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Conformational Characteristics of Poly(ethyl methacrylate). Dipole Moment Measurements and Calculations

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ABSTRACT: Dipole moment measurements of poly(ethyl methacrylate) (PEMA) have been performed in four different solvents, benzene, 1,4-dioxane, carbon tetrachloride, and toluene, in a temperature range of about 20–100 °C. Experimental measurements have been theoretically analyzed on the basis of rotational isomeric state formalism. Energetic and geometric parameters proposed for poly(methyl methacrylate) are found to give a reasonable account of the experimentally measured values, in general. However, the change in average dipoles with temperature is found to exhibit a substantial dependence on the type of solvent, which indicates the importance of specific solvent–polymer interaction on the conformational characteristics of the chain.

Introduction

A large number of papers have been published on the conformational characteristics and dipole moment measurements of poly(methyl methacrylate) (PMMA)[1–7] and poly(methyl acrylate) (PMA)[8–13] chains in dilute solutions. However, the published data related to the experimental dipole moment measurements of poly(ethyl methacrylate) (PEMA) in solutions are limited.

In the present study we first report experimental results on dipole moment measurements of PEMA chains in various solvents over a wide range of temperature. The variation of dipole moment with temperature is found to exhibit a clear dependence on solvent, which indicates a change in short-range interactions at a given temperature. Several samples of PEMA with known molecular weights are used for experimental work. The experimental results are compared with the predictions of the the rotational isomeric state (RIS)[14] model of chain equilibrium statistics.

Experimental Methods and Results

Sample Preparation. The ethyl methacrylate monomer was a product of the Rohm and Haas Co. It was washed with 5% NaOH solution and H_2O, dried with $MgSO_4$, and freshly distilled under reduced pressure before use (bp 54 °C at 10^4 Pa). Bulk polymerization of the monomer was carried out at 80 °C under reduced pressure, using 2,2′-azobis(isobutyronitrile) as initiator. The polymer obtained was dissolved in acetone, precipitated in a methanol/water mixture, filtered, and dried in a vacuum oven overnight. Two samples of PEMA were obtained by using the above procedure. The molecular weights of the polymers were determined by viscometry using the relationship

$$[\eta] = 3.46 \times 10^{-5} M^{0.81} \qquad (1)$$

for methyl ethyl ketone solutions at 35 °C.[15] The viscosity average molecular weights of PEMA samples were found to be $M_v = 7.0$ 10^5 and 4.0×10^5. The second sample was selected for dielectric work. The samples, resulting from free-radical polymerization, are accepted to be atactic.

Dielectric Measurements. All dielectric measurements were performed on a WTW Model DM-01 dipole meter operating at a frequency of 2 MHz. The type of the cell used was DFL1 with a working range of dielectric constant of 1.8–7. The temperature of the cylindrical measuring cell could be controlled to less than ±0.05 °C. The instrument was calibrated at every working temperature with air ($\epsilon_0 = 1.000$) and by using liquids with well-known dielectric constants (cyclohexane, benzene, toluene, and 1,4-dioxane).[16] All of the solvents used for calibration and dielectric measurements were purified according to standard procedures and freshly distilled.[17] Dielectric constants ϵ of solvents and solutions were determined by using the method of evaluation of the dipole meter constants.[18] The uncertainties in ϵ were ±0.002.

Dielectric measurements were performed at constant temperature (±0.05 °C), and all solutions were prepared by weighing both components. Dielectric increments of PEMA solutions were measured at several temperatures ranging from 20 to 90 °C. The dependence of the dielectric constant (ϵ) on the weight fraction (ω) of polymer is linear for concentrations smaller than $\omega \approx 1.0 \times 10^{-2}$; all measurements have been made for concentrations smaller than this value. As a typical example, the dependence of dielectric constants on weight fractions of PEMA in toluene solutions is given in Figure 1. Similar plots were constructed for PEMA solutions of benzene, 1,4-dioxane, and carbon tetrachloride at a wide range of temperature.

Refractive Indices and Densities. The refractive index increment value at 25 °C in benzene, $(dn/dc) = 0.007$ mL/g, is used for the dipole moment calculations of PEMA. This value is in good agreement with the values reported for PMMA[19] and PMA[11] under similar conditions. Refractive index increment values of PEMA in toluene, 1,4-dioxane, and carbon tetrachloride are calculated by using the relationship

$$\left(\frac{dn}{dc}\right)_A - \left(\frac{dn}{dc}\right)_B = \frac{n_B - n_A}{\rho_p} \qquad (2)$$

where n_A and n_B denote the refractive indices of solvents A and B, respectively, and ρ_p is the density of PEMA ($\rho_p = 1.11$ g/mL).[20] The densities and refractive index values of all solvents are calculated from literature data[21] and used in dipole moment calculations.

Mean-square dipole moments (esu) per repeat unit of the polymer chain were calculated from an appropriate form of the Guggenheim–Smith equation[22,23]

$$\langle \mu^2 \rangle / x = \frac{27kTM_0}{4\pi N(\epsilon_1 + 2)^2 d_1}\left[\left(\frac{d\epsilon}{d\omega_2}\right)_{\omega_2 \to 0} - \left(\frac{dn^2}{d\omega_2}\right)_{\omega_2 \to 0}\right] \qquad (3)$$

where x is the number of repeat units in the polymer, M_0 is the molar weight of a repeat unit, k is the Boltzmann constant, N is Avogadro's number, T is the absolute temperature, d_1 is the solvent density, ϵ is the static dielectric constant, n is the refractive index for visible light (546 nm for the increments), ω_2 is the weight

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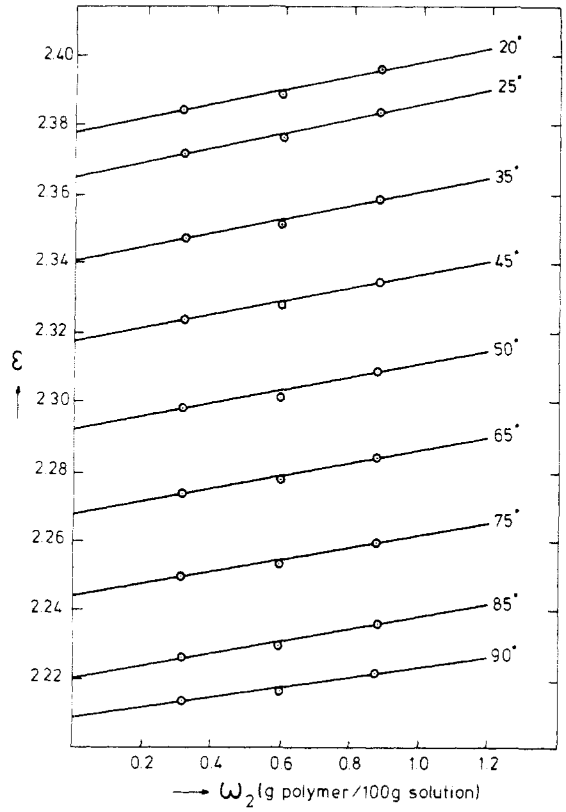

Figure 1. Dependence of dielectric constants on weight fraction of PEMA in toluene solution at the indicated temperatures.

Table I
Values of $(d\epsilon/d\omega_2)_{\omega_2\to 0}$ for PEMA at Different Temperatures in Different Solvents

	$(d\epsilon/d\omega_2)_{\omega_2\to 0}$			
T, °C	benzene	toluene	1,4-dioxane	carbon tetrachloride
20	2.16	2.04	2.46	3.42
25	2.02	3.13	2.44	3.39
30				3.42
35	1.96	2.02	2.49	3.27
45	1.85	2.00	2.35	3.27
55	1.75	1.95	2.39	2.24
65	1.63	1.87	2.31	3.12
70	1.61			3.16
75		1.74	2.20	
85		1.73	2.18	
90		1.53	2.20	

fraction of the polymer, and the subscript 1 refers to values for pure solvent.

Experimental Results. It has been established in an earlier dielectric work on PMA chains that $\langle\mu^2\rangle/x$ does not depend on x for polymers having molecular weights comparable to our PEMA samples.[12] Therefore, we have not fractionated our polymeric samples for dielectric measurements. Table I shows the values of $(d\epsilon/d\omega_2)_{\omega_2\to 0}$ for PEMA at all measureed temperatures for all solvents.

Values of $\langle\mu^2\rangle/x$ computed according to eq 3 were reduced to the dimensionless dipole moment ratio $D_x = \langle\mu^2\rangle/(x\mu_0^2)$, where μ_0 is the dipole moment of a repeat unit. We have determined the dipole moment of n-butyl acetate as $\mu_0 = 1.86$ D in benzene solutions, which is in agreement with the reported dipole moment value of this compound in the same solvent ($\mu_0 = 1.85$ D, 25 °C).[24] This value was used as the dipole moment, μ_0, of the repeat unit. Figure 2 shows the experimental values of dipole moment ratios as a function of temperature for PEMA in four solvents.

Rotational Isomeric State Calculations of Mean-Square Dipole Moments

Following the conventional conformational analysis of vinyl chains, two types of statistical weight matrices are defined: (i) $\mathbf{U}'$ for the pair of bonds flanking the C^α atom and (ii) $\mathbf{U}_m''$ and/or $\mathbf{U}_r''$ for the adjacent pair of bonds within the meso (m) and/or racemic (r) diads, respectively. Those matrices may be expressed as a function of four interaction parameters, α, β, ρ, and ψ, according to[7]

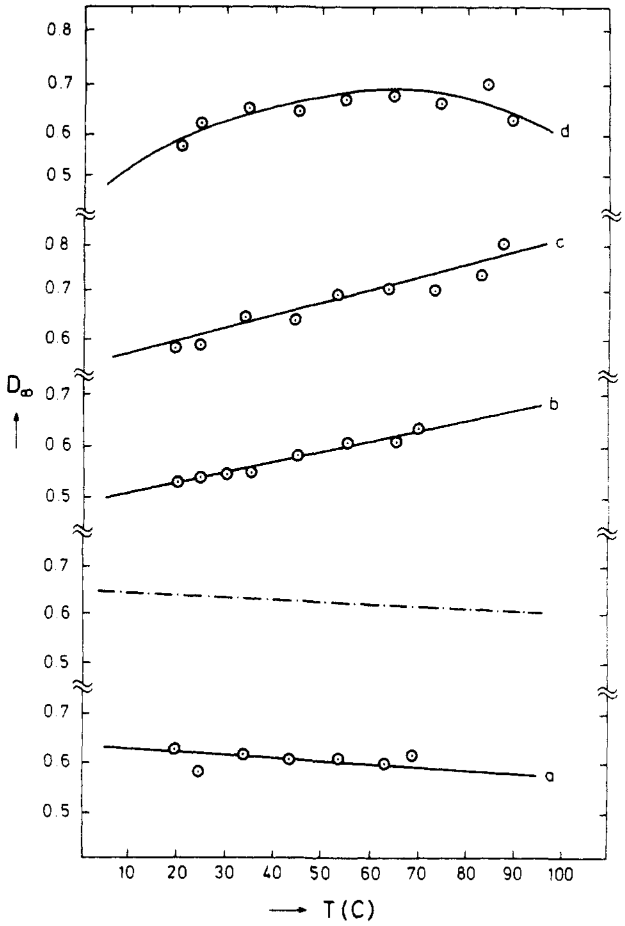

Figure 2. Dependence of D_∞ on temperature for PEMA in (a) benzene, (b) carbon tetrachloride, (c) 1,4-dioxane, and (d) toluene. The dot-dashed curve is theoretically obtained by using the RIS formalism.

$$\mathbf{U}' = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 0 & \psi \\ 1 & \psi & 0 \end{bmatrix} \tag{4}$$

$$\mathbf{U}_m'' = \begin{bmatrix} 1 & \alpha & \beta\rho \\ \alpha & \alpha^2/\beta & \alpha\rho \\ \beta\rho & \alpha\rho & \rho^2 \end{bmatrix} \tag{5}$$

$$\mathbf{U}_r'' = \begin{bmatrix} \beta & \alpha & \rho \\ \alpha & \alpha^2/\beta & \alpha\beta \\ \rho & \alpha\rho & \beta\rho^2 \end{bmatrix} \tag{6}$$

provided that three states t, g, and $\bar{g}$ are accessible per bond. A meso diad of the PEMA chain, in all-trans conformation, is shown in Figure 3. In view of the differences in the shape and size of isomeric minima in the conformational energy maps, the above energy parameters are expressed as[25]

$$\zeta = \zeta_0 \exp\{-E_\zeta/RT\} \tag{7}$$

where ζ stands for α, β, ρ, and ψ. For PMMA, the following optimal values have been deduced from energetic considerations[7]

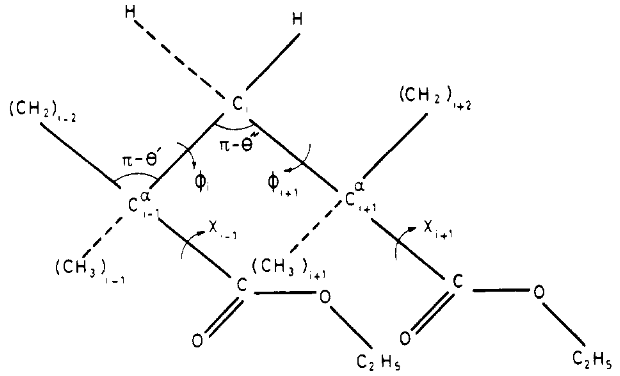

Figure 3. Schematic representation of a meso diad of PEMA, in the all-trans configuration.

$$\begin{aligned}\alpha &= 0.85 \exp\{-E_\alpha/RT\}\\ \beta &= 0.77 \exp\{-E_\beta/RT\}\\ \rho &= 0.87 \exp\{-E_\rho/RT\}\\ \psi &= 1.00 \exp\{-E_\psi/RT\}\end{aligned} \tag{8}$$

with $E_\alpha = 0.991$, $E_\beta = -0.358$, $E_\rho = 1.016$, and $E_\psi = 2.5$ kcal/mol.

The three-state scheme adopted by Sundararajan for the conformational analysis of PEMA[7] will be used in the present study. The presence of an ethyl group instead of the methyl group at the end of the ester side group will be assumed to be of negligible significance in prescribing the statistics of the backbone. Accordingly, energy parameters obtained for PMMA will be adopted in the following. In view of the limitations of the semiempirical functions conventionally used in conformational calculations, the energy parameter will be varied within reasonable ranges to achieve agreement with experimental results.

The unperturbed mean-square dipole moment $\langle \mu^2 \rangle_0$ is computed from

$$\langle \mu^2 \rangle_0 = Z^{-1} \mathcal{G}_0 [\prod_{k=1}^{x-1} U' \mathcal{G}_k'] \mathcal{G}_x \tag{9}$$

where the configurational partition function, Z, and the generator supermatrices U', $\mathcal{G}_0$, and $\mathcal{G}_x$ are evaluated following procedures previously described.[26,27] In particular, $\mathcal{G}_k$ takes the form

$$\mathcal{G}_k = \begin{bmatrix} \mathbf{G}'(\mathrm{t}) & 0 & 0 \\ 0 & \mathbf{G}(\mathrm{g}) & 0 \\ 0 & 0 & \mathbf{G}'(\bar{\mathrm{g}}) \end{bmatrix} [\mathbf{U}'' \otimes \mathbf{E}_5] \begin{bmatrix} \mathbf{G}''(\mathrm{t}) & 0 & 0 \\ 0 & \mathbf{G}'' & 0 \\ 0 & 0 & \mathbf{G}''(\bar{\mathrm{g}}) \end{bmatrix} \tag{10}$$

E is the identity matrix of order 5, ⊗ denotes the direct product, the terminal matrices $\mathcal{G}_0$, $\mathcal{G}_x$, $\mathbf{U}_0$, and $\mathbf{U}_x$ retain their previous definitions,[27] and $\mathbf{G}'$ and $\mathbf{G}''$ are the related generator matrices[27,28] for the first and second bond of a given diad, as indicated by the superscripts. Their arguments refer to the isomeric states t, g, and ḡ. They are given by

$$\mathbf{G} = \begin{bmatrix} 1 & 2\mu^{\mathrm{T}}\mathbf{T} & \mu^2 \\ 0 & \mathbf{T} & \mu \\ 0 & 0 & 1 \end{bmatrix} \tag{11}$$

Here **T** is the transformation matrix for expressing vectors or tensors of a given bond-based coordinate system in the preceding bond-based frame along the chain.[14,27] μ and μ^{T} are the dipole vector per repeat unit and its transpose. **G** assumes different forms depending on the tacticity of the diad in conformity with the prescription[26]

$$\begin{aligned}\mathbf{G}_{\mathrm{m}}' &= \mathbf{G}(\mathbf{T}^{*\prime})\\ \mathbf{G}_{\mathrm{r}}' &= \mathbf{G}(\mathbf{T}')\\ \mathbf{G}_{\mathrm{m}}'' &= \mathbf{G}(\mathbf{T}^{*\prime\prime})\\ \mathbf{G}_{\mathrm{r}}'' &= \mathbf{G}(\mathbf{T}^{*\prime\prime})\end{aligned} \tag{12}$$

where $\mathbf{T}^* \equiv \mathbf{T}$ diag (1, 1, −1) is the transformation matrix operating between left-handed and right-handed coordinate systems, which are assigned to levo (*l*) and dextro (*d*) bonds, respectively; the primes indicate the pairs of bonds on which the transformation matrices operate. It should be noted that the levo and dextro terminology is used here to indicate bond chirality and is not related to optical activity. The bond angles $\theta' = 110°$ and $\theta'' = 124°$ (see Figure 3) are used in the present study together with the rotational angles tabulated in ref 7. Those values apply to both *d* and *l* bonds, inasmuch as a left-handed coordinate system is assigned to the latter.

The direction of the dipole moment vector with respect to the local bond-based frame of a C^α–C bond is determined as follows. It is well established that the ester group is planar with the OR group trans to the C^α–C* bond. Energetic calculations indicate that the two states defined by the C^α–C* torsional angles $\chi = 0°$ and 180° are the most stable.[29] The $\chi = 180°$ configuration corresponds to the case where the C*═O* bond is cis to C^α–CH_3. It possesses a conformational energy of ca. 0.1 kcal/mol higher than that of the $\chi = 0°$ configuration. In conformity with the approach used in the calculation of the dipole moment of poly(methyl acrylate) by Tarazona and Saiz,[13] an effective dipole moment, μ_e, is evaluated per repeat unit, by weighting the contribution of both configurations by their Boltzmann factors. By adopting $\Delta E = 0.12$ kcal/mol for the excess energy of the $\chi = 180°$ state with respect to the $\chi = 0°$ state, using bond angles $CC^\alpha C = 110°$ and $CC^\alpha CH_3 = 109.5°$, and taking $\tau = 126°$ where τ is the angle the dipole moment vector makes with the C^α–C* bond (i.e., μ_e is almost parallel to C*═O*), μ_e equates to $\mu_e(0.233–0.333 \pm 0.432)^{\mathrm{T}}$ at 300 K, and the magnitude μ_e and μ_e becomes $0.593\mu_0$ where $\mu_0 = 1.85$ D as mentioned above. The preaveraging over χ prior to RIS calculations leads to a reduction in the magnitude of the dipole vector assigned to each unit. μ_e is readily inserted into eq 13, which is used in eqs 9–12, to computer D_x.

For a thorough understanding of the dependence of D_∞ on the orientation of the dipole moment of the ester group, calculations were performed as a function of τ, as illustrated in Figure 4. The curves are representative of atactic chains of 100 units with a Bernouillian distribution of meso and racemic diads, subject to conformational energy parameters equal to (a) $E_\alpha = 0.8$, $E_\beta = -0.5$, and $E_\rho = 0.5$, (b) $E_\alpha = 0.991$, $E_\beta = -0.358$, and $E_\rho = 1.016$, (c) $E_\alpha = 0.5$, $E_\beta = -0.5$, and $E_\rho = 0.5$, and (d) $E_\alpha = 1.0$, $E_\beta = 0.0$, and $E_\rho = 0.5$ kcal/mol. Those values lie within a range of ±0.5 kcal/mol with respect to those given by eq 8. Figure 4 calls attention to the importance of the direction of the dipole moment of the ester group in prescribing the average dipole of the chain. Examination of the curves in relation to experimental results shows that $115° < \tau < 130°$ is a reasonable range.

The optimal choice of energy parameters applicable to PEMA is determined from extensive calculations carried out for a variety of energy values, as displayed in Figure 5. The curves represent D_∞ values as a function of E_α for (a) $E_\beta = -0.5$ and $E_\rho = 0.5$, (b) $E_\beta = -0.5$ and $E_\rho = 1.0$, (c) $E_\beta = -1.0$ and $E_\rho = 0.5$, (d) $E_\beta = 0$ and $E_\rho = 0.5$, and (e)

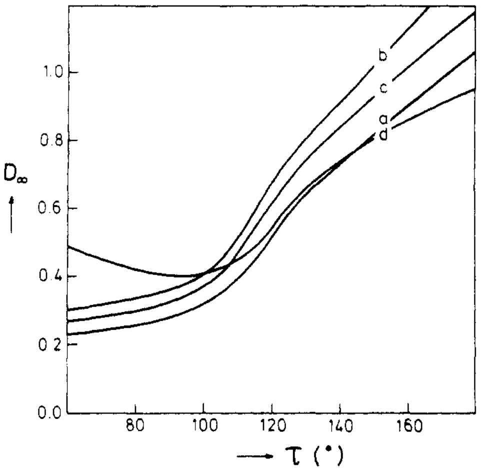

Figure 4. Dependence of D_∞ on the direction of the dipole moment in the ester group. Curves are obtained for atactic chains at 300 K, with the energy parameters (a) $E_\alpha = 0.8$, $E_\beta = -0.5$, and $E_\rho = 0.5$, (b) $E_\alpha = 0.991$, $E_\beta = -0.358$, and $E_\rho = 1.016$, (c) $E_\alpha = 0.5$, $E_\beta = -0.5$, $E_\rho = 1.0$, and (d) $E_\alpha = 1.0$, $E_\beta = 0.0$, and $E_\rho = 0.5$ kcal/mol.

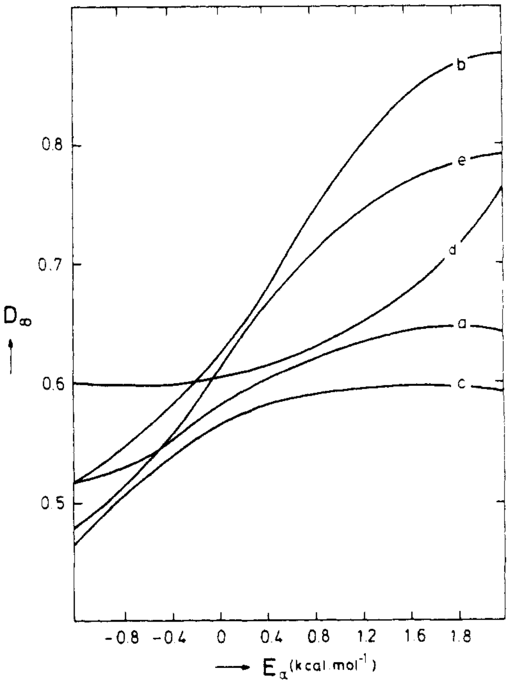

Figure 5. Dependence of D_∞ on conformational energy parameters. Curves are obtained for atactic chains at 300 K, as a function of E_α with the use of the energy parameters (a) $E_\beta = -0.5$ and $E_\rho = 0.5$, (b) $E_\beta = -0.5$ and $E_\rho = 1.0$, (c) $E_\beta = -1.0$ and $E_\rho = 0.5$, (d) $E_\beta = 0$ and $E_\rho = 0.5$, and (e) $E_\beta = -1.0$ and $E_\rho = 1.0$ kcal/mol.

$E_\beta = -1.0$ and $E_\rho = 1.0$ kcal/mol. From comparison with experimental data, the set $E_\alpha = 0.8$ kcal/mol, $E_\beta = -0.5$ kcal/mol, and $E_\rho = 0.5$ kcal/mol is adopted for PEMA to investigate the dependence of D_∞ on tacticity and temperature; ω_m in the abscissa of Figure 6 refers to the weight fraction of meso diads in the chain. A substantial dependence on tacticity is observed. On the basis of the polymerization mechanism, our sample is expected to be atactic, with $\omega_m = 0.5$. As to the temperature dependence, which is displayed by the dashed curve in Figure 2, the coefficient $d \ln D_\infty / dT = -8.6 \times 10^{-4}/°C$ is found to agree with the measurements carried out in benzene, while the positive slope observed with carbon tetrachloride, dioxane, and toluene is not reproduced by the theory. The latter may be attributed to specific polymer–solvent interaction in the presence of those solvents, which is not rigorously considered in the conventional RIS calculation scheme.

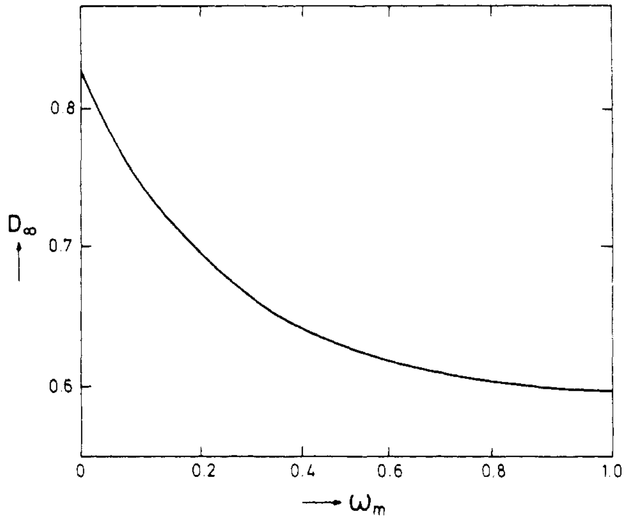

Figure 6. Dependence of D_∞ on chain tacticity. ω_m indicates the fraction of meso diads in the chain.

Discussion

Mean-square dipole moments for isotactic (meso) and syndiotactic (racemic) chains were calculated at various degrees of polymerization up to $x = 100$. The ratios D_x rapidly approach their limits D_∞ with an increase in x.[24] Experimental results of dipole moment measurements for PMA chains also indicate that the values of D_x are insensitive to x, within the range of molecular weights studied in the present work.[11]

Experimental data about the variation of D_∞ with temperature have cumulated steadily during the last 20 years. Peculiar changes in the variation of dipole moment ratios with temperature have been reported for various polymer–solvent systems.[2,4,11,30–34] The present analysis demonstrates that, for PEMA, a reasonable agreement is obtained between experiments and theory as far as the magnitudes of the average dipoles are concerned. The latter is achieved by a slight readjustment of the energy parameters determined from PMMA.[7] However, a correct interpretation of the temperature dependence of dipole moments necessitates a more thorough examination of the specific polymer–solvent interaction and cannot be accounted for by a conventional RIS formalism based on unperturbed chain characteristics, unless the latter is modified so as to incorporate the specific solvent effect.

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Registry No. PEMA, 9003-42-3; benzene, 71-43-2; toluene, 108-88-3; 1,4-dioxane, 123-91-1; carbon tetrachloride, 56-23-5.