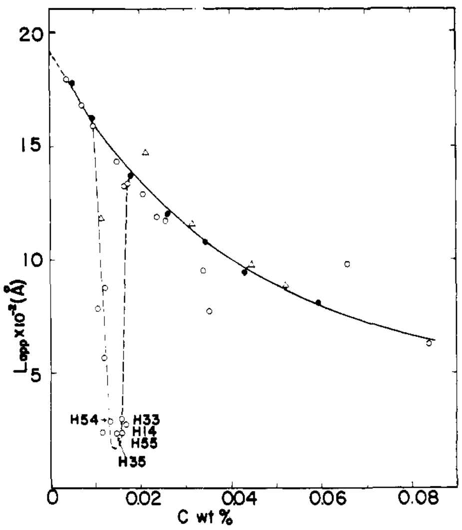

Figure 1. Plot of L_{app} vs. concentration for PS (TSK F-1500) in CCl_4 at 25 °C: (○) sealed samples prepared separately over a period of several months and measured at $\lambda_0 = 632.8$ nm; (●) solutions at various concentrations prepared by dilution and measured at $\lambda_0 = 632.8$ nm; (△) results from ref 10.

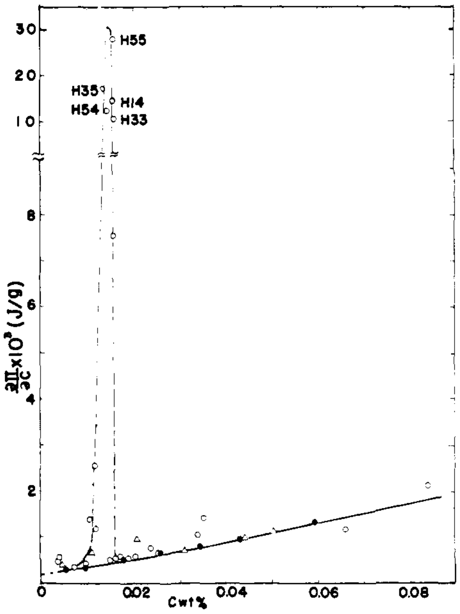

Figure 2. Plot of $(\partial\pi/\partial C)_{P,T}$ vs. concentration for two different methods of sample preparation at 25 °C: (○) sealed polymer solutions; (●) polymer solutions prepared by the dilution method; (△) results from ref 10. $\lambda_0 = 632.8$ nm.

we have to reexamine some of the accepted methods of polymer solution preparation. We must always be cautious with respect to possible gel formation, and freezing should surely be avoided.

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Measurement of the Specific Refractive Index Increment of Polyelectrolytes in Aqueous Salt Solutions with the Chromatix KMX-16 Differential Refractometer

M. MANDEL,* F. A. VARKEVISSER, and
C. J. BLOYS VAN TRESLONG

Department of Physical Chemistry, Gorlaeus Laboratories, University of Leiden, 2300 RA Leiden, The Netherlands.

Received August 26, 1981

The absolute value of the molar mass of polyelectrolytes can be determined from the Rayleigh light scattering intensity of their aqueous solutions with additional low molar mass electrolytes but an accurate value of the limiting specific refractive index increment at constant chemical potential of the electrolyte, $(\Delta n/\Delta C_p)_{\mu_s}{}^{\circ}$, is required.[1,2] Usually a series of polyelectrolyte solutions of different macromolecular concentrations C_p are equilibrated through a semipermeable membrane with the same electrolyte solution of equilibrium concentration C_s. This electrolyte solution is also used as the reference solvent for the measurement of the refractive index (RI) increment, Δn, in a differential refractometer. The manufacturer of the Chromatix KMX-16 laser differential refractometer recommends[3] for the determination of Δn to multiply ΔX, the difference between the corrected instrument reading for solution and solvent, by the instrumental constant k obtained from calibration with different NaCl solutions. The refractive index increments of those solutions with respect to pure water can be established through the accurate RI measurements of NaCl solutions by Kruis.[4] A linear relation between Δn and ΔX is a prerequisite for such a procedure. We have found that this linearity cannot be established over the total range of this refractometer, however, and therefore the specific RI increment of polyelectrolyte solutions should be determined in a slightly different way than usually performed.

We have used 33 different NaCl solutions (prepared from NaCl (Merck, Urtitersubstanz) dissolved in conductivity water) over a broad range of concentrations ($0.46 < C_s < 3.6$ g/100 g of H_2O) for the calibration of the refractometer. Some of the solutions were measured again after a few days. The Δn values were calculated from a cubic equation in C_s fitted to the data of Kruis (after interpolation to $\lambda_v = 633$ nm, the wavelength of the laser used) corresponding to seven different concentrations of NaCl ($0.33 < C_s < 6.9$ g/100 g of H_2O).

$$\Delta n/C_s = (1.735 \pm 0.002) \times 10^{-3} - (2.7 \pm 0.2) \times 10^{-5}C_s + (1 \pm 2) \times 10^{-6}C_s^2 \quad (1)$$

This equation differs from that given by Chromatix[3] as we did not use the two lowest NaCl concentrations measured by Kruis, the Δn of which may be less accurate. The difference between the two equations is not significant, however, and our least-squares fit turns out to be slightly better. The result of the calibration is shown in Figure 1, where $\Delta n/\Delta X$ is plotted against ΔX. In the same figure have also been represented the values of $\Delta n/\Delta X$ measured for several NaCl concentrations, $C_s < 0.4$ g/100 g of H_2O ($\Delta X < 5000$). It is clear that ΔX is *not* a linear function of Δn over the total range investigated. For $\Delta X < 5000$ the value of $\Delta n/\Delta X$ increases with ΔX, contrary to what is observed for $\Delta X > 5000$. The reproducibility for $\Delta X < 10000$ is poor. The data for $10000 < \Delta X < 45000$ could be fitted to a cubic equation in ΔX

$$\Delta n/\Delta X = (1.3858 \pm 0.0009) \times 10^{-7} - (3.2 \pm 0.8) \times 10^{-14}\Delta X + (8 \pm 15) \times 10^{-20}\Delta X^2 \quad (2)$$

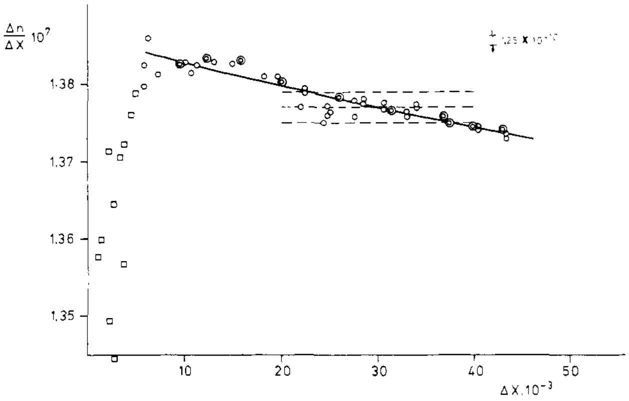

Figure 1. Calibration of the Chromatix KMX-16 refractometer, with NaCl solutions; Δn is the RI increment of a solution with respect to pure water calculated with (1) and ΔX is the difference between corrected instrument readings for solution and water. The drawn curve corresponds to (2) fitted to the 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 (□).

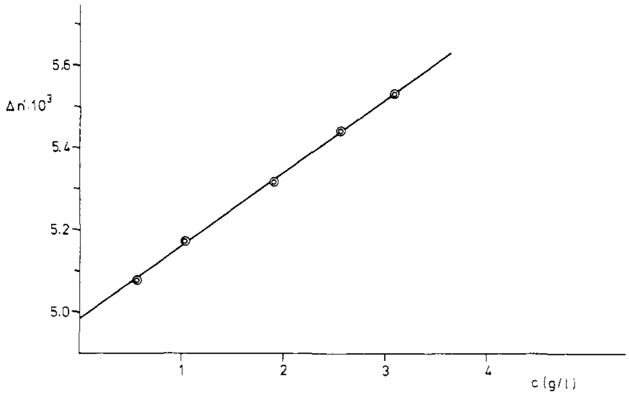

Figure 2. $\Delta n'$ vs. C_p for sodium poly(styrenesulfonate) ($M_w \simeq 10^6$ g mol^{-1}; Pressure Chemical Co.) in aqueous 0.5 M NaCl. The straight line obeys the equation $\Delta n' = (4.983 \pm 0.005) \times 10^{-3} + (0.179 \pm 0.003) \times 10^{-3}C_p$, with a standard deviation of 0.005×10^{-3} 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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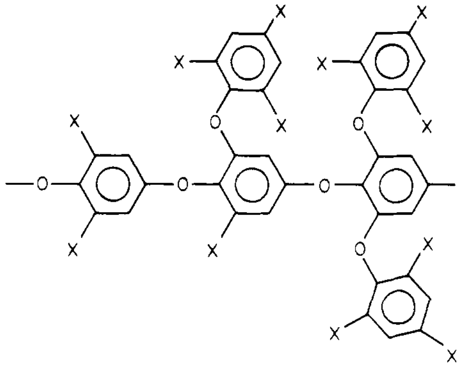
Comparison of the Structures of Poly(dibromophenylene oxides) Produced by Free Radical Initiation and by Decomposition of Copper Tribromophenoxide

JOHN F. HARROD* and ALAN SHAVER

Chemistry Department, McGill University, Montreal, Quebec, H3A 2K6 Canada. *Received October 21, 1981*

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.



1

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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