

Poly(benzimidazole) and Substituted Poly(benzimidazoles): Novel, Electroactive, and Conducting Polymers Possessing High Catalytic and Coordination Properties

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Received 14 July 1998; accepted 25 September 1999

ABSTRACT: Benzimidazoles and substituted benzimidazoles were electropolymerized on a Pt electrode using acetonitrile containing 0.1 M NaClO₄. The polymers are electroactive and conducting. They have a high electrocatalytic effect on the reduction of H⁺, O₂, and CO₂ and exhibit high coordination ability. The properties of the polymers depend on the extent of conjugation in the monomer. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 112–115, 2000

Key words: electropolymerization; conductivity; poly(benzimidazoles); electroactivity; electrocatalysis; coordination

INTRODUCTION

Benzimidazoles are biologically important compounds found in vitamin B₁₂, metalloproteins, etc. They exhibit antitumor, antibacterial, anthelmintic, fungicidal, and virucidal properties.^{1–3} They have proven coordination and corrosion-inhibition abilities.^{4–6} Chemically prepared poly(benzimidazoles) are thermally stable and therefore have applications at elevated temperatures in the aerospace field.

Ever since the report that conjugated polymers could be tailored to achieve high conductivity,^{7,8} there has been phenomenal growth in research on organic conducting polymers. The presence of conjugated “π-bonds” in benzimidazoles can make them potential candidates for producing conducting polymers. A review of the literature surprisingly reveals no information on the electrochemical polymerization of benzimidazoles and the conducting properties of the resulting polymers.

We have found that benzimidazole (BI) and substituted benzimidazoles, namely, 2-mercaptobenzimidazole (MBI), 2-amino-2-phenylbenzimidazole (AmPhBI), 2-phenylbenzimidazole (PhBI), and 2,6-bisbenzimidazylpyridine (bBPy) (structures given in Fig. 1) on electropolymerization produce electroactive and conducting polymers. They are potential electrocatalysts for the reduction of O₂, CO₂, and H⁺ and possess coordination ability. The properties are functions of conjugation; the longer the conjugation in the monomer, the better the properties of the resulting polymers.

EXPERIMENTAL

Monomers, NaClO₄ (all AR), and acetonitrile (AN) were used as received. A detailed experimental procedure is discussed elsewhere.⁹

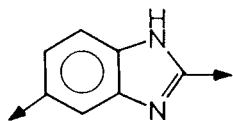
RESULTS

Cyclic voltammetric parameters during the electrooxidation of the monomers are collected in Ta-

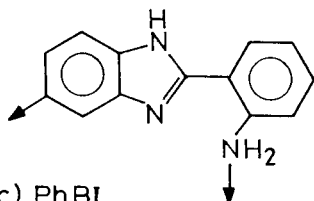
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Journal of Applied Polymer Science, Vol. 77, 112–115 (2000)
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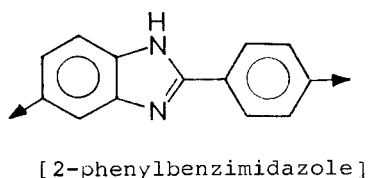
(a) BI (Benzimidazole)



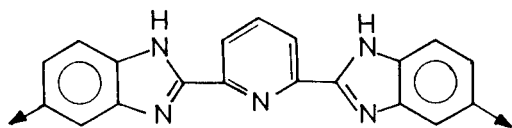
(b) AmPhBI [2-amino-2-phenylbenzimidazole]



(c) PhBI



(d) bBPy [2,6-bisbenzimidazylpyridine]



(e) MBI [2-mercaptobenzimidazole]

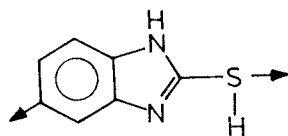


Figure 1 Structures of benzimidazole and substituted benzimidazoles (\rightarrow indicates possible position of linkages in the polymer). (a) Benzimidazole (BI), (b) 2-amino-2-phenylbenzimidazole (AmPhBI), (c) 2-phenylbenzimidazole (PhBI), (d) 2,6-bisbenzimidazylpyridine (bBPy), (e) 2-mercaptobenzimidazole (MBI).

ble I. All the monomers gave an anodic peak during the forward scan and a cathodic peak during the reverse scan. Additionally, AmPhBI gave an anodic peak at +1.14 V (assignable to the oxidation of the amino group¹⁰), and MBI's was +2.16 V (when the potential range was extended up to +2.4 V.) This peak was due to the oxidation of the —SH group^{11–14}). The height of all the peaks decreased slightly and attained steady values after three cycles. However, the peak at +2.16 V, ob-

served during the oxidation of MBI, disappeared after five cycles.

On repeated cycling the electrode was gradually coated with a yellow-colored film. The films were insoluble in acetone, methanol, chloroform, and ethanol; sparingly soluble in DMF, acetonitrile, and DMSO; but dissolved in hot concentrated H_2SO_4 and aqueous NaOH.

These polymeric films were electroactive when cycled between 0 and 1.8 V in acetonitrile containing 0.1 M NaClO_4 . The corresponding cyclic voltammetric parameters are collected in Table II.

Table II also contains the conductivity values and electrocatalytic effects of these polymers. H_2O_2 and CO are the respective products from the reduction of O_2 and CO_2 .

A known amount of the films on Pt (typically 10-nm film on $1 \times 1 \text{ cm}^2$ Pt) was exposed to Cu^{2+} solutions for 1 h. Then the film was removed, washed with water, and dissolved in concentrated HNO_3 , and the copper content was analyzed spectrophotometrically¹⁵ (Table II).

DISCUSSION

Based on IR data (Table III), electroactivity, and also, on earlier literature about poly(BI),^{16–25} we can reasonably propose the possible position of linkages in the polymer, shown as arrow marks in Figure 1. BI coordinates via tertiary nitrogen in neutral solution, while in alkaline solutions it

Table I Cyclic Voltammetric Parameters during Electropolymerization of Benzimidazoles on Pt in AN Containing 0.1M NaClO_4

Monomer	Anodic Peak Potential ($E_{p,a}/V$)	Cathodic Peak Potential ($E_{p,c}/V$)
BI	1.3	1.1
AmPhBI	0.52 (1.14) ^a	0.50
PhBI	0.75	0.70
bBPy	0.90	0.68
MBI	1.44 (2.16) ^b	1.08

^a Due to oxidation of NH_2 group.¹⁰

^b Polymer coating was obtained only when potential was extended to 2.4 V, when a peak due to —SH group^{11–14} appeared at 2.16 V.

Potential Range 0 to 1.5 V versus SCE; Monomer Concentration = 10 mM; Scan rate = 100 mV/sec.

[BI = benzimidazole, AmPhBI = 2-amino-2-phenylbenzimidazole, PhBI = 2-phenylbenzimidazole, bBPy = 2,6-bisbenzimidazylpyridine, MBI = 2-mercaptobenzimidazole]

Table II Properties of Pt/Poly(benzimidazoles) Film (10 nm)

		BI	AmPhBI	PhBI	bBPy	MBI
Electroactivity ^a (V)	$E_{p,a}$	+1.5	+0.3	+0.7	+1.0	+1.36
	$E_{p,c}$	+1.1	+0.06	+0.6	+0.8	+1.2
Conductivity ^b (S/cm)		1×10^{-3}	1×10^0	1×10^{-2}	1×10^{-2}	1×10^{-4}
Electrocatalytic activity ^c ($i_p/\mu A$)	H ⁺ ^d	18.9	18.1	21.2	17.5	10.2
	O ₂ ^e	15.9	21.2	19.0	19.8	15.1
	CO ₂ ^f	10.2	16.8	15.3	15.0	8.2
Copper content in the film ^g (mg)	pH 5	Nil	Nil	Nil	Nil	Nil
	pH 7	0.10	0.12	0.10	0.10	0.12
	pH 9	0.14	0.15	0.16	0.15	0.15

^a In AN–0.1M NaClO₄; SR = 100 mV/sec; potential range (0 to 1.5V).

^b By four-probe method.

^c SR = 200 mV/sec.

^d CF₃COOH (0.2M) + CF₃COONa (0.2M), pH 3.0; plain Pt = 14.1 μA .

^e O₂ = saturated 0.05M H₂SO₄; plain Pt = 10.4 μA .

^f CO₂ = saturated AN–Et₄NClO₄; plain Pt = 6.0 μA .

^g Solution copper content = 1.27 mg; exposure time = 1 h.

[BI = benzimidazole, AmPhBI = 2-amino-2-phenylbenzimidazole, PhBI = 2-phenylbenzimidazole, bBPy = 2,6-bisbenzimidazylpyridine, MBI = 2-mercaptobenzimidazole]

coordinates via imine nitrogen. Because it's a cation, in acid solution it loses the ability to coordinate. Films exposed to alkaline and neutral solutions contained greater amounts of copper, while that exposed to an acidic solution did not contain

any copper (Cu²⁺ actually forms coordination complexes with the films—data not shown). These results reveal that both tertiary nitrogen and imine nitrogen of the benzimidazole ring are not involved in polymerization and further cor-

Table III IR Spectral Data

Monomer	Bands Due to cm ⁻¹	In Monomer	In Polymer	Remarks
BI ^a	$\nu_{C=C}$, $\nu_{C=N}$; 1550	Not found	Found	Substituted heterocyclic ring in the polymer.
MBI ^b	ν_{S-H} ; 2590	Found	Not found	C—S—C linkage in the polymer.
	ν_{C-S-C} ; 1227	Not found	Found	
PhBI ^c	1,4-substituted phenyl ring 1140, 764, 700	Not found	Found	1,4 substitution in the phenyl ring of the polymer film.
Am-PhBI ^d	NH ₂ group; 3380	Found	Not found	C—N—C linkage in the polymer.
bBPy ^e	BI ring vibration 440, 1277 In plane C—H ring breathing modes and deformation	Found	Not found	Possible linkage is through C-5 of BI ring.

^a 1620, 1600 & 1500 (aromatic $\nu_{C=C}$ and $\nu_{C=N}$); 3400 ν_{N-H} ; 1566 (N—H in plane bending of BI) and 1000, 935, 750, 660 (BI ring vibration).

^b 3200 (ν_{N-H}): ~ 1630 ($\nu_{C=C}$ & $\nu_{C=N}$); 1317 (ν_{C-N} & δ_{N-H}); 1262, 1007, 630, 480 (BI ring vibrations).

^c 3200 (ν_{N-H}): 1560 ($\nu_{C=C}$ & $\nu_{C=N}$); 1527 (N—H in plane bending of BI ring); 1405, 1273, 1000, 967 (BI ring vibration); 1311 (ν_{C-N} & δ_{N-H} of BI).

^d ~ 1040 (ν_{C-N} of amino phenyl group); 1205 ($\nu_{C=C}$ and $\nu_{C=N}$); 1320 (ν_{C-N} & δ_{N-H} of BI); ~ 750, 620 (BI ring vibration).

^e 3514 (ν_{N-H}); ~ 1620 ($\nu_{C=N}$ and $\nu_{C=C}$); 1600 ($\nu_{C=C}$ skeletal in plane vibration); ~ 1566 (ν_{N-H} in plane vibration); 1377, 1315 (δ_{N-H} & ν_{C-N}); 1141 (ortho substituted pyridine ring vibration); 1001 (BI ring vibration); 760 (N—H, C—H out of plane deformation); 753 (out of plane deformation of BI and C—H out of plane deformation of pyridine ring).

[BI = benzimidazole, AmPhBI = 2-amino-2-phenylbenzimidazole, PhBI = 2-phenylbenzimidazole, bBPy = 2,6-bisbenzimidazylpyridine, MBI = 2-mercaptobenzimidazole]

NOTE: a–e are found both in the respective monomer and polymer.

roborate the possible positions of linkages proposed.

Conductivity and catalytic effect increased in the order MBI < BI < bBPy < PhBI < AmPhBI, while the $E_{p,a}$ values increased in the reverse order. A look at the structure of the monomers reveals the extent of conjugation increases, which happens in this order: BI = MBI < PhBI = AmPhBI < bBPy. In the case of MBI, the presence of a C—S—C linkage hinders the extended conjugation, and consequently the polymers obtained from it have poor quality. On the other hand, in AmPhBI the amino group helps in retaining the extended conjugation through poly(aniline)-like²⁶ linkage. Hence, poly(AmPhBI) has superior properties. Thus the quality of the film can be improved considerably by extending the conjugation in the monomer and retaining it in the polymer.

S.T. expresses her gratitude to the principal and management of Al-Ameen College, Bangalore, for their encouragement.

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