass das bei 260 bis 300°C sich bildende Vorpolymere sowohl Benzimidazol als auch Hydroxybenzimidazol enthält, dagegen aber keine Phenoxybenzimidazolstrukturen. Experimentelle Hinweise deuten auf einen Mechanismus hin, der einen anfänglichen Verbrauch an Phenol berücksichtigt und nachfolgende Bildung von Wasser unter Aufbau von Benzimidazolstrukturen. Die im Vacuum durchgeführte Polymerisation bei 400°C ergibt Polybenzimidazole.

Résumé

On a étudié la condensation de l'isophthalate de phényle et du tétra-2,2',3,3'-aminobiphenyl en poly-2,2'-(*m*-phénylène)-5,5'-bibenzimidazole dans le vide ou en atmosphère inerte. L'évidence obtenue à partir des études spectrales du polymère et du composé modèle (le diphenylbibenzimidazole), de l'analyse élémentaire et de l'analyse de l'effluent volatil indique que le prépolymère formé entre 260°C à 300°C contient à la

fois du benzimidazole et de l'hydroxybenzimidazoline, mais est essentiellement dépourvu de structure phenoxybenzimidazoliques. On a établi un mécanisme admettant une perte initiale de phenol, suivie par une libération d'eau pour donner des structures benzimidazoliques. Ce mécanisme est basé sur les données expérimentales. La polymérisation dans le vide jusqu'à 400°C donne le polybenzimidazole.

Received by editor May 17, 1966

Submitted for publication August 24, 1966