clearly from our living polymerization of vinyl ethers in nonpolar solvents.

The present study has provided the first direct spectroscopic evidence for the propagation reaction involving the activation of a covalent species in "cationic" polymerization of vinyl compounds, and this mechanism is of key importance for the formation of perfect living polymers. As we previously pointed out,[23] covalent species per se are not capable of polymerizing monomers, but they can react electrophilically with a carbon–carbon double bond when activated (e.g., by iodine) or when highly nucleophilic monomers are employed.[25] Therefore, this work has accounted for the longstanding apparent contradiction between the pseudocationic theory[21,22] and our experimental results on the styrene polymerization by trifluoroacetic acid.[23]

Registry No. 1, 95314-34-4; 3, 95314-33-3; HI, 10034-85-2; I_2, 7553-56-2; IBVE, 109-53-5.

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Two-Step Synthesis of Alkyl- and Alkenylbenzoxazole Polymers

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ABSTRACT: The conversion of several commercial and new AB monomers to polyamides and polybenzoxazoles was carried out through a two-step process. The monomers include 3-hydroxy-4-aminobenzoic acid and its 4,3 isomer, the analogous derivative of phenylacetic acid, 3-hydroxy-4-aminocinnamic acid and its isomer, and the two hydrocinnamic acid derivatives with HO and NH_2 in the 3- and 4-positions. Treatment of these monomers with a triphenylphosphine reaction mixture led to formation of polyamides containing hydroxyl substituents on the aromatic rings of the backbones. These polymers were characterized by IR, ^{13}C NMR, and TGA. Thermal cyclization of the polyamides gave the corresponding polybenzoxazoles in excellent yields and with viscosities up to 2.1 dL/g. IR was used to monitor the dehydration process and to characterize the polybenzoxazoles. TGA data for these polyheteroaromatics indicate reasonable thermal stability for the all-aromatic polymers as well as those containing alkene and a single methylene group in the polymer backbone. The two polymers containing CH_2CH_2 backbone units displayed catastrophic weight loss over a very narrow temperature range. This behavior is attributed, in part, to a thermal unzipping of the polymer backbone. Carbon NMR data are presented on new monomers and polyamides.

Introduction

Polymers with heteroaromatic repeat units have been known for many years to exhibit good thermal and oxidative stability. Polybenzimidazoles,[1] polybenzothiazoles,[2] and polybenzoxazoles[3] were first reported in the late 1950s and early 1960s and have since been under widespread investigation. Both AA–BB and AB monomer systems have been employed in the synthesis of high molecular weight polymers.[4] The thermal stability in nitrogen atmosphere of the completely aromatic AB polymers prepared from the various 3,4-disubstituted benzoic acid derivatives reportedly decreased in the order benzimidazole > benzothiazole > benzoxazole.[4] In air, however, the reported order of stability for AA–BB polymers was benzo-

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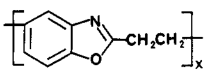
thiazole > benzoxazole > benzimidazole.[5]

In addition to the all-aromatic AB polymers, which are infusible and generally insoluble,[6] several polymers which contain alkyl chains have been described. The earliest such benzoxazole polymers were prepared from the ω-(3-amino-4-hydroxyphenyl) derivatives of propionic acid, 3-methylbutyric acid, and 5-methylhexanoic acid.[7] Thermal polymerization of the propionic acid monomer under nitrogen atmosphere with gradual temperature increase from 195 to 285 °C gave a polymer 1 which was molded at 400 °C into films. The films swelled slightly in concentrated sulfuric acid but were unaffected by other solvents.



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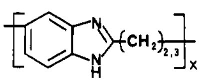

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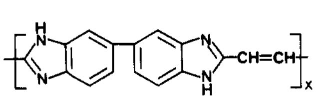

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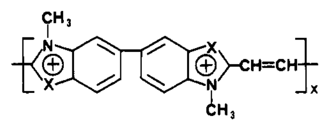

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Two benzimidazole AB polymers with ethylene[8] and trimethylene[9] chains attached at the 2- and 5-positions (2) have been described. These were obtained from, respectively, 3-(3,4-diaminophenyl)propanoic acid and 4-(3,4-diaminophenyl)butanoic acid and their various salts and esters. Thermal melt and solid-state polymerizations were used in both cases to give polymers with a maximum viscosity of 0.45 dL/g. Attempts to further increase molecular weights gave insoluble products. Several AA–BB polybenzimidazoles containing backbone methylene chains have also been synthesized, and studies reported of their thermal degradation,[10] crystallinity,[11] and electrical properties.[12]

Benzimidazole and benzothiazole polymers have been described which contain backbone unsaturation in the form of alkene chains conjugated to the heteroaromatic rings. These polymers were all obtained with AA–BB monomer systems. The earliest report employed melt polymerization with maleic anhydride to give low molecular weight products.[13] The polyphosphoric acid (PPA) method was later used with both fumaric[14] and maleic acid,[15] and 3,3′-diaminobenzidine to give a polymer with structure 3. A low viscosity was reported for the former, but the latter gave an intrinsic viscosity of 0.79 dL/g. Copolymerization of terephthalic acid with fumaric acid somewhat increased the viscosity values from 0.10 to 0.16 dL/g with a 2:1 diacid ratio[14] although at a 4:1 ratio it jumped to 0.60 dL/g. Similar copolymerization with maleic acid, however, actually led to a decrease in viscosity compared to the homopolymer.

A novel application of the Knoevenagel reaction led to both benzimidazolium[16] and benzothiazolium containing[17] polymers with backbone alkene groups (4). Starting monomers were 2,2′-dimethylbis(heteroaromatics) and various dialdehydes. Yields were generally low and the highly colored polymers obtained were insoluble. Characterization involved thermal analysis and conductivity measurements.

We have recently been involved in examining new AB polyheteroaromatic systems containing benzimidazole and benzoxazole units in the polymer backbone along with alkyl and alkenyl groups. A preliminary report on the polybenzoxazoles[18] was followed by an extended description of the monomer and polymer synthetic procedures.[19] We have now further characterized the monomers and polymers with IR and NMR spectroscopy. The thermal cyclization process from the hydroxy-substituted polyamides to the polybenzoxazoles has been examined in detail with IR and TGA. Finally, the thermal stabilities of the polybenzoxazoles which had been characterized by viscosity and spectroscopy were determined and compared to the parent polymers obtained from benzoic acid derivatives.

Experimental Section

The starting materials *p*-hydroxybenzaldehyde, 3-hydroxy-4-nitrobenzaldehyde, and *p*-hydroxyphenylacetic acid were purchased from Aldrich Chemical Co. and used as received. The monomers 3-amino-4-hydroxybenzoic acid and 4-amino-3-hydroxybenzoic acid were purchased from Pfaltz and Bauer and used without purification. Other monomers were synthesized as previously described.[19] Reagent-grade pyridine was distilled over KOH under nitrogen. Hexachloroethane was sublimed 3 times. Other chemicals and solvents were reagent grade or purified prior to use. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 583-B. Proton nuclear magnetic resonance spectra were obtained on a Varian EM-390 with a Me_2SO-d_6–$CDCl_3$ mixture as solvent. Carbon NMR spectra were measured on a Varian CFT-20 or a JEOL FX-90Q in either Me_2SO-d_6 or *N*,*N*-dimethylacetamide (DMAc) as solvent. Chemical shifts were measured as ppm downfield from internal Me_4Si or calculated from solvent peak positions. Thermal gravimetric analysis (TGA) data were obtained on a Du Pont 900 thermal analyzer under a N_2 atmosphere at a heating rate of 10 °C/min. Microanalyses were performed by Galbraith Laboratories, Nashville, TN, and M-H-W Laboratories, Phoenix, AZ. Measured values for C, H, and N were within ±0.3% of calculated values for all new compounds. The inherent viscosities were measured in a Cannon-Ubbelohde viscometer at 30 ± 0.2 °C with 98% sulfuric acid unless otherwise indicated. A polymer concentration of 0.2 g/(100 mL) was used for all viscosity measurements.

General Polyamide Synthesis.[19] Monomer (4.0 mmol) and triphenylphosphine (4.8 mmol) were dissolved in 10 mL of pyridine. Hexachloroethane (6.0 mmol) was added in one portion to the rapidly stirring solution which immediately turned yellow to amber red in color depending on the monomer. Heat evolution and polymer precipitation occurred within 30 s. The mixture was stirred for 30 min more and 100 mL of CH_3OH was added. The solid polymer was collected by filtration, washed sequentially with 300 mL of H_2O and 200 mL of CH_3OH, and then dried in vacuo for 12 h.

Thermal Cyclization of Polyamides to Polybenzoxazoles. The polyamide (0.2–1.0 g) was placed in a polymerization tube under vacuum and then immersed in a preheated oil bath at 220–260 °C for times required for complete cyclization as monitored by IR spectroscopy.[19]

Solution Polymerization in Polyphosphoric Acid (PPA). The PPA (20.0 g) was placed in a 50-mL flask equipped with an inlet and outlet needle for nitrogen flow. The flask was heated under nitrogen to 160 °C for 3 h with stirring and then cooled to room temperature. The monomer (0.5 g) was then added and the solution heated under nitrogen to the required temperature and kept there for 3–10 h. The solution was then poured into 300 mL of CH_3OH or water with rapid stirring. The polymer was collected by filtration, stirred with dilute $NaHCO_3$ solution overnight, and then filtered again. The polymer was then washed with H_2O and CH_3OH and dried under vacuum at 100 °C for 10 h.

Polymerization in a Sealed Tube. The monomer (0.5 g) was placed in a polymerization tube and the tube kept under vacuum for several hours. It was then sealed, placed into a preheated oil bath at 200–270 °C (depending on structure), and kept at that temperature for 1–6 h. The tube was cooled and opened to remove the polymer. In case of incomplete cyclization, the polymer was washed with boiling methanol and heated under vacuum again at higher temperature until cyclization was complete.

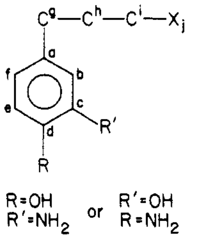
Results and Discussion

Monomer Synthesis and Characterization. 3,4-Di-

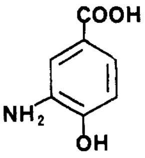
Table I
^{13}C Chemical Shifts (in ppm from Me_4Si) of Monomers[a]

monomer	a	b	c	d	e	f	g	h	i	j
7	125.97	114.38	136.47	143.04	115.6	117.5	40.75	173.46		
	126.9	116.7	134.7	140.9	117.6	120.2				
7a	125.34	115.52	136.67	143.29	115.53	117.52	40.24	172.39	51.64	
	128.0	116.7	134.7	140.7	117.6	120.2				
8	131.8	114.0	136.2	142.4	114.0	116.1	30.1	35.9	173.9	
	133.8	116.4	133.8	139.9	116.7	119.9				
8a	131.36	114.39	136.34	142.39	114.39	116.01	30.0	35.54	172.9	51.18
	134.3	116.4	133.8	139.9	116.7	119.9				
9	129.0	114.5	144.0	134.5	114.5	119.1	29.9	35.9	174.0	
	131.8	116.5	142.1	131.6	116.6	121.9				
10	125.8	114.4	137	146.9	114.4	118.7	145.8	112.8	168	
	128.0	116.9	133.3	143.7	116.2	120.4				
10a	125.63	114.4	137.11	147.25	114.14	119.09	145.85	112.93	167.18	51.22
	128.2	117.0	133.5	143.9	116.4	118.8				
11	122.3	113.0	143.9	140	112.4	122.4	145.3	113.7	168.2	
	126	117	141.6	135.4	116.1	122.4	145.3			
11a	121.96	113.46	143.73	140.74	113.04	122.69	145.91	110.72	167.35	51.05
	126.2	117.1	141.8	135.6	116.3	122.5				

[a] Top row: observed values. Bottom row: calculated values from substituent effects in Table II.



substituted cinnamic and hydrocinnamic acids (8–11) and their ester derivatives were prepared from the intermediate hydroxynitrocinnamic acids. The nitro intermediates were obtained in two steps from the appropriate hydroxybenzaldehyde according to literature methods applied to analogous compounds.[20,21] Details of the synthetic procedures, yields, and characterization data for all monomers were reported previously.[19] New compounds 8–11 gave acceptable elemental analysis values. Compounds 5 and 6 were available commercially. Monomer 7 was synthesized according to literature methods[22] and gave satisfactory melting point and spectral data.



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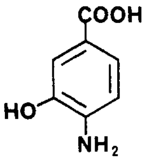

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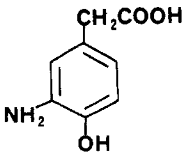

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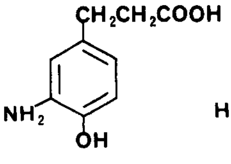

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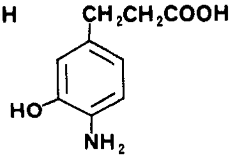

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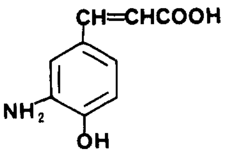

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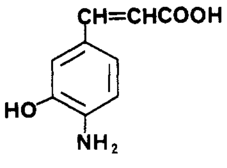

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Table II
^{13}C NMR Substituent Effects for Monosubstituted Benzenes Relative to 128.5 ppm

	position[a]			
substituent	C_1	ortho	meta	para
CH_2CH_2COOH	11.7	−0.2	0	−2.2
$CH_2CH_2COOCH_3$	12.2	−0.2	0	−2.2
CH_2COOH	4.8	0.1	0.98	−1.2
CH_2COOCH_3	5.9	0.3	0.9	−1.4
$CH{=}CHCOOH$	5.9	0.3	−0.5	1.6
$CH{=}CHCOOCH_3$	6.1	0.4	−0.3	1.8
NH_2	18.0	−13.3	0.9	−9.8
OH	26.9	−12.7	1.4	−7.3
$NHCOCH_3$	11.1	−9.9	0.2	−5.6
C_6H_5CONH	10.8	−7.9	−0.1	−4.19
$C_6H_5NHC{=}O$	6.8	−0.8	−0.3	2.7

[a] Chemical shift in ppm relative to C_6H_6 = 128.5 ppm, taken from ref 24 and 25.

The complete IR, ^1H NMR, and ^{13}C NMR spectra of all new compounds 8–11 and their methyl esters (except for 9) were obtained.[23] Table I lists the calculated (top line) and observed (bottom line) ^{13}C chemical shifts for monomers 7–11, **7a**, **8a**, **10a**, and **11a** (the **a** indicates methyl ester). Calculated values were obtained by summing the appropriate values for monosubstituted benzenes listed in Table II. Excellent agreement was observed (±2–3 ppm) for all but a few carbons. This agreement plus the splitting observed in off-resonance decoupled spectra for hydrogen-containing carbons confirms the assignments indicated.

Polyamide Synthesis. The overall goal for synthesis of the hydroxy-substituted polyamides involved their conversion to the corresponding polybenzoxazoles (Figure 1). The normal methods of formation of polybenzoxazoles employing thermal polymerization of acid or ester monomers in polymerization tubes and in polyphosphoric acid (PPA) did not work well with the new monomers 8–11. Insoluble or low molecular weight polymers were obtained in most cases as indicated in Table III, although the PPA procedure in our hands did give products for monomers 5 and 6 that were comparable to literature values.[6]

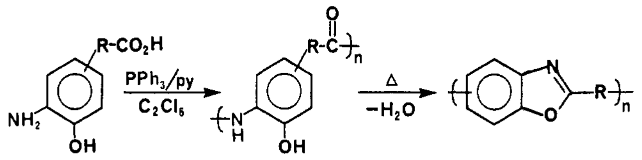


Figure 1. General two-step synthesis of polybenzoxazoles involving selective formation of hydroxy-substituted polyamide followed by thermal cyclization.

Table III
Inherent Viscosities at 30 °C for 0.2 g/dL in 98% H_2SO_4

	viscosity, dL/g			
monomer	polyamide	polybenzoxazole from polyamide	polymer made in sealed tube	polymer made in PPA
5	0.20	1.28		0.91[a]
6	0.18	1.20		0.86[b]
7	0.13	0.64	0.24	low
7a			0.18	
8	0.25	2.14	0.69	low
8a			0.24	
9	0.21	0.95	0.59	
10	0.14	0.55		
10a			insoluble	insoluble
11	0.49	0.59		
11a			insoluble	insoluble

[a] Previously reported values:[4,6] 0.72–2.21 from PPA; 1.04 from $SOCl_2$ + phenol two-step process. [b] Previously reported values:[4,6] 1.08–1.40 from PPA; 0.32 from $SOCl_2$ + phenol two-step process.

We are aware of only two other reports of synthesis of hydroxy-substituted polyamides from AB monomers such as those employed here. The first involved a two-step reaction of monomers **5** and **6** with $SOCl_2$ followed by treatment with phenol in pyridine.[4] A low-viscosity material was obtained for **5** which displayed both amide and ester bands in the IR. However, monomer **6** had reacted almost completely to the cyclized oligomer. These intermediates were thermally converted to polybenzoxazoles with inherent viscosities of 1.04 and 0.32 dL/g, respectively.

The second report only mentioned reaction of monomer **5** with triphenyl phosphite, pyridine, and LiCl dissolved in *N*-methylpyrrolidone as solvent.[26] The product polymer had an inherent viscosity of 0.1 dL/g at 0.5 g/dL in 5% LiCl-*N*,*N*-dimethylacetamide. The polyamide structure was indicated although no spectral evidence was given to substantiate lack of ester formation. The report indicated that viscosity values for all-para monomers (such as *p*-aminobenzoic acid) were much higher in the organic solvent than in H_2SO_4, the solvent used in our viscosity studies. Thus, their value of 0.1 dL/g probably corresponds to a lower molecular weight than we obtained for monomer **5** (0.2 dL/g at 0.2 g/dL concentration).

The synthetic procedure employed in our work was based on previously reported methods for synthesis of unsubstituted polyesters, polyamides, and polyureas.[26–30] Various acid-activating groups were examined including PCl_3, $POCl_3$, and diphenyl and triphenyl phosphites. We found that the system employing triphenylphosphine, hexachloroethane, and pyridine[27] was very mild and provided a high degree of selectivity for amide rather than ester bond formation during polymerization. This method was applied several times each to the monomers **5**–**11**.

Polyamide Characterization. In general, the viscosities of the polyamides obtained for the monomers studied (Table III) were not high despite the fact that polymer yields were close to quantitative in all cases. We attribute this to precipitation of the growing polymer chains early in the reaction due to insolubility in pyridine. Surprisingly, thermal treatment of these intermedate polymers led to excellent polybenzoxazole viscosities, which will be discussed in a later section. It would nonetheless be desirable to obtain hydroxy-substituted polyamides with higher viscosities and molecular weights to study their film and fiber-forming capabilities. Synthetic improvements are presently being investigated.

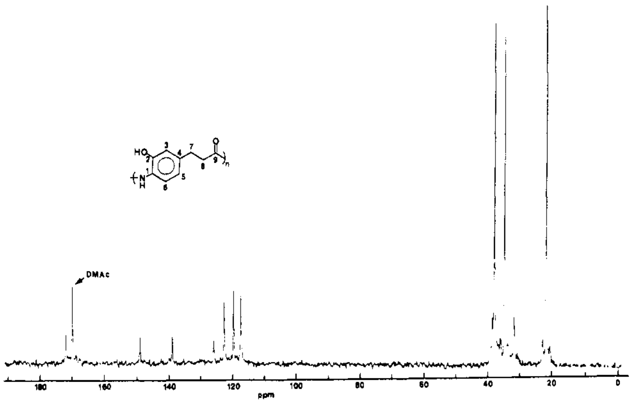


Figure 2. ^{13}C NMR spectrum of polyamide from **9** in DMAC with 6% LiCl.

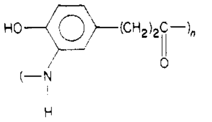
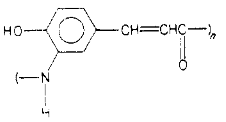
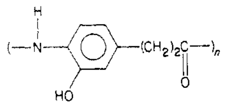
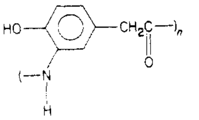
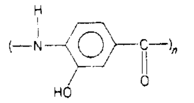
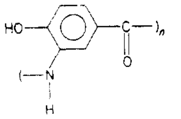
The IR spectra of the new saturated and unsaturated polyamides were consistent with model compounds and known analogues. All polyamides synthesized displayed amide I and amide II bands in the ranges 1640–1660 and 1510–1540 cm^{-1}, respectively. The conjugated-double-bond peaks of the unsaturated polyamides were shifted to ca. 1600 cm^{-1} and contributed to the strong aromatic peaks at that position. In addition, the intense peak at 810 cm^{-1} for these polymers is consistent with trans alkene units. The strong broad absorption centered at 3240 cm^{-1} and characteristic of the phenolic OH group was observed in all polyamides. Peaks associated with C–O, C–N, NH, and the 1,2,4-trisubstituted benzene structures were also evident in all spectra.

The most conclusive spectral evidence for the proposed polyamide structures, and especially for selective amide rather than ester formation, was provided by ^{13}C NMR. Most spectra were obtained with 6% LiCl in DMAc although DMF, Me_2SO, and H_2SO_4 were employed in some cases. All chemical shifts reported in Table IV are for the DMAc system. Spectra for polyamides from **8** and **10** were published previously[19] and that for **9** is given in Figure 2. The calculated chemical shifts in Table IV were obtained by summing substituent parameters in Table II and are all within ±3 ppm of the observed values. The most important observation concerning the spectra of all polyamides described here is that only one set of peaks was observed in each case. No ester carbonyl peaks nor duplication of peaks was found, clearly indicating formation of only amide linkages during polymerization.

Polyamide Cyclization. Thermal conversion of the hydroxy-substituted polyamides to the polybenzoxazoles was followed by both TGA under nitrogen and IR. Table V lists the TGA data for all polyamides. In all cases, two major thermal transitions were observed. The first began between 210 and 240 °C, corresponding to dehydration to the benzoxazole structures. The second began between 430 and 620 °C and involved polymer degradation and depolymerization.

The calculated values of weight loss for 1 equiv of water per repeat unit and measured values for the first transition are compared in Table V. Greater weight loss was observed in most cases than could be accounted for only by dehydration. Large-scale cyclization in vacuo led to iso-

Table IV
^{13}C Chemical Shifts (in ppm) of Hydroxy-Substituted Polyamides[a]

polymer	a	b	c	d	e	f	g	h	i
	131.8 133.6	121.7 119.8	126.8 126.9	146.5 143.3	116.5 116.0	124.5 124.0	30.9	38.3	171.6
	127.8 127.5	120.9 120.4	126.2 126.6	150.1 147.3	116.2 115.7	125.3 125.7	141.2	118.9	165.0
	138.1 137.1	116.5 115.4	148.2 145.5	125.0 124.7	118.8 120.0	121.7 121.2	30.9	37.8	171.4
	126.2 127.3	122.5 120.1	125.7 127.8	146.2 144.1	116.2 116.9	124.4 124.4	38.4	165.4	
	130.6 129.4	115.9 114.9	147.7 147.2	129.4 129.3	120.4 121.7	117.7 120.3	164.3		
	126.7 127.9	120.2 121.2	124.0 126.3	151.7 150.2	115.2 115.4	122.8 124.2	164.3		

[a] Top line: values of each entry were observed. Bottom line: values were calculated from substituent effects in Table II. Positions a–i same as in Table I.

Table V
TGA Data of Hydroxy-Substituted Polyamides[a]

polyamide from	1st transn, °C start	1st transn, °C end	wt loss during 1st transn, %	theo H_2O loss, %	2nd transn, °C start	2nd transn, °C end	wt loss during 2nd transn, %	temp between 2 transns, %	wt loss between 2 transns, %	compn at 1000 °C, wt %
5	240	390	18.75	13.3	620	800	24.4	230	0	48
6	230	470	20	13.3	600	800	25.6	200	1.25	40
7	220	320	17.5	12.08	430	700	28.8	110	1.25	46.9
8	220	330	11.25	11.04	460	550	40.6	130	1.25	41
9	210	340	11.4	11.04	460	570	36.9	120	6.25	40.6
10	230	380	16.3	11.18	430	780	31	50	1.9	40
11	240	380	12.5	11.18	430	780	31.9	50	1.0	39

[a] 10 °C/min under N_2.

lation of a white sublimate which was identified as triphenylphosphine oxide by IR, NMR, and melting point. This material may have been physically entrapped in the precipitating polymer during formation. However, large increase in polymer viscosities after cyclization and ^{13}C NMR observation of peaks in the polyamides other than those attributable to $Ph_3P{=}O$ suggests that phosphine–carboxylic acid adducts may have been formed at the polymer chain ends before precipitation but were unable to react further. Thermal treatment of these polyamides with active chain ends would thus have led to chain extension as well as benzoxazole formation.

The onset and duration of the two thermal transitions were found to depend strongly on the repeat unit structures. For the alkyl monomers **7–9**, both the onset temperatures and widths of the first transition were lower than for the parent compounds **5** and **6** and alkenyl species **10** and **11**. We attribute this to greater flexibility of the methylene-containing polymers which allows easier and more rapid intramolecular attack and chain reorganization. A more complex structural relationship was observed for the second transition, which will be described in the next section.

IR analysis of the thermal dehydration process was carried out for each polyamide to determine optimal temperature and time required for complete reaction. Figure 3 contains IR spectra taken before, during, and after cyclization of the polyamide from monomer **8**. Arrows pointing up indicate peaks which disappeared and those pointing down (just below the top spectrum) indicate new peaks. Complete loss of, e.g., the amide I and II peaks and the appearance of characteristic benzoxazole peaks[31] at 1608–1630 and 1244–1266 cm^{-1} confirm product structure and completeness of cyclization.

Polybenzoxazole Characterization. Viscosities for the product polybenzoxazoles are given in Table III along with those of the precursor polyamides. The significant increase observed on thermal treatment cannot be attributed entirely to formation of the more rigid heterocyclic units. Repeat units for the parent polyamides from **5** and **6** are fairly rigid before cyclization while those of the methylene-containing polybenzoxazoles possess flexibility in the repeat units comparable to that of the polyamides. In addition, the viscosities of the soluble polybenzoxazoles obtained in PPA were low for all monomers but **5** and **6** while the sealed-tube method gave significantly lower

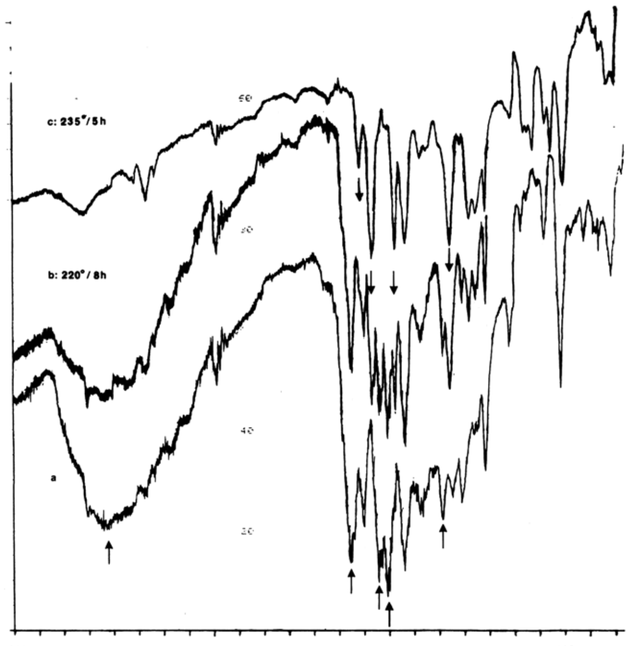


Figure 3. IR spectra of (a) polyamide from **8**, (b) partially cyclized polymer after 8 h at 220 °C, and (c) completely cyclized polybenzoxazole after 5 h more at 235 °C.

Table VI
Calculated and Observed Values for Chemical Composition of Polybenzoxazoles

polymer from monomer	composn, %					
	calcd			found		
	C	H	N	C	H	N
5	71.8	2.56	11.97	70.20	3.02	10.02
6	71.8	2.56	11.97	69.25	3.54	9.44
7	73.28	3.82	10.69	73.03	4.08	10.49
8	74.48	4.8	9.65	74.14	4.91	9.61
9	74.48	4.8	9.65	73.46	4.99	9.34
10	75.52	3.49	9.79	71.19	4.19	8.64
11	75.52	3.49	9.79	71.10	3.79	8.82

values than the two-step procedure. We conclude that the initial formation of polyamides is mild and selective and does not result in decarboxylation, degradation, or cross-linking, all of which have been observed for the more vigorous reactions examined. The intermediate polyamides retain activated carboxylic acid end groups after precipitation which, in thermal treatment under vacuum, lead to chain extension along with benzoxazole formation. The overall result is a high-yield synthesis of polybenzoxazoles with acceptable viscosities even when alkyl and alkenyl groups are present which can undergo side reactions under other conditions.

Table VI gives the elemental analyses of the various polybenzoxazoles obtained. Generally, carbon and nitrogen values were low while hydrogen values were high. Polymers from the alkyl-containing monomers **7–9** gave the closest agreement to calculated values. The direction of the differences between calculated and observed values suggests the presence of adsorbed and difficult-to-remove water. Support for this possibility comes from residual OH absorption at 3150 cm^{-1} in most of the polybenzoxazole IR spectra, and small weight losses observed between 200 and 450 °C in TGA scans.

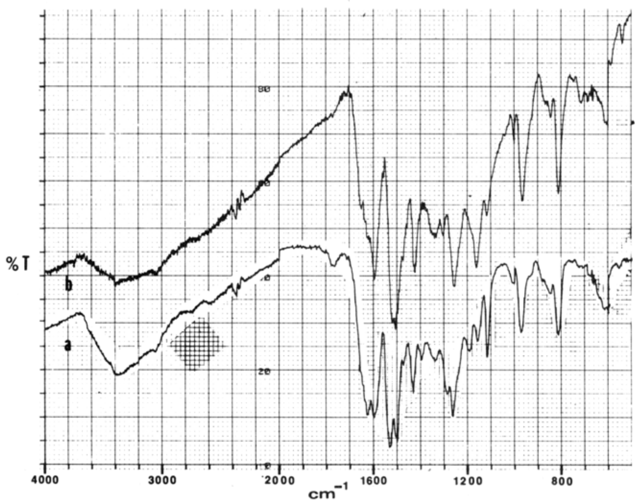


Figure 4. IR spectra of unsaturated polybenzoxazole from (a) monomer **10** and (b) monomer **11**.

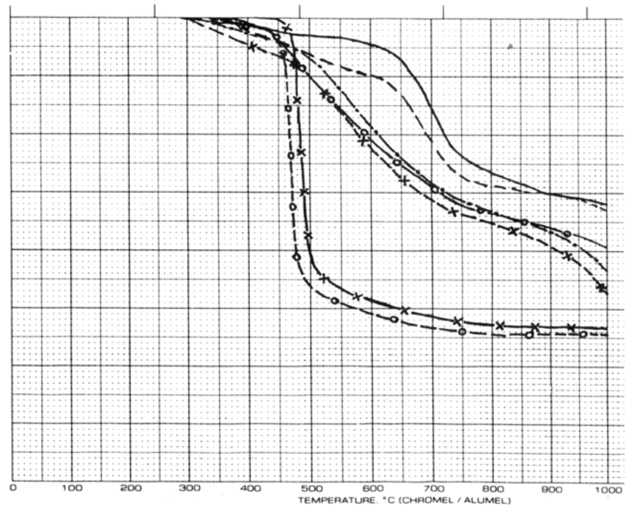


Figure 5. TGA plots for polybenzoxazoles from **5–11** with a heating rate of 10 °C/min under nitrogen: (—) **5**, (- - -) **6**, (—o—) **7**, (—×—) **8**, (- - -o- - -) **9**, (- - -×- - -) **10**, (—●—) **11**.

Additional characterization of the polybenzoxazoles involved IR spectroscopy and TGA. In general, characteristic benzoxazole bands[31] were observed at 1602–1630 and 1244–1266 cm^{-1}. The 1,2,4-substitution pattern on the benzene nucleus displayed the expected peak at 812–855 cm^{-1}. Conjugation in the polymers of monomers **10** and **11** led to the highest (1628–1630 and 1256–1266 cm^{-1}) and lowest (812–813 cm^{-1}) values in these respective ranges. Figure 4 gives the spectra of these two polymers and shows the additional alkene peaks at 965 (trans double bond) and 1600 cm^{-1}. This latter is somewhat weak even for a conjugated alkene and it may be that the two peaks at 1600 and 1628 cm^{-1} represent more complex combination bands of the C=N and C=C groups.

Figure 5 summarizes the TGA behavior of all of the polybenzoxazoles examined. As expected, the two parent compounds with all-aromatic backbones displayed the best thermal stability in terms of onset temperature for weight loss and percent weight retained at 1000 °C. The monomethylene polymer and the two alkenyl derivatives were similar in behavior, showing the lowest onset temperatures while retaining approximately 50% initial weight at 1000 °C. The weight lost below 500 °C for these three polymers could be due to adsorbed moisture, incomplete cyclization, or retained phosphine derivatives. However, their IR spectra indicate that further cyclization can account for only a small part of this weight loss region.

The thermal behavior of the two CH_2CH_2-containing polymers was the most unusual. Both isomers displayed essentially no weight loss below 450 °C in contrast to the other polybenzoxazoles. Apparently there were no retained or adsorbed byproducts and cyclization was complete. These conclusions are consistent with high molecular weight indicated by excellent viscosities for these polymers, especially for the polymer from 3-amino-4-hydroxyhydrocinnamic acid (**8**).

The most surprising observation for these two polymers was the catastrophic weight loss observed between 450 and 500 °C. Both the narrowness of the transition range (50 °C equals 5 min) and the amount of weight lost were remarkable, especially in comparison to the polymer containing a single backbone methylene group. We believe that these two species undergo a chain depolymerization that involves initial bond breaking followed by rapid radical unzipping. Thermolysis product identification and mechanistic studies of this process are currently under way.

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Acetylene–Carbon Monoxide Copolymers. Synthesis and Characterization

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ABSTRACT: Acetylene has been copolymerized with carbon monoxide to copolymers containing from 5 to 13 mol % of CO. Copolymer films were obtained at −78 °C with $\bar{M}_n \sim 4000$; only powdery products were formed at 25 °C with $\bar{M}_n \sim 1000$. The comonomer compositions in copolymers were determined by elemental analysis, radioassay of copolymers containing ^{14}CO monomer, and ^{13}C NMR. Carbonyl absorptions were observed by both IR and ^{13}C NMR. The copolymers have increasingly higher trans structure with the increase of CO content. TGA shows loss of CO at low temperatures. Pyrolysis GC-MS found CO, CO_2, H_2O, and CH_3CHO in addition to the previously observed products for polyacetylene. The copolymers are completely amorphous and are without the fibrillar morphology characteristics of polyacetylene. The CO units in the copolymers are easily protonated. The copolymers have undoped room-temperature conductivities, σ_{RT}, greater than the undoped *trans*-$[CH]_x$. Upon doping of the copolymers, their σ_{RT} increased greatly to within one-half to one-third of the values for similarly doped *trans*-$[CH]_x$.

Introduction

One of the structural requirements for a conducting polymer is an extended conjugated backbone. However, the question about the value of n for $-(CH{=}CH)_n-$ needed to exhibit electronic transport upon doping has not been seriously addressed. If carrier migration is mainly via the polymer backbone, then the value of n should be as large as possible. If the function of conjugation is to decrease the energy difference for the $\pi-\pi^*$ transition, i.e., the energy gap, then according to the Hückel molecular orbital theory $\Delta E = 4\beta \sin [\pi/2(n + 1)]$,[2] where β is the exchange integral. The values of ΔE for polyenes are independent of values of n for $n \geq 10$. Finally, an unpaired spin or a charge in $[CH]_x$, polyacetylene, is delocalized; the former was estimated from EPR line width[3] to have $n = 6$–8 and the latter was said[4] to have a domain width of ca. $n = 8$–10. However, in order to sustain a moving domain excitation, soliton, the conjugated backbone should have very large values of n. To elucidate the relationship between conjugation length and electrical conductivity, it will be in-

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