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ADHESIVE AND ANTICORROSIVE POLYMERIC COATINGS OBTAINED FROM POLYBENZAZOLES (PBI and PBO)

İlkay ÖZAYTEKİN*, İbrahim KARATAŞ**

*Engineering and Architecture Faculty, Department of Chemical Engineering,
Selcuk University, 42031, Konya, Turkey
e-mail: ozaytekin@selcuk.edu.tr
**Art and Science Faculty, Department of Chemistry, Selcuk University, 42031, Konya, Turkey
e-mail: ikaratas@selcuk.edu.tr
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Abstract: In this study, polybenzimidazole and polybenzoxazole having high molecular weights were prepared with 3,3'-diaminobenzidine, 1,2,4,5-tetraaminobenzene or 3,3'-dihydroxybenzidine and various dihydroxamoyl chloride. The characterization of polymers was performed with the assistance of the analyses of inherent viscosity, FT-IR and the elemental analysis. Moreover, the adhesion properties and the resistance properties against corrosion were examined for the synthesized polymers. The effects upon adhesion and anticorrosion properties of polymers due to the presence of terminal functional groups (CCl=NOH, NH_2) or the functional groups of main chain (-C=N-, -C=NH-, -C-O-, -S-S-, -O-) bonded to the structure of the polybenzazoles were determined.

Key words: Polybenzoxazole, Polybenzimidazole, Coating.

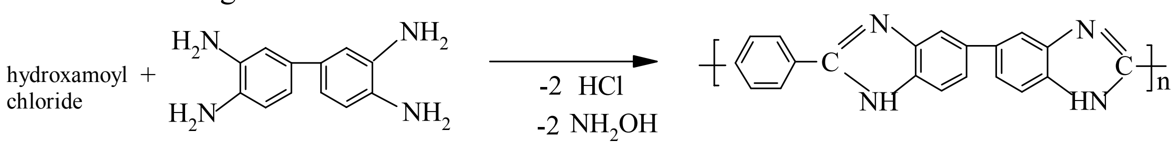
POLİBENZAZOLLERDEN ELDE EDİLEN ADHESİF VE ANTİKORROZİF KAPLAMALAR (PBI ve PBO)

Özet: Bu çalışmada yüksek molekül ağırlığına sahip polibenzimidazol ve polibenzoksazoller 3,3'-diaminobenzidin, 1,2,4,5-tetraaminobenzen veya 3,3'-dihidroksibenzidin ile çeşitli dihidroksamoil klorur bilesiklerinden sentezlendi. Polimerlerin karakterizasyonu, logaritmik viskozite sayısı, elemental analiz ve FT-IR analizleri ile belirlendi. Bununla birlikte sentezlenen polimerlerin adhezyon özellikleri ve korozyona karşı dayanıklılık özellikleri incelendi. Polimerlerin adhezyon ve antikorozyon özelliklerine, polibenzazollerin yapısında bulunan asıl zincirdeki fonksiyonel grupların (-C=N-, -C=NH-, -C-O-, -S-S-, -O-) veya polimerin uc fonksiyonel gruplarının (CCl=NOH, NH_2) etkileri belirlendi.

Anahtar kelimeler: Polibenzoksazol, Polibenzimidazol, Kaplama

INTRODUCTION

Polybenzimidazole (PBI) is amine-based resin and was first polymerized by scientists in 1950s. In 1961, the aromatic PBIs with extreme thermal and oxidative stabilities were synthesized by H. Vogel and C. S. Marvel. A most versatile and practical synthesis of benzazoles (PBI and PBO) has been provided by the interaction of o-phenylenediamin, 3,3'-dihydroxy-4,4'-diaminobiphenyl with carboxylic acid and various diphenyl esters. Besides, many studies for the synthesis of PBI and PBO were performed (KORSHAK & TEPLYAKOV 1971, KORSHAK et al. 1974, KORSHAK et al. 1989, VOGEL & MARVEL 1961, VOGEL & MARVEL 1963, WRASIDLO & LEVINE 1964, GAJIWALA & ZAND 2000, WOLFE & ARNOLD 1981, IMAI et al. 1965, MOYER et al. 1965, KUBOTA&NAKANISHI 1964, UEDA et al. 1986, KIM & LEE 2001). In this study, different from the previous studies, the polybenzazoles were synthesized by reacting various dihydroxamoylchlorides with 3,3'-diaminobenzidine, 1,2,4,5-tetraaminobenzene and 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB). The reaction of the synthesized (PBI)s can be seen in Figure 1.



Poly[2,2'-(p-phenylene)-5,5'-bis(benzimidazole)]

Figure 1. The reaction of synthesized polybenzimidazoles

The coatings of polybenzimidazoles and polybenzoxazoles have better chemical resistance against many harsh chemical environments than many other high performance polymers (IURA et al. 1996, IZYEEV et al.). The PBI coating films were hydrothermally degraded and delaminated from the underlying steel substrates after 14 days at high temperatures (SUGAMA 2004).
In this study, the adhesion and anticorrosive features of synthesized polymers on steel articles were determined at room temperature for 10 days. The functional groups (C=N and C=C double bound, -S-S-, -O- and NH_2) in the aromatic ring of the synthesized polymers are suitable to obtain polymeric coatings (Ahmetli et al. 2006, FRIEDRICH et al. 2005). As a result, the synthesized polybenzoxazoles and polybenzimidazoles have highly adhesive property, and they are resistant against corrosion due to chemical attack (CARRON et al. 1993, IURA et al. 1996, IZYEEV et al. 1967, DAVID 1996).

EXPERIMENTAL

Materials and Reagents

4-hydroxybenzaldehyde, 3,3'-diaminobenzidine, 3,3'-dihydroxybenzidine and 1,2,4,5-tetraaminobenzentetrahydro chloride were obtained from Merck and TCI Japan.

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Instrumentation

The solution NMR spectra was obtained by the "Bruker Avance DPX-400" spectrometer, and the elemental analyses for carbon, hydrogen, nitrogen and sulphide were carried out in the laboratories of the Scientific and Technical Research Council of Turkey (TUBITAK). FT-IR Spectra was obtained with the "Perkin Elmer 1605" spectrometer and the viscometric measurements were performed at a constant temperature of 25 ±0,5 ˚C using solvent at the "Oswald" viscometer.

The Synthesis of Hydroxamoyl Chloride

The starting materials of terephthalohydroxamoyl chloride, 4,4'-bis(phenylhydroxamoyl chloride)ether, 4,4'-bis(phenylhydroxamoyl chloride)disulphide and 4,4'-bis(phenyl hydroxamoyl chloride) were obtained by passing chloride gas (which was dried and passed under safe conditions) through the $CHCl_3$ solutions of terephthaldoxime and the CCl_4 solutions of bis(4-farmaldoximephenyl)ether, bis(4-formaldoximephenyl)disulphide and 4,4'-biphenyldialdoxime by stirring for 2h (KARATAŞ & TÜZÜN 1989, RHEINBOLD 1926).

Terephthalohydroxamoyl chloride : (mp:195 ˚C, yield: 81 %). 'H-NMR (DMSO): δ 12.11 (s, 1H), 11.82 (s, 2H), 6.5-7.4 (m, 4H, J: 7 Hz). Elem. Anal. Calcd. for $C_8H_6N_2O_2Cl_2$ (%): C:41.20, H: 2.58, N:12.00 Cl: 30.50 Found: C: 41.93, H: 2.60, N:12.62, Cl:31.20.

4,4'-bis(phenylhydroxamoyl chloride)ether : (mp:133-134 ˚C, yield: 70 %). 'H-NMR (DMSO): δ 12.61 (s, 1H), 11.97 (s, 1H), 6.9-7.8 (m, 8H, J: 8.7 Hz). Elem. Anal. Calcd. for $C_{14}H_{10}N_2O_3Cl_2$ (%): C:51.90, H: 3.09, N:8.64 Cl: 21.60 found: C: 50.50, H: 3.16, N:9.03, Cl:20.80.

4,4'-bis(phenylhydroxamoyl chloride)disulphide : (mp:177-178 ˚C, yield: 68 %). 'H-NMR (DMSO): δ 11.37 (s, 2H), 7.87-7.53 (m, 8H, J: 1.92 Hz). Elem. Anal. Calcd. for $C_{14}H_{10}N_2O_2S_2Cl_2$ (%): C:45.20, H: 26.90, N:75.30, Cl: 18.82, S:17.20 found: C: 45.30, H: 27.00 N:75.30, Cl:19.20, S:18.00.

4,4'-bis(phenylhydroxamoyl chloride) : (mp:170-172 ˚C, yield: 60 %). 'H-NMR (DMSO): δ 11.35 (s, 1H), 7.88 (q, 8H, J: 17.43 Hz). Elem. Anal. Calcd. for $C_{14}H_{10}N_2O_2Cl_2$ (%): C:54.50, H: 3.25, N:9.10, Cl: 22.73 found: C: 54.00, H: 3.95, N:9.01, Cl:21.98.

The General Synthesis of Polybenzazole (Polybenzimidazole and Polybenzoxazole)

Poly(benzimidazole)s and poly(benzoxazole)s were synthesized by gently heating stoichiometric mixture of 3,3'-diaminobenzidine 1,2,4,5-tetraaminobenzene, or 3,3'-dihydroxybenzidine and the aforementioned dihydroxamoyl chlorides in dry DMF under nitrogen atmosphere; then the mixture was slowly heated to a maximum temperature of 30˚C for 3h. The viscous polymerization mixture was poured into water, and the precipitated polymers were filtered, washed several times with water and ether, then dried in vacuum at 80˚C for 24h. At the end of this experiment, the polymers namely poly[2,2'-(p-phenylene)-5-benzobis(imidazole); PBI-1, poly(2,2'-(p-phenylene)-5,5'-bis(benzimidazole)); (PBI-2), poly[2,2'-(p-phenylene)-5,5'-bis(benzoxazole)]; PBO-1, poly[2,2'-(p,p'-diphenyleter)-5-benzobis(imidazole)]; PBI-3, poly[2,2'-(p,p'-diphenyleter)-

5,5'-bis(benzimidazole)]; PBI-4, poly[2,2'-(p,p'-diphenyleter)-5,5'-bis(benzoxazole)]; PBO-2, poly[2,2'-(p,p'-diphenyldisulphide)-5-benzobis(imidazole)]; PBI-5, poly[2,2'-(p,p'-diphenyldisulphide)-5,5'-bis(benzimidazole)); PBI-6, poly[2,2'-(p,p'-diphenyldisulphide)-5,5'-bis(benzoxazole)]; PBO-3, poly[2,2'-(p,p'-diphenylene)-5-benzobis (imidazole)]; PBI-7, poly[2,2'-(p,p'-diphenylene)-5,5'-bis(benzimidazole)]; PBI-8 and poly[2,2'-(p,p'-diphenylene)-5,5'-bis(benzoxazole)]; PBO-4 were obtained.

The Investigation of Coating Properties of PBI and PBO

10 % polymer solution in DMSO was prepared for the investigation of coating properties (adhesion, anti-corrosion) of PBI and PBO. A film with 100-120 μm thickness was applied to the surface of a 50×100×1 mm steel plate that was first dried at room temperature then in an oven at 100˚C for 4 h. The adhesion properties and the corrosion properties against the chemical conditions (in the solutions of 3% NaCl, 10% NaOH, 10% HCl) of the polymer film on the metal surface were determined.

The Determination of The Adhesion Properties of The Coatings

The adhesion property of the coatings obtained from the PBI and PBO were determined using the Lattice method. The polymer coatings on the metal surfaces were divided into equal and small squares (1mm × 1mm) by a razor blade. An insutape was suddenly pulled. As a result of this operation, the % of adhesion was calculated by the following expression:

$$\text{Adhesion }\% = \left(\frac{a-b}{a} \right) \times 100$$

where a: total number of the squares; b: number of squares removed from the coating

Determination of The Corrosion Resistance

Polymer coatings (100-120 μm thick) were formed on the metal surfaces by using the prepared polymer solution and exposed to 3% NaCl, 10% NaOH, 10% HCl, pure water and open air for 10 days. Then, the plates were removed from this medium and the amount of decomposition observed with the naked eye was taken as a measure of the corrosion resistance.

The Determination of Chloride Ion

The amount of the chloride ion was determined by using the chlorine ion electrode.

RESULT AND DISCUSSION

In our study, different from the previous studies, the polybenzazoles were synthesized from dihydroxamoylchlorides with 3,3'-diaminobenzidine, 1,2,4,5-tetraaminobenzene and 3,3'-dihydroxy-4,4'-diaminobiphenyl (HAB). The characterization of polymers was performed with the assistance of the analyses of inherent viscosity, FT-IR and the elemental analysis. The data obtained by our analyses were in agreement with the ones in the literature (GAJIWALA & ZAND 2000, IMAI et al. 1965, KIM 2005, UEDA et al. 1986).

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PBI and PBO are soluble only in strong acids, such as MSA, TFA and conc. H_2SO_4 (KIM et al. 2005, UEDA et al. 1986). In this study, the synthesized polymers were dissolved in conc. H_2SO_4. The polymers with this procedure generally have inherent viscosities in the range of 2,2-4,8 dL/g, as measured in conc. H_2SO_4 at 30 ˚C. Some physical properties, the results of elemental and inherent viscosity analyses are shown in Table 1 and the assignments of bands for polybenzazoles backbones are given in Table 2.

Table 1. Some physical properties, the data of the elemental analysis and the analysis of the inherent viscosity in conc. H_2SO_4 at 30 ˚C of the polybenzazoles.

Compound	Colour	M.p. (˚C)	Yield %	Found (Calcd.) % C	H	N	S	[η] dL/g
PBI-1	Black	> 350	67	77.87 (72.41)	4.49 (3.45)	26.4 (24.14)	- -	4.2
PBI-2	Brown	> 350	72	76.41 (77.92)	5.72 (3.89)	20.38 (18.18)	- -	3,2
PBO-1	Black	> 350	60	77.63 (77.42)	3.40 (3.23)	8.80 (9.03)	- -	4,0
PBI-3	Dark brown	> 350	74	75.02 (74.10)	3.58 (3.70)	20.63 (17.28)	- -	4.2
PBI-4	Dark brown	> 350	60	80.12 (78.00)	3.68 (3.00)	15.40 (14.00)	- -	3,5
PBO-2	Brown	> 350	52	80.12 (77.61)	3.68 (3.48)	15.40 (6.97)	- -	3.1
PBI-5	Dark brown	> 350	75	65.3 (64.52)	3.70 (3.23)	15.43 (17.20)	17.32 17.20	4.0
PBI-6	Brown	> 350	57	73.42 (69.64)	3.98 (3.57)	11.87 (12.5)	15.10 (14.29)	2.7
PBO-3	Brown	> 350	58	75.02 69.33	3.58 3.11	5.63 6.22	13.85 14.22	2.2
PBI-7	Dark Brown	> 350	78	78.13 (77.92)	2.96 83.89)	18.58 (18.18)	- -	3.7
PBI-8	Dark Brown	> 350	69	84.40 (81.25)	4.09 (4.16)	14.52 (14.58)	- -	4.8
PBO-4	Dark Brown	> 350	60	76.41 80.83	3.72 3.63	8.38 7.25	- -	2.7

Table 2. FT-IR Spectrum data of Polybenzazoles

Polymers	N-H stretching (cm^{-1})	C=N stretching (cm^{-1})	Ring-vibration characteristic of conjugation between benzene and imidazole ring (cm^{-1})	CH_{arom} (cm^{-1})
PBI-1	3410	1614	1514	3050
PBI-2	3440	1618	1547	3046
PBO-1	-	1640	-	3072
PBI-3	3395	1620	1522	3045
PBI-4	3430	1608	1518	3067
PBO-2	-	1647	-	3076
PBI-5	3450	1670	1570	3040
PBI-6	3400	1607	1514	3045
PBO-3	-	1642	-	3065
PBI-7	3420	1620	1583	3054
PBI-8	3418	1610	1583	3042
PBO-4	-	1635	-	3063

In the early studies, the PBI and PBO coating films were examined considering the steel's adhesion properties and the corrosion resistance against the organic solvents and heat (SUGAMA 2004, IURA et al. 1996). Highly resistant property against heat and chemical attack have been previously determined for the polybenzazole coatings. In our study, the polybenzazoles were also used as the coating materials of steel. The solutions in DMSO of synthesized polybenzazole were used for forming film in the the dip coating method. Furthermore, the effect of terminal groups of polymer structure on the coating properties was studied. It was determined that the adhesion properties of PBI and PBO having groups (-S-S-, -O-, -C=N-, -C-NH-) on the main chain and ($-NH_2$, CCl=NOH) at the terminal group in their structures were increased (AHMETLİ et al. 2006, FRIEDRICH et al. 2005). PBI-5, PBI-6 and PBO-3 had higher adhesion properties depending on the presence of (-S-S-) on the main chain.

Upon analysis, it was determined that the polymers having the terminal groups of ($-NH_2$) in their polymer structures and coated on metal surfaces had higher adhesion and anti-corrosion properties as in literature (FRIEDRICH et al. 2005). Some polymers had lower coating property because just one or two hydroxamoyl chloride terminal groups were present in the polymer structure. The proposed terminal groups of the polymer structure were shown in Figure 2 and the related results are presented in Table 3. The microscope image of PBI and PBO coated on the metal surfaces after the adhesion test is given in Figure 3.

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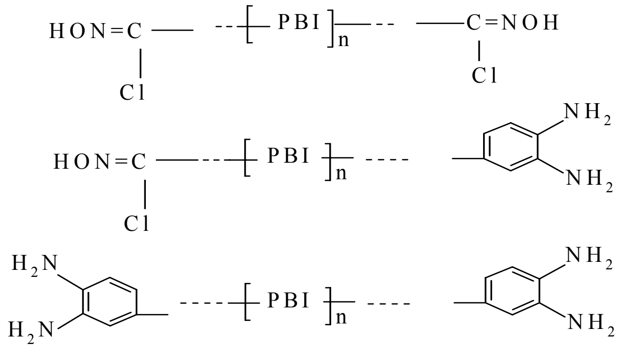

Figure 2. The proposed terminal groups to polymer structure

Table 3. Adhesion and corrosion resistance properties of PBI and PBO structures

Polymer	Proposed Terminal groups -CCl=NOH	Adhesion (%)	Corrosion Resistance 3%NaCl	10%NaOH	water	10%HCl
PBI-1	HON=CCl-...-$(PBI)_n$-..$Ar(NH_2)_2$	100	++	+	++	-+
PBI-4	$(NH_2)_2$Ar-..-$(PBI)_n$-..$Ar(NH_2)_2$	85	++	++	++	-
PBO-2	$(NH_2)_2$Ar-..-$(PBO)_n$-..$Ar(NH_2)_2$	100	++	++	++	-
PBI-6	$(NH_2)_2$Ar-..-$(PBI)_n$-..$Ar(NH_2)_2$	87	++	++	++	-
PBO-3	HON=CCl-...-$(PBO)_n$-..$Ar(NH_2)_2$	94	++	+	++	-+
PBI-5	HON=CCl-...-$(PBI)_n$-..$Ar(NH_2)_2$	100	++	+	++	-+
Other polymers	-	-	-	-	-	-

-, No resistance, -+, little, +, medium resistance, ++,high resistance

PBI-4 **PBI-1** **PBO-2**

Figure 3. Microscope image of PBI and PBO coated on metal surfaces after the adhesion test.

The corrosion resistances of PBI and PBO that will be used under aggressive conditions were analyzed by the "Microscopic Analysis Method". The corrosion resistances of PBI and PBO coated on metal surfaces were investigated for 10 days in 3 % NaCl, 10 % NaOH, 10 % HCl solutions in the atmosphere. It was observed that the coatings were resistant against 3% NaCl and 10% HCl solutions, and no degradation occured on the coatings. Additionally, PBI-1, PBO-2, PBO-3, PBI-4, PBI-5 and PBI-6 had no corrosion in 3% NaCl for 10 days.

The effect of the quantity of the hydroxamoyl chloride or amino groups of the terminal groups of the polymers was observed against corrosion resistance for 10 days in 10% NaOH solution. However, it was determined that the resistance of the coatings against 10% NaOH solution decreased depending on the presence of (-CCl=NOH) terminal group in the structure of the polymer. The main reason for this is considered as the formation of the chemical bond between the hydroxamoyl chloride group and NaOH.

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REFERENCES

AHMETLI G, ŞEN N, PEHLIVAN E, DURAK S, 2006. Adhesive and Anticorrosive Polymeric Coatings Obtained From Modified Industrial waste Oligostyrenes, *Progress in Organic Coatings*, 55, 262-267.

CARRON KT, LEWIS ML, DONG J , DING J , XUE G and CHEN Y, 1993. Surface enhanced Raman scattering and cyclic voltammetry studies of synergetic effects in the corrosion inhibition of copper by polybenzimidazole and mercaptobenzimidazole at high temperature, *Journal of Materials Science*, 28(15), 4099-4103.

DAVID EG, 1996. Encapsulated Ferromagnetic Particles Suitable for High Temperature Use, *US Patent 5563001*, General Motors Corporation, 8 October.

FRIEDRICH JF, MIX R, KÜHN G, 2005. Adhesion of Metals To Plasma-Induced Functional Groups At Polymer Surfaces, *Surface and Coatings Technology*, 200 (1-4), 565-568.

GAJIWALA HM, ZAND R, 2000. Synthesis And Characterization of Thermally Stable Polymers Containing Phenazine, *Polymer*, 41, 2009-2015.

IMAI Y, TAOKA, I, UNO K, IWAKURA Y, 1965. Polybenzoxazoles and Polybenzthiazoles, *Macromolecul Chemistry*, 83, 167-179.

IURA K, ONISHI Y, ITOH T, 1996. Varnish-Coated Heat-Resistant Roll for Copying Machine, and Method of Producing The Same, *US Patent 5,549,946*, Sumitomo Wiring Systems, Ltd. August 27.

IZYNEEV AA, TEPLYAKOV MM, SAMSONOVA VG, MAKSIMOV AD, 1967. Polyazoles, *Russian Chemical Review*, 36, 912-932.

KARATAŞ İ, TÜZÜN C, 1989. Terephthalohydroximoyl Chloride, *Organic Preparations and Procedures International*, 21, 517.

KIM JH, LEE JK, 2001. Hydroxy-Substituted Polyenaminonitrile asa Soluble Precursor for Rigid-Rod Polybenzoxazole, *Bulletin of the Korean Chemical Society*, 22, 999-1004.

KIM YJ, 2005. Synthesis of High Molecular Weight Polybenzoxazoles in Polyphosphoric Acid and Investigation of Their Hydrolytic Stability Under Acidic Conditions, *Hıgh Performance Polymers*, 17, 377-401.

KORSHAK VV, KAZAKOVA GV, RUSANOV AL, 1989. Catalytıc Methods of Synthesızıng Polybenzazoles Review, *Polymer Scıence*. U.S.S.R., 1, 4-21.

KORSHAK VV, KRONGAUZ YS, RUSANOV AL, TRAVNIKOVA AP, 1974. Polybenzoxazoles and Benzthiazoles Containing 2-Benzimidazolyl Side Groups, *Vyskomol Soedin*, A16, 9, 1996-2001.

KORSHAK VV, TEPLYAKOV MM, 1971. Synthesis Methods and Properties of Polyazoles, *Journal of Macromolecular Science - Reviews; Macromolecular Chemistry*, C5(2), 409-450.

KUBOTA T, NAKANISHI R, 1964. Preparation of Fully Aromatic Polybenzoxazoles, *Journal of Polymer Science* Part:B, 2, 655-659.

MOYER WW, COLE C, ANYOS TJ, 1965. Aromatic Polybenzoxazoles, *Polymer Science* Part: A3, 2107-2121.

RHEINBOLD H, 1926. Über die Reactionsweiser des Nitrosyl Chlorids, *Liebigs Annalen Chemistry*, 451, 161.

SUGAMA T, 2004. Hydrothermal Degradation of Polybenzimidazole Coating, *Materials Letters*, 58, 1307-1312.

UEDA M, SUGITA H, SATO MJ, 1986. Synthesis of Poly(benzoxazole)s by Direct Polycondensation of Dicarboxylic Acids With 3,3'-Dihydroxybenzidine Dihydrochloride Using Phosphorus Pentoxide/Methanesulfonic Acid As Condensing Agent and Solvent, *Polymer Science Part: A, Polymer Chemistry*, 24, 1019-1026.

VOGEL H, MARVEL CS, 1961. Polybenzimidazoles; New Thermally Stable Polymer, *Journal of Polymer Science*, L, 511-539.

VOGEL H, MARVEL CS, 1963. Polybenzimidazoles. II., *Journal of Polymer Science* Part A, 1, 1531-1541.

WOLFE JF, ARNOLD FE, 1981. Rigid-Rod Polymers. 1. Synthesis And Thermal Properties of para-Aromatic Polymers With 2,6-Benzobisoxazole Units In The Main Chain, *Macromolecules*, 14, 909-915.

WRASIDLO W, LEVINE HH, 1964. Polybenzimidazoles. I. Reaction Mechanism and Kinetics, *Journal of Polymer Science* Part A, 2, 4795-4808.