

Estimation of the effective conjugation length of oligo-*p*-phenylenes from specific refractive index increments of solutions

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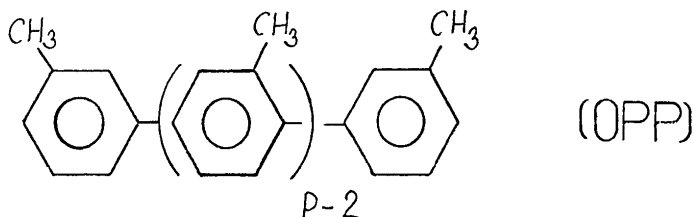
Summary

An unusually strong molecular weight dependence of the specific refractive index increment which has been reported for solutions of oligomers ($M < 10^3$) of *p*-2-methyl phenylene is attributed to the exaltation of polarizability of phenylene units. The saturation length is estimated to be $l_s \cong 6$ phenylene units.

Introduction

The specific refractive index increment ν of dilute polymer solutions is known (1) to depend on the molecular weight in the low-molecular weight region, usually below 10^4 . Bodman (2), Margerison et al. (3), and Lorimer and Jones (4) have interpreted this dependence as an end-group effect. As the proportion of chain repeating units to end groups increases, the specific refractive index increment approaches a limiting value. The effect is the larger the larger the difference in molar refractivities and molar volumes of end groups and chain repeating units.

An unusually strong molecular weight dependence has been observed with oligomers ($M < 10^3$) of *p*-2-methyl phenylene (OPP) (5) although the end groups and the repeating units have the same structure. The present note attributes this fact to the exaltation of polarizability of phenylene units, a typical property of molecules with conjugated bonds.



Results and discussion

Experimental ν values for OPP in cyclohexane and toluene (at 25 °C and wave length 546 nm) have been taken from the paper by Ziegler et al. (5) and have been completed by the values for high-molecular weight phenyl-substituted polyphenylenes (PPP, $M \times 10^4 = 1$ to 4) in benzene and tetrahydrofuran (6). They were converted to the specific refractivity R (according to Lorenz and Lorentz), the molar refractivity $[R]$ and the molar polarizability α , by means of the equations

$$R = (n_1^2 - 1) \cdot \bar{\nu}_2 / (n_1^2 + 2) + 6n_1 \nu / (n_1^2 + 2)^2 \quad (1)$$

$$[R] \equiv R \cdot M_0 P = (4/3) \pi \cdot N_A \cdot \alpha \quad (2)$$

where n_1 is the solvent refractive index, $\bar{\nu}_2$ is the partial specific polymer volume, M_0 is the molecular weight of the chain repeating unit, P is the number of repeating units in the polymer chain, and N_A is the Avogadro constant. The value of $\bar{\nu}_2 = 0,84 \text{ cm}^3/\text{g}$ (toluene at 25 °C) was taken from the paper by Claesson et al. (7).

The specific refractivities R were compared with the theoretical values R' calculated from the theoretical molar refractivities $[R']$ according to

$$R' = [R'] / M \quad (3)$$

The $[R']$ values were obtained as the sum of bond refractivities $[R']_i$ that make up the molecule

$$[R'] = \sum_i [R']_i \cdot m_i \quad (4)$$

where m_i is the number of bonds of type i in the molecule. The following values of $[R']_i$ were employed (8,9): 1.676, 1.296 and 2.688 for C-H, C-C (aliphatic) and C-C (aromatic), respectively.

In Fig. 1, specific refractivities R are plotted against the number P of phenylene units. The values for high-molecular weight PPP samples are assumed to be close to the limiting values (R_∞). The R values for solutions in toluene are higher than those for cyclohexane by about 3% at $P \leq 6$ and by 7% for $P = 8$. It is actually impossible to explain these differences as they may be due to solvent effects on the molecular refractivity or on the partial specific volume used in Eqn. (1) or to inaccuracy of experimental data.

Fig. 1 shows that, except of the dimer where $R'=R$, experimental values of R are higher than the calculated ones R' , the difference $R - R' \equiv \delta R$ increasing from $\delta R = 0$ at $P = 2$ to 0.06 at $P \rightarrow \infty$. To exclude the possibility that the increase in R is due to the molecular weight dependence of the partial specific volume, the values of $\bar{\nu}_2$ were calculated which would bring experimental and theoretical data in coincidence. They would decrease from $0.84 \text{ cm}^3/\text{g}$ (i.e., the experimental value for high-molecular weight polymers) to an improbably low value of $0.64 \text{ cm}^3/\text{g}$. It may be concluded that the strong molecular weight dependence of the specific refractive index increment is due neither to the end-group effect on R nor the chain length dependence of $\bar{\nu}_2$.

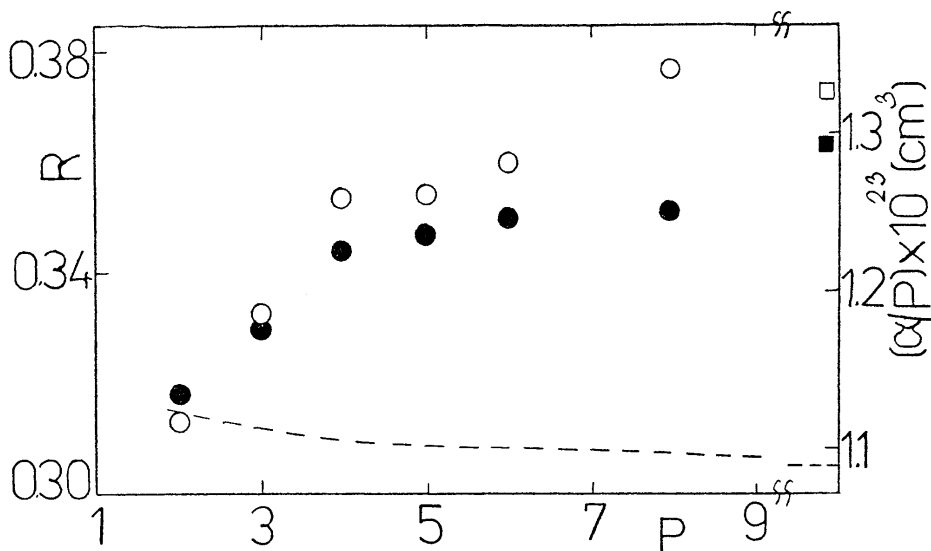


Figure 1. Values of R (left scale) and α/P (right scale) of OPP in dependence on the number P of phenylene units.

R values were calculated with Eqn. (1) from ν values for oligomers OPP (● cyclohexane, ○ toluene (5)) and for high-molecular-weight PPP (■ tetrahydrofuran, □ benzene (6)). Dotted curve was calculated from bond contributions to refractivity with Eqns. (3,4). Values of α/P were calculated with Eqn. (2).

The difference δR between experimental and calculated specific refractivities indicates exaltation, i.e., non-additivity of bond contributions to refractivity. Note that ν values for dilute solutions of derivatives of poly(thiophene), which considerably exceed those of usual polymers, were also attributed to exaltation of refractivity (10, 11).

Optical exaltation is assumed to be a consequence of increased polarizability of the electronic system forming the bonds (8). This is a typical property of compounds with π -conjugated bonds or groups where the propagation of an electrical influence is easily transmitted from one part of the molecule to another due to the presence of mobile electrons along the conjugated system (8).

Fig.1 also presents a plot of the values of α/P , i.e., the polarizability per phenylene unit. The dependence is asymptotic but approaches a constant value (saturation) already at $P \geq 6$ (saturation length, l_s).

Quantum mechanics shows that the polarizability is the component of the dipole moment (induced by incident light) that oscillates at the transition frequency corresponding to an excited state m . It is given (12) by the equation

$$\alpha = (2/\hbar) \sum_m \frac{\omega_{0m}}{\omega_{0m}^2 - \omega^2} |\langle \Psi_0 | \mu | \Psi_m \rangle|^2 \quad (5)$$

where \hbar is the Planck constant and $\langle \Psi_0 | \mu | \Psi_m \rangle$ is the dipole transition moment for state m . Hence, the polarizability is determined by the sum of all the dipole transition moments, each being weighted by the energy term. It can be seen that, at a fixed frequency of the incident light ω , this term increases with a decrease in ω_{0m} . In conjugated systems, the absorption maxima are displaced to longer frequency, the displacement being the higher the higher the number of conjugated bonds. Thus, the exaltation of polarizability and its increase with an increase in the number of conjugated bonds can qualitatively be explained.

Long ago, Gilham and Hey (13) found that (i) the frequency of UV absorption maxima of oligo(p-phenylene)s ($P=2$ to 7) decreased with increasing number P of phenylene units, (ii) the intensity of absorption increased in this series, and (iii) the extent of the displacement of the maxima decreased significantly with the lengthening of the chain. The chain length dependence of the frequency of absorption maxima was later confirmed theoretically by Dewar (14), and Murrell and Longuet-Higgins (15).

Item (iii) is in line with the results of quantum mechanical calculations showing that the frequency of absorption maxima should decrease asymptotically to a limiting value. While the facts sub (i) and (ii) belong to arguments supporting the conjugation of chain units in poly(p-phenylene)s (16-18), items (i) and (iii) may serve to qualitatively explain the exaltation of polarizability of OPP samples and its asymptotic dependence on the number of benzene rings.

The chain length dependence of electronic properties of conjugated polymer chains is well known (19-21). In such chains, the molecular polarizability increases with a high power (a=2-3) of the number of chain repeating units, and the polarizability per repeat unit (α / P) is an increasing function of the chain length. However, at some length (conjugation length l_c), the electrons of the chain are no longer correlated, so the polarizability per repeat unit approaches a constant value.

It is useful to compare the saturation length l_s estimated from Fig.1 with the values of effective conjugation length l_{eff} derived from other experiments. From a study of ESR revealing the existence of unpaired electrons in poly(p-phenylene)s, the conclusion was advanced that the unpaired electron is delocalized over 3-5 or 2-4 phenylene units (cf. 18). From fluorescence measurements of oligo(p-alkyl phenylene)s, Pasco and Baker (22) have recently assessed $l_{eff} = 4$ units with slight dependence on the size of the alkyl group (methyl to hexyl). Similar values (4-5 units) have been calculated theoretically for the delocalization of photogenerated radical cations (23-25). The l_{eff} values ($l_{eff} = 5$ to 7 units (26,27)) reported for poly(p-phenylene-vinylene), which differs from poly(p-phenylene) by vinyl groups interposed between phenylene rings, and for substituted poly(thiophene)s ($l_{eff} \approx 6$ units (28-31)), another member of the family of polymers with conjugated rings, are in the same range.

When comparing various characteristics of conjugation, the following facts should be taken into consideration: (i) As pointed out by Silbey (19), there is no firmly established connection between the conjugation length l_c (which is a measure of coplanarity of chain units) and the lengths at which various physical properties approach a constant value and, moreover, it is not clear whether there are not different conjugation lengths for different properties. In view of this, the results of experiments are expressed in terms of the saturation length l_s or the effective conjugation length l_{eff} rather than the conjugation length l_c . - (ii) The electronic properties of conjugated chains are affected by small chemical defects or structural differences (chains ends, cross-links, structural irregularities, substituents, rotation planarity, etc.). OPP chains discussed in this note were synthesized by a method which guarantees linearity and uniformity in both the molecular weight and structure. On the contrary, samples studied in some of other papers were prepared by polymerization techniques where some of the above defects could not be excluded with certainty. (iii) The accuracy of estimation of the conjugation characteristics is not high. This impedes a discussion of structural effects.

The effect of rotation on the conjugation length has been discussed by Rossi et al. (32), assuming the bond vectors to be parallel to each other and only rotations in a plane perpendicular to the direction of the chain to be allowed. The conformational conjugation length l_c , which is a measure of coplanarity of chain units, is related by the equation

$$l_c = \left(\ln \langle \cos 2\varphi \rangle \right)^{-1} \quad (6)$$

to the average rotation angle $\langle \varphi \rangle$ which depends on two components of the effective potential for torsional motions, viz., a „conjugation term“ and a „steric hindrance term“. The latter has origin in steric hindrance due, e.g., to substituents.

Molecular mechanics calculations (33) predict non-planar conformations for isolated poly(p-phenylene) with an energy minimum at a torsional angle of about 45° between the planes of phenylene rings and small barriers at 0° and 90° . As demonstrated (33) by ^{13}C -NMR, the torsion angle is decreased to 20 - 30° in solutions. The conformational conjugation length l_c calculated with the latter values and Eqn (6) would be 3.7 to 1.4 phenylene units. The $\langle \varphi \rangle$ values which would correspond to $l_c = 6$ and $l_{eff} = 4$ units are lower (16 and 17.5° , respectively).

When comparing the calculated and experimental results, the following factors cannot be neglected: (i) While the OPP samples have one methyl group per phenylene unit, calculations of l_c were done for unsubstituted rings. Molecular mechanics minimization performed with alkyl substituted biphenyls has shown that the position and length of alkyl groups have impact on the coplanarity of phenylene rings (34). (ii) There is an uncertainty in the form of the model rotation potential used by Rossi et al. (32). (iii) The effects of bending, waggings and stretching motions have been neglected in the theory. However, molecular mechanics calculations predict out-of-plane bending deformations occurring at the atoms at either end of the backbone single bond and resulting in nonplanar conformations (35). (iv) Solvent effects have not been considered.

In view of these limitations, the correspondence of experimental and theoretical characteristics of conjugation is fair.

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