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Behavior

Kerr Constant of Poly (Methyl Phenyl Siloxane)

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SUMMARY

The molar Kerr constant at infinite dilution of atactic (W_m=0.5) poly (methyl phenyl siloxane) (PMPS) with $\overline{M}_v = 8\ 10^5$, was determined from experimental measurements of electrical birefringence on its solutions in p-dioxane at 21 ± 1 °C. The experimental result is $<_m K>/x = (1.9 \pm 0.5)\ 10^{-25}$ $m^5V^{-2}mol^{-1}$; the large estimated error of this result is due to the surprisingly low value of $<_m K>/x$ of the PMPS. The theoretical value of this magnitude, calculated according to the RIS model is $<_m K>/x = 1.6\ 10^{-25}\ m^5V^{-2}mol^{-1}$ wich is in good agreement with the experimental result. Moreover, theoretic- ical analysis indicates that the reason for the low value of this magnitude, is that the dipole contribution to $<_m K>/x$ is negative although not large enough to overcome the positive contribituion of polarizability.

INTRODUCTION

Stress-optical behavior of atactic poly (methyl phenyl siloxane) (PMPS) has been reported in a previous paper (LLORENTE et al. 1985). It was found that for this polymer unlike many other systems (LIBERMAN et al. 1972; LIBERMAN et al. 1974; STEIN 1976; MARK and LLORENTE 1981; LLORENTE et al. 1983; RIANDE at al. 1984 a,b; SAIZ et al. 1984 a,b) the concordance between experimental (measured in unswollen networks) and theoretical (calculated with the rotational isomeric state model RIS) values of the optical configuration parameter Δa is excellent; however when the network is swollen with decaline, the experimental results of Δa depart from the calculated value. It seemed that intermolecular correlations in the amorphus solid utilized in the strain birefringence measurements are smaller for asymmetric chains than for symmetric ones (RIANDE et al. 1984 a; SAIZ et al. 1984 b; LLORENTE et al. 1985), and in particular they should be negligible in the case of PMPS. The variation of Δa with the degree of swelling of the sample was qualitatively explained by a modification of the optical parameters by the presence of the solvent in the sense of decreasing the anysotropy of the side groups of the chains.

Under these circumstances, it seemed interesting to investigate the molar Kerr constant $<_mK>/x$ of PMPS in order to check the agreement between theoretical and experimental values of this magnitude whose scheme of calculation is formally identical to that of Δa. Such a study would give valuable information about both the energy and the optical parameters of this polymer. This is the aim of the present paper in wich we undertake the study of $<_mK>/x$ of PMPS both from the experimental and theoretical points of view.

EXPERIMENTAL SECTION

a) Materials: A sample of PMPS was kindly provided by Dr. J.R. Falender from Dow Corning Co. (Midland, MI, USA). The polymer was fractionated at 25°C usind toluene-methanol as solvent as the solvent/non solvent system. One of the fractions was selected for the present study; it was purified by precipitation with methanol from a toluene solution at room temperature; the polymer was then separated by filtration and dried under vacuum until the weight remainded constant. The viscosity average moleculer weigth of the studied fraction was $\overline{M}_v = 8\ 10^5$; the stereochemistry of the sample , determined by ^{1}H NMR, gave a fraction of meso dyads of $W_m=0.5$ and its density, measured by picnometry was found to be $\rho = 1.115$ gcm^{-1} (LLORENTE et al. 1985). The p-dioxane (Panreac) used as solvent was purified according to standard procedures (PERRIN et al. 1966) and stored over 4Å molecular sieves (Merck).

b) Apparatus: The experimental set up used for the present measurements was described elsewhere (MENDICUTI and SAIZ 1984 a,b; FLORY at al. 1981). Briefly, the ligth source was a 5 mW He-Ne laser (SPECTRA-PHYSICS 120S) operating at $\lambda = 632.8$ nm; birefringence δ produced by electric fields E up to 3 10^6 Vm^{-1} were transformed into rotation of the plane of polarization of the incoming radiation by means of a quarter-wave plate and them compensated with a Faraday coil. The ligth detector was a photomultiplier (PACIFIC PRECISION INSTRUMENTS 062) whose signal was fed into a lock-in amplifier (PRINCETON APPLIED RESEARCH 128A) and then monitored in a recorder. Kerr constants B of the measured liquids were evaluated as:

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

where l is the length of the cell.

c) Results: All the measurements were carried out at room temperature

(21 ± 1 °C). The molar Kerr constant of the polymer was computed as : (SAIZ et al. 1977; FLORY et al. 1981; MENDICUTI and SAIZ 1984 a)

$$<_{m}K>/x = 54\,\lambda n\{\lim_{m\to 0}(\Delta B/m) + V_s B_o\}\{(n^2+2)(\varepsilon+2)\}^{-2} \qquad (2)$$

where $\Delta B = B - B_o$ is the difference between the B constant of each solution and the pure solvent; V_s is the molar volume of the solute and n, ε are respectively the refractive index and dielectrical constant of solvent for wich the values $n = 1.4224$, $\varepsilon = 2.2090$ where used (WEAST and ASTLE 1981). A value $B_o = 0.0705\ 10^{-14}\ Vm^{-2}$ was measured for pure p-dioxane at 21°C. A molecular weigth $M_o = 136.1$ corresponding to the repeat unit of PMPS was used in the evaluation of m and V_s, therefore, the result of eq. 2 gives the molar Kerr constant at infinte dilution per repeat unit.

Figure 1 shows the extrapolation of $\Delta B/m$ to $m\to 0$; substitution of the intercept into eq. 2 gives $<_{m}K>/x = (1.9 \pm 0.5)\ 10^{-25}\ m^5V^{-2}mol^{-1}$. The large estimated error is due to the low birefringence exhibited by the sollutions of PMPS that introduces substantial uncertainties into ΔB.

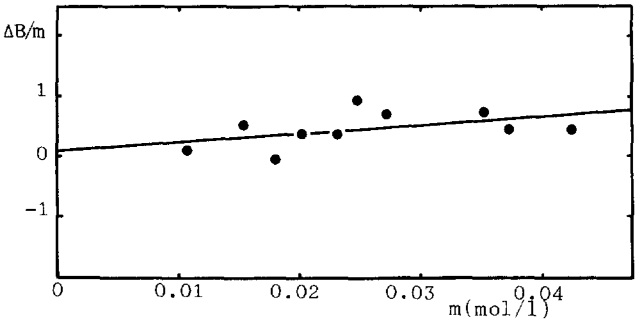

Fig. 1: Ratios of the difference $\Delta B = B - B_o$ to the molarity m (in mol/l) plotted against m for PMPS.

THEORETICAL CALCULATIONS

a) Geometry: Figure 2 shows a segment of the isotactic PMPS chain in its planar all-trans conformation. Values of 143° and 109.5° were used for the valence angles between bonds meeting at the O and Si atoms respectively; rotational isomers were placed at $\phi = 0°$, ±120° (MARK and KO 1975).

b) Energy Parameters and Statistical Weight Matrices: The energy parameters, taken from MARK and KO (1975), are: $E_\sigma = 0.35$, $E_\omega = 1.60$, $E_{\omega'} = -2.50$,

$E_{\omega''} = -0.90$, $E_{\omega'''} = -0.50$ and $E_{\delta} = -1.00$, all in Kcal/mol. The statistical weight matrices representing each pair of squeletal bonds of the chain were described by LLORENTE et al. (1985).

c) Anisotropic Part of the Polarizability Tensors: Two different contributions are needed in order to evaluate the anisotropic part of the polarizability tensor $\underset{\sim}{\hat{\alpha}}$ of the chain of PMPS, namely $\underset{\sim}{\hat{\alpha}}_i$ representing the contribution of skeletal bonds O-Si (bonds like i in Fig. 2) and $\underset{\sim}{\hat{\alpha}}_{i+1}$ representing the contribution of skeletal bonds Si-O (like i+1 in Fig. 2) plus the side groups attached to the Si atom. Using the standard nomenclature, these two tensors can be written as:

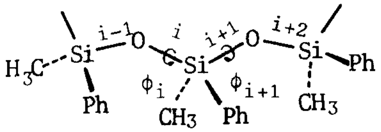

Fig. 2: A segment of the isotactic PMPS chain shown in its planar all-trans conformation.

$$\underset{\sim}{\hat{\alpha}}_i = \underset{\sim}{\hat{\alpha}}_{SiO} = \Delta\alpha_{SiO}\ \underset{\sim}{J}$$

$$\underset{\sim}{\hat{\alpha}}_{i+1} = \underset{\sim}{\hat{\alpha}}_{SiO} + \underset{\sim}{T}\ \underset{\sim}{\hat{\alpha}}_{SiPh}\ \underset{\sim}{T}^T + \underset{\sim}{T}'\ \underset{\sim}{\hat{\alpha}}_{SiCH_3}\ \underset{\sim}{T}'^T =$$

$$= \Delta\alpha_{SiO}\ \underset{\sim}{J} + \underset{\sim}{T}\ \{\Delta\alpha_{SiPh}\ \underset{\sim}{J} + \Delta\alpha^{+}_{SiPh}\ \underset{\sim}{J}^{+}\}\ \underset{\sim}{T}^T + \underset{\sim}{T}'\ \{\Delta\alpha_{SiCH_3}\ \underset{\sim}{J}\}\ \underset{\sim}{T}'^T \qquad (3)$$

where $\underset{\sim}{J} = \mathrm{diag}(2/3,-1/3,-1/3)$, $\underset{\sim}{J}^{+} = \mathrm{diag}(0,1/2,-1/2)$ and $\underset{\sim}{T}$, $\underset{\sim}{T}'$ represent the transformation matrices required to bring the coordinate systems attached to Si-Ph and Si-CH_3, respectively, into coincidence with the reference frame associated with skeletal bond i+1 (SUTER and FLORY 1977). The values of the optical parameters used in the present calculations are summarized in Table I. Sustitution of these parameters and the geometry of the PMPS into eq. 3 gives:

$$\underset{\sim}{\hat{\alpha}}_i = \mathrm{diag}(0.866,-0.433,-0.433)$$

$$\underset{\sim}{\hat{\alpha}}_{i+1} = \begin{bmatrix} -1.213 & -2.175 & 0.639 \\ -2.175 & -0.972 & -0.905 \\ 0.639 & -0.905 & 2.185 \end{bmatrix} \qquad (4)$$

both in units of 10^{-24} cm^3.

d) Results: Values of the molar Kerr constant per repeat unit were calculated as (SUTER and FLORY 1977).

$$<_mK>/x = (2\pi N/15kTx)\ \{<\mu^T\underset{\sim}{\hat{\alpha}}\mu>/kT + <Tr(\underset{\sim}{\hat{\alpha}}\ \underset{\sim}{\hat{\alpha}})>(\varepsilon-1)/(n^2-1)\} \qquad (5)$$

A dipolemoment $|\mu| = \pm 0.6$ D was used for the Si-O and O-Si skeletal bonds (MARK 1968; SUTON and MARK 1971; LIAO and MARK 1973).

TABLE I: Optical Parameters ^{a} (in 10^{-24} cm^3)

$\Delta\alpha_{SiPh} = 5.1$	$\Delta\alpha_{Si\text{-}O} = 1.3$
$\Delta\alpha^{+}_{SiPh} = -3.0$	$\Delta\alpha_{SiCH_3} = 1.25$

a) Evaluated by LLORENTE et al. (1985) from literatura values of bond and group polarizabilities.(LIBERMAN et al. 1972; PATTERSON and FLORY 1972; SUTER and FLORY 1977; ARMSTRONG et al. 1981).

Standard methods of matrix multiplication scheme (FLORY 1969; 1974) were used to calculate values of $<_mK>/x$ at different degrees of polymerization x, up to $x = 100$; asymptotic limits of $<_mK>/x$ versus x were reached for $x = 60$-70 (differences between values computed at $x = 60$ and $x = 100$ are ca. 2%); all the values reported below were calculated at $x = 100$. Monte Carlo simulations with Bernoullian placement of meso and racemic dyads were used to generate chains with each desired fractions of meso dyads W_m; values reported below for $0 < W_m < 1$ are averages over 20 chains thus generated. Figure 3 shows $<_mK>/x$ as function of W_m and Table II shows the variation $<_mK>/x$ with the parameters used on the calculation.

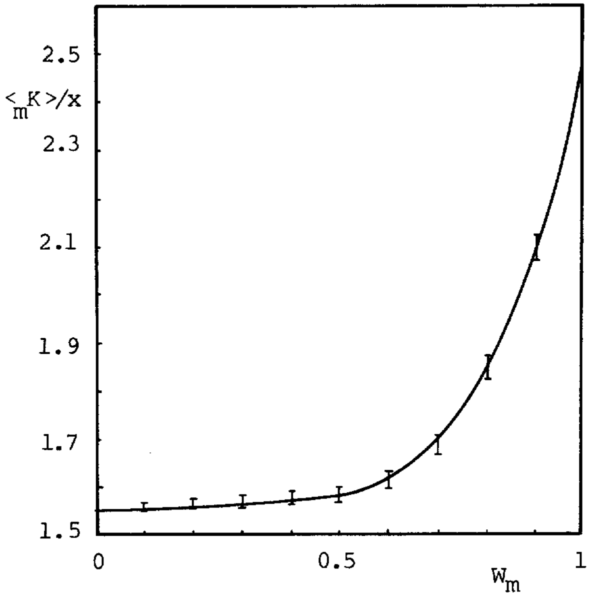

Fig. 3: Molar Kerr constant at infinite dilution per repeat unit $<_mK>/x$, as a function of the fraction of meso dyads W_m calculated at 21°C for chains consisting on $x = 100$ repeat units with energies given in the text and optical parameters of Table I. Values shown for $0 < W_m < 1$ are averages over 20 Monte Carlo Chains and the vertical bars represent standard errors of the averages.

TABLE II : Variation of $\langle {}_{m}K\rangle/x$ with temperature, dipole moment, conformational energies and optical parameters used in the calculations.

Parameter (p)	$10^2\,\delta\{\langle {}_{m}K\rangle/x\ (10^{-25} m^5 V^{-2} mol^{-1})\}/\delta p$		
	$W_m = 0$	$W_m = 0.5$	$W_m = 1.0$
T	0.3	0.6	2.5
μ	-190	-106	-140
E_σ	-34	2	354
E_ω	-0.8	3	3
$E_{\omega'}$	-40	-67	-344
$E_{\omega''}$	121	88	324
$E_{\omega'''}$	-48	-26	-340
E_δ	6	41	317
$\Delta\alpha_{SiPh}$	66	73	109
$\Delta\alpha^{+}_{SiPh}$	-39	-22	-43
$\Delta\alpha_{SiO}$	-84	-35	-186
$\Delta\alpha_{SiCH_3}$	18	15	77

DISCUSSION

The small value found for $\langle {}_{m}K\rangle/x$ of PMPS is due to the fact that, the two contributions to this magnitude (eq. 5) are of opposite sign, namely the term $\langle \mu^T \underset{\sim}{\hat{\alpha}} \mu\rangle$ is negative while $\langle Tr(\underset{\sim}{\hat{\alpha}}\ \underset{\sim}{\hat{\alpha}})\rangle$ is positive. The negative sign of $\langle \mu^T \underset{\sim}{\hat{\alpha}} \mu\rangle$ is due to the contributions to this term arising from the components xx and xy of $\underset{\sim}{\hat{\alpha}}_{i+1}$ (eq. 4); moreover, since the dipole moments of the Si-O and O-Si bonds are opposed and include a large valence angle ($\theta = 143°$) there is a substantial cancellation of μ_i for each two consecutive bons of the chain , therefore the resulting $\langle \mu^T \underset{\sim}{\hat{\alpha}} \mu\rangle$, besides being negative is too small in absolute value to overcome the positive contribution of $\langle Tr(\underset{\sim}{\hat{\alpha}}\ \underset{\sim}{\hat{\alpha}})\rangle$.

As Table II shows, a consequence of the opposite sign of the two contributions to $\langle {}_{m}K\rangle/x$ is that this magnitude decreases when μ increases since the term $\langle \mu^T \underset{\sim}{\hat{\alpha}} \mu\rangle$ increases in absolute value. A variation of the optical parameters modifies both $\langle \mu^T \underset{\sim}{\hat{\alpha}} \mu\rangle$ and $\langle Tr(\underset{\sim}{\hat{\alpha}}\ \underset{\sim}{\hat{\alpha}})\rangle$; however the variation of $\langle \mu^T \underset{\sim}{\hat{\alpha}} \mu\rangle$ is smaller than that of $\langle Tr(\underset{\sim}{\hat{\alpha}}\ \underset{\sim}{\hat{\alpha}})\rangle$ due to the partial cancellation of the contributions to μ above mentioned; thus, the modification of $\langle Tr(\underset{\sim}{\hat{\alpha}}\ \underset{\sim}{\hat{\alpha}})\rangle$

still is the dominant one and $\langle {}_mK\rangle/x$ increases when the anisotropy of the side groups is increased (ie. when $\Delta\alpha_{SiPh}$, $\Delta\alpha_{SiCH_3}$ or the absolute value of $\Delta\alpha^{+}_{SiPh}$ are increased). An increase of $\Delta\alpha_{SiO}$ increases the elements of $\hat{\alpha}_{\sim i}$ but decreases the absolute value of those of $\hat{\alpha}_{\sim i+1}$ since the contributions from the side groups and the backbone to this tensor have opposite sign; this second effect is more important since the elements of $\hat{\alpha}_{\sim i+1}$ are larger and therefore contribute more to $\langle \mathrm{Tr}(\underset{\sim}{\hat{\alpha}}\ \underset{\sim}{\hat{\alpha}})\rangle$; consequently, $\langle \mathrm{Tr}(\underset{\sim}{\hat{\alpha}}\ \underset{\sim}{\hat{\alpha}})\rangle$ and $\langle {}_mK\rangle/x$ decrease when $\Delta\alpha_{SiO}$ increases.

The variations of $\langle {}_mK\rangle/x$ with the energy parameteres summarized in Table II are small; the largest modification is produced by a change in $E_{\omega''}$ and even for this one, a variation of roughly 2 kcal/mol is required to duplicate the calculated value of $\langle {}_mK\rangle/x$ whereas for instance in PDET (MENDICUTI and SAIZ, 1984a), the same effect is produced by a change of 0.5 kcal/mol in one of the conformational energies. Again this behavior can be explained by the negative and small value of $\langle \mu^T\underset{\sim}{\hat{\alpha}}\mu\rangle$; any change of one of the energy parameters modifies $\langle \mu^T\underset{\sim}{\hat{\alpha}}\mu\rangle$ and $\langle \mathrm{Tr}(\underset{\sim}{\hat{\alpha}}\ \underset{\sim}{\hat{\alpha}})\rangle$ in opposite sense and the resulting effect on $\langle {}_mK\rangle/x$ is small.

Figure 3 shows that $\langle {}_mK\rangle/x$ is also relatively insensitive to W_m except in the region of highly isotactic chains. The term $\langle \mu^T\underset{\sim}{\hat{\alpha}}\mu\rangle$ exhibits small variations with W_m since the cancellation between two successive dipole moments is independent of the tacticity of the chain; the term $\langle \mathrm{Tr}(\hat{\alpha}\hat{\alpha})\rangle$ increases sharply when W_m approaches 1 due to the predominance of tt conformation on the meso dyads and this is the reason for the increase of $\langle {}_mK\rangle/x$ in the region of high W_m.

The theoretical result of $\langle {}_mK\rangle/x$ calculated for $W_m = 0.5$ is 1.6 $10^{-25} m^5 V^{-2} mol^{-1}$ which agrees with the measured value within the limit of experimental error. Exact agreement with the experimental value of 1.9 10^{-25} $m^5 V^{-2} mol^{-1}$ would be reproduced with a modification of $\Delta\alpha_{SiPh}$ of about 10% of its value or by an adjustment of all the optical parameters within ±0.2 $Å^3$; any of this two modifications has little incidence into the calculated values of the optical configuration parameter Δa (LLORENTE et al., 1985), more specifically, the value of Δa calculated after any of those modifications of the optical parameters is still in good agreement with the experimental result of Δa measured in the unswollen sample.

From the comparison of our experimental and theoretical values of $\langle {}_mK\rangle/x$ we can conclude that the set of conformational energies given in the text and optical parameters of Table I with uncertainties of ±0.2 $Å^3$, wich have proven to reproduce some conformational properties of the PMPS, are also able to reproduce the molar Kerr constant of this polymer. However, given the large experimental error due to the very low value of $<_m K>/x$ and its relative insensitivity to the parameters used in the calculation, the conformational energies can not be optimized from this comparison.

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