Electrochemical and Chemical Polymerization of Imidazole and Some of Its Derivatives

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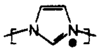
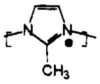
ABSTRACT: Imidazole, 1-methylimidazole, 2-methylimidazole, 4-methylimidazole, and benzimidazole were subjected to electrochemical and chemical oxidation. Chemical oxidation yields oligomers with higher molecular weight (DP > 12) than anodic oxidation (DP > 6) as detected by laser desorption mass spectrometry (LDMS). The oligomers have a relatively simple structure in which imidazole moieties are linked by N–N bonds. 1-Methylimidazole does not polymerize, and benzimidazole seems to react through the benzene carbon atoms as well as through the nitrogen atoms. Solubility of these products varies with the substituent group on the imidazole ring. We propose a variation of Diaz's mechanism of pyrrole polymerization that we base on cyclic voltammetry, spectral analysis, pH effects, laser desorption mass spectrometry, and computer calculations. The mechanism involves stepwise removal of an electron from the N-3 atom to produce a radical cation that then couples. LDMS data suggest that chemical polymerization occurs by rapid dimerization of imidazole followed by slower polymerization of the dimers. LDMS of electrochemical polymerization products suggests that polymerization occurs by addition of one imidazole unit at a time. None of these products exhibits electrical conductivity.

Introduction

Imidazole has a structure similar to that of pyrrole, thiophene, and triazole, which are known to undergo oxidative polymerization to produce electrically conducting polymers. Imidazole has been studied extensively in enzyme chemistry.[1,2] It is used as an initiator in enzyme reactions.[3] Trofimenko[4] first reported in 1967 that polymerization of imidazole with boranes involves formation of N–B–N linkages. Davies[5] reported copolymerization of acrylic acid with 1-methylimidazole in 1973. Tripathy[6] recently reported the electrochemical oxidation of imidazole but did not report the structure of the polymeric product. We now report the electrochemical and chemical oxidation of imidazole, its 2-methyl and 4-methyl derivatives, benzimidazole, and 1-methylimidazole. We have labeled the polymeric products of the first four of these compounds as follows (1-methylimidazole is included as compound V:



I



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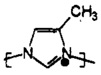

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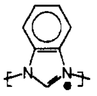

IV

V

Experimental Section

Materials. Imidazole, 1-methylimidazole, 4-methylimidazole, and benzimidazole (Aldrich) were used as obtained. 2-Methylimidazole was recrystallized before use. Acetonitrile (AN) and tetrabutylammonium fluoroborate (TBAFB) have been described.[7] Ammonium persulfate was used as received.

Apparatus. Constant-potential electrolyses (CPE) and cyclic voltammetry (CV) instrumentation have been described.[7] ^{1}H and ^{13}C NMR spectra were taken with a Bruker 360 FT NMR instrument. Infrared spectra were obtained with a Beckman FT 1100 FTIR spectrometer. Differential scanning calorimetry and thermal gravimetric analyses were measured with a DuPont thermal analysis system. pH values were measured with an Orion Model 520 pH meter. Laser desorption mass spectral data were recorded using a Nicolet 2000 Fourier transform mass spectrometer interfaced with a Tachisto 215 pulsed CO_2 laser.[8] X-ray diffraction analysis (XDS 2000 Scintag Inc. instrument; operating conditions, 40 kV and 35 mA) was performed on powder held onto glass with double-sided sticky tape.

Electrochemical Polymerization. We carried out the electrolyses at monomer concentrations of 0.2 M for all the imidazole species. We ran the constant-potential electrolyses (Table 1) in a constant-temperature bath at 45 °C to increase the solubility of the monomer in the AN solvent and to increase the rate of the oxidation reaction. We analyzed only the coating from the electrode, even though we found some precipitate in the bulk. These coatings were peeled off the electrode surface, washed with AN to remove the electrolyte, and then dried under vacuum for at least 24 h. In all cases, these films were very brittle; peeling them off the electrode was quite difficult.

Chemical Polymerization. Imidazole (3.4 g, 0.05 mol) was dissolved in 200 mL of water, and 11.4 g (0.05 mol) of ammonium persulfate was added to the solution. On stirring, the solution changed from colorless to dark brown. The solution became viscous and precipitate started to form in a matter of hours. After standing overnight, the precipitate, I, was filtered and washed with acetone and dried under vacuum for more than 24 h.

The same procedure was applied to 1-methylimidazole, 2-methylimidazole, and 4-methylimidazole; however, 1-methylimidazole and 4-methylimidazole did not react with ammonium persulfate; i.e., no color change or precipitate was observed. Benzimidazole (6.4 g, 0.05 mol) was dissolved in a water/acetone solution, and 11.4 g of ammonium persulfate was added. The solution turned brown and then red in a few hours. An orange solid precipitated within a day.

Computer Calculation Data. Semiempirical molecular orbital calculations were carried out on imidazole, its 1-methyl, 2-methyl, and 4-methyl derivatives, and benzimidazole employing a LCAO method as modified by Anderson to take into account nuclear repulsion between atoms. Details of this method have been described.[9] The method employs a force field minimization model. Calculation results include net charge distributions, MO energies, and total energy, which account for the effect of HOMO energy of a methyl group or benzene ring fused to the imidazole molecule. These calculations indicate that the unsubstituted (unprotonated) nitrogen atom has the highest net negative charge (−0.95 to −0.99) and therefore should be the most easily oxidized site in the molecule.

Discussion

Physical Properties. The electrochemical products were all deposited as brittle films on the platinum electrodes. Soluble materials and precipitated material were not investigated except in the case of V, which did

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Table 1. Oxidation Products and Their Solubilities[a]

monomer	imidazole	2-methylimidazole	4-methylimidazole	benzimidazole	1-methylimidazole
peak potential (V) vs Ag/Ag$^+$	1.5, 2.6	1.9, 2.3	1.8	2.0, 2.3	3.1
CPE potential (V) vs Ag/Ag$^+$	2.8	2.9	2.9	2.6	2.8
oxidation product	dark brown coating	dark brown coating	brown coating	dark brown coating	black precipitate
DMSO	VS	VS	VS	VS	VS
water	SS	PS	PS	I	
DMF	I	SS	PS	SS	
THF	I	I	I	I	
chloroform	I	I	I	I	

[a] VS: very soluble. SS: slightly soluble. PS: partly soluble. I: insoluble.

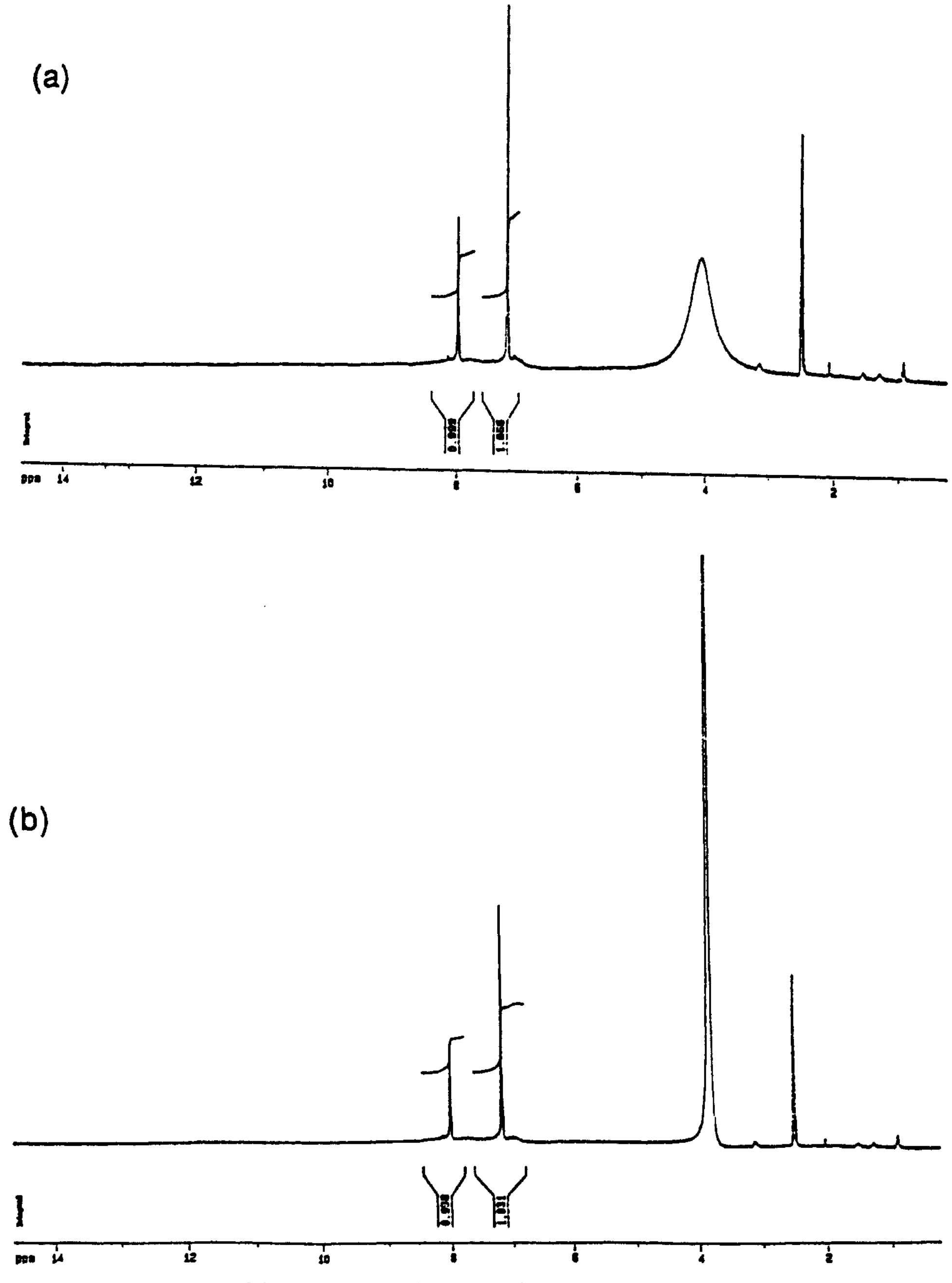


Figure 1. 360-MHz proton NMR spectra (DMSO-d_6) of the oxidation product of imidazole (a, top); after adding D_2O (b, bottom).

not form a film on the electrode. The potentials at which each oxidation product was obtained and relevant solubilities are shown in Table 1. Except for **IV**, all the imidazole oxidation products exhibit some water solubility, and all, including **IV**, are insoluble in $CHCl_3$. None of the products exhibited any measurable electrical conductivity by the standard four-probe method on pressed pellets.

The physical properties of oxidation products **I–IV** correspond to those of polymeric materials: Their elemental analyses (Table 2) and NMR spectra (vide infra) indicate that these oligomers retain the imidazole repeat unit; the viscosities observed for solutions of **I–IV** are consistent with the polymeric or oligomeric nature of these products. H_2O solutions of the oxidation products of **I–IV** have near neutral pHs.

NMR Spectra. The ^1H NMR spectra of **I–IV** show a broad resonance between 4 and 8 ppm, which disappears when D_2O is added to the NMR tube. In its place a new water peak (from H_2O in the D_2O) appears at 4.1–4.2 ppm. This was observed with all four of these products. Figure

Table 2. Elemental Analyses of Polyimidazoles I–IV

	% C	% H	% N	% O[a]	ash
		sample			
imidazole	41	4.01	36.76		
2-methylimidazole	41.22	4.54	27.98	23.09	2.2
4-methylimidazole	46.53	5.59	29.19	20.11	1.5
		ratio			
	C	H	N	O	
imidazole	2.9	3.3	2.2		
2-methylimidazole	4	5.2	2.3	1.6	
4-methylimidazole	4	5.4	2.1	1.3	

[a] Oxygen analysis was performed because no fluorine was found.

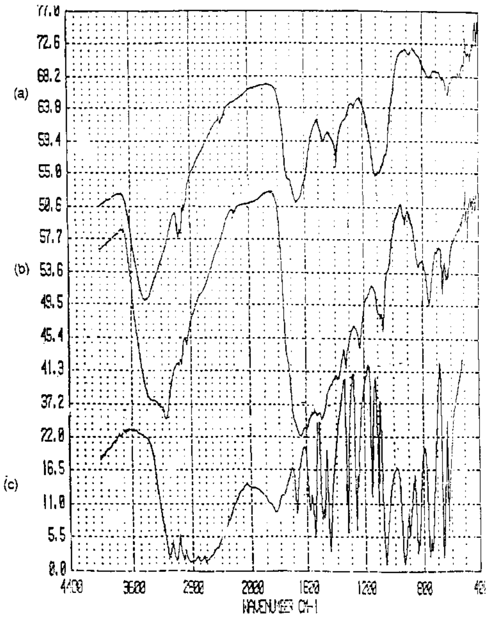


Figure 2. FTIR spectra (KBr pellet) of the oxidation product of (a) imidazole prepared in water solution, (b) imidazole prepared in acetonitrile, and (c) imidazole monomer.

1 exemplifies this effect in the proton NMR spectra of I before and after addition of D_2O. After smoothing out the broad bands with D_2O, the integrations are consistent with the repeat monomer unit less the amine proton. This observation seems to rule out water as a major constituent of these products.

NMR spectra of the oxidation product of V show mostly aliphatic carbons. Adding D_2O to this product does not smooth its spectrum. These results suggest that the aromatic ring structure has been lost.

Decoupled and undecoupled proton NMR spectra of I indicate that C_2, C_4, and C_5 bear one proton each in the oxidized product.

The ^1H NMR spectra of I and II prepared by ammonium persulfate oxidation, obtained after addition of D_2O, are identical to those of the electrochemically produced products except that they show slight downfield shifts.

Both proton and carbon-13 NMR spectra show clearly that the oxidation products of **I–III** retain all their C–H protons, and only the N–H protons are lost during oxidation. The latter is further demonstrated by the FTIR spectra of oligomers **I–IV**, which show the loss of the broad band at 2500–2900 cm^{-1} due to hydrogen-bonded N–H. Figure 2, the FTIR spectrum of **I**, is typical. These results are consistent with N–N linkages between repeating imidazole units. Also consistent with N–N linkages is the fact that V, the *N*-methyl derivative, does not form a regular polymeric product but instead loses its aromaticity.

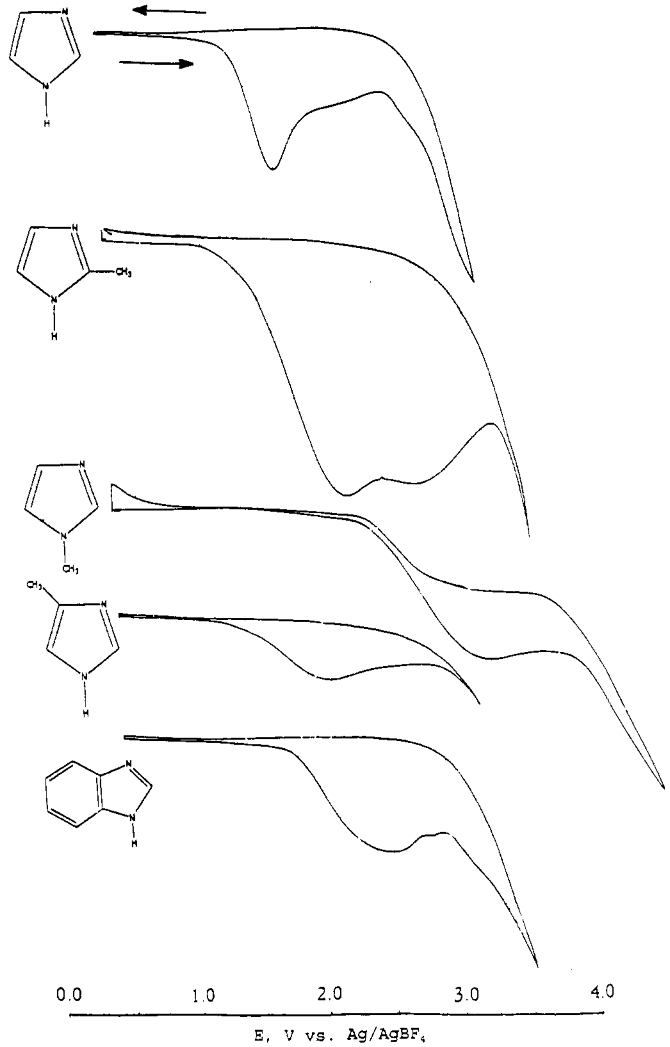


Figure 3. Cyclic voltammetry of imidazole and its derivatives vs Ag/Ag$^+$. The solvent is CH_3CN; the supporting electrolyte is TBAFB; scan rate = 200 mV/S. The sweep direction is shown by the arrows in the CV of imidazole.

CVs of imidazole and its derivatives are shown in Figure 3. Imidazole, 2-methylimidazole, and benzimidazole show two oxidation peaks below 3 V vs Ag/Ag$^+$. 4-Methylimidazole and 1-methylimidazole show only one oxidation peak. The latter shows no oxidation peak under 3 V. The remaining compounds, all of which have unsubstituted nitrogen, have at least one oxidation peak under 2.2 V. In these compounds, proton tautomerization can occur between N-1 and N-3. This tautomerization is verified by ^1H and ^{13}C NMR spectra (vide infra and Figure 4). The methyl group attached to N-1 of 1-methylimidazole prohibits tautomerization, which may result in a higher oxidation potential than those observed for the remaining imidazole derivatives.

Further evidence for N–N bonding lies in the sharpened C-4 and C-5 resonances in the ^{13}C NMR spectra of I and II as exemplified in Figure 4. We explain this loss of broadening by loss of tautomerization, which renders C-4 and C-5 equivalent.

An interesting aspect of the NMR spectra is that there are no significant downfield shifts observed for the imidazole ring carbons and hydrogens. The major differences are in peak intensity. The two peaks in the aromatic region (C-2 and C-4/C-5) exhibit an intensity reversal due to the loss of tautomerization between C-4 and C-5. The differences are shown in Figure 4. Trofimenko[4] reported similar small shifts for imidazole–borane polymers as did Salamone for vinylimidazolium salts.[10]

Both chemically and electrochemically prepared products appear to be ionic in nature. The evidence for this

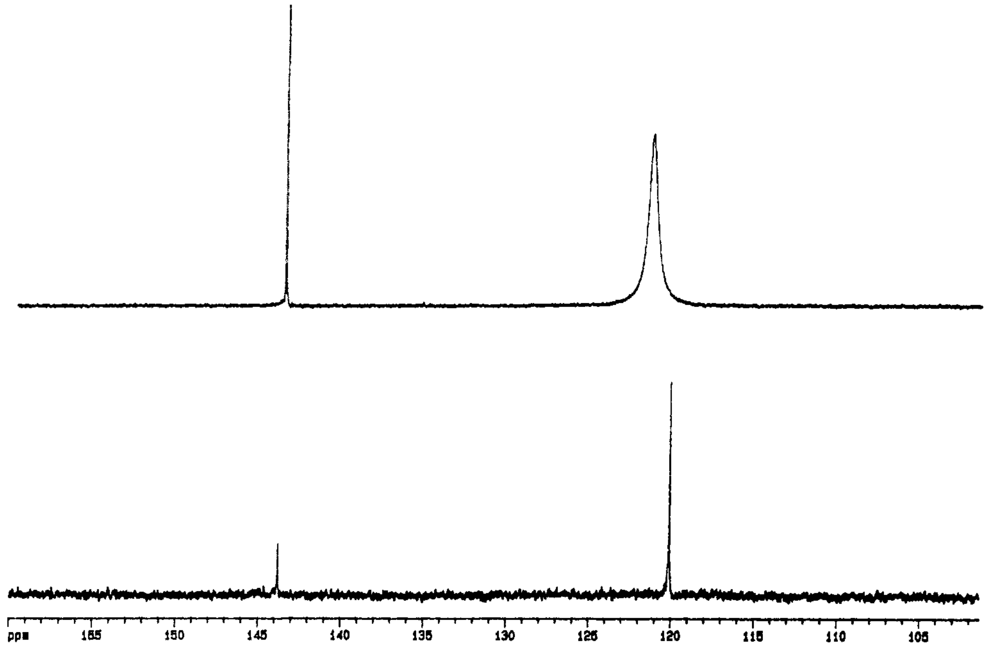


Figure 4. 360-MHz ^{13}C NMR spectra (DMSO-d_6) of 2-methylimidazole. Peak broadening due to tautomerization: (top) monomer; (bottom) polymer product.

Table 3. Data from Mass Spectra of Electrochemically Prepared Polyimidazole[a]

MIP (*m/z*)	region	correspond to
133, 135, 137	dimer	2RU - 1, 2RU + 1, 2RU + 3
201	trimer	3RU
267	tetramer	4RU - 1
333	pentamer	5RU - 2
399	hexamer	6RU - 3
459	heptamer	7RU - 10
661	decamer	10RU - 9

[a] MIP: most intense peaks. RU: repeating unit.

Table 4. Data from the Mass Spectrum of Electrochemically Prepared Poly(2-methylimidazole)

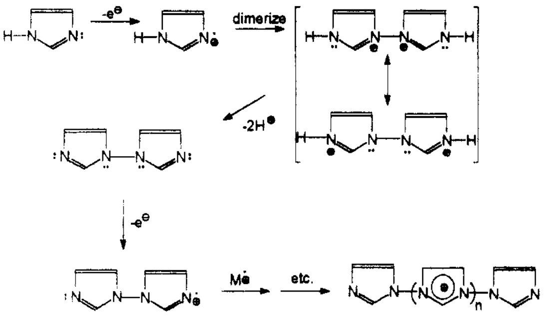
MIP (*m/z*)	region	correspond to
161, 165	dimer	2RU - 1, 2RU + 3
242, 243	trimer	3RU - 1, 3RU
323	tetramer	4RU - 1
403	pentamer	5RU - 2
483	hexamer	6RU - 3

is that they are high-melting, crystalline, water-soluble, and $CHCl_3$-insoluble. Although the reactions were carried out in the absence of oxygen or water, elemental analyses show ca. one oxygen atom per repeat unit. Tripathy and co-workers have reported the same result.[6] The products are hygroscopic and absorb water during workup. In the electrochemically produced oligomers, the only anion that should have been incorporated is fluoroborate. Elemental analyses showed no fluorine, however. We suggest that atmospheric water reacts with the fluoroborate ion to produce hydroxide ion and fluoroboric acid, which is lost in washing. The presence of hydroxide ion in the products is confirmed by a 5–10% weight loss at 120 °C during TGA analysis, which we ascribe to loss of water through decomposition.

The ^{13}C NMR spectrum of **IV** (Figure 5) indicates that, although the ring structure is retained, a large number of new resonances appear, suggesting that reaction has also occurred at the benzene ring to cross-link the product. Otherwise, benzimidazole seems to react as **I–III**. We are currently exploring this reaction.

FTIR Spectra. Strong absorption bands at 3400 and 1660 cm^{-1}, characteristic of water and/or hydroxide ion,[11] are prominent in the FTIR spectrum of **I** (Figure 2). Comparison of the spectrum of **I** prepared in water with that prepared in acetonitrile suggests that they differ only in DP, with the former having the simpler spectrum and therefore the higher molecular weight. This assumption is strengthened by the complete correspondence of resonances in the NMR spectra of these two products.

Scheme 1. Mechanism of the Electrochemical Polymerization of Imidazole



Laser Desorption Mass Spectra. Laser desorption mass spectra (LDMS) of electrochemically produced **I–III** are shown in Figures 6–8, respectively. The LDMS spectrum of **II** prepared chemically is shown in Figure 9.

The LDMS spectrum of electrochemically prepared **I** shows evidence of oligomers and of oligomer fragments consisting of up to 10 repeat imidazole units ($C_3H_3N_2^+$, $m/z = 67$). Peak intensities do not show a characteristic oligomer intensity distribution; instead, the oligomer intensities consistently decrease with increasing mass, a behavior characteristic of ion fragments. The pattern of peaks shown in Table 3 suggests that trimers consist of exactly three imidazole units (3RU), tetramers consist of four imidazole units minus one hydrogen atom (4RU - 1), pentamers consist of 5RU - 2, hexamers consist of 6RU - 3.

The LDMS spectrum of **II** (Figure 7) confirms a repeat unit of $m/z = 81$ ($C_4H_5N_2^+$) and shows oligomer fragments containing up to six repeat units. Table 4 shows a pattern similar to that shown in Table 3 for **I**.

The LDMS spectrum of **III** (Figure 8) also shows oligomer fragments of up to six repeat units (Table 5).

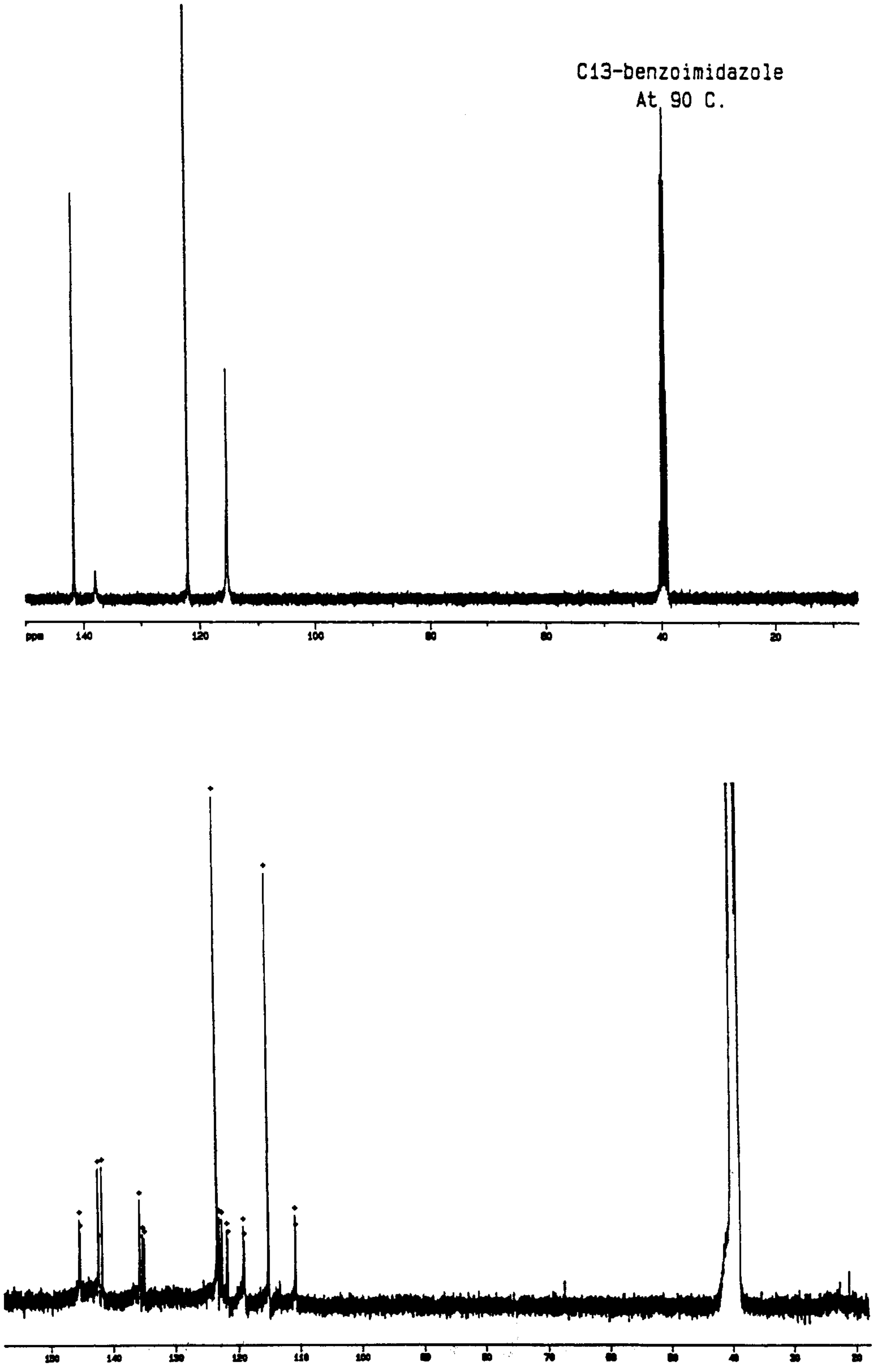


Figure 5. 360-MHz ^{13}C NMR spectra (DMSO-d_6) of benzimidazole (top) and the oxidation product (bottom).

Mechanism of Electrochemical Polymerization. We find that, during anodic oxidation, the pH drops as the reaction proceeds (Figure 9). At sufficiently low pHs, the reaction slows down (Figure 10). These findings agree with the mechanism proposed by Diaz[12] for the electrochemical production of polypyrrole. In that mechanism, a one-electron oxidation step produces a radical cation. Coupling of two radical cations and loss of two protons produces a neutral dimer. This dimer undergoes further oxidation and combines with another monomer radical cation to produce another dication, which becomes neutral when it loses two protons. Combination of monomer radical cations with oligomer radical cations, followed by elimination of protons continues, and the polymer chain grows. In the case of imidazole, an analogous mechanism for the growth of polymer would lead to bonding between nitrogen radical cations (Scheme 1). The mechanism for imidazole polymerization differs from pyrrole polymerization in one important way, however: oligomers with more than two imidazole units must bear a positive charge on each repeating unit except the two end ones (Scheme 1). The positive charge must be balanced by a counterion, which we propose is OH^- in the isolated polymer. For $n = 1$, the molecular formula is $[(C_3H_3N_2)_3]^+OH^-$. In the LDMS for $n = 1$ the main peak observed corresponds to $[(C_3H_3N_2)_3]^+$. The LDMS of higher oligomers exhibit

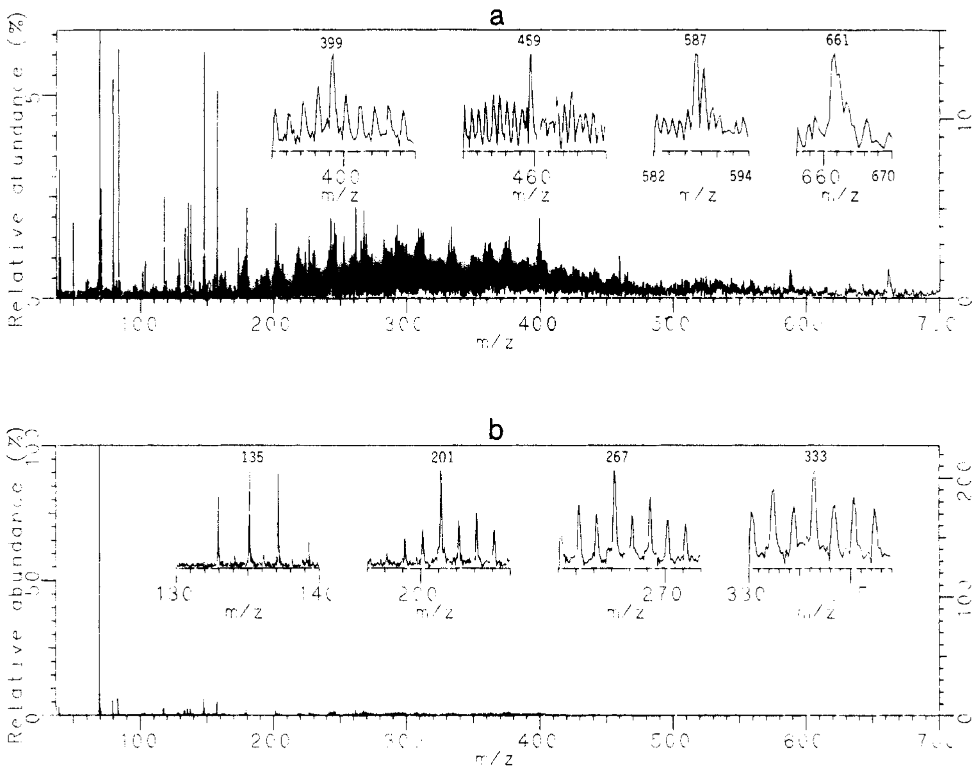


Figure 6. Mass spectrum of electrochemically prepared polyimidazole.

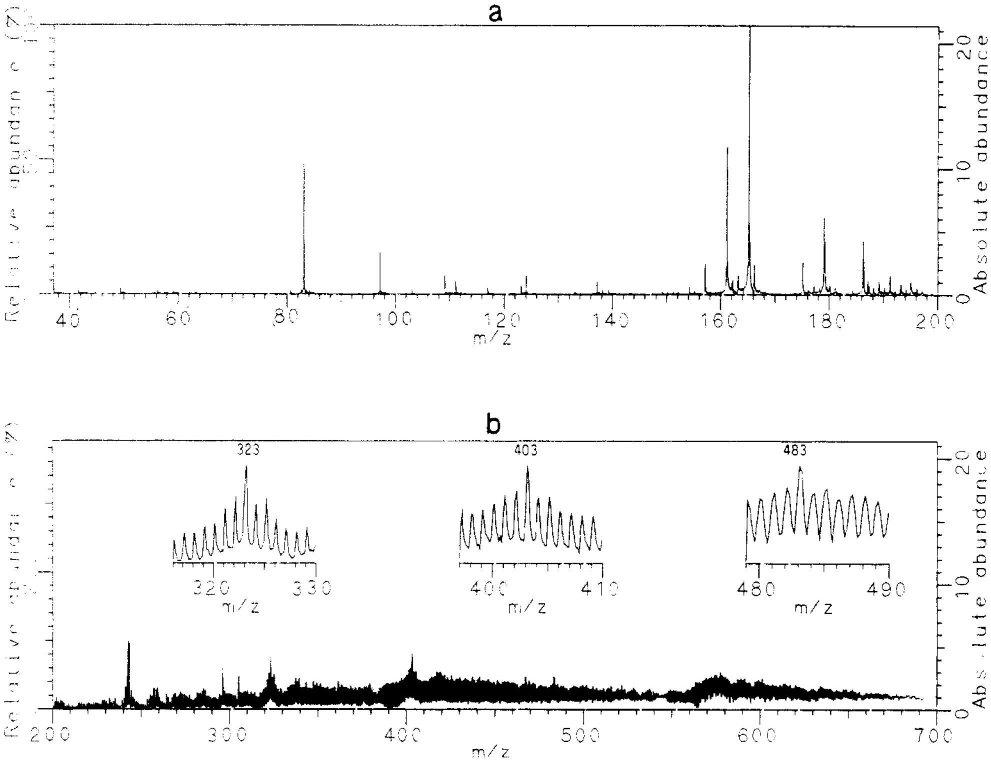
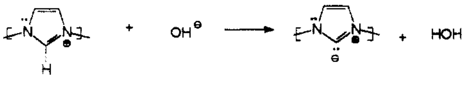
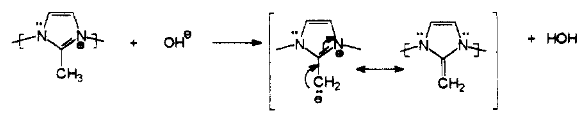


Figure 7. Mass spectrum of electrochemically prepared poly(2-methylimidazole).

hydrogen deficiencies. We explain these on the basis that, to be detected in the mass spectrometer, the oligomer must bear one positive charge. To achieve a monopositive charge, the hydroxide ion deprotonates the ring in the mass spectrometer, as shown in the following equation:



An alternative with 2-methyl-substituted imidazole is



This process of deprotonation is consistent with the masses observed: 3RU for $n = 1$, 4RU − 1 for $n = 2$; 5RU − 2 for $n = 3$; and 6RU − 3 for $n = 4$ (see Scheme 1 for the value of n) because removal of 0, 1, 2, and 3 protons, respectively, leads to monopositively charged ions. We note also that the desorbed ions are not sodium- or potassium-attached, which is usually observed when

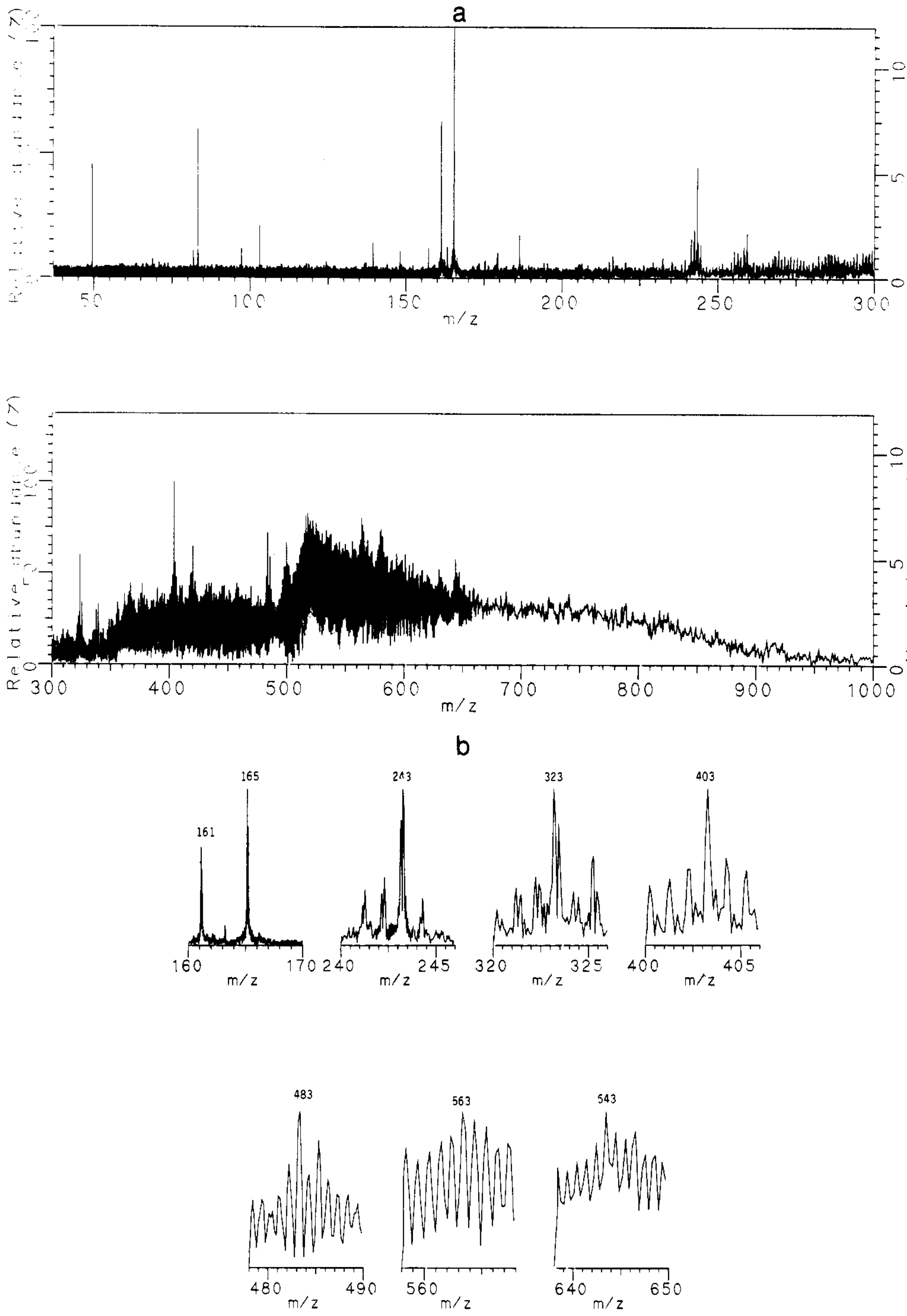


Figure 8. (a) Mass spectrum of poly(4-methylimidazole) prepared electrochemically. (b) High-resolution portions of a.

neutral polymers are laser desorbed. The absence of sodium- or potassium-attachment is a further indication that the electrochemically prepared polymers are ionic in nature. The required deprotonation also explains why a distribution of oligomers is not observed; i.e., the required deprotonation to produce a monopositive ion becomes more difficult as *n* increases. The Diaz mechanism is also consistent with our observation that pH decreases as the reaction proceeds and that, at low pH, the reaction rate decreases.

Oxidation products of **I** and **II**, obtained by chemical oxidation, resemble those produced electrochemically except that they exhibit larger downfield NMR shifts. We believe these differences arise because the chemically produced oligomers have higher DPs than we observed for the electrochemically produced polymer. The higher DPs are confirmed by LDMS (vide infra).

A structure consistent with the above data is shown in Scheme 1 for **I**.

The LDMS of chemically induced 2-methylimidazole presents some interesting data. In Figure 11a and Table 6 we see three pairs of peaks 16 mass units apart: m/z = 347 and 363, m/z = 509 and 525, m/z = 671 and 687, suggesting sodium and potassium attachment. When potassium chloride was added to the sample (Figure 11b), the peaks due to m/z = 525 and 687 were enhanced, confirming that these correspond to K^+-containing ions. Two additional peaks appear at m/z = 849 and 1011, corresponding to $\{(81)(10) + K\}^+$ and $\{(81)(12) + K\}^+$, respectively. The observed K^+-attached oligomers are all in the spectrum $\{(81)_n + K\}^+$, where n = 4, 6, 8, 10, 12. The fact that the oligomers are observed as K^+-attached seems to indicate that the oligomers are laser desorbed as neutral molecules, which then attach to K^+ in the gas phase. This

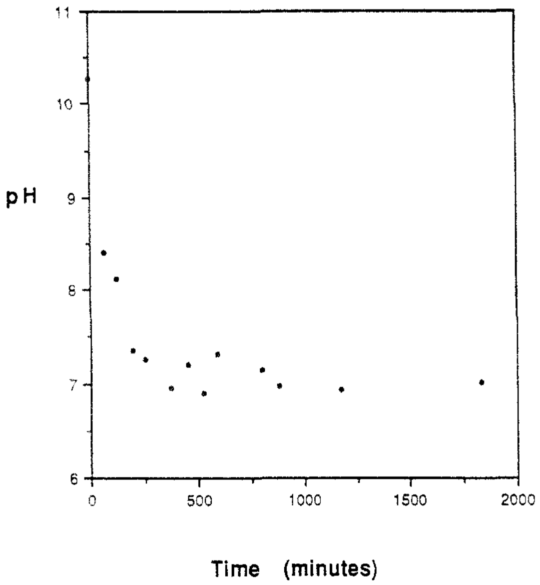


Figure 9. Imidazole oxidation in water solution: pH vs time.

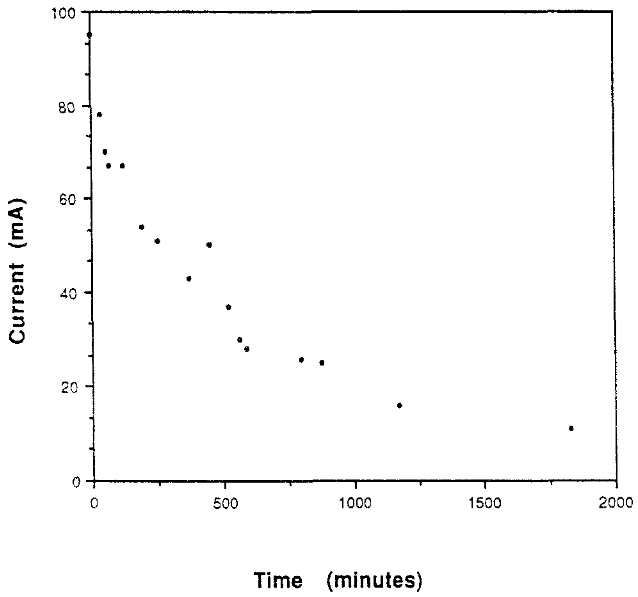


Figure 10. Imidazole oxidation in water solution: current vs time.

Table 5. Mass Spectral Data of Electrochemically Prepared Poly(4-methylimidazole)

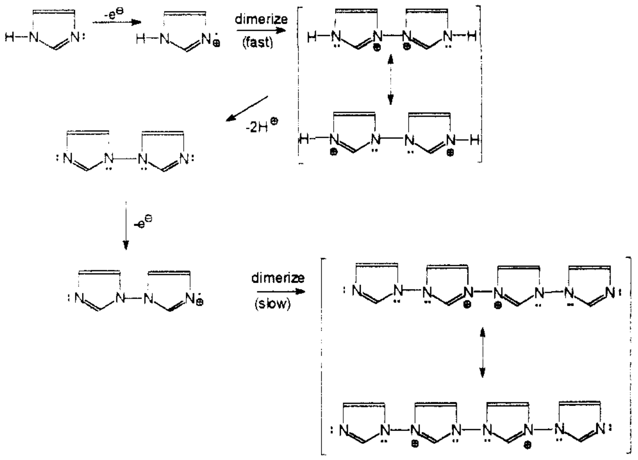
MIP (*m*/*z*)	region	correspond to
161, 165	dimer	2RU − 1, 2RU + 3
243	trimer	3RU
323	tetramer	4RU − 1
403	pentamer	5RU − 2
483	hexamer	6RU − 3

Table 6. Data of the Mass Spectrum of Poly(2-methylimidazole) Prepared Chemically

MIP (*m*/*z*)	region	correspond to
363	tetramer	4RU + K^+
525	hexamer	6RU + K^+
687	octamer	8RU + K^+
849	decamer	10RU + K^+
1011	dodecamer	12RU + K^+

is supported by the observation that no hydrogen deficiency is observed for the chemically prepared polymer. We do not understand at this point how the polymer can be neutral; it is impossible to write a neutral structure that corresponds to a repeating unit with mass = 81.

Scheme 2. Mechanism of the Chemical Polymerization of the Imidazole Dimerization Mechanism



The chemical polymerization mechanism is clearly different from that for electrochemically produced polymer because the chemically produced oligomers differ in mass by two repeating units. Chemical polymerization seems to produce dimers by a fast reaction sequence followed by a slower polymerization of dimers (Scheme 2). We expect the formation of tetramers from dimers to be slower than the formation of dimers from monomers because the positive charges cannot be lost through deprotonation.

In contrast, electrochemical polymerization appears to initiate on the electrode surface with monomer units adding one at a time.

Another difference between the LDMS of chemical polymerization and that of anodic polymerization is that intensity distributions in the former suggest an oligomeric distribution rather than fragmentation.

X-ray Diffraction Analysis. X-ray diffraction spectra of **I**, **II**, and **IV** are shown in Figure 12. The monomers show high crystallinity as expected. Polymer samples **I** and **II** both have an intense peak at $2\theta = 27.5°$, with the peak for **I** much more intense than that for **II**. **IV** shows a completely amorphous structure. We calculate the preferred spacing between polymer chains in the polymer matrix to be 2.54 Å for both **I** and **II**.

Conclusions

(1) Polyimidazole and its 2-methyl, 4-methyl, and benzo derivatives were prepared electrochemically. All of these except the 4-methyl derivative were also prepared chemically. The slight differences in chemical shift between the electrochemically and chemically prepared compounds may be due to different molecular weight distributions.

(2) Imidazole, 2-methylimidazole, and 4-methylimidazole polymerize through the nitrogen atoms. Benzimidazole undergoes reactions at the benzene ring carbon atoms. 1-Methylimidazole does not form an electrode coating.

(3) The solubility of the polyimidazoles varies with the position of the substituent on the imidazole ring.

(4) Pressed pellets of these materials show no significant conductivity.

(5) LDMS show that polyimidazole, poly(2-methylimidazole), and poly(4-methylimidazole) prepared electrochemically have DP > 6. Poly(2-methylimidazole) prepared chemically has DP > 12.

(6) Oligomer distributions as seen in the LDMS of chemically produced polymer suggest addition of dimer units in the rate-controlling step of that polymerization process.

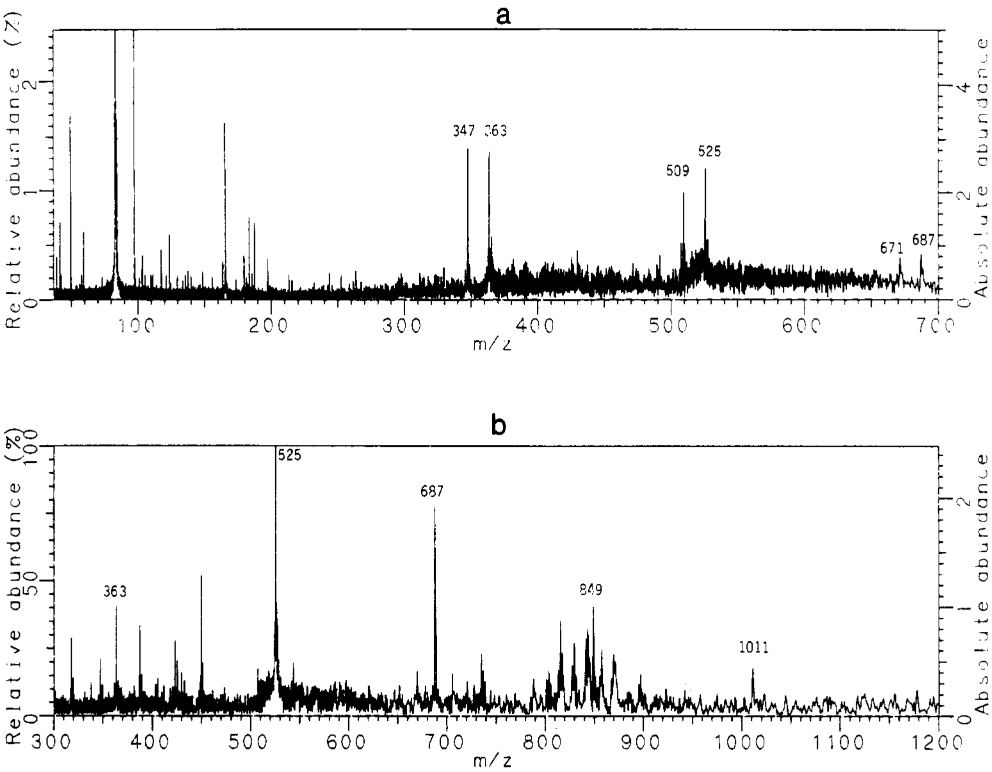


Figure 11. Mass spectra of chemically prepared poly(2-methylimidazole): (a) sodium ion and potassium ion attached; (b) KCl added.

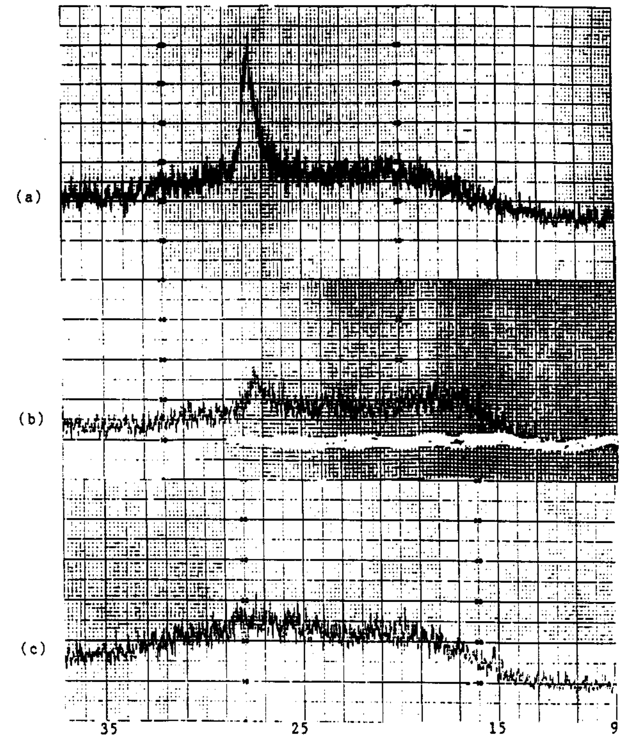


Figure 12. X-ray diffraction spectra of (a) polyimidazole, (b) poly(2-methylimidazole), and (c) poly(benzimidazole).

(7) Fragmentation patterns and hydrogen loss observed in the LDMS of these polymers suggest that electrochemical and chemical polymerization occur by different mechanisms.

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References and Notes

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