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Further Studies of the Structure of Poly(dihalophenylene oxides) Using Carbon Nuclear Magnetic Resonance Spectroscopy

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ABSTRACT: Decomposition of copper(II) trihalophenoxides in acetonitrile yields poly(dihalophenylene oxides) of lower molecular weight than previously available. The C NMR spectra of these polymers at 50 MHz indicate that earlier assignments, based on spectra of higher molecular weight polymers at 20 MHz, were incorrect. The new assignments are based on a polymer structure consisting of a 1,4-catenated backbone substituted in the ortho positions by trihalophenoxy groups. The density of substitution depends on the nature of the halogen leaving group. A bromine in the 4-position favors 1,4-catenation over *o*-phenoxylation in both 4-bromo-2,6-dichlorophenoxide- and 2,4,6-tribromophenoxide-derived polymers. In polymers derived from 2,4,6-trichloro- and 2-bromo-4,6-dichlorophenoxides 1,4-catenation and ortho substitution take place at roughly equal rates. The previously proposed mechanism for the polymerization reaction is modified to account for the new structure.

Introduction

In view of their structural and steric similarity to the commercially successful poly(2,6-dimethylphenylene oxide) it might be expected that poly(2,6-dihalophenylene oxides) would also exhibit useful mechanical properties together with exceptional oxidative stability.[1] Yet, despite the fact that poly(dihalophenylene oxides) have been known in various forms for over 60 years,[2–7] none has yet been prepared with sufficiently attractive physical properties to warrant commercial exploitation as a structural polymer.

For a number of years we have attempted to devise methods to synthesize poly(2,6-dichlorophenylene oxide) with a minimum of defects in the chain.[4,8] This goal has to a considerable degree been frustrated by the difficulty encountered in determining the detailed nature of the imperfections which occur in polymers of this kind. Some significant progress was achieved earlier by the application of ^{13}C FT NMR spectroscopy, but even this method gave equivocal results due to the generally poor quality of the spectra obtainable with the polymers and instrumentation available at the time.[9] More recently we have devised methods for synthesis of polymers of considerably lower molecular weight than previously available. Using these low molecular weight polymers together with more advanced instrumentation has allowed a considerable advance in our ability to make structural assignments. The results of these studies are the subject of the present paper.

Experimental Section

Synthesis of Polymers. All of the polymers used in the present work were prepared by stirring the appropriate copper(II) trihalophenoxide (10 g) in acetonitrile (250 mL) for about 1 h at room temperature. The resulting solid was filtered off and extracted with toluene to dissolve the polymer. The toluene extract was added dropwise to a large excess of methanol containing a few drops of concentrated HCl. After filtration, the polymer was reprecipitated three times and dried for 24 h at 100 °C in a vacuum oven. A list of the polymers together with chemical analyses and molecular weight data is given in Table I. The copper phenoxides were prepared by literature methods.[10]

Determination of Molecular Weights and Intrinsic Viscosities. Values for $\bar{M}_w$ for each of the polymers studied were determined at 25 °C in toluene. Measurements were carried out with a Chromatix KMX-6 low-angle laser light scattering instrument. Using standard polystyrene calibrants, we found that the instrument was able to reproduce molecular weights to within 6% in the relevant range. In all cases, the second virial coefficients were found to be close to zero for the dihalophenylene oxides.

Intrinsic viscosities were determined at 30 °C in toluene, using an Ubbelohde viscometer with a drop time of ca. 250 s for pure toluene.

Measurement of NMR Spectra. The spectra were measured in $CDCl_3$ solution at a concentration of ca. 20% by weight. The Varian XL-200 spectrometer was operated in the pulsed Fourier transform mode at 50.3088 MHz with a pulse angle of 90°, a repetition rate of 0.5 s, and a probe temperature of 25 °C. Decoupled spectra were measured with modulated square-wave proton decoupling with a modulation frequency of 200 Hz.

Chemical and Physical Properties of the Polymers. The chemical compositions of the low molecular weight polymers used in the present work are essentially identical with those obtained previously.[3,4,6] The analyses of the polymers derived from trichloro- and tribromophenoxides correspond closely to those of the poly(dihalophenylene oxides). That of the polymer from 4-bromo-2,6-dichlorophenoxide corresponds closely to a poly(dihalophenylene oxide) with a Cl:Br ratio of ca. 7:1 and that of the polymer from 2-bromo-4,6-dichlorophenoxide to a poly(dihalophenylene oxide) with a Cl:Br ratio of ca. 3:1.

The $\bar{M}_w$ and $[\eta]$ data in Table I have been combined with similar data for high molecular weight polymers to produce the Mark–Houwink plots shown in Figure 1 Contrary to our earlier conclusion,[9] the new data suggest that the lines for 4-bromo-2,6-dichloro- and trichlorophenoxide-derived polymers are not coincident. The best-fit parameters for the polymers were found to be $\alpha = 0.30$, $K = 1.96 \times 10^{-3}$ and $\alpha = 0.32$, $K = 2.32 \times 10^{-3}$, respectively.

^{13}C NMR Spectra of Polymers. All four polymers gave reasonable quality spectra with a relatively small number of scans (ca. 10 000 vs. ca. 40 000 for higher molecular weight materials at 20 MHz[9]) in both the proton-coupled and -decoupled modes. The spectra are shown in Figures 2–5 and the δ values for the various resonances are tabulated in Table II. The calculated δ values for the model structures in Table II were obtained from aryl carbon shielding parameters taken from literature tabulations.[11] The relevant parameters are listed in Table III.

Discussion

Assignment of Spectra. Polymers from 4-Bromo-2,6-dichlorophenoxide.

A high molecular weight polymer derived from 4-bromo-2,6-dichlorophenoxide had previously been observed to give unusually sharp and simple ^{1}H and ^{13}C spectra compared to other dichlorophenylene oxides.[9] In fact, the ^{13}C spectrum corresponded almost exactly to that expected for poly(2,6-dichloro-1,4-phenylene oxide), but the presence of substantial amounts of bromine in the polymer (by elemental analysis) belied this apparent simplicity. It was suspected that the lines due to 2,6-dichloro units were artifically exaggerated, relative to those of the units carrying bromine, by a large difference in line width. This suspicion is borne out by the spectrum of the low molecular weight polymer shown in Figure 2, where a new sharp line due to a carbon atom bearing a hydrogen is clearly evident at $\delta = 132$.

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Table I
Analysis and Molecular Weight Data of Polymers Used for NMR Study

parent phenol	$\overline{M}_w$	[η], dL/g	% C	% H	% Cl	% Br	% C
4-bromo-2,6-dichloro	15 150	0.051	41.85	1.18	35.6	11.55	
2,4,6-trichloro	14 930	0.035	45.15	1.30	43.47		10.00
2,4,6-tribromo	9 900	0.026	28.54	1.05		64.5	
2-bromo-4,6-dichloro	9 800	0.027	39.43	1.16	27.70	21.86	10.08

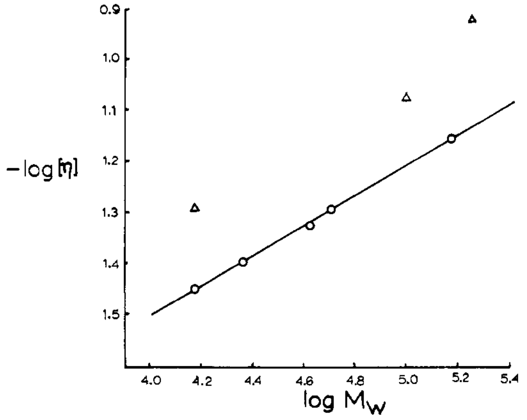


Figure 1. Mark–Houwink plots for the polymers obtained from 2,4,6-trichlorophenoxide (○) and 4-bromo-2,6-dichlorophenoxide (△).

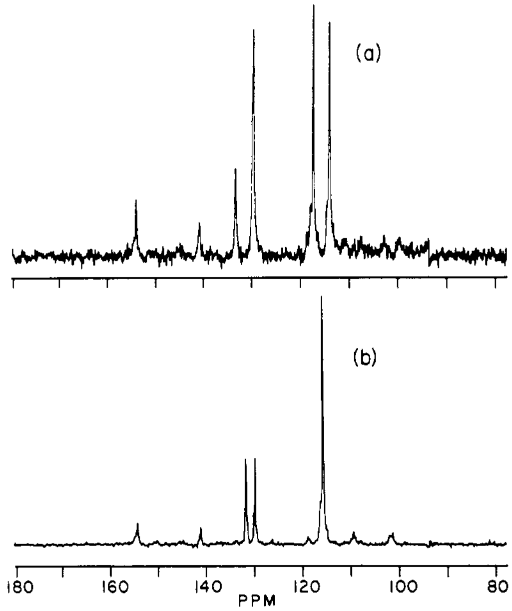


Figure 2. Proton-coupled (a) and -decoupled (b) spectra of polymer based on 4-bromo-2,6-dichlorophenoxide.

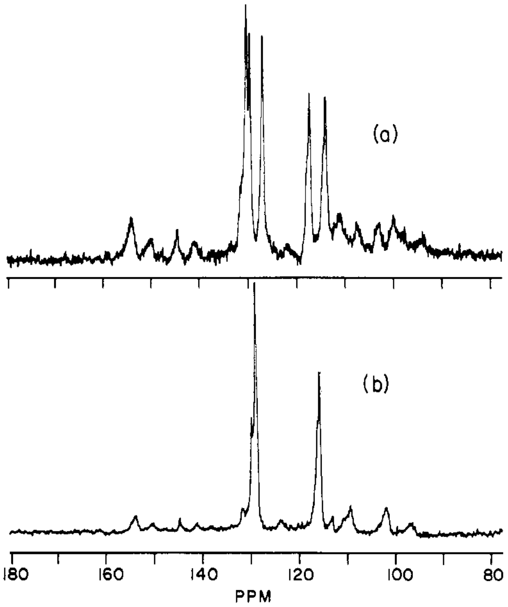


Figure 3. Proton-coupled (a) and -decoupled (b) spectra for polymer derived from 2,4,6-trichlorophenoxide.

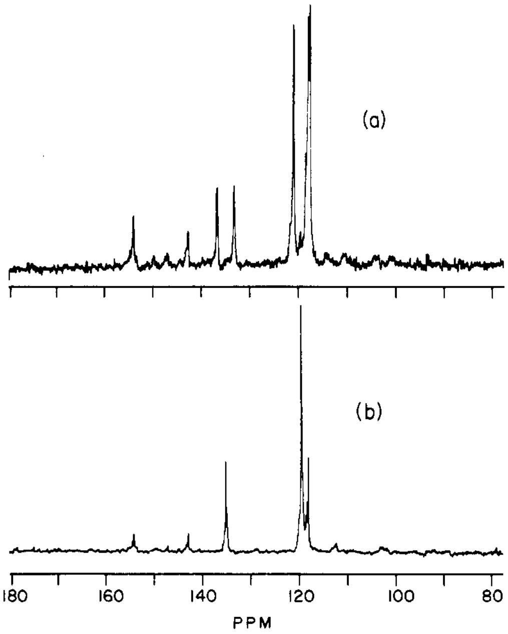


Figure 4. Proton-coupled (a) and -decoupled (b) spectra for polymer derived from 2,4,6-tribromophenoxide.

In earlier attempts to assign the spectra of these polymers[9] it was concluded that the major spectral features could be accounted for on the assumption that the polymers are largely copolymers of 1,4- and 1,2-coupled units, as represented in structures 2, 4, 6, and 8 of Table II. If such were the case, then the structure of the polymer from 4-bromo-2,6-dichlorophenoxide would on the average have 1,4- and 1,2-coupled units in the ratio of 3:1 to satisfy the analytically observed Cl:Br ratio of ca. 7:1. For reasons to be outlined at length below, we now favor an alternative model in which the analytical and spectral asperities are attributed to the presence of trihalophenoxyl substituents along the polymer backbone, such as represented in structures 1, 3, 5, and 7 of Table II.

In terms of peak positions, there is not a great deal of difference between the calculated values for the two models if it is allowed that the 1,4-/1,2-coupled copolymer contains some branches to account for the high-field resonances observed in all of the polymers ($\delta < 115$). These resonances, all due to carbons bearing hydrogen, can only be accounted for on the assumption that they are in rings carrying three or four phenoxyl substituents. The deviations of these resonances from calculated values are large, presumably due to the inadequacy of the unsubstituted phenoxyl shift parameter used in the calculation.

A close examination of the relative intensities of the lines of the proton-coupled spectrum in Figure 2 indicates that

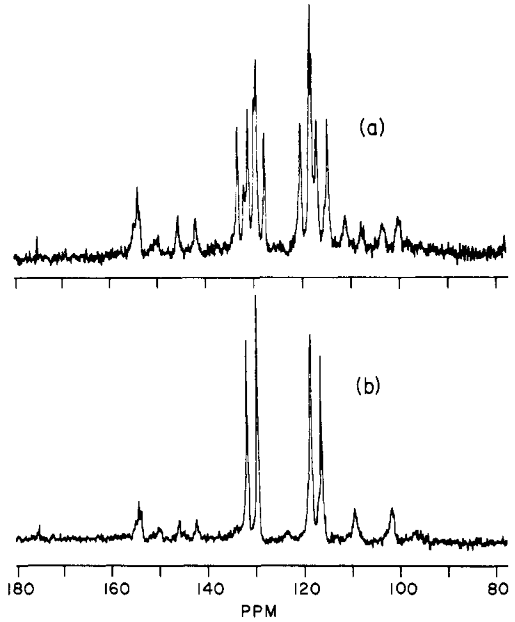


Figure 5. Proton-coupled (a) and -decoupled (b) spectra for polymer derived from 2-bromo-4,6-dichlorophenoxide.

structure 1 is more likely than 2. If structure 2 is assumed, the doublet at $\delta = 132.5$ must be assigned to the unique proton-bearing carbon atom C_7. This then requires that there be a similar doublet accidentally degenerate with the observed higher doublet at $\delta = 115.7$, due mainly to C_3. Since we require a 3:1 ratio of 1,4- to 1,2-coupled units, the lines supposedly due to C_9 and C_7 of structure 2 are anomalously intense. On the other hand, in structure 1, chemical analysis requires a 2:1 ratio of 1,4-coupled units to branch units and the ratio of C_2 to C_{13} is 2:1, which conforms reasonably well to the assignment of the $\delta = 132.5$ resonance to C_{13}. The assumption of structure 1 also provides a natural explanation for the resonances at $\delta =$ 103 and 111 at the intensity observed. It is also worth noting that the assignment of the $\delta = 132.5$ resonance of C_7 of structure 2 involves a substantial downfield discrepancy between calculated and observed values whereas in all other cases the discrepancy is upfield. A similar anomaly occurs for each polymer. Finally, it should be noted that there is no obvious resonance in Figure 1 that can be assigned to either C_{14} of 1 or C_8 of 2. It is not unreasonable that the very weak signal at $\delta = 118.7$ could be the missing signal, but why it is so weak is not clear.

The possibilities that the polymers may contain some 1,2-coupled units, some branches of degree of polymerization greater than unity, and/or some doubly branched units cannot be excluded on the basis of the present data, but it can be asserted with reasonable confidence that structure 1 represents the major features of the polymer.

Polymers from Trichlorophenoxide and Tribromophenoxide. By arguments similar to those developed above, it may be concluded that the polymers derived from trichlorophenoxide have structures best represented by **3**. The relative intensities of the peaks assigned to C_2 and C_{13} are now reversed compared to the polymer from the 4-bromophenoxide, to the extent that the branch units probably are more frequent than the 1,4-coupled units. Part of the reason for the high density of branch trichlorophenoxyl groups is the occurrence of significant double branching, as indicated by the very high-field resonance at 95 ppm, attributable to units carrying four phenoxyl substituents.

Except for the upfield shift of the resonances due to bromine-bearing relative to chlorine-bearing carbons, the spectrum of the polymer derived from tribromophenoxide shows a striking similarity to that of the polymer from 4-bromo-2,6-dichlorophenoxide and clearly indicates a significantly lower density of branched units relative to poly(dichlorophenylene oxide). The possible reason for this difference is discussed further below.

Polymer from 2-Bromo-4,6-dichlorophenoxide. The greater potential for structural variation and the great similarity of the calculated shifts for the various possible structural units make assignments for this polymer more equivocal than the others. Nevertheless, certain conclusions can be drawn with some confidence.

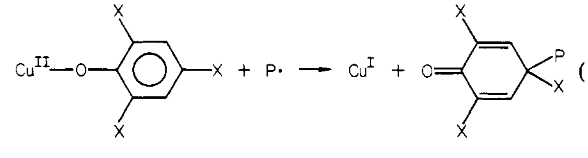
In the first place, the relatively intense resonances at ca. 102 and 110 ppm indicate the presence of a high abundance of branch units bearing three phenoxyl substituents. It is not possible to distinguish between such units bearing a single chlorine and those bearing a bromine since the resonances due to the carbons bearing halogen are expected to be degenerate with those of other halogen-bearing carbons.

Secondly, the resonances at 115–121 ppm conform closely to those expected for a 1,4-coupled unit and those at 128–134 ppm to a 2,4,6-trihalophenoxyl group. The relative intensities of the resonances in the proton-coupled spectrum indicate that these units are present in roughly equal amounts and in amounts not greatly different from that of the singly branched units.

Finally, a broad weak resonance at ca. 97 ppm is indicative of some doubly branched units, bearing four phenoxyl substituents.

Since the original intent of putting bromine in the 2-position was to promote 1,2-coupling, it is obviously important to consider the possibility of 1,2-coupled dichlorophenoxyl units in this polymer. The problem is the same as that alluded to earlier in the discussion of structure 1 vs. structure 2 in that the assignment of any observed resonance to C_9 of structure 8 requires the postulation of an anomolous discrepancy between observed and calculated shift values. It must be emphasized, however, that, given the large variations of line width encountered in these polymers, a resonance in the appropriate region might remain undetected due to excessive broadness. This point is of some importance since the presence of some 1,2-coupled dichlorophenoxyl units would help to restore the Cl:Br ratio to the experimentally determined value of ca. 3:1. Such a value is not possible if a significant number of 1,4-coupled units is present, but the dichloro units are not.

Mechanistic Implications of the Modified Structure. The structures now assigned to the poly(dihalophenylene oxides) are quite different from those previously assumed and the difference is such as to require a major modification of the mechanism previously proposed for the decomposition of (trihalophenoxy)copper(II) complexes.[8] The essential feature of the earlier mechanism was that propagation occurred by the rapid transfer of a phenoxyl ligand to an attacking polymer radical (P·) as in eq 1.

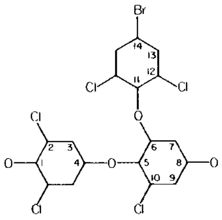
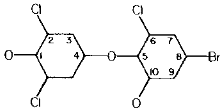
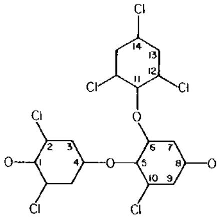
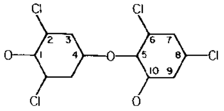
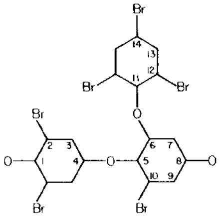
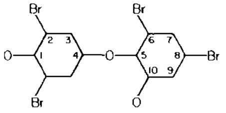


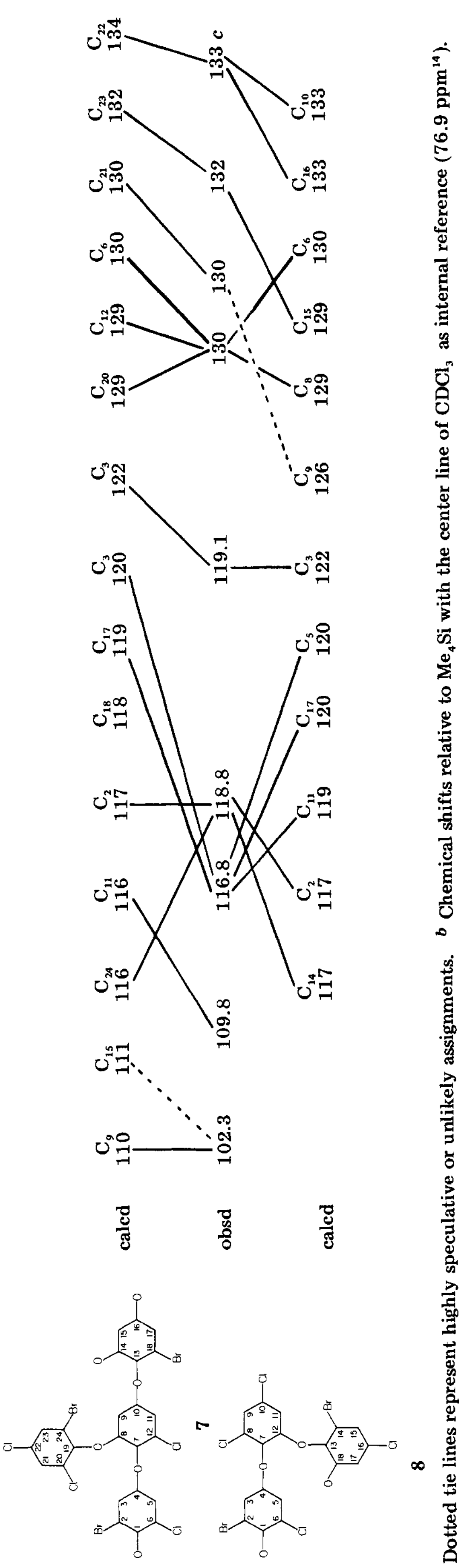
(1)

P· = polymer radical

Although this mechanism allows for attack at either the 2- or 4-position, and thus eventually 1,4- or 1,2-coupling, it does not permit branching. It was assumed earlier[8] that

Table II
Correlation Table for Observed and Calculated Chemical Shift Data[a,b]

structure	chemical shift, ppm														
	calcd	C_7 110	C_9 116	C_3 120	C_{14} 121	C_{12} 130	C_2 130	C_{10} 130	C_{13} 133	C_5 144	C_6 152	C_1 154	C_4 155	C_8 156	C_{11} 158
1	obsd	103	111	115.7	118.7	129.7	132.5	142	155						
 **2**	calcd	C_3 120	C_8 121	C_9 123	C_7 129	C_2 130	C_6 130	C_5 148	C_{10} 152	C_1 154	C_4 155				
	calcd	C_7 110	C_9 116	C_3 120	C_{14} 127	C_2 130	C_{10} 130	C_{13} 130	C_{12} 131	C_5 144	C_6 152	C_1 154	C_4 155	C_8 156	C_{11} 157
3	obsd	95	101	109	115.8	123	129	130.5	132	142	145	150	154.2		
 **4**	calcd	C_3 120	C_9 120	C_7 127	C_2 130	C_6 130	C_8 134	C_5 148	C_{10} 152	C_1 154	C_4 155				
	calcd	C_7 111	C_2 118	C_{10} 118	C_9 119	C_{12} 119	C_{14} 123	C_3 124	C_{13} 136	C_5 148	C_6 154	C_4 157	C_8 157	C_1 160	C_{11} 164
5	obsd	104	114	118.5	119.8	135.6	143.4	147	150	154.5					
 **6**	calcd	C_2 118	C_6 118	C_8 122	C_3 124	C_7 124	C_9 132	C_5 152	C_{10} 153	C_4 157	C_1 160				



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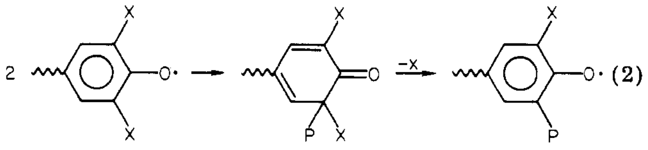
[a] Dotted tie lines represent highly speculative or unlikely assignments. [b] Chemical shifts relative to Me_4Si with the center line of $CDCl_3$ as internal reference (76.9 ppm[14]). [c] Values for oxygen-bound carbons omitted for clarity.

Table III
Chemical Shift Parameters for Calculated Chemical Shifts[a,b]

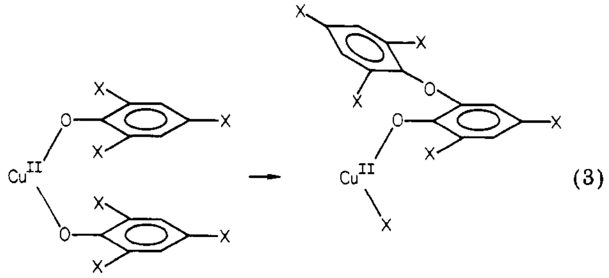
substituent	Δδ contribution C-1	ortho	meta	para
OPh	+29.2	−9.4	+1.6	−5.1
Cl	+6.4	+0.2	+1.0	−2.0
Br	−5.4	+3.3	+2.2	−1.0

[a] Data from ref 11. [b] The shift parameters are relative to $\delta^{C_6H_6} = 129$.

whatever branching occurred would arise through direct coupling of free polymeric radicals; thus



The high density of monomeric branches, postulated to explain the ^{13}C NMR spectra reported above, is not easily explained on the basis of such a mechanism. It is our belief that the presently observed structures and the mechanistic data reported earlier can only be reconciled on the assumption that ortho substitution by trihalophenoxyl groups and chain extension to poly(phenylene oxide) proceed by competing and independent mechanisms. An appealing mechanism is one where chain extension occurs by reaction 1 with a fairly high selectivity for attack at the 4-position, while ortho substitution occurs by an intramolecular process involving two adjacent phenoxyl ligands at a single copper center; thus



A reaction such as (3) might go in a concerted manner, or it might involve reductive elimination of an ortho-substituted cyclohexadienone to produce a Cu(0) species, followed by reoxidation of Cu(0) to Cu(I) by halogen atom abstraction and to Cu(II) by phenoxyl radical capture. The known structural features of bis(phenoxy)copper(II) complexes, particularly the close stacking of the phenoxyl groups[12] and the proximity of the *o*-chlorine atoms of the phenoxy ligand to the copper,[13] are particularly suggestive of the concerted reaction possibility.

That reaction 1 should show high regioselectivity for the 4-position is not surprising in view of the steric encumbrance of the 2-positions in the bis(phenoxo)copper(II) complexes.

On the basis of the above model, all of the observed structural details of the four polymers presently described can be rationalized. In the case of the 4-bromo-2,6-dichlorophenoxide-derived polymer chain, extension proceeds at roughly twice the rate of intramolecular coupling and the same is true for the tribromophenoxide-derived polymer. With the trichlorophenoxide-derived polymer the intramolecular coupling competes more favorably with chain extension, to the extent that the rates are more or less equal, and the same seems to be roughly true of the 2-bromo-4,6-dichlorophenoxide-derived polymer. All of this points to the fact that, while relative rates of (1) and (3) do not change greatly on substituting bromine for chlorine, reaction 1 is slightly favored by the presence of bromine in the 4-position.

If the above mechanism is correct, significant differences in structure should be observed between polymers produced by decomposition of copper complexes and polymers produced with classical free radical initiators. Some preliminary studies of poly(dibromophenylene oxide) show this to be the case. The results of that study will be published elsewhere.

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References and Notes

(1) Hay, A. S. *Polym. Eng. Sci.* **1976**, *16*, 1.
(2) Hunter, W. H.; Joyce, F. E. *J. Am. Chem. Soc.* **1917**, *39*, 2640.
(3) Blanshard, H. S.; Finkbeiner, H.; Russell, G. A. *J. Polym. Sci.* **1962**, *58*, 469.
(4) Carr, B. G.; Harrod, J. F.; van Gheluwe, P. *Macromolecules* **1973**, *6*, 498.
(5) Stamatoff, G. S. U.S. Patent 3 228 910, Jan 11, 1966.
(6) Tsuruya, S.; Yonezawa, T. *J. Catal.* **1975**, *36*, 48.
(7) Hedayatullah, M.; Denivelle, L. *C. R. Hebd. Seances Acad. Sci.* **1962**, *254*, 2369.
(8) Carr, B. G.; Harrod, J. F. *J. Am. Chem. Soc.* **1973**, *95*, 5707.
(9) Harrod, J. F.; van Gheluwe, P. *ACS Symp. Ser.* **1979**, *No. 104*, 52.
(10) Harrod, J. F. *Can. J. Chem.* **1969**, *47*, 637.
(11) Stothers, J. B. "Carbon-13 Spectroscopy"; Academic Press: New York, 1972; p 197.
(12) Vogt, L. H.; La Placa, S.; Bednowitz, A. 155th National Meeting of the American Chemical Society, Inorganic Division, San Francisco, May 1968; Abstr. No. 123.
(13) Bullock, J. I.; Dobson, R. J.; Povey, D. C. *J. Chem. Soc., Dalton Trans.* **1974**, 2037.
(14) Abraham, R. J.; Loftus, P. "Proton and Carbon-13 NMR Spectroscopy"; Heyden and Son: New York, 1978; p 10.

Observations by High-Resolution Carbon-13 Nuclear Magnetic Resonance of Cellulose I Related to Morphology and Crystal Structure

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ABSTRACT: High-resolution solid-phase ^{13}C NMR spectra were obtained on celluloses from cotton linters, ramie, hydrocellulose prepared from cotton linters, *Acetobacter xylinum*, and *Valonia ventricosa*. The spectra from cotton, ramie, and hydrocellulose are virtually identical. Peak positions for all peaks are the same for the cotton, *Acetobacter*, and *Valonia* celluloses although there are differences in resolution and in the intensity of two broad resonances attributed to C-4 and C-6. These differences are ascribed to differences in the morphology of the samples. The higher resolution obtained in the NMR spectra of *Acetobacter* and *Valonia* celluloses plus the improved resolution obtained at an applied field of 4.7 T relative to 1.4 T shows definite multiplicity in the resonances assigned to C-1 and C-4. It is argued that this multiplicity is higher than two and reflects the fact that there must be more than two anhydroglucose residues per unit cell in the crystal structure of cellulose I.

Introduction

Although there is no concensus regarding the structure and morphology of cellulose I, the majority of recent X-ray diffraction and computer modeling studies support a proposed structure with parallel cellulose chains.[1-5] Recent evidence for native cellulose is overwhelmingly in favor of elementary fibrils, 3.5 × 3.5 nm in cross section, which may aggregate into larger microfibrils.[6-13] The exact size and structure of the microfibrils found in nature is somewhat dependent upon the biological source of the cellulose and the electron microscopic techniques used to observe the microfibrils. Cotton microfibrils apparently range in size from 10 to 50 nm with an average around 25 nm, bacterial cellulose (*Acetobacter xylinum*) occurs in ribbonlike structures with an average crystallite size of 7 nm, and algal cellulose (*Valonia ventricosa*) is found in highly uniform coherent ribbons 10 × 20 nm in cross section.[11] Little detailed crystallographic or morphological information exists regarding bacterial cellulose but it is thought that one of the major differences between different celluloses lies in the perfection of the packing of elementary fibrils into microfibrils, with *Valonia* cellulose representing a high degree of regularity and order, cotton much less regularity and order,[11] and *Acetobacter* an intermediate degree of lateral order.[12] This regularity of *Valonia* cellulose is underscored by the fact that X-ray fiber diffraction is usually done on it.[1-4]

The solid-state NMR spectrum of cellulose has been reported in earlier publications.[14,15] In our earlier work we concluded that the various resonance regions showed rather uniform chain mobilities; thus we suggested that the morphology of the sample might affect the appearance of the NMR spectrum.[15] The work reported here supports this conclusion by comparing the solid-state NMR spectra of several morphologically different samples of cellulose I.

Experimental Section

Several preparations of cellulose will be discussed below. Cotton linters which were washed, bleached, and double cut (chemical cotton) were obtained from Hercules Chemical Co.[16] A sample of hydrocellulose was prepared from the chemical cotton by the methods of Rowland et al.,[17] which involved boiling the sample for 40 min in 2.5 M HCl. A sample of ramie was obtained from Fischer, Dottikon, Switzerland.[18] Algal cellulose was obtained