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Kerr Constant of Dimethyl Terephthalate and Poly (Diethylene Glycol Terephthalate)

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SUMMARY

Electrical birefringence of Dimethyl Terephthalate(DMT) and Poly (Diethylene Glycol Terephthalate)(PDET) in p-dioxane solutions were measured at 20°C. The results were used to compute molar Kerr constants of both compounds at infinite dilution. The experimental results were $<{}_mK>= = 780$ and $<{}_mK>= -732$, both in units of 10^{-27} m^5 V^{-2} mol^{-1}, for DMT and PDET respectively. Theoretical analysis of $<{}_mK>$ of DMT indicates that the inductive effects that prevent the additivity of $\hat{\underset{\sim}{\alpha}}$ tensors of benzene and ester groups account for about 12% of the value of $<{}_mK>$. The $\hat{\underset{\sim}{\alpha}}$ tensor obtained for DMT was used, together with literature values of all the non optical parameters, to calculate $<{}_mK>/x$ of PDET according to the RIS model. The concordance between theoretical and experimental results of this magnitude is excellent.

INTRODUCTION

During the last years, the stress-optical behavior of many polymeric systems have been studied both theoretical and experimentally (STEIN et al. 1954; ISHIKAWA et al. 1969; LIBERMAN et al. 1971, 1974; LLORENTE et al. 1983; RIANDE et al. 1984; SAIZ et al. 1984). In most of the systems studied far, the experimental values of the optical configuration parameter Δa are substantially larger than the theoretical results obtained with the rotational isomeric state model (RIS); in some cases, the discrepancy amounts to even one order of magnitude.

The apparent inability of the RIS model for the interpretation of Δa may be due either to the non-additivity of the anisotropic part of the polarizability tensors $\hat{\underset{\sim}{\alpha}}_i$ of the repeating units along the chain, or to uncertainties in the parameters used, either in the optical (i.e. the $\hat{\underset{\sim}{\alpha}}_i$ tensors) or in the energetic (i.e. conformational energies) ones.

It is hard to believe in an intrinsic failure of the RIS model when it has succeded in the interpretation of many other conformation dependent properties, among others, the molar Kerr constant, whose calculation is formally identical to that of Δa (SAIZ et al. 1977; IRVINE et al. 1983), of a wide variety of polymeric systems. As with respect to the parameters used in the calculation, they offer the guarantee of reproducing experimental results of the systems studied, or at least of some model compounds.

The present paper tries to give some information on this topic. We have selected the Poly (Diethylene Glycol Terephthalate) (PDET), whose conformational statistics have been well determined (RIANDE 1977) and whose stress-optical behavior has been studied by some of us (RIANDE et al. 1984) finding that there is a noticeably discrepancy between theoretical and experimental values of Δa. We have performed experimental measurements of the molar Kerr constants, ${}_mK$ of PDET and Dimethyl Terephthalate (DMT) as model compound for a segment of the repeating unit of the polymer. The results of ${}_mK$ of the DMT molecule is used to optimize the $\underset{\sim}{\hat{\alpha}}_i$ tensors of the repeat unit of the PDET chain; these $\underset{\sim}{\hat{\alpha}}_i$ tensors are then used, together with the geometrical parameters used in the calculations of other magnitudes (RIANDE 1977 ; RIANDE et al. 1984) to calculate ${}_mK$ of the polymer according to the RIS model. A comparison between theoretical and experimental values of ${}_mK$ for this polymer will provide a good test for deciding whether or not the RIS model is applicable for the calculation of the $\underset{\sim}{\hat{\alpha}}$ tensor of a polymeric chain by addition of the contributions from the repeating units.

EXPERIMENTAL PART

a) Materials: The polymer PDET, was obtained and purified as explained elsewhere (RIANDE 1977); a sample having a number average molecular weigth (measured in a Hitachi vapor pressure osmometer) $\overline{M}_n = 11{,}700$ and a density of 1.31 gcm^{-1} at 20°C was used for this work. The model compound DMT, (Merck) had a purity over 99% and was used as received. The solvent p-dioxane (Panreac) was purified according to standard procedures (PERRIN et al. 1966) and stored over 4A molecular sieves (Merck).

b) Apparatus: The Kerr cell and experimental set up used for the present work is similar to those described (FLORY et al. 1981) with the only noteworthy modification of replacing the compensator by a quarter wave plate and a Faraday coil (BUCKINGHAM and SUTER 1976). A 5 mW He-Ne laser (SPECTRA-PHYSICS, model 120S) operating at $\lambda = 632.8$ nm was used as ligth source. Birefringences δ produced by electric fields E up to 3×10^6 Vm^{-1} were measured and the Kerr constants B of the measured liquids were evaluated as:

$$B = \delta / 2\pi l E^2 \qquad (1)$$

c) Results: Kerr constants B of neat p-dioxane and of DMT or PDET solutions in p-dioxane were obtained at room temperature (20 ± 1°C). A value of $B_o = 0.077 \times 10^{-14} mV^{-2}$ was obtained for pure p-dioxane; with this result and the values of B for the solutions, the increments $\Delta B = B - B_o$ were evaluated an the molar Kerr constant of the solutes were computed as (SAIZ et al. 1977; FLORY et al. 1981):

$$_mK = \frac{54\lambda n\{\lim_{m\to 0}(\Delta B/m) + V_s B_o\}}{(n^2+2)^2\ (\varepsilon+2)^2} \qquad (2)$$

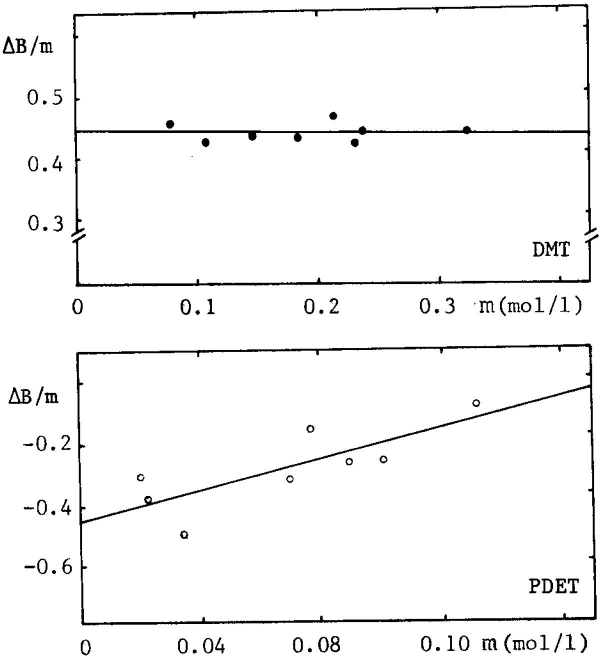

Fig. 1: Ratios of the diference $\Delta B = B - B_o$ to the molarity (in mol/l) plotted againts m for DMT and PDET.

Figure 1 shows the extrapolation of $\Delta B/m$ to $m \to 0$ for DMT and PDET respectively. Substitution of the intercepts of their corresponding straight lines into eq. 2 gave values of $_mK = 780$ and -732 in units of $10^{-27}\ m^5V^{-2}mol^{-1}$ for DMT and PDET respectively.

THEORETICAL ANALYSIS

a) Dimethyl Terephthalate (DMT)

The molar Kerr constant of a molecule in a given conformation, neglecting the contributions from hyperpolarizabilities (SUTER and FLORY 1977; FLORY et al. 1981), can be evaluated as:(*)

$$_mK = (2\pi N/15KT)\{(\vec{\mu}^T \hat{\underset{\sim}{\alpha}} \vec{\mu})/KT + |(\varepsilon-1)/(n^2-1)|\,\mathrm{Tr}(\hat{\underset{\sim}{\alpha}}\hat{\underset{\sim}{\alpha}})\} \qquad (3)$$

Eq. 3 has to be averaged over all the possible conformations of the molecule, in order to obtain $<_mK>$ which is directly comparable with the experimental results. This averaging is very simple to perform in the case of DMT since this molecule has only two stable conformations: the one shown in Fig. 2 that will be refered to as trans because of the relative orientation of

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(*) Molar Kerr constant defined by eq. 2 and 3 differ from those of LE FEVRE et al. (1972) by a factor of 9.

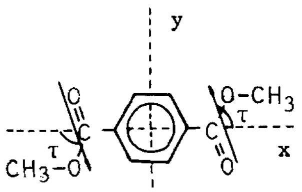

Fig. 2: The DMT molecule shown in its <u>trans</u> conformation.

the two ester groups, and the <u>cis</u> conformation obtained by rotation of 180° over one of the C-C* bonds. According to SAIZ et al. 1981, the <u>cis</u> orientation has an energy $E_\gamma = 0.05$ kcal mol^{-1} higher than <u>trans</u> which is mainly due to interactions between the dipole moments of both ester groups that are defined by $\mu_E = 1.89$ D with an orientation given by $\tau = 123 \pm 3°$.

The dipole moment of the two conformations of DMT refered to a coordinate systems like the one shown in Fig. 2 are:

$$\vec{\mu}^T(\underline{\text{trans}}) = (0,0,0) \quad \text{and} \quad \vec{\mu}^T(\underline{\text{cis}}) = (0,-2\mu_E \sin\tau, 0) \tag{4}$$

The molecule of DMT can be formally obtained by condensation of two molecules of methyl acetate with one of benzene, with elimination of two molecules of CH_4. Taking into account that the CH_4 molecule has spherical symmetry so that $\hat{\underset{\sim}{\alpha}}(CH_4) = 0$, the $\hat{\underset{\sim}{\alpha}}$ tensor of the DMT molecule in a given conformation assumed that all the tensors are expressed in the same coordinates system and representing by $\hat{\underset{\sim}{\alpha}}(E)$ the tensor of the Methyl acetate molecule, could be written as:

$$\hat{\underset{\sim}{\alpha}}(\text{DMT}) = \hat{\underset{\sim}{\alpha}}(\text{B}) + 2\hat{\underset{\sim}{\alpha}}(\text{E}) \tag{5}$$

Eq. 5 implies strict additivity of the $\hat{\underset{\sim}{\alpha}}$ tensors; however, it has been found (IRVINE et al. 1983) that this condition is not fulfilled when groups having large electron delocalization are involved. In these cases, there are inductive effects that could noticeably modify the $\hat{\underset{\sim}{\alpha}}$ tensors. We represent by $\underset{\sim}{\delta}$ the possible correction for the non additivity of tensors, and write:

$$\hat{\underset{\sim}{\alpha}}(\text{DMT}) = \hat{\underset{\sim}{\alpha}}(\text{B}) + 2\hat{\underset{\sim}{\alpha}}(\text{E}) + \underset{\sim}{\delta} \tag{6}$$

Substitution of the tensor $\hat{\underset{\sim}{\alpha}}(B)$ given by FLORY and SUTER (1977) and $\hat{\underset{\sim}{\alpha}}(E)$ of FLORY et al. (1981), together with the transformations required to write all the tensors in the coordinate system of Fig. 2, gives the tensors for the two conformations of the DMT molecule. These two tensors differ in the non diagonal terms; however, the incidence of these non diagonal terms in the value of $<_m K>$ of this molecule is c.a. 0.1% these terms may thus be neglected and, with this approximation:

$$\hat{\underset{\sim}{\alpha}}(\underline{\text{cis}}, \text{DMT}) = \hat{\underset{\sim}{\alpha}}(\underline{\text{trans}}, \text{DMT}) = (\Delta\alpha_{DMT} + \delta)\underset{\sim}{J} + (\Delta\alpha^+_{DMT} + \delta^+)\underset{\sim}{J}^+ \tag{7}$$

where $\Delta\alpha_{DMT} = \Delta\alpha_B + 2\Delta\alpha_E = 6.94$ Å^3; $\Delta\alpha^+_{DMT} = \Delta\alpha^+_B + 2\Delta\alpha^+_E = 5.42$ Å^3; $\underset{\sim}{J}$ and $\underset{\sim}{J}^+$ are diagonal matrices defined as $\underset{\sim}{J} = \text{diag}(2/3,-1/3,-1/3)$ and $\underset{\sim}{J}^+ = \text{diag}(0,1/2,-1/2)$.

Averaging of eq. 3 over the two conformations of DMT, with substitution of the numerical constants at T = 298K yields:

$$10^{27}\langle {}_mK\rangle = 6.935\ \{98.84\gamma\mu_E^2\sin^2\tau(\eta^+/2-\eta/3)/(1+\gamma) + 1.1(2\eta^2/3+\eta^{+2}/2)\} \qquad (8)$$

with $\gamma = \exp(-E_\gamma/RT)$, $\eta = \Delta\alpha_{DMT} + \delta$ and $\eta^+ = \Delta\alpha^+_{DMT} + \delta^+$; with μ_E in D and η, η^+ in Å^3, the units of $\langle {}_mK\rangle$ are $m^5V^{-2}mol^{-1}$.

With the values of the parameters mentioned above, and taking $\delta = \delta^+ = 0$ (i.e. neglecting the inductive effects), eq. 8 gives $\langle {}_mK\rangle = 684\ 10^{-27}$ $m^5V^{-2}mol^{-1}$, which is noticeably different of our experimental value of 780 in the same units. This comparison indicates that the inductive effects are not negligible.

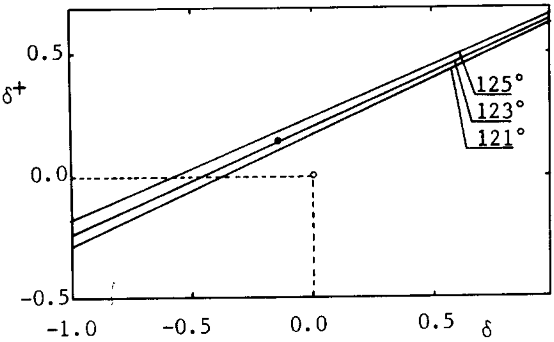

Fig. 3 Values of δ and δ^+ required to fit the experimental result of $\langle {}_mK\rangle$ for DMT at several orientations of the dipole moment of the ester group (see Fig. 2).

A quantitative information about the inductive effects can be obtained by equalling eq. 8 to our experimental result and solving for δ^+ at several values of δ. Fig. 3 shows the loci of the values δ, δ^+ that reproduce the experimental result of $\langle {}_mK\rangle$ of DMT at three differents values of the τ angle. As Fig. 3 indicates, the results are not much sensitive to the value of τ, and moreover, it is possible to reproduce the experimental result of $\langle {}_mK\rangle$ of DMT with rather small values of δ and δ^+, i.e. the modification produced in the $\hat{\alpha}_{DMT}$ tensor by the inductive effects are not large, although their incidence in the calculated value of $\langle {}_mK\rangle$ amounts to c.a. 12%.

This second conclusion may seem surprising taking into account that IRVINE et al. (1983) found that in the case of Methyl Benzoate, the value of δ amounted to about 28% of $\Delta\alpha_{MB}$. However, it is quite intuitive to think that in DMT, the inductive effects should be much smaller than in MB because of cancellation between the effects of both ester groups. This intuition is confirmed by the results of the direction of dipole moments in ester grups reported by SAIZ et al. (1981); they determined the angle τ for Dimethyl trans-1,4 Cyclohexanedicarboxilate (CDC), Methyl p-Chlorobenzoate (MCB), Methyl p-Bromobenzoate (MBB) and DMT. A value $\tau = 122°$ was obtained for CDC and this result could be used as representative for the situation in which there are not inductive effects since the ring joining both ester groups is not aromatic. The results for MCB and MBB were 113° and 117° respectively, and their difference respect to the value for CDC indicates that there are strong inductive effects in these two compounds, and moreover, the intensity of these effects changes with the group placed in p- respect to the ester. However, the value $\tau = 121°$ obtained for DMT confirms the idea of cancellation of inductive effects among the two ester groups. Relying on the analysis of those results, we have selected, from Fig. 3, a set of values of δ and δ^+ as close as possible to the $\delta = \delta^+ = 0$ situation; specifically, we have used $\delta = -0.14$ Å^3 and $\delta^+ = 0.14$ Å^3, in all the following calculations.

b) Poly (Diethylene Glycol Terephthalate) (PDET)

Figure 4 shows a segment of the PDET chain. Literature values (RIANDE 1977; RIANDE et al. 1984) were used for all parameters (i.e. geometry, conformational energies etc...) of this polymer. Specifically, the $\hat{\alpha}_i$ tensors for all the segments of the chain are given by RIANDE et al. (1984) and have been used in the present work with the only modification of including $\delta = -0.14$, $\delta^+ = 0.14$ in the $\hat{\alpha}_{DMT}$ tensor that represents the virtual C*-C* bond; the non diagonal terms of this tensor that were neglected in the analysis of the DMT molecule were nevertheless taken into account in the calculations for the polymer.

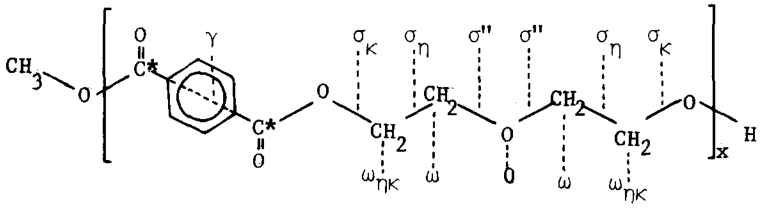

Fig. 4: The PDET chain shown in its planar all-trans conformation. Statistical weights (defined as $\zeta = \exp(-E_\zeta/RT)$) are represented above/below the skeleton for first/second order interactions.

Standard procedures of matrix multiplication scheme (FLORY 1969; 1974) were used to generate chains of PDET consisting of x = 100 repeat units and to compute averaged values of $<_m K>$ according to eq. 3. The ratios $<_m K>/x$ reach asymptotic limits at x = 30-40 (typical differences between the results for x = 10 and x = 100 are c.a. 4%). All the values that we present below were calculated at x = 100.

With $\delta = -0.14$, $\delta^+ = 0.14$ Å^3 and the literature values of all the other parameters we obtained $<_m K>/x = -768\ 10^{-27}\ m^5 V^{-2} mol^{-1}$. Table I summarizes the variation of $<_m K>$ with the parameters used in the calculation for both the

DMT model compound and the PDET polymer.

The concordance between theoretical and experimental results of $<_{m}K>/x$ of the polymer is very satisfactory. The discrepancy between both values is smaller than 5% which is about the estimated error of our experimental determination. Moreover, as Table I indicates, a small variation of some parameters (for instancean increase of $E_{\sigma\eta}$ by c.a. 0.03 kcal mol^{-1}) would bring the theoretical value of $<_{m}K>/x$ in exact agreement with the experimental result. Neither this modification of energies nor the incorporation of δ and δ^{+} to the $\underset{\sim}{\hat{\alpha}}$ tensor of DMT has noticeably effect on the values of the optical configuration parameter Δa of this polymer (see Table IV of RIANDE et al. (1984).

TABLE I : Variation of the Molar Kerr constant of DMT and PDET with the Parameters used on calculation.

PARAMETER	$\delta(<_{m}K>)/\delta(\text{parameter})$*		PARAMETER	$\delta(<_{m}K>)/\delta(\text{parameter})$*	
	DMT	PDET		DMT	PDET
$E_{\sigma\kappa}$	-	-790.4	θ_3	-	-20.3
$E_{\sigma\eta}$	-	1422.5	θ_4	-	20.4
$E_{\sigma''}$	-	-584.1	$\Delta\phi$	-	-6.6
$E_{\omega\kappa\eta}$	-	-97.3	δ	-203.5	-123.4
E_{ω}	-	-119.4	δ^{+}	454.6	53.4
E_{γ}	-378.7	796.4	μ	447.7	-722.6
θ_1	-	-11.3	τ	-9.4	15.5
θ_2	-	-4.0	T	-4.0	13.3

* Energies in kcal mol^{-1}; Angles in degrees; Polarizabilities in Å^{3}; Dipole moments in D; Temperature in K.

We conclude that the value of $<_{m}K>/x$ calculated with the RIS model for PDET is in excellent agreement with the experimental value. This concordance indicates that the RIS model is applicable to the calculation of the $\underset{\sim}{\hat{\alpha}}$ tensor of a polymeric chain through addition of contributions from the repeat units. Therefore, disagreement between theoretical and experimental values of Δa reported for many systems (among others this same polymer with the very same set of parameters used here), should be due to specific effects taking place in the amorphous solid state, but not to a failure of the RIS model.

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