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Dipole Moments of Poly(*p*-chlorostyrene) Chains

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ABSTRACT: The mean-squared dipole moments $\langle\mu_x^2\rangle$ of poly(*p*-chlorostyrene) (PPCS) chains have been calculated as a function of stereochemical composition using the rotational isomeric state analysis recently published for polystyrene. The dipole moment ratio $D_\infty \equiv \lim_{x\to\infty}(\langle\mu_x^2\rangle/x\mu_0^2)$, where μ_x is the dipole moment of the *x*-meric chain and μ_0 is the dipole moment of the structural unit, is calculated to be less than unity at all stereochemical compositions: 0.59 for syndiotactic, ca. 0.55 throughout the atactic range, and 0.78 for isotactic. Unfavorable correlation of the individual dipoles is thus implied. The low value for syndiotactic is attributed to the approximate antiparallelism of the resultant moments for successive sequences $|\mathrm{tt}|_y$ of *y* trans,trans dyads. The mutual correlation of dipoles in sequences of the preferred |tg| conformation for the isotactic chain is poor, but the more favorable mutual orientation of resultant moments for successive sequences is responsible for the larger ratio D_∞. The calculations are in good agreement with the average, $D_\infty = 0.54 \pm 0.07$, of experimental results for atactic PPCS estimated to contain ca. 35% meso dyads. The temperature coefficient is calculated to be negative in agreement with available experiments.

The conformations accessible to a vinyl polymer chain $-(\mathrm{CHR{-}CH_2}-)_x$, in which the substituent is a planar group, can be adequately represented by two rotational states, trans (t) and gauche (g), for each bond of the chain skeleton.[2-4] The gauche-bar ($\bar{\mathrm{g}}$) state, in which the planar substituent is tilted inward with respect to the incident dyad, is effectively suppressed by steric interactions (see below). Conformational energy calculations on polystyrene[2b,3] (PS) with R = C_6H_5, on poly(methyl acrylate)[4] (PMA) with R = $COOCH_3$, and on the disubstituted homologue of PMA, poly(methyl methacrylate)[2a] (PMMA), show the energy of the $\bar{\mathrm{g}}$ conformation to be excessive, a conclusion that may be anticipated from critical examination of models.

The two-state scheme has been applied to stereochemical equilibria in oligomers of PS,[5] to the analysis of unperturbed dimensions expressed by the characteristic ratio $C_n = \langle r^2\rangle_0/nl^2$ of the PS chain,[2b] and to its optical anisotropy.[6] It has been employed also to treat the electric birefringence of poly(*p*-chlorostyrene) (PPCS) and poly(*p*-bromostyrene)[7] (PPBS). As was pointed out previously,[8] para substitution with Cl or Br does not materially affect the conformational energy. Hence, the conformational energies calculated for PS[2b] should be applicable also to the latter derivatives of this polymer. Advantages of the newer model over the three-state scheme used previously[9-11] accrue principally from refinements in the locations of rotational isomeric states for the meso and racemic dyads and in their relative energies. Apart from procedural simplifications resulting from reduction in the number of rotational states to be considered, rejection of conformations involving $\bar{\mathrm{g}}$ states for one or more bonds of the chain are of minor significance, inasmuch as the statistical weights previously employed[5,8-11] in the three-state model reduced $\bar{\mathrm{g}}$ conformations to low incidence.

The present study explores the use of the two-state scheme for treating the mean-square dipole moments $\langle\mu_x^2\rangle$ of *x*-meric PPCS chains of variable stereochemical compositions. Calculations are carried out also on the dependences of the dipole moments on temperature. The results are directly relevant to the interpretation of the electrical birefringence of these chains,[7] as characterized by the molar Kerr constant, $_{\mathrm{m}}K$, which is determined principally by the configurationally averaged quantity $\langle\boldsymbol{\mu}^{\mathrm{T}}\hat{\alpha}\boldsymbol{\mu}\rangle$, where $\boldsymbol{\mu}^{\mathrm{T}}$ is the transpose of the dipole moment vector $\boldsymbol{\mu}$ for the molecule as a whole and $\hat{\alpha}$ is the anisotropic polarizability tensor of the molecule. A number of experimental studies[12-19] of the dipole moments of PPCS have been conducted over ranges of temperature. We compare these results with theoretical calculations.

Structural Geometry, Statistical Weights, and Computational Procedure

A planar substituent such as phenyl, represented as R in Figure 1, is restricted to an orientation about the C–R bond such that its plane is approximately perpendicular to the plane of the two skeletal bonds (e.g., bonds $i-1$ and i in Figure 1) flanking the substituted carbon.[2a,11,20] Steric repulsions by hydrogens of the adjoining methylene groups impose this constraint. In the $\bar{\mathrm{g}}$ conformation in which the C–R bond assumes the position of the methine C–H in Figure 1, the planar R group, oriented as stated, impinges on one of the groups, R, CH_2, or H, pendant to the neighboring substituted carbon of the dyad embracing the $\bar{\mathrm{g}}$ bond.[2,4] According to calculations of the conformational energy of PS,[2b] occurrence of a $\bar{\mathrm{g}}$ conformation entails an energy of at least 5 kcal mol^{-1}. Neglect of this state is well justified therefore, and we adopt the statistical weight matrices employed previously. These are[2b]

$$\mathbf{U}' = \begin{bmatrix} 1 & 1 \\ 1 & 0 \end{bmatrix} \tag{1}$$

for a pair of bonds flanking a substituted carbon, irrespective of the configurations of the adjoining dyads, and

$$\mathbf{U}_{\mathrm{m}}'' = \begin{bmatrix} \omega'' & 1/\eta \\ 1/\eta & \omega/\eta^2 \end{bmatrix} \tag{2}$$

$$\mathbf{U}_{\mathrm{r}}'' = \begin{bmatrix} 1 & \omega'/\eta \\ \omega'/\eta & 1/\eta^2 \end{bmatrix} \tag{3}$$

for the bond pairs within a meso and a racemic dyad, respectively. The statistical weights are here normalized to unity for racemic,tt. The first-order parameter η measures the preference for trans over gauche. The second-order parameters ω,

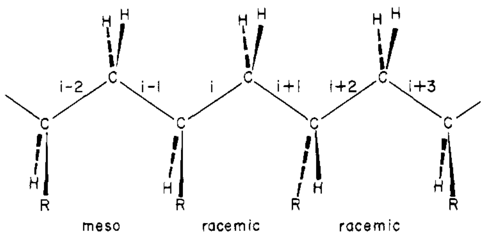


Figure 1. Portion of a vinyl chain in the planar, all-trans conformation.

Table I
Averaged Locations of Conformations (from ref 2b)

State	$\langle\varphi'\rangle$, $\langle\varphi''\rangle$, deg Meso	$\langle\varphi'\rangle$, $\langle\varphi''\rangle$, deg Racemic
tt	22, 22	9, 9
tg[a]	6, 110	20, 87
gg	92, 92	105, 105

[a] Includes gt with $\langle\varphi'\rangle$ and $\langle\varphi''\rangle$ interchanged.

ω', and ω'' express the effects of repulsions between juxtaposed pairs CH_2- - -CH_2, CH_2- - -C_6H_5, and C_6H_5- - -C_6H_5, respectively.

According to the conformational energies previously calculated, with minor adjustments to optimize agreement with experimental results on configuration-dependent properties,[2b]

$$\eta = 0.8\exp(200/T) \tag{4}$$

$$\omega = \omega' = 1.3\exp(-1000/T) \tag{5}$$

$$\omega'' = 1.8\exp(-1100/T) \tag{6}$$

Mean values of the torsion angles φ' and φ'' for the first and second bonds of a dyad (e.g., bonds i and $i+1$ in Figure 1), respectively, were determined by taking Boltzmann averages over the several domains of each dyad. Results for a temperature of 300 K are given in Table I.

The generator matrix for $\mu_x{}^2$, the square of the dipole moment for the x-meric polymer chain CH_3–(CHR–CH_2)$_x$–H in a specified conformation, is[10,21]

$$\mathbf{G}_{j;\xi} = \begin{bmatrix} 1 & 2\mu_0{}^{\mathrm{T}}\mathbf{T}_\xi & \mu_0{}^2 \\ 0 & \mathbf{T}_\xi & \mu_0 \\ 0 & 0 & 1 \end{bmatrix}_j \tag{7}$$

where μ_0 is the dipole moment associated with the jth skeletal bond of the chain, μ_0 being expressed as a column vector in the reference frame of bond j; $\mu_0{}^{\mathrm{T}}$ is its transpose and $\mu_0{}^2$ is the square of its magnitude; $\mathbf{T}_\xi$ is the transformation relating the reference frame of bond $j+1$ to that of bond j. This transformation depends on the supplement θ of the skeletal bond angle at the junction of bonds j and $j+1$ and on the torsional angle of rotation φ_j about bond j in the conformation denoted by ξ.

In keeping with the computations of conformational energies[2b] which provide the basis for the present analysis of dipole moments, we take $\theta' = 66°$ at the methylenic carbon and $\theta'' = 68°$ at the substituted carbon. Other bond angles at the latter carbon may be assigned tetrahedral values in sufficient approximation. The dipole moment μ_0 of the repeating unit is collinear with the C^α-phenyl bond. It is fixed therefore in the reference frame of the following skeletal bond (e.g., bond i in Figure 1). On the basis of the closely agreeing dipole moments of p-chlorotoluene (1.88 D),[22] p-chloro-*tert*-butylbenzene (1.91 D),[23] and p-chlorocumene (1.91 D),[7] all measured in carbon tetrachloride, we take $\mu_0 = 1.90$ D. This value of μ_0 replaces 1.68 D used in the earlier investigation[8] of the dipole moments of PPCS chains. Substitution of it in eq 7 together with $\langle\varphi'\rangle$ taken from Table I completes the evaluation of $\mathbf{G}_\xi'$ for the first bond of a dyad in state ξ. The matrix $\mathbf{G}''$ for the second bond is obtained similarly with μ null. Then for the x-meric chain in a conformation fully specified by $\{\xi\}$[21,24]

$$(\mu_x{}^2)_{\{\xi\}} = \mathbf{G}_1 \prod_{k=1}^{x-1} (\mathbf{G}'\mathbf{G}'')_{k,\xi_k} \mathbf{G}_x \tag{8}$$

where ξ_k denotes the conformation of dyad k, $\mathbf{G}_1 = [1 \quad 0 \quad 0]$ is the first row of the matrix shown in eq 7 with $\mu_0 = 0$, and $\mathbf{G}_x$ is its final column with μ_0 therein representing the last p-chlorophenyl group in the chain.

The statistical mechanical average over all conformations is given by[24]

$$\langle\mu_x{}^2\rangle = Z^{-1}\mathcal{G}_0\left(\prod_{k=1}^{x-1}\mathcal{U}'\mathcal{G}_k\right)\mathcal{G}_x \tag{9}$$

where Z is the configuration partition function evaluated by serial multiplication of the statistical weight matrices, eq 1–3;[10–21]

$$\mathcal{U}' = \mathbf{U}' \otimes \mathbf{E}_5 \tag{10}$$

where $\mathbf{E}_5$ is the identity of order five, ⊗ denotes the direct product, and[24]

$$\mathcal{G}_0 = [\mathbf{G}_1 \quad 0] \tag{11}$$

$$\mathcal{G}_k = \begin{bmatrix} \mathbf{G}_t{}' & 0 \\ 0 & \mathbf{G}_g{}' \end{bmatrix} (\mathbf{U}_k{}'' \otimes \mathbf{E}_5) \begin{bmatrix} \mathbf{G}_t{}'' & 0 \\ 0 & \mathbf{G}_g{}'' \end{bmatrix} \tag{12}$$

$$\mathcal{G}_x = \begin{bmatrix} \mathbf{G}_x \\ \mathbf{G}_x \end{bmatrix} \tag{13}$$

For a meso dyad, for example, $\mathcal{G}_k$ is given by

$$\mathcal{G}_{\mathrm{meso}} = \begin{bmatrix} \omega''(\mathbf{G}_t{}'\mathbf{G}_t{}'') & \eta^{-1}(\mathbf{G}_t{}'\mathbf{G}_g{}'') \\ \eta^{-1}(\mathbf{G}_g{}'\mathbf{G}_t{}'') & \omega\eta^{-2}(\mathbf{G}_g{}'\mathbf{G}_g{}'') \end{bmatrix} \tag{14}$$

All results are expressed as the dimensionless ratios

$$D_x = \langle\mu_x{}^2\rangle / x\mu_0{}^2 \tag{15}$$

Results of Calculations

Mean-square dipole moments for isotactic (meso) and for syndiotactic (racemic) chains at 300 K were calculated at various degrees of polymerization up to $x = 100$. The ratios D_x rapidly approach their limits D_∞ with increase in x. Extrapolation was carried out by plotting D_x against $1/x$; the projected increase in D_x beyond $x = 100$ amounted to only ca. 0.3% of the limiting value.

Monte Carlo methods were employed to generate atactic chains of specified stereochemical composition. Meso and racemic dyads were distributed at random (Bernoullian distribution), being subject only to the a priori expectation w_{m} of a meso dyad. Matrices $\mathbf{U}''$ and $\mathcal{G}$ were introduced in the serial multiplications required to obtain Z and $\langle\mu_x{}^2\rangle$ (see eq 9 and 12) according to the character, meso or racemic, of each dyad of the Monte Carlo chain. Calculations were carried out at intervals of 0.1 in w_{m} over the range $0.1 \le w_{\mathrm{m}} \le 0.9$. For each value of w_{m}, 20 chains of $x = 100$ units were generated. Averages were extrapolated as above to obtain D_∞ at each stereochemical composition. The extrapolations beyond $x = 100$ invariably were smaller than the standard errors d in the averages.

Results are shown in Figure 2. Error bars for the atactic chains cover ranges ±d. They resemble results of previous calculations[8] carried out using the three-state scheme with choice of corresponding locations of rotational isomeric states.

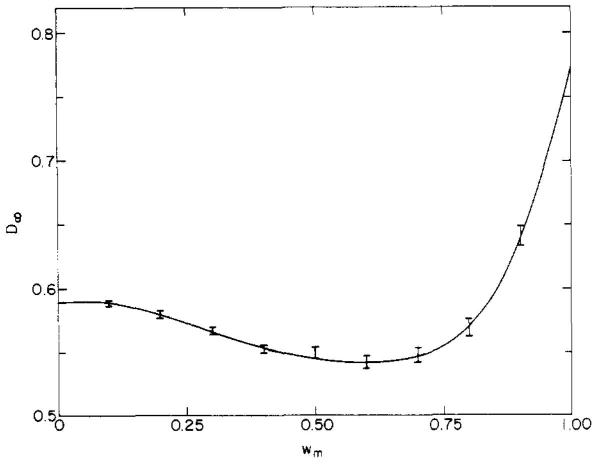


Figure 2. The dipole moment ratio for PPCS calculated as a function of stereochemical composition expressed by the a priori expectation w_m of a meso dyad. Vertical lines for $0.1 \leq w_m \leq 0.9$ represent $\pm d$ where d is the standard error in the average for 20 Bernoullian Monte Carlo chains for each value of w_m in this range.

For all stereochemical compositions the mean correlations between individual dipoles in the chain are negative, as is indicated by values of D_∞ less than unity. The ratio D_∞ is smaller for the syndiotactic ($w_m = 0$) than for the isotactic chain ($w_m = 1$). The curve passes through a shallow minimum near $w_m = 0.6$.

The value of D_∞ calculated for the syndiotactic chain is sensitive to the parameter η. It increases 10% if η is increased 7%, which approximates the uncertainty in η according to experiments on stereochemical equilibria in oligomers of PS.[5] The effect of η decreases with w_m. At the limit $w_m = 1$, a 7% increase in η *decreases* D_∞ about 1%. Dependences on other statistical weights are negligible, within the ranges of allowable variation, for all values of w_m.

The effect of temperature on the dipole moment ratio is shown in Figure 3 for four values of w_m. The temperature coefficients are consistently negative. The syndiotactic chain shows the greatest dependence on temperature; the atactic chain with $w_m = 0.5$ is least dependent thereon.

Comparison of Calculations with Experiments

A number of published investigations[12–19] on the dipole moments of PPCS polymers provide data from which D_∞ may be evaluated. With choice of $\mu_0 = 1.90$ D in each instance, and adjustment of results, where necessary, to a temperature of 300 K, we obtain values of D_∞ ranging from 0.41 to 0.70. Although a variety of solvents were used, there is no obvious correlation with solvent type. Perturbations of the chain configuration by effects of excluded volume should not, of course, affect $\langle \mu_x{}^2 \rangle$ in a chain such as PPCS in which the moment μ_0 is symmetrically oriented with respect to the chain backbone. It is most significant that the values of D_∞ are consistently smaller than unity. Averaging the results quoted, we obtain $D_\infty = 0.54 \pm 0.07$.

All of the polymers used in the investigations cited above were prepared by free-radical polymerization, generally carried out somewhat above room temperature. The fact that the characteristic ratio for PPCS thus prepared is close to that of polystyrene[25,26] suggests that their stereochemical compositions are similar. According to NMR measurements[27] on the latter polymer $w_m \approx 0.35$. A similar stereochemical composition is indicated for atactic PPCS according to measurements of its optical anisotropy and Kerr constant.[7] Taking $w_m = 0.35 \pm 0.05$ as a plausible mean value, we find from Figure 2 that $D_\infty = 0.55–0.57$, in excellent agreement with the average value deduced from experiments.

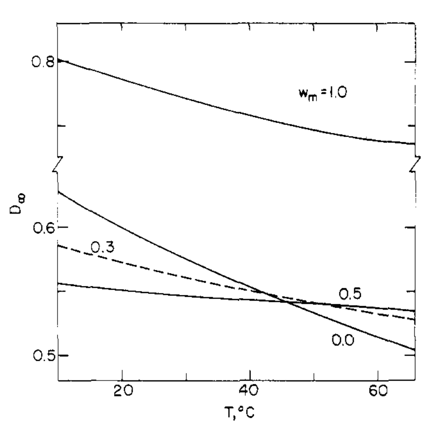


Figure 3. Dependence of the dipole moment ratio on temperature for the stereochemical compositions w_m indicated.

Experimental measurements permitting evaluation of the temperature coefficient of the mean-square dipole moment are more limited. Burshtein and Stepanova[16] found -4×10^{-3} K^{-1} for d ln $\langle \mu^2 \rangle / dT$ over the range 10–60 °C. For higher temperatures they report a positive value which, however, may have been vitiated by loss of solvent (toluene); Baysal, Lowry, Yu, and Stockmayer[17] give values of -4×10^{-3} and -6×10^{-3} K^{-1} near 300 K. A negative temperature coefficient is thus indicated, in confirmation of theory, but the evidence at hand does not permit a quantitative comparison.

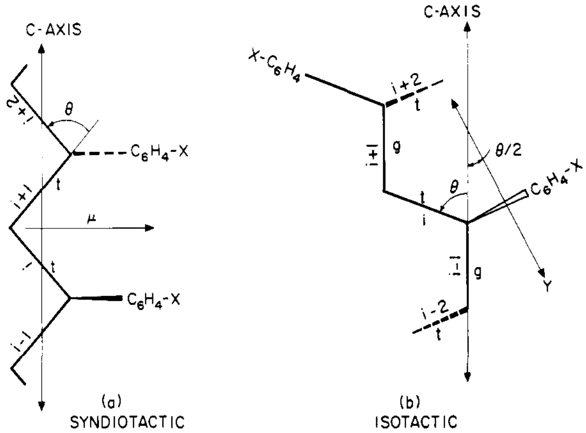
We conclude that theoretical calculations are in satisfactory agreement with available experimental results on the dipole moments of "atactic" PPCS. This agreement is obtained using parameters deduced from conformational energies calculated for polystyrene, with minor adjustments to optimize conformity with experimental results pertaining to that polymer, notably with stereochemical equilibria for oligomers of PS[5] and with dimensions of PS and PPCS.[2b,25–27] The agreement of calculated dipole moments with those observed by experiment has been achieved without benefit of adjustment of parameters.

Discussion

The adverse correlations between dipoles in the PPCS chain manifested in values of D_∞ less than unity and the lower D_∞ for the syndiotactic compared to the isotactic chain find rational explanation in the structure and predominant conformations of this chain.

Consider first the syndiotactic chain ($w_m = 0$). At the level of approximation of the following analysis, let all bond angles be symmetrical tetrahedral and the rotational states be located at $\varphi_t = 0°$ and $\varphi_g = 120°$. In the all-trans conformation thus defined the individual dipoles are oriented alternatingly above and below the plane of the backbone, as shown in Figure 4a. They are directed at angles $\pm(\pi - \theta)/2$ from the plane of the backbone, θ being the supplement of the tetrahedral bond angle. The resultant moment for a sequence of y units (y even) so conformed is $y\mu_0 \cos [(\pi - \theta)/2] = y\mu_0/3^{1/2}$. It is perpendicular to the chain axis (C) and in the plane of the backbone as shown in Figure 4a.

Sequences of the preferred dyad conformation |tt| are preponderantly interrupted by the |gg| conformation; see eq 1–3. For $\varphi_g = 120°$, the dipole moments of two sequences thus joined would be antiparallel as was pointed out previously.[8] The resultant ratio $\langle \mu_x{}^2 \rangle / x$ for a chain adhering to the geometrical parameters adopted here would vanish in the limit $x \rightarrow \infty$. Departures of θ', θ'' and of φ_t and φ_g from these "symmetrical" values and the occasional occurrence of a |tg| or |gt| conformation appear to be responsible for departures from this prediction. The low value of D_∞ for the syndiotactic chain



(a) SYNDIOTACTIC (b) ISOTACTIC

Figure 4. Preferred conformations for syndiotactic (a) and isotactic (b) chains. Axes of propagation of the preferred conformations are labelled C. The axis Y in (b) is normal to the plane of the phenyl group.

is nevertheless attributable to the unfavorable mutual orientation of the moments for successive $|tt|$ sequences. It is to be noted however that the moments μ_0 within a given sequence correlate favorably. Hence, the greater the average length of a sequence, the greater will be $\langle \mu_x^2 \rangle$ for the chain as a whole. The sequence length is estimated[2b,7] to be about $y = 4$ units at 300 K. Its decrease with temperature provides an explanation for the negative temperature coefficient calculated for D_∞.

Perpetuation of the chirally related, preferred conformations $|gt|$ or $|tg|$ for the isotactic chain ($w_m = 1$) yields the Natta–Corradini 3_1 helix. A sequence $|gt|_{y_1}$ may be followed by a sequence $|tg|_{y_2}$, but the reverse combination is forbidden; see eq 1. The principal mode of return from a $|tg|$ sequence to its enantiomorph $|gt|$ of opposite chirality involves interposition of a $|tt|$ dyad between the two sequences; this conformation entails a higher energy. Calculations[2b,7] carried out using the parameters given above and a temperature of 300 K indicate an average sequence length $y \approx 3.5$ units, too few for a well-defined helix, to be sure. Ignoring this qualification on the terminology adopted here, we observe that the C–R bonds of successive units, and hence their group dipole moments, make angles θ with the axes (C) of the 3_1 helix, as shown in Figure 4b. Thus, the resultant of y units so conformed is $y\mu_0/3$. If $y/3$ is integral, transverse components vanish. For "helices" of the lengths calculated for the isotactic PPCS chain, they may contribute appreciably to $\langle \mu_x^2 \rangle$ for the molecule as a whole. Ignoring them within the context of the present qualitative account, we observe that successive helical sequences interrupted in either of the ways indicated above meet at an angle θ. Hence, they are positively correlated, in contrast to the relationship between successive sequences $|tt|_y$ in the syndiotactic chain.

Thus, the contribution per unit in the preferred conformation of the isotactic chain is smaller than for the syndiotactic chain ($\mu_0/3$ compared to $\mu_0/3^{1/2}$), and the average sequence length is smaller also. The correlations between successive sequences are favorable in the isotactic chain, however, instead of adverse as in the syndiotactic form. Consequently, the mean-squared moments are larger for isotactic PPCS. The moment ratio D_∞ nevertheless remains smaller than unity.

These interpretations gain support from the electric birefringence as expressed in the molar Kerr constant $_mK$ calculated[7] on the basis of the same conformational parameters. The resultant dipole moment for $|tt|$ sequences of the syndiotactic chain is parallel to the planes of the phenyl groups. Hence, $_mK$ is large and positive. The resultant dipole moment of the preferred (helical) conformation of the isotactic chain is oriented at an angle $\theta/2$ from the cylindrical axis of the phenyl group, i.e., the Y axis in Figure 4b, in the approximations adopted above. Hence, its direction is more nearly normal than parallel to the plane of the phenyl group. The Kerr constant consequently is calculated to be negative and large.[7]

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