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# Effect of the Pendant Ester Group Orientations on the Dipole Moment of Poly(alkyl acrylate)s

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ABSTRACT: The dipole moment analysis of vinyl polymers carrying polar side groups such as poly(methyl acrylate) (PMA), poly(methyl methacrylate) (PMMA), and poly(ethyl methyacrylate) (PEMA) has been performed by the expanded matrix algebra method with due consideration of the ester group orientations. The stereochemical characteristics of the pendant ester groups have been exactly treated by introducing a Bernoullian probability $\lambda$ representing the occurrence of the cis conformation around the first articulated $C^{\alpha}-C^{*}$ bond. Special care is required for the orientational correlation of the neighboring ester groups when the skeletal conformations around the two successive bonds are both in trans. Such a meso-*tt* effect has been accommodated by assigning probability $\lambda'$ or $(1 - \lambda')$ to the proper elements of the statistical weight matrix. Experimental observations were found to be satisfactorily reproduced with $\lambda = 0.3-0.4$, indicating that the trans conformation is more preferred for the ester group. The orientational correlation $\lambda' = 0.8-0.9$ suggests that the meso-*tt* effect is substantial. For the purpose of comparison, we have adopted the two-state scheme of Yoon et al. for PMA and the three-state scheme of Sundararajan for PMMA and PEMA. The results of calculations were compared with those derived by the conventional method, in which an effective dipole moment is used to represent the contribution from the pendant ester group. Possible errors inherent to the approximation involved in the preaveraging scheme are critically discussed.

## Introduction

It has been widely accepted that the ester group involved in the side chain of poly(alkyl acrylate)s is planar with bond $O-R'$ trans to bond $C^{\alpha}-C^{*}$ (cf. Figure 1), and two isomeric orientations of the ester group are permitted around the latter bond: $\chi = 0$ to the cis conformation in which bond $C^{*}{=}O^{*}$ is cis to $C^{\alpha}-R$ and $\chi = \pi$ to the trans in which these two bonds are trans to each other.[1,2] According to Saiz et al.,[3] the dipole moment of the ester group is almost antiparallel to the $C^{*}{=}O^{*}$ bond, directed at an angle of 123 ± 3° from the $C^{\alpha}-C^{*}$ bond. Strictly speaking, as pointed out by Ojalvo et al.,[4] these two orientations must be treated separately when one formulates the generator matrix $\mathbf{G}_k$ in a given reference frame ($k$) as required in the rotational isomeric state (RIS) calculation:

$$\mathbf{G}_k = \begin{pmatrix} 1 & 2\bar{\mathbf{m}}^T\mathbf{T} & m^2 \\ 0 & \mathbf{T} & \bar{\mathbf{m}} \\ 0 & 0 & 1 \end{pmatrix}_k \tag{1}$$

where $\bar{\mathbf{m}}$ is a column matrix for the dipole moment expressed in the coordinate system affixed to the skeletal bond associated with the $k$th α-carbon: $m = 0$ for the first bond of every dyad. The matrix $\mathbf{T}$ effects the transformation required to convert the components of a vector defined in reference frame $i + 1$ to those in reference frame $i$. In the molecular system under consideration, $\bar{\mathbf{m}}$ depends on the rotations of both the side $C^{\alpha}-C^{*}$ and the corresponding skeletal bond. When the ester groups in the side chain are allowed to take either of the two alternate orientations, the statistical weight matrices, commonly called **U**-matrices, must be expanded accordingly. For the sake of simplicity, an effective dipole moment derived by preaveraging the dipoles of the two orientations of the ester group has been sometimes used in estimating the dielectric properties of polymers.[5−7]

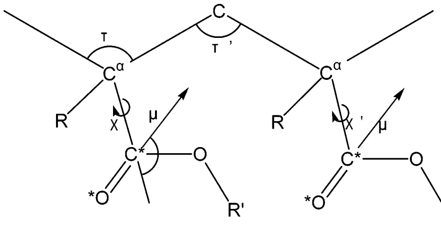

**Figure 1.** Schematic representation of a meso dyad in the trans−trans conformation: poly(methyl acrylate) ($R = H$; $R' = CH_3$) and poly(methyl methacrylate) ($R = R' = CH_3$), and poly(ethyl methacrylate) ($R = CH_3$; $R' = CH_2CH_3$). The pendant ester groups are taken to be trans to the C−R bond. In this conformation, the directions of the neighboring ester dipoles are nearly parallel.

$$\mu_{\text{eff}} = \lambda\mu^0 + (1 - \lambda)\mu^{\pi} \tag{2}$$

where $\mu^0$ and $\mu^{\pi}$ represent respectively the dipole of the ester group in the $\chi = 0$ and $\pi$ orientation, with $\lambda$ and $1 - \lambda$ being the corresponding weight factors. The effective dipole moment $\mu_{\text{eff}}$ thus estimated can be accommodated in the **G** matrix defined for the skeletal bond in the conventional manner.[5−9]

As easily shown by a proper model, an exceptionally strong dipole−dipole interaction, either repulsive or attractive, may take place when the two successive

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skeletal bonds of a meso dyad are in the trans–trans state (cf. Figure 1). If the two adjacent ester groups take the same orientation, i.e., $(\chi, \chi') = (0, 0)$ or $(\pi, \pi)$, the dipoles must be situated nearly parallel to each other at a separation of only ca. 2.5 Å. An alternate orientation such as $(\chi, \chi') = (0, \pi)$ or $(\pi, 0)$ should be more favorable in the *tt* state. Such a meso-*tt* effect can be properly handled by the expanded matrix algebra technique.

One of the purposes of this paper is to examine the difference between the exact and approximate enumeration techniques mentioned above. We will treat poly(methyl acrylate) (PMA) by the expanded matrix algebra method and compare the results with those derived by employing the preaveraging technique.

In a preceding work,[2] we have studied the mean-square dipole moment of poly(methyl methacrylate) (PMMA) having various tacticities by using the expanded matrix algebra method on the basis of the six-state **U**-matrix scheme prescribed by Vacatello and Flory.[10] A satisfactory reproduction of experimental observations of the dipole moment of the polymer including low molecular weight oligomers was achieved. For the PMMA system, Sundararajan[11] has presented a three-state **U**-matrix scheme almost at the same time as Vacatello and Flory. The neutron scattering function of the glassy polymer has been elucidated by using these two schemes: the six-state scheme exhibited slightly better agreement with the experimental curve.[12] In view of the reasonably small difference between the two results, we have treated the mean-square dipole moment of PMMA on the basis of the three-state scheme of Sundararajan in this work.

Experimental measurements[13−17] of the dipole moment of PMA samples synthesized by radical polymerization having a statistical content of meso dyads $P_m \approx 0.5$ were reported to give the characteristic ratio of the mean-square dipole moment, $D$ $(=\langle M^2\rangle/x\mu^2) = 0.67 \pm 0.01$ at $T \approx 300$ K,[7] where $x$ is the degree of polymerization and $\mu$ the dipole moment of the monomeric residue. As summarized in our preceding paper, the dipole moment ratios of PMMA ranges from $D = 0.71$ (isotactic),[18,19] to 0.64 (atactic with $P_m = 0.21$),[19] to 0.58 (syndiotactic),[18] all determined in benzene at 30 °C. An atactic poly(ethyl methacrylate) (PEMA) sample has been prepared and the dipole moments were measured in four different solvents, benzene, 1,4-dioxane, carbon tetrachloride, and toluene, over the temperature range 20–100°C by Kuntman et al.[5] The dipole moment ratio was found to be in the range 0.62–0.72 at 25 °C when recalculated on the basis of $\mu = 1.73$ D in place of $\mu = 1.86$ D as used in the original paper.[5] The agreement with the corresponding value of PMMA is reasonable, indicating that the addition of a methyl group at the side-chain terminals has little effect. Unless otherwise noted, PMMA and PEMA will be commonly designated as poly(alkyl methacrylate) (PAMA) in the following section.

## Theoretical Framework

A schematic representation of a meso dyad situated along the skeletal chain is shown in its planar trans conformation in Figure 1. The mean-square dipole moment of a given polymer chain can be conventionally expressed by[8,9,20,21]

$$\langle M^2\rangle = Z^{-1} g_0 \left(\prod_{k=1}^{x-1} g_k' g_k''\right) g_x \tag{3}$$

where $g_k'$ and $g_k''$ are respectively the generator matrices defined for the first and second bond of the $k$th dyad, $g_0$ and $g_x$ are respective row and column matrices defined for the two terminal bonds, and $Z$ is the conformational partition function. These generator matrices are given in a general form such as

$$g_k = ((\mathbf{U} \otimes \mathbf{E}_5)||\mathbf{G}||)_k \tag{4}$$

where $\mathbf{E}_5$ is the identity matrix of order 5, **U** the statistical weight matrix, and $||\mathbf{G}||$ may be derived by assembling **G** matrices (eq 1) for the appropriate rotational states of bond $k$ in the diagonal array. The **G** matrix contains information regarding the individual bond rotations expressed in the proper reference frame.

The expanded matrix algebra method enables us to derive an exact RIS average, rotation around the articulated side-chain bond being properly taken into account. In practice, Bernoullian probability $\lambda$ is used to treat the orientational characteristics of the ester group: $\lambda$ for $\chi = 0$ and thus $(1 - \lambda)$ for $\chi = \pi$. The mean-square dipole moment can then be expressed by

$$\langle M^2\rangle = Z^{-1}(\lambda g_0(0)\ (1-\lambda) g_0(\pi)) \left[\prod_{k=1}^{x-1} \begin{pmatrix} g_k' & \\ & g_k' \end{pmatrix} \times \begin{pmatrix} \lambda g_k''(0) & (1-\lambda) g_k''(\pi) \\ \lambda g_k''(0) & (1-\lambda) g_k''(\pi) \end{pmatrix}\right] \begin{pmatrix} g_x \\ g_x \end{pmatrix} \tag{5}$$

where $g(0)$ and $g(\pi)$ represent the generator matrices for $\chi = 0$ and $\pi$ respectively.

As briefly mentioned in the preceding section, special care is required for the orientational correlation of the neighboring ester groups involved in the meso-dyad. When the skeletal conformations around the two successive bonds are both trans (meso-*tt*), the two adjacent ester groups may not be allowed to choose the $\chi = 0$ or $\pi$ position arbitrarily. According to the previous estimation for the meso-*tt* isomer of PMMA,[2] the energy difference between the parallel and alternate orientations amounts to 4.68 kJ mol$^{-1}$. As shown in ref 2, this effect can be easily accommodated in the expanded statistical weight matrix scheme by assigning the parameter $\lambda'$ or $(1 - \lambda')$ to the proper element of the $\mathbf{U}''_m$ matrix (see eqs 6 and 8).

In treating the dipole moment of PMA, we have adopted the two-state scheme previously proposed by Yoon et al.,[22,23] which has been used in the estimation of the conformational characteristics such as unperturbed dimensions, stereochemical equilibria of oligomers, and NMR coupling constants. According to their energy calculation, contribution from one of the gauche states (designated as $\bar{g}$) is negligibly small due to severe steric interactions. The locations of the trans and gauche minima are somewhat (~10°) displaced from the regular 3-fold position. The bond angles are estimated to be $\tau = 112°$ and $\tau' = 114°$ respectively for $\angle CC^{\alpha}C$ and $\angle C^{\alpha}CC^{\alpha}$. The statistical weight matrices are formulated in the $2 \times 2$ form:[22, 23]

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

$$\mathbf{U}''_m = \begin{pmatrix} \omega'' & 1/\eta \\ 1/\eta & \omega/\eta^2 \end{pmatrix} \tag{6}$$

$$\mathbf{U}''_r = \begin{pmatrix} 1 & \omega'/\eta \\ \omega'/\eta & 1/\eta^2 \end{pmatrix}$$

Here a set of parameters deduced to attain agreement with various experimental observations is given as[22]

$$\begin{aligned} \omega &\approx 1.3 \exp(-800/T) \\ \omega' &\approx 1.4 \exp(-800/T) \\ \omega'' &\approx 1.2 \exp(-6.27/RT) \\ \eta &\approx 1.0 \exp(-1.25/RT) \end{aligned} \tag{7}$$

where the conformational energies are expressed in kJ mol$^{-1}$.

To take account of the meso-*tt* effect ($\lambda'$), the $\mathbf{U}''_m$ matrices for the meso dyad (eq 6) must be expanded to a 4 × 4 size.[2] The angle between the unit dipole and the C$^{\alpha}$–C* bond of the ester group was taken to be 123° for PMA in the following calculations.[3,7]

The conformational energy parameters specifically applicable to PEMA chains are not found in the literature. Following Kuntman et al.,[5] we assume that the difference between PEMA and PMMA is small, and the three-state scheme proposed for the latter chain by Sundararajan[11] may be commonly applicable:

$$\mathbf{U}' = \begin{pmatrix} 1 & 1 & 1 \\ 1 & 0 & \psi \\ 1 & \psi & 0 \end{pmatrix}$$

$$\mathbf{U}''_m = \begin{pmatrix} 1 & \alpha & \beta\rho \\ \alpha & \alpha^2/\beta & \alpha\rho \\ \beta\rho & \alpha\rho & \rho^2 \end{pmatrix} \tag{8}$$

$$\mathbf{U}''_r = \begin{pmatrix} \beta & \alpha & \rho \\ \alpha & \alpha^2/\beta & \alpha\rho \\ \rho & \alpha\rho & \beta\rho^2 \end{pmatrix}$$

where

$$\begin{aligned} \alpha &= 0.85 \exp(-E_{\alpha}/RT) \\ \beta &= 0.77 \exp(-E_{\beta}/RT) \\ \rho &= 0.87 \exp(-E_{\rho}/RT) \\ \psi &= 1.00 \exp(-E_{\psi}/RT) \end{aligned} \tag{9}$$

Conformational energy parameters derived from semiempirical energy calculations were slightly modified to improve agreement with the experimental data of the unperturbed dimension for the isotactic and highly syndiotactic chains. A set of parameters thus derived are as follows: $E_{\alpha} = 2.5-4.2$, $E_{\beta} = -2.1$ to $-4.2$, $E_{\rho} = 4.25$, and $E_{\psi} = 10.45$, the unit used being kJ mol$^{-1}$. The displacements of the rotational state from the regular 3-fold position were estimated on the basis of the energy contour diagram by Sundararajan. The torsion angles ($\varphi$) around the skeletal bonds are tabulated for each dyad in Sundararajan's table:[11] meso, ($\varphi_t$, $\varphi_t$) = (−2.8°, −2.8°), ($\varphi_t$, $\varphi_g$) = (1.8°, 112.8°), ($\varphi_t$, $\varphi_{\bar{g}}$) = (−4.1°, −115.8°), ($\varphi_g$, $\varphi_g$) = (119.3°, 119.3°), ($\varphi_g$, $\varphi_{\bar{g}}$) = (113.0°, −109.4°), ($\varphi_{\bar{g}}$, $\varphi_{\bar{g}}$) = (−118.3°, −118.3°); racemic, ($\varphi_t$, $\varphi_t$) = (1.7°, 1.7°), ($\varphi_t$, $\varphi_g$) = (−4.2°, 119.2°), ($\varphi_t$, $\varphi_{\bar{g}}$) = (3.5°, −109.9°), ($\varphi_g$, $\varphi_g$) = (111.9°, 111.9°), ($\varphi_g$, $\varphi_{\bar{g}}$) = (124.0°, −111.1°), ($\varphi_{\bar{g}}$, $\varphi_{\bar{g}}$) = (−111.9°, −111.9°). The bond angles $\tau = 110°$ and $\tau' = 124°$ were adopted.[11] To facilitate comparison, the angle between the unit dipole and the C$^{\alpha}$–C* bond was set equal to 126° for PAMA, the same value being used in Kuntman et al.'s work.[5]

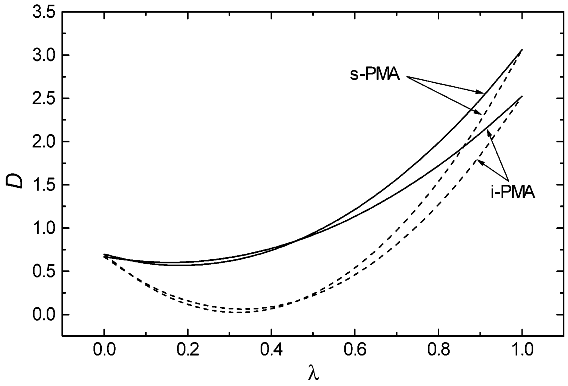

**Figure 2.** Variation of the dipole moment ratio $D$ with the orientation probability of the ester group $\lambda$, calculated for the perfectly isotactic and syndiotactic PMA chains comprising 1000 units at 300 K. The solid curves represent the results obtained by the expanded matrix algebra method and the dashed ones are those from the preaveraging method. For the purpose of comparison, the meso-*tt* effect is not considered in the former calculations (i.e., $\lambda' = 0.5$).

Consideration of the $\lambda'$ effect for the meso-*tt* arrangement requires expansion of the $\mathbf{U}''_m$ matrix to a 6 × 6 scheme. Calculations were performed for chains having the degree of polymerization $x = 1000$. For stereoirregular chains, stereochemical sequences were generated by the Monte Carlo technique and averages were taken over 100 chains.

## Results

**PMA (R = H, R′ = CH$_3$ in Figure 1).** The dipole moment ratios $D$ calculated for the stereoregular PMA chains at 300 K are plotted as a function of the orientation probability $\lambda$ of the pendant ester group in Figure 2: while the solid curves are the results obtained by using the expanded matrix algebra method as prescribed above, those derived according to the preaveraging method are shown by the dashed curves for comparison. In the former calculations, the meso-*tt* effect is neglected by setting $\lambda' = 0.5$. In Figure 2, the difference originating from the mathematical description is substantial except for both extremes, i.e., $\lambda = 0$ and 1. While the values of $D$ derived by the expanded matrix algebra method remain above 0.5 over the entire range of $\lambda$ for both isotactic and syndiotactic chains, those obtained from the preaveraging method tend to decrease to almost nil around $\lambda = 0.3-0.4$.

The effect arising from the strong dipole–dipole interaction expected in the meso-*tt* state was first examined for the isotactic PMA chain for given values of $\lambda$. The dipole moment ratio $D$ was found to decrease monotonically with an increase of $\lambda'$ at any value of $\lambda$.

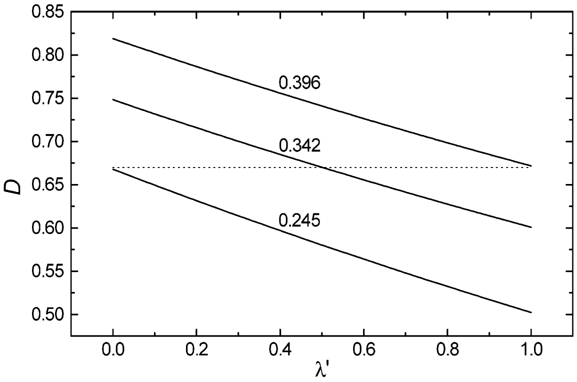

**Figure 3.** Meso-*tt* effect ($\lambda'$) on the dipole moment ratio *D*, the orientation probability $\lambda$ required for the calculation being noted with each curve. Calculations were carried out for the atactic PMA chains ($P_m = 0.5$) of 1000 units at 300 K. The experimental value is shown by the dashed line.

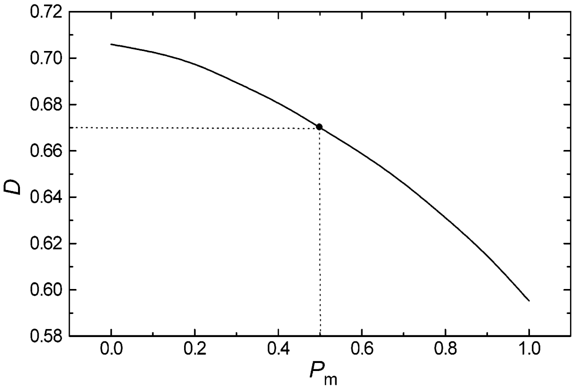

**Figure 4.** Dependence of the dipole moment ratio of PMA chains on the stereochemical constitution, $P_m$. Calculations were carried out for the Monte Carlo chains with 1000 unit at 300 K. A set of parameters $\lambda = 0.377$ and $\lambda' = 0.815$ are so chosen as to fit the experimental range $D = 0.67 \pm 0.01$ (shown by the solid circle) at $P_m = 0.5$.

In Figure 3, the values of *D* calculated for atactic PMA chains ($P_m = 0.5$) are plotted as a function of $\lambda'$ for given values of $\lambda$. The experimental value ($D = 0.67$) reported for PMA samples prepared by a radical polymerization is shown by the dotted line. Values of $\lambda$ consistent with the experimental observation are found in the range 0.245 to 0.396. The orientational correlation of the neighboring ester groups in the meso-*tt* state requires $\lambda' > 0.5$, yielding a probable estimate of $\lambda$ to be 0.342 to 0.396.

Shown in Figure 4 is the variation of *D* with the fraction of meso dyad $P_m$ at 300 K. Calculations were carried out for PMA sequences generated by Monte Carlo method, the orientation probabilities $\lambda$ (0.377) and $\lambda'$ (0.815) being kept invariant. This set of $\lambda$ and $\lambda'$ has been so chosen as to reproduce the experimental value of *D* (0.67) at $P_m = 0.5$. The characteristic ratio *D* decreases monotonically with $P_m$ over the range 0 to 1.

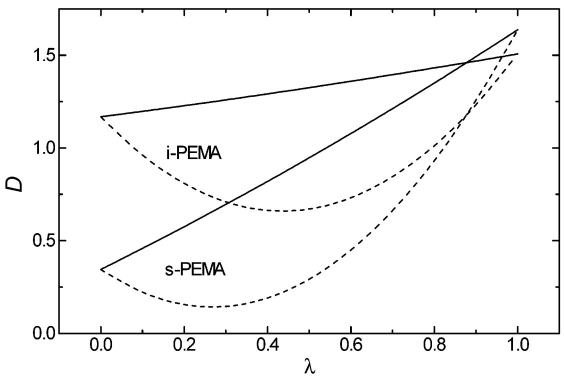

**Figure 5.** Variation of the dipole moment ratio *D* with the orientation probability of the ester group $\lambda$, calculated for the perfectly isotactic and syndiotactic PAMA chains comprising 1000 units at 300 K. The conformational energy parameters required for the calculation were taken from Kuntman et al.'s set. The solid curves represent the results obtained by the expanded matrix algebra method and the dashed ones are those from the preaveraging method. For the purpose of comparison, the meso-*tt* effect is not considered in the former calculations (i.e., $\lambda' = 0.5$).

**PAMA ($R = CH_3$, $R' = CH_3$ or $CH_2CH_3$ in Figure 1).** The dipole moment ratios calculated for the stereoregular syndiotactic and isotactic PAMA chain (300 K) are plotted against $\lambda$ in Figure 5, where the results derived from the two different mathematical models are compared. In these calculations, the value of $\lambda'$ required for the isotactic chain has been kept invariant at 0.5. The conformational energy parameters required are borrowed from those proposed by Kuntman et al.:[5] $E_\alpha = 3.34$, $E_\beta = -2.09$, $E_\rho = 2.09$, and $E_\psi = 10.45$ kJ mol$^{-1}$. The solid curves are those obtained by the expanded matrix algebra and the broken curves by the preaveraging method. While the values of *D* derived by the expanded matrix algebra method vary almost linearly with an increase of $\lambda$ from 0 to 1, the curves are concave for those obtained by the preaveraging method. Essentially the same plot is shown for PMA in Figure 2: although some sizable differences in *D* may be noted in the vicinity of $\lambda = 1.0$, the general trend of the curves is similar between the two figures. For the isotactic PAMA chain, the magnitude of *D* was found to decrease monotonically with increase of $\lambda'$ at any given values of $\lambda$.

In the preceding work,[2] a set of orientation probability parameters $\lambda = 0.270$ and $\lambda' = 0.865$ were found to give a reasonable reproduction of the experimental data of the mean-square dipole moment of isotactic and atactic PMMA. The same values of $\lambda$ and $\lambda'$ were adopted for PEMA in this work. Variation of *D* with the conformational energy parameters were examined for the atactic PEMA chain with $P_m = 0.5$. In Figure 6, the curves calculated according to eq 8 for the temperature of 300 K are plotted as a function of $E_\beta$ for a variety of combinations of $E_\alpha$ and $E_\rho$: (a) $E_\alpha = 4.18$ and $E_\rho = 4.18$, (b) $E_\alpha = 6.27$ and $E_\rho = 4.18$, (c) $E_\alpha = 2.09$ and $E_\rho = 4.18$, (d) $E_\alpha = 4.18$ and $E_\rho = 2.09$, and (e) $E_\alpha = 4.18$ and $E_\rho = 6.27$, with the units being in kJ mol$^{-1}$. In all these calculations, $E_\psi$ was assumed to be 10.45 kJ mol$^{-1}$. The probable range of the conformational energy parameters may be elucidated from the corresponding experimental value of *D* (0.62−0.72): $E_\alpha = 2.09-6.27$, $E_\beta = 0 \sim -2.92$, $E_\rho = 2.09 \sim 4.18$, with the units being kJ mol$^{-1}$ (see Figure 6). These estimates are reasonably compatible with the parameter set proposed for the unperturbed dimension by Sundararajan[11] as well as that used for the dielectric properties by Kuntman et al.[5] The dipole moment of the chain is relatively insensitive to the variation of $E_\alpha$. Figure 7 is the plot of *D* vs $\lambda'$ obtained by the parameters of Kuntman et al., the value of $\lambda$ being kept invariant as indicated for each curve. To reproduce experimental data, a value of $\lambda < 0.35$ is required, which is in a reasonable agreement with those found in the present work for PMA as well as a set of values ($\lambda = 0.270$ and $\lambda' = 0.865$) derived by

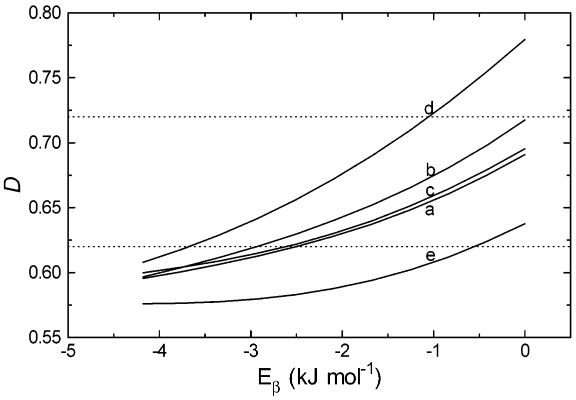

**Figure 6.** Dipole moment ratio $D$ calculated as a function of the conformation energy parameters for atactic PEMA chain ($P_m = 0.5$) at 300 K. The results are plotted as a function of $E_\beta$; other parameters were assigned values such as: (a) $E_\alpha = 4.18$ and $E_\rho = 4.18$; (b) $E_\alpha = 6.27$ and $E_\rho = 4.18$; (c) $E_\alpha = 2.09$ and $E_\rho = 4.18$; (d) $E_\alpha = 4.18$ and $E_\rho = 2.09$; (e) $E_\alpha = 4.18$ and $E_\rho = 6.27$ kJ mol$^{-1}$, $E_\psi$ being set equal to 10.45 kJ mol$^{-1}$. In these calculations, the values of $\lambda$ and $\lambda'$ required are taken from the previous analysis of PMMA ($\lambda = 0.270$ and $\lambda' = 0.865$). To facilitate comparison, the observed range of $D$ (0.62−0.72) is shown by the two dotted horizontal lines.

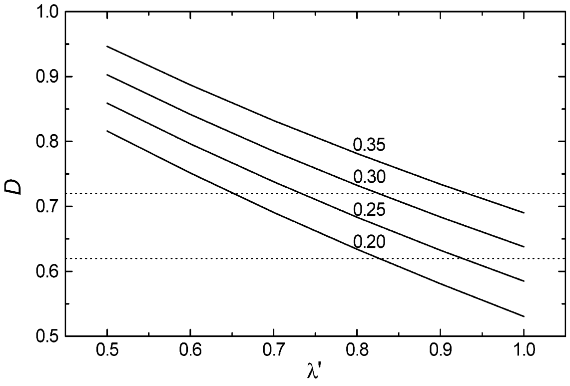

**Figure 7.** Meso-*tt* effect ($\lambda'$) on the dipole moment ratio $D$, the orientation probability $\lambda$ required for the calculation being noted with each curve. Calculations were carried out for the atactic PAMA chains ($P_m = 0.5$) of 1000 units at 300 K. For dotted lines, see the caption to Figure 6.

using six-state scheme in the previous treatment of PMMA.[2]

Variation of the dipole moment ratio $D$ with the stereochemical constitution $P_m$ was also examined in the three-state scheme. The $D$ vs $P_m$ plot previously reported for PMMA on the basis of the six-state scheme of Vacatello and Flory (Figure 5 of ref 2) was confirmed: as before, the curve exhibits a shallow minimum at around $P_m = 0.15$. Since the two curves closely resemble with each other, the diagram is not shown here. Kuntman et al.[5] have reported a $D$ vs $P_m$ plot for PEMA on the basis of the preaveraging method. Their calculation suggested a monotonic decrease of $D$ from the syndiotactic ($D =$ ca. 0.8 at $P_m = 0.0$) to the isotactic side ($D =$ ca. 0.6 at $P_m = 1.0$), which is inconsistent with the trend of our calculation[2] as well as the experimental findings of Shima et al.[18] on PMMA. Finally it may be interesting to note that the same plot of PMA is convex (cf. Figure 4) in opposite to that of PAMA.

## Discussion

The mean-square dipole moment of polymer chains carrying pendant ester groups have been studied in this work by the two-state and three-state schemes, respectively, for PMA and PAMA, and previously by the six-state scheme for PMMA. As shown in Figures 2 and 5, the divergence between the expanded matrix algebra and the preaveraging methods reaches maximum around $\lambda = 0.5$, gradually diminishing to zero at either $\lambda = 0$ or 1. In these calculations, the meso-*tt* effect is ignored by setting $\lambda' = 0.5$ (see eq 11 of ref 2). The difference between the two approaches may be demonstrated by a simple analysis on a dimer (or a dyad) model. The mean-square dipole moments expressed in these two schemes take somewhat different algebraic form. According to the expanded matrix algebra method,

$$\langle M^2\rangle_e = \lambda^2 \langle(\mu_1^0 + \mu_2^0)^2\rangle + \lambda(1-\lambda)[\langle(\mu_1^0 + \mu_2^\pi)^2\rangle + \langle(\mu_1^\pi + \mu_2^0)^2\rangle] + (1-\lambda)^2\langle(\mu_1^\pi + \mu_2^\pi)^2\rangle \quad (10)$$

where subscripts 1 and 2 designate the two separate dipoles $\mu$ of the dimer, and the orientations of these dipoles are distinguished by superscripts 0 and $\pi$. In the preaveraging scheme, it should be given as

$$\langle M^2\rangle_p = \langle[\lambda\, \mu_1^0 + (1-\lambda)\mu_1^\pi + \lambda\, \mu_2^0 + (1-\lambda)\mu_2^\pi]^2\rangle \quad (11)$$

Taking the difference between these two equations,

$$\langle M^2\rangle_e - \langle M^2\rangle_p = \lambda(1-\lambda)[(\mu_1^0 - \mu_1^\pi)^2 + (\mu_2^0 - \mu_2^\pi)^2] \quad (12)$$

and dividing by $x\mu^2$ ($x = 2$), we obtain an expression such as

$$D_e - D_p = 2\lambda(1-\lambda)(1 - \cos\delta) \quad (13)$$

where subscripts e and p respectively represent the expanded matrix algebra and the preaveraging method, and $\delta$ denotes the angle between $\mu^0$ and $\mu^\pi$. The difference thus derived does not contain any term associated with the relative orientation of the two dipoles, and thus it is effective independent of the stereochemical constitution of the dimer. The treatment presented above can be generalized for polymeric systems carrying multiple dipoles or including more than two orientational states of the side group. As may be demonstrated by a simple manipulation, the difference between the solid and broken curves shown in Figures 2 and 5 are satisfactorily explained by adopting $\delta = 114$ and 108° respectively for PMA and PAMA. The orientational correlation ($\lambda'$) inherent to the meso-*tt* conformation cannot be handled in such a simple manner.

The conformational energy parameter sets adopted in the present treatment are mostly identical with those previously used in estimating the other conformation-dependent properties such as the unperturbed dimensions and their temperature coefficients. In our calculations of the dipole moment of PMA and PAMA, experimental observations have been successfully reproduced by adjusting orientation probabilities, $\lambda$ and $\lambda'$, of the ester group. A value of $\lambda \sim 0.3$ amounts to the preference of the trans ($\chi = \pi$) over the cis conformation ($\chi = 0$) by about 2.1 kJ mol$^{-1}$ at 300 K in terms of the simple Boltzmann expression. This result is in opposite to that predicated from the force field calculation[3], which suggests that the trans has an energy of ca. 0−0.82 kJ mol$^{-1}$ higher than the cis orientation. A value of $\lambda' \sim 0.8$ for the meso-*tt* effect corresponds to an energy difference of about 3.7 kJ mol$^{-1}$ between the parallel and alternate orientations of the ester dipole.

In Ojavo et al.'s treatment of PMA,[4] the two orientations of the ester group have been considered in elucidating the statistical weight matrices comprising four rotational states. Nevertheless, they adopted the preaveraged dipole moment for the repeat unit as defined by eq 2 in calculating the mean-square dipole moment of the polymer. In their model, the direction of the dipole moment of the ester group was assumed to make an angle of 40° with respect to the C*═O* bond, which was later surpassed by the more elaborate model (with the displacement angle of ∼0°) proposed by Saiz et al.[3]

Experimental values of the temperature coefficient $d(\ln\langle M^2\rangle)/dT$ are somewhat divergent for both PMA and PAMA. Kotera at al.[16] reported a slight increase of $D$ over a range 20−50 °C for an atactic PMA. Masegosa et al.[17] noted for the same polymer that the slightly positive $D$ vs $T$ plot (20−30 °C) abruptly exhibited a sharp disruption in the region 30−35 °C, yielding a maximum at about 30 °C and a minimum at around 35 °C. According to Kuntman et al.,[5] the temperature coefficient of PEMA could be positive or negative depending on the solvent and temperature. More recently, Shima et al.[18] carried out dielectric studies on highly stereoregular PMMA samples: $d(\ln\langle M^2\rangle)/dT \sim 0$ and $3.72 \times 10^{-3}$ K$^{-1}$ respectively for isotactic and syndiotactic chains. In our previous paper,[2] the experimental values of Shima et al. have been shown to be consistent with the theoretical treatment using the six-state scheme. The temperature coefficients of atactic PMA and PAMA are predicted to be positive in our calculation.

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