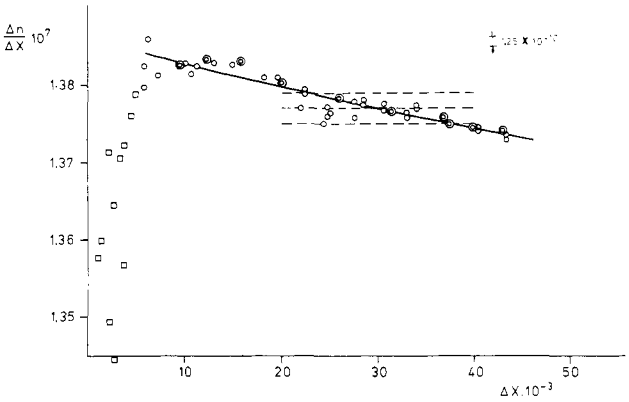

Figure 1. Calibration of the Chromatix KMX-16 refractometer, with NaCl solutions; Δn is the RI increment of a solution with respect to pure water calculated with (1) and ΔX is the difference between corrected instrument readings for solution and water. The drawn curve corresponds to (2) fitted to the experimental values for $\Delta X > 5000$ (○). The broken lines represent $k = (1.377 \pm 0.002) \times 10^{-7}$. Measurements at $\Delta X < 5000$ are also indicated (□).

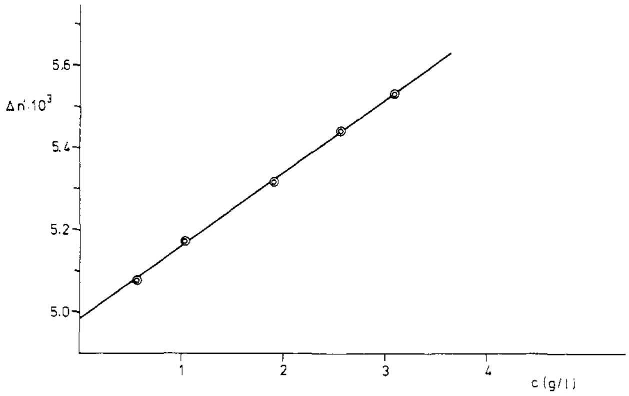

Figure 2. $\Delta n'$ vs. C_p for sodium poly(styrenesulfonate) ($M_w \simeq 10^6$ g mol^{-1}; Pressure Chemical Co.) in aqueous 0.5 M NaCl. The straight line obeys the equation $\Delta n' = (4.983 \pm 0.005) \times 10^{-3} + (0.179 \pm 0.003) \times 10^{-3}C_p$, with a standard deviation of 0.005×10^{-3} in $\Delta n'$. Here $36800 < \Delta X < 40200$ and the value k given in the text has been used.

with a standard deviation of 1.3×10^{-10} in the experimental values with respect to the least-squares curve. The value of $\Delta n/\Delta X$ decreases 0.7% from $\Delta X = 10000$ to $\Delta X = 45000$. In the range 20000–40000 the total variation is only half of that figure and here a constant $k = \Delta n/\Delta X = (1.377 \pm 0.002) \times 10^{-7}$ may be assumed. Values of Δn calculated from ΔX with this constant k do not differ by more than 0.2% from those obtained from (2) in the given range; generally the agreement is better.

It may therefore be concluded that the best results with the Chromatix KMX-16 will be obtained with ΔX values lying in the range of 10000–45000 and higher but with a *calibration equation* such as (2) or with ΔX values in a smaller range and $\Delta X > 10000$ (such as $20000 < \Delta X < 40000$) with a *calibration constant k*. For polyelectrolyte–electrolyte solutions measured against the polymer-free electrolyte solution as a reference the polymer concentrations satisfying these conditions may sometimes be too high to yield a satisfactory *limiting* value of the specific RI increment. With a given low C_p higher values of ΔX can be measured if *pure water* is used as a reference solvent instead of the electrolyte solution. The $\Delta n' \equiv n - n_0$ values of the different dialyzed polyelectrolyte solutions (of RI n) with respect to pure water (with RI n_0) thus obtained can be fitted by a least-squares procedure to a linear (or quadratic) equation in C_p. As the electrolyte solution in Donnan equilibrium with the polyelectrolyte–electrolyte solutions must have a RI increment Δn_s independent of C_p, it follows that

$$\Delta n' = \Delta n_s + (\Delta n/\Delta C_p)_{\mu_s}{}^{\circ}C_p + \ldots \qquad (3)$$

The intercept of the line thus yields Δn_s and the slope the specific RI increment of the polyelectrolyte–electrolyte system. An example of such a determination is given in Figure 2. This procedure has the additional advantage that through the use of higher ΔX values their relative accuracy is increased and, furthermore, the influence of small changes in the concentration of the reference electrolyte solution, e.g., by evaporation, manifesting itself by a nonnegligible intercept in a plot of $\Delta n \equiv n - n_s$ vs. C_p, can be eliminated.

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Comparison of the Structures of Poly(dibromophenylene oxides) Produced by Free Radical Initiation and by Decomposition of Copper Tribromophenoxide

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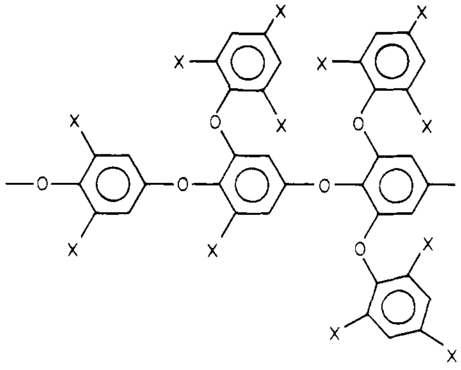
An earlier paper assigned the ^{13}C NMR spectra of a number of poly(dihalophenylene oxides).[1] On the basis of these assignments, it was concluded that the polymers consisted mainly of the structural units shown in 1.



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It was tentatively suggested that the high density of trihalophenoxyl substituents on the backbone could be the result of a specific intramolecular substitution process accompanying the propagation reaction during decomposition of the copper trihalophenoxide complexes, from which the polymers were synthesized. To test this hypothesis, a sample of poly(dibromophenylene oxide) was prepared by a free radical induced decomposition of alkaline, aqueous tribromophenol. The ^{13}C NMR spectrum of this polymer was compared with that of a polymer derived from decomposition of copper tribromophenoxide. If the high density of tribromophenoxyl substituents in the latter polymer arises from a specific, intramolecular substitution reaction within the coordination sphere of copper(II), its structure should differ substantially from that

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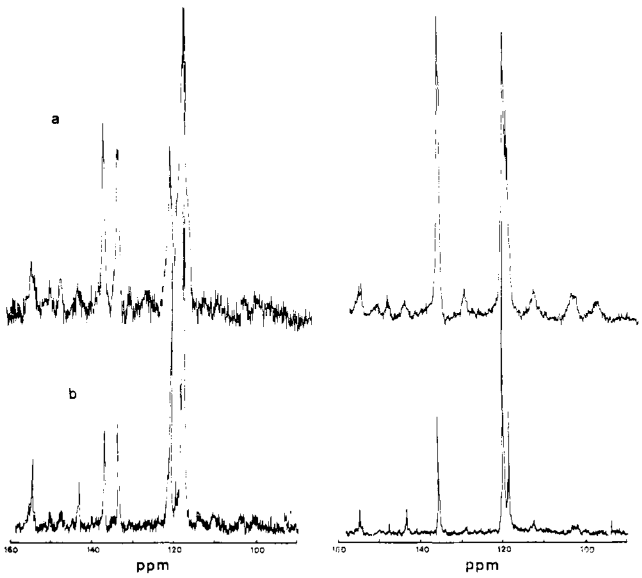
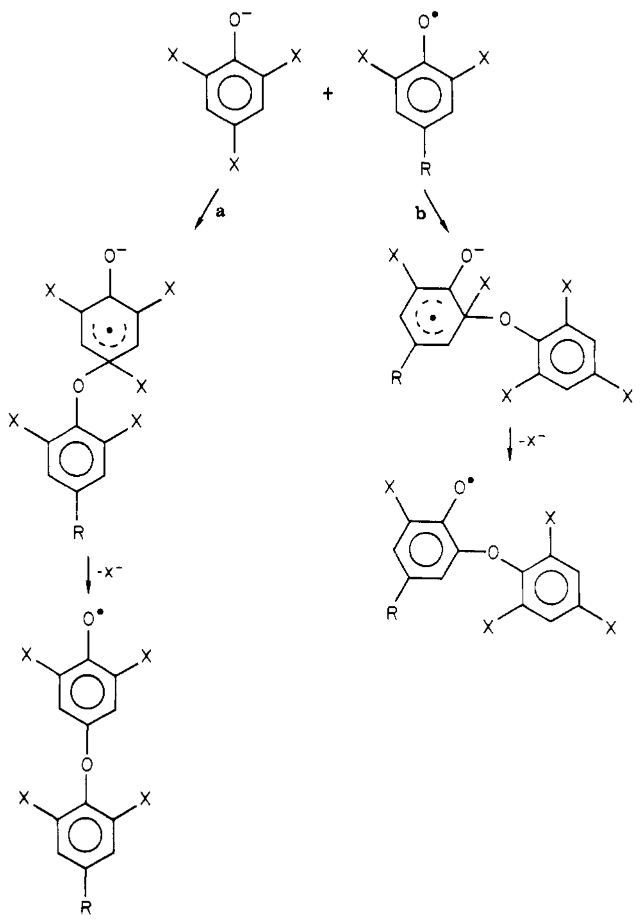


Figure 1. ^{13}C NMR spectra of poly(dibromophenylene oxides): (a) free radical polymerized; (b) copper phenoxide decomposition. Left-hand side, proton-coupled spectra; right-hand side, proton-decoupled spectra.

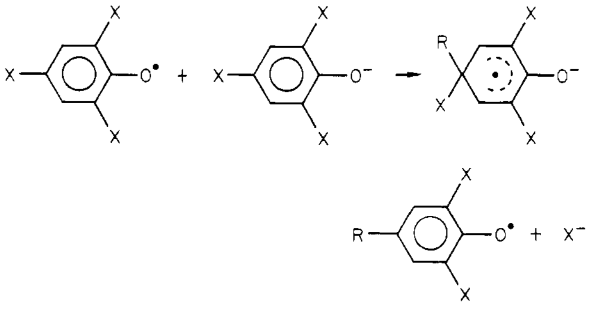
of a polymer formed under conditions where such a specific effect cannot occur.

As can be seen from Figure 1, the differences between the two samples are not very great. The slightly broader resonances of the free radical initiated polymer probably reflect a higher molecular weight. The enhanced resonances at 97, 104, and 112 ppm in the radical-initiated polymer are due to greater amounts of hydrogen-bearing carbon atoms in rings substituted with three and four oxygen substituents. The most important aspect of the spectra is, however, that the resonance at 135.6 ppm, due to the hydrogen-bearing carbons of tribromophenoxyl units, is even more intense in the radical-initiated polymer, relative to the resonance at 119.8 ppm, than in the copper phenoxide derived polymer. This observation indicates that the proportion of tribromophenoxyl units is higher in the free radical than in the copper phenoxide polymer. It is thus unnecessary to invoke a specific copper-related mechanism to explain the high return of trihalophenoxyl groups in these polymers. On the other hand, the genesis of structures of both polymers is now problematical.

Scheme I



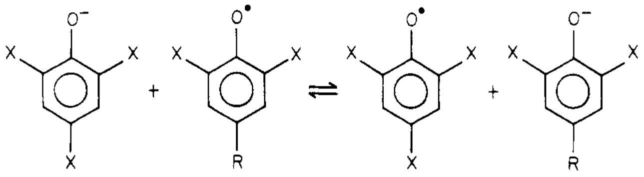
Although little is known for sure of the mechanism of radical-initiated halogen displacement of the kind under discussion, it is generally assumed that propagation occurs by attack of a phenoxyl radical on a phenolate ion.[2,3] If this hypothesis is correct, the polymer radical produced in a reaction such as (1) should attack a phenoxide ion in



(1)

R → trihalophenoxyl

either the ortho or para position to give polymer with extended branches, rather than monomeric branches. This dilemma is partially resolved by the assumption that polymer radicals are in rapid equilibrium with phenoxide ions by the electron-transfer process 2.[4] This leads to most



(2)

of the radicals being monomeric, since the mole fraction of monomer with respect to active end groups remains high for most of the reaction. The further assumption of a high regioselectivity for attack of phenoxyl radicals at the ortho position of phenoxide ions provides a complete explanation of the polymer structure. This assumption predicts the initial transformation of the starting monomer, trihalophenoxide, into new "monomers", the mono- and bis(trihalophenoxyl)-substituted phenoxides. The new monomers could then propagate in a 1,4-coupling reaction, according to (1). Unfortunately, while it successfully accounts for the polymer structure, this model fails to account for the observation that, in both the copper phenoxide and free radical reactions, relatively high molecular weight polymer appears early in the reaction and long before the trihalophenoxide is significantly depleted.

The central difficulty in explaining these results is to have a mechanism which only allows attack of ortho positions of a rapidly propagating polymer terminus by monomeric species, while at the same time only allowing the polymer end to attack monomer at the para position. A model that appears to satisfy these conditions is one that admits to two different halide-displacement mechanisms as depicted in Scheme I. Branch a of Scheme I represents an attack of a phenoxyl radical with high selectivity at the para position of a phenoxide ion, while branch b represents the attack of a phenoxide ion at the ortho position of a phenoxyl radical. It is not necessary to postulate high selectivity for the latter reaction since attack at the para position would also give products in agreement with experimental observation. The selectivity of branch a is necessary to explain the apparent absence of 1,2-enchainment. It is envisaged that propagation occurs rapidly by branches a and b simultaneously during the lifetime of a radical.

Given the differences between generation of phenoxide and phenoxyl radicals in aqueous alkali and in a copper complex in a low dielectric organic solvent (or even in a solid copper complex), it is quite remarkable that the polymer structures are so similar.

Experimental Section

The synthesis of poly(dibromophenylene oxide) by decomposition of copper tribromophenoxide in acetonitrile has been described previously.[1] The free radical polymerization of tribromophenoxide was effected by a modification of a procedure reported by Stamatoff.[5] To a solution of tribromophenol (3.3 g) in deaerated distilled water (100 mL) containing sodium hydroxide (0.4 g) was added potassium persulfate (0.1 g). The solution was stirred for 12 h and a further aliquot of initiator was added (0.1 g). After a further 12 h at room temperature the reaction mixture was heated to 80 °C for 1 h and then filtered. The resulting polymer was dried, redissolved in a few milliliters of toluene, and reprecipitated in a large excess of methanol containing a small amount of hydrazine. The resulting white polymer was filtered, washed with methanol, and dried in a vacuum oven overnight at 100 °C; yield 1.8 g (75%).

The ^{13}C NMR spectra were recorded for solutions in $CDCl_3$ (ca. 20% w/v) with a Varian XL-200 spectrometer. Operating conditions were the same as described previously.[1]

Acknowledgment. This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada.

References and Notes

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Comment on "Interpretation of the Excimer Kinetics of Poly(*N*-vinylcarbazole) and 1,3-Dicarbazolylpropane in Dilute Solutions" (*Macromolecules* 1981, *14*, 405)

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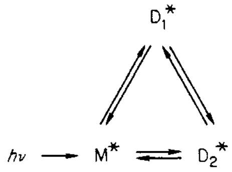
In a recent paper[1] time-resolved fluorescence measurements were reported for poly(*N*-vinylcarbazole) in solution. Results were interpreted in terms of a kinetic scheme, Scheme I, where M* represents an uncomplexed monomer carbazole chromophore, D_1* a high-energy excimer site emitting at λ_{max} 370 nm, and D_2* a sandwich excimer emitting at λ_{max} 420 nm. In this scheme it will be noted that only one high-energy excimer, D_1*, is postulated and that the low-energy D_2* is populated through both the high-energy excimer and directly from the monomer, with the latter being the favored route. Although structural difference between samples of poly(*N*-vinylcarbazole) prepared under nonidentical conditions may preclude exact comparison of fluorescence decay data, in the light of our own experiments on these systems, we wish to make the following comments upon this interpretation.

Scheme I



(a) The attributing of the component with a 60-ps decay as due to monomer M* in Scheme I is in agreement with the work of Ghiggino et al.[2] In our experiments we were not able to resolve this component.

(b) In the experiments of Ng and Guillet,[1] the analysis of the fluorescence decay recorded at 420 nm revealed a component with a lifetime of 60 ps with a negative preexponential factor, suggesting that the growth of the low-energy "sandwich" excimer was due to the decay of the monomeric species. This observation was said to explain the slow growing in of the low-energy emission band observed in time-resolved emission spectra reported previously.[3,5,6] Examination of these, however, reveals that little sandwich excimer fluorescence may be observed during the first few nanoseconds following excitation and, consequently, the main route to the formation of the sandwich excimer must involve a rise time considerably longer than the 60 ps suggested.[1] Indeed nanosecond rise times have already been reported by Tagawa et al.[4] (2 ns) and Roberts et al.[3] (2.6 ns). This rise time corresponds to the decay of a species emitting at 370 nm and is assigned to either a "relaxed monomeric" moiety[4] or a *third* excimer.[3] The conclusion reached by us was that the low-energy excimer was excited principally via this high-energy species and not from the directly excited monomer.

(c) It is necessary to consider why the rise times of 2[4] or 2.6 ns[3] clearly seen by us and other workers were not seen by Ng and Guillet.[1] We believe the choice of wavelength used to monitor the sandwich excimer fluorescence was unfortunate. At this wavelength the high-energy excimer also emits, and thus measured decays will not correspond purely to those of the sandwich excimer. The lifetime observed by Ng and Guillet in the range 2.3–3.0 ns has a small positive preexponential factor. We believe this is due to simultaneous observation of the *decay* of the component at 380 nm and the *rise* of the 420-nm component, leading to almost complete cancellation of *A* factors. In experiments performed in our laboratory, in order to measure decay parameters which were independent of the fluorescence wavelength, thus corresponding to the emission from solely the low-energy excimer, it was necessary to observe at wavelengths longer than 450 nm.

(d) We accept that the observation by Ng and Guillet of a negative preexponential factor for the 60-ps decay time in the emission at 420 nm indicates that the low-energy excimer *is* populated directly from the excited monomer, although in view of the above discussion we maintain this to be a minor process.

(e) Ng and Guillet presented no evidence for a second high-energy emitting species as observed by Roberts et al.[3]

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