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Calculation of the Dipole Moment of Poly(methyl acrylate) with a Two-Rotational-States Scheme

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ABSTRACT: Dipole moments of poly(methyl acrylate) (PMA) are calculated with the rotational isomeric scheme with two states per bond previously used by Flory and co-workers to calculate some other conformation-dependent properties of this polymer. When the dipole moment of the ester group lateral to the chain is placed in the orientation deduced by the semiempirical method recently reported, calculated values of the dipole moment are in excellent agreement with experimental results without any kind of adjustment of the energy parameters obtained by Flory and co-workers. The two-states scheme is therefore able to reproduce all the experimental magnitudes reported to date for this polymer, i.e., dimensions, dipole moments, stereochemical equilibria, and NMR coupling constants.

Introduction

The conformational characteristics of poly(methyl acrylate) (PMA) were studied by Flory and co-workers.[1] Their conformational energy calculations allowed them to disregard the g^- rotational isomer because of its high energy, and consequently they proposed a rotational isomeric scheme with two states per bond (with trans (t) and gauche (g) states at $\phi_t = 10°$ and $\phi_g = 110°$) containing four energy parameters (η, ω, ω' and ω'') for this polymer. Comparison of theoretical and experimental values of some conformation-dependent properties (i.e., dimensions, stereochemical equilibria in the dimeric and trimeric oligomers, and NMR coupling constants) permitted the optimization of these energy parameters and the choice of a "best set" which reproduced the experimental values for all these magnitudes.

Some years later, Ojalvo et al.[2] tried to calculate the dipole moment $\langle\mu^2\rangle$ of PMA chains. This kind of calculation requires a previous knowledge of the modulus and the direction of the dipole moment in the repeat unit μ_0. Methyl propionate was taken as a model compound for μ_0 and Le Fevre's experimental value[3] in benzene solution at 25 °C, $|\mu_0| = 1.76$ D, was used. Unfortunately, no experimental determination of the direction of the dipole μ_0 for methyl propionate or any other suitable model compound was available at that time, and methyl formate was used as a model compound for this direction, so that μ_0 was assumed to make an angle of $\gamma \simeq 40°$ with the C=O bond ($\tau \simeq 81°$; see below) as Curl[4] reported to be the case for methyl formate. The introduction of the μ_0 vector thus defined (modulus 1.76 D, orientation $\tau \simeq 81°$) lead Ojalvo et al. to conclude that the two-states model previously used for PMA was not suitable for the calculation of the dipole moment; consequently they proposed a four-states scheme obtained by splitting each rotational isomer into two different states according to the position of the lateral ester group (this splitting required the use of two new energy parameters) and a modification of the direction of μ_0 by assuming that the C–H bond attached to the tertiary carbon had a noticeable contribution to the dipole moment of the repeating unit.

Recently, Saiz et al.[5] presented a semiempirical method of determining the direction of the dipole moment and applied it to elucidate the actual direction of this vector in the ester group. They came to the conclusion that the dipole moment in esters RCOOR′, in which R and R′ are alkyl or aryl groups (but not hydrogen), is roughly antiparallel to the C=O bond, directed at an angle $\tau = 123 \pm 3°$ from the R–C bond (see figure 1).

The analysis presented by Saiz et al.[5] is directly applicable to the repeat unit of the PMA chain; in fact, one of the compounds they studied, dimethyl *trans*-1,4-cyclohexanedicarboxylate (CDC), may be regarded as the junction of two segments $CH_2CH(COOCH_3)CH_2$ of the polymer. Thus it seems interesting to find how this new information on μ_0 affects the calculation of the dipole moment in the PMA chain, and this is the aim of the present paper.

Table I
Energy Parameters for PMA[a]

$p = p_0 \exp(-E_p/RT)$

parameter (p)	preexp factor (p_0)	energy, kcal mol^{-1} (E_p)
η	1.0	−0.3 ± 0.1
ω	1.3	1.6
ω'	1.4	1.6
ω''	1.2	1.5 ± 0.3

[a] Taken from ref 1.

Calculation Method

Following Flory's scheme, only two rotational states t and g, placed at the averaged values $\phi_i = 10°$ and 110°, respectively, were allowed for the backbone of the chain; the pertinent statistical weight matrices were thus[1,6]

$$U' = \begin{bmatrix} 1 & 1 \\ 1 & 0 \end{bmatrix} \qquad U_m'' = \begin{bmatrix} \omega'' & 1/\eta \\ 1/\eta & \omega/\eta^2 \end{bmatrix}$$
$$U_r'' = \begin{bmatrix} 1 & \omega'/\eta \\ \omega'/\eta & 1/\eta^2 \end{bmatrix} \tag{1}$$

The "best set" of values of the energy parameters obtained by optimization of theoretical results of dimensions, stereochemical equilibria, and NMR coupling constants is summarized in Table I and is used throughout the calculations.

It has been well established that the methyl ester group is planar, with the O–CH_3 bond trans to the C^α–C* bond.[4,7-10] In the case of PMA, there is still a degree of freedom for rotation around the C^α–C* bond; we denote this rotation by χ and assign the value $\chi = 0$ to the conformation in which the bond C* = O* is cis to the C^α–H bond, as represented in Figure 2. Force field calculations performed for methyl isobutyrate[5] showed that, among the six local minima obtained by rotation of χ, the cis conformation ($\chi = 0$) is the preferred one; the trans conformation ($\chi = 180°$) has an energy of ca. 0–0.2 kcal mol^{-1} higher than cis, and all the others have energies of at least 1.5 kcal mol^{-1} above that of cis. We let E_ρ denote the energy of trans over cis, assign statistical weights ρ =

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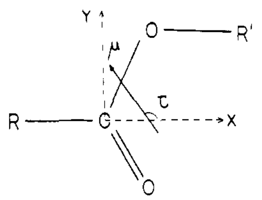

Figure 1. Direction of the dipole moment of the ester group.

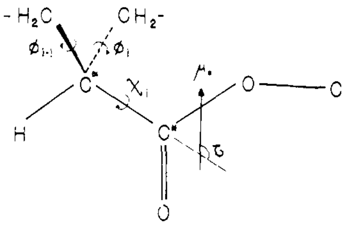

Figure 2. Lateral group of the PMA chain shown in its preferred cis (χ = 0) conformation.

$\exp(-E_\rho/RT)$ and 1 to these two orientations[11] of the lateral group, respectively, and disregard all other local minima.[12]

A straightforward procedure for incorporating this rotational freedom into the scheme of calculation would be to assume that the χ angle of the lateral group is independent of the rotations ϕ over the backbone, so that the contribution μ_0 of each repeating unit may be averaged over χ prior to its introduction into the scheme for averaging over ϕ angles.

This assumption implies that the dipole–dipole interactions are negligible. Some exploratory calculations were carried out in order to check the magnitude of such interactions. Partial charges to reproduce $|\mu_0|$ = 1.76 D and τ = 123° ($q_{C^*} = -q_{O^*} = 0.298$; $q_{CH3} = -q_O = 0.005$) were assigned; a value of ϵ = 3.0 was used for the dielectric constant of the medium. The results prove dipole–dipole interactions to be important only for meso-tt, for which the differences between cis–cis and cis–trans orientations amounted to about 0.4 kcal mol^{-1}. However, this conformtion has a small statistical weight and therefore has little influence in the calculation of the dipole moment of the chain. For the preferred conformations meso-tg and racemic-tt, this difference amounted to ca. 0.1 kcal mol^{-1}.

We let μ_{eff} denote the "effective" contribution of each repeating unit to the dipole moment of the chain and evaluated μ_{eff} as an average of the two orientations over χ; i.e., $\mu_{eff} = (1 + \rho)^{-1}\{\mu_0(\text{cis}) + \rho\mu_0(\text{trans})\}$. For instance, with $|\mu_0|$ = 1.76 D, τ = 123°, and E_ρ = 0.3 kcal mol^{-1}, we obtain μ_{eff} = col (−0.48, 0.71, 0.58) D and $|\mu_{eff}|$ = 1.03 D at 300 K in the coordinate system affixed to skeletal bond CH_2–C^α.

Results and Discussion

Monte Carlo chains consisting of 100 repeating units were generated with a Bernoullian distribution of meso and racemic dyads, and their square averaged dipole moments $\langle\mu^2\rangle$ were computed according to standard procedures.[13,14] Dipole ratios $D_x = \langle\mu^2\rangle/\mu_0^2$ (note that $\mu_0 \neq \mu_{eff}$) were evaluated and extrapolated to $x \rightarrow \infty$; the projected variation of D_x beyond x = 100 was in the range of 1–2% of its limiting value. Values of D_∞ presented below for intermediate tacticities (i.e., $0 < W_m < 1.0$, with W_m being the fraction of meso dyads) are averages over the results for ten chains generated as explained above.

Figure 3 shows the variation of D_∞ with the angle τ governing the orientation of the dipole moment of the ester group. The most important features of this figure can be easily explained: D_∞ is minimal when τ = 90° so that the dipole moments of cis and trans orientations of the ester group are exactly antiparallel; these two vectors cancel each other out when both have the same probability of occurrence (i.e., when E_ρ = 0); consequently, D_∞ should increase as τ departs from 90°. The value of τ was reported to be[5] ca. 123°, and as can be seen in Figure 3, D_∞ for the atactic polymer ranges from about 0.55 to about 0.85 for this value of τ when the energy E_ρ changes from 0 to 0.3 kcal mol^{-1}.

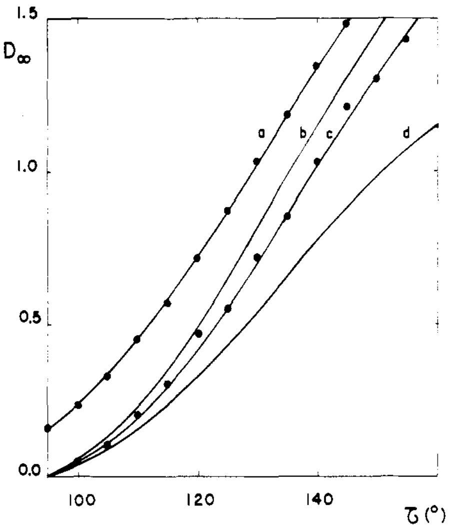

Figure 3. Variation of D_∞ with the orientation of the dipole moment of the ester group, τ, calculated at 300 K with (a) W_m = 0.5, E_ρ = 0.3; (b) W_m = 0.0, E_ρ = 0.1; (c) W_m = 0.5 E_ρ = 0.0; and (d) W_m = 1.0, E_ρ = 0.0. Values shown for atactic samples are averages over ten Monte Carlo chains; standard errors of calculations are roughly represented by the size of the circles. Energies are given in kcal mol^{-1}.

Figure 4 represents the variation of D_∞ with the energy E_ρ governing the relative stability of trans vs. cis orientation of the ester group. It may seem surprising that D_∞ is neither minimal at E_ρ = 0 nor symmetric with respect to that value, whereas $|\mu_{eff}|$ is minimal ($|\mu_{eff}|$ = 0.96 D) at E_ρ = 0 (when the cancellation between $\mu_0(\chi = 0)$ and $\mu_0(\chi = 180°)$ is maximal), and furthermore, $|\mu_{eff}|(E_\rho) = |\mu_{eff}|(-E_\rho)$; for instance, $|\mu_{eff}|$ = 1.13 D for E_ρ = ±0.5 kcal mol^{-1}. However, D_∞ for the whole chain depends not only on the magnitude of μ_{eff} but also on its orientation, which governs the reinforcement or cancellation of contributions from successive units; i.e. $|\mu_{eff}|$ depends on correlations of one χ rotation, whereas D_∞ depends also on correlations over ϕ rotational angles. This second effect can be easily shown for a racemic dyad; in its preferred tt conformation the two dipole moments of its units will add their respective projections over the plane of the backbone; these projections are 1.04, 0.55, and 0.07 D at 300 K for E_ρ = 0.5, 0, and −0.5 kcal mol^{-1}, respectively. Therefore, although $|\mu_{eff}|$ is the same for E_ρ = ±0.5 kcal mol^{-1}, D_∞(syndiotactic) will be sensibly lower for E_ρ = −0.5 than for E_ρ = 0.5 kcal mol^{-1}.

The reported value of E_ρ lies in the range[5] 0–0.2 kcal mol^{-1}, and as Figure 4 indicates, the results of D_∞ for atactic (W_m = 0.5) PMA are 0.55–0.75 for this range of E_ρ. Experimental measurements of the dipole moment of PMA samples synthesized by radical polymerization and thus having a statistical content of $W_m \simeq 0.5$[15] give [16-19] D_∞ = 0.67 ± 0.01 at $T \simeq$ 300 K. As is apparent from figures 3 and 4, this experimental result is reproduced when the parameters E_ρ and τ are in the range 0–0.2 kcal/mol and 123°, as its was concluded they should be,[5] and with all the other parameters having the values of the "best set" that reproduces some other conformation-dependent properties.

The variation of D_∞ with the isotactic fraction W_m calculated with τ = 123° and two different values of E_ρ is

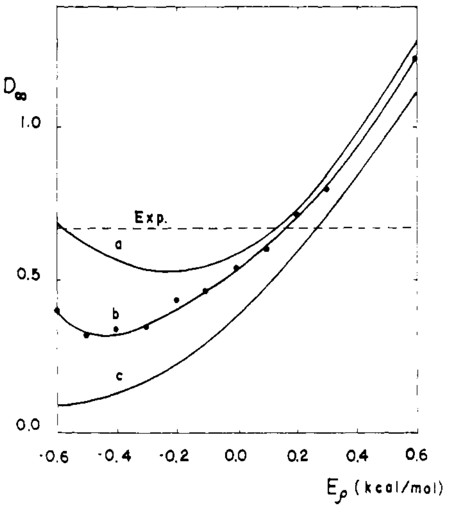

Figure 4. Variation of D_∞ with the energy E_ρ of cis vs. trans orientations of the ester group calculated at 300 K with $\tau = 123°$ and (a) $W_m = 0.0$, (b) $W_m = 0.5$; and (c) $W_m = 1.0$. See caption to Figure 3.

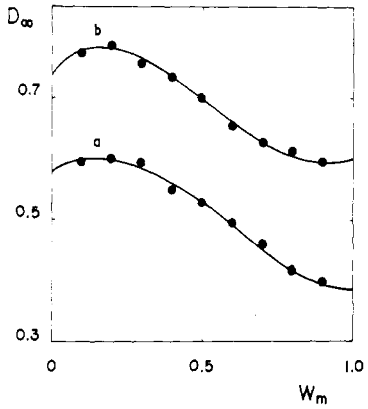

Figure 5. Variation of D_∞ with the fraction of meso dyads (W_m) of the chains calculated at 300 K with $\tau = 123°$ and (a) $E_\rho = 0.0$ and (b) $E_\rho = 0.3$. See caption to Figure 3.

shown in Figure 5. D_∞ is larger for syndiotactic than for isotactic polymer although the difference, due to the preference of syndiotactic polymer for the tt conformation, in which the projections of μ_0 over the backbone plane add, is small.

The variation of D_∞ with temperature is presented in Figure 6. This variation grows larger as E_ρ departs from 0 and its contribution to the temperature coefficient increases; for instance, D_∞ of the syndiotactic sample decrease by ca. 8% when $E_\rho = 0.3$ and by 1.5% when $E_\rho = 0$ in the range 290–320 K. Experimental measurements of the temperature coefficient of D_∞ indicate that it is very small and therefore quite difficult to determine with accuracy; thus whereas Kotera et al.[18] reported a net increase of about 5% in the range 290–320 K for atactic sample, Masegosa et al.[19] obtained an overall decrease of about 1% for the same range of temperatures with a transition at about 308 K. The computation of the temperature coefficient for atactic samples is difficult since the standard error of the calculation reoughly equals the variation of D_∞ with T; however, theoretical results seem to indicate a slightly negative temperature coefficient, in qualitative accordance with the overall results on Masegosa et al.,[16] although no transition is obtained. A transition similar to the experimental one could be obtained if the value of ρ were assumed to suddenly increase at a given temperature either by a decrease of E_ρ(E_ρ should decrease by ca. 0.2 kcal mol^{-1} in order to lower D_∞ by 30%) or by the introduction of a preexponential factor representing an entropic term.[2] However, there is no quantitative explanation for any one of these changes although qualitatively and just as a possibility one could imagine some kind of solvent effect that, in a cooperative way, might stabilize trans vs. cis orientation of the ester group.

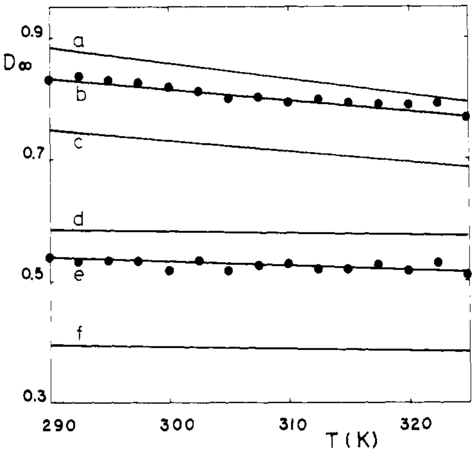

Figure 6. Variation of D_∞ with temperature calculated with $\tau = 123°$ and (a) $W_m = 0.0$, $E_\rho = 0.3$, (b) $W_m = 0.5$, $E_\rho = 0.3$; (c) $W_m = 1.0$, $E_\rho = 0.3$; (d) $W_m = 0.0$, $E_\rho = 0.0$; (e) $W_m = 0.5$, $E_\rho = 0.0$; and (f) $W_m = 1.0$, $E_\rho = 0.0$. See caption to Figure 3.

Throughout all our calculations we have used the same energy parameters selected by Yoon et al.,[1] summarized in Table I; therefore, the scheme still reproduces the results these authors obtained for dimensions, stereochemical equilibria, and NMR coupling constants. We therefore conclude that the two-isomers scheme, with the proper orientation of the dipole moment and a realistic value of the stability of trans vs. cis orientation of the ester group, is able to reproduce all the experimental magnitudes reported to date for this polymer.

Registry No. PMA, 9003-21-8.

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(11) The preexponential factor ρ_0 is roughly equal to unity since the variation of E vs. χ is about the same in the vicinities of $\chi = 0$ and $\chi = 180°$.
(12) Crystalline aliphatic polyesters are reported to have planar-zig-zag conformation ($\chi = 120°$); see, for instance: Takokoro, H. "Structure of Crystalline Polymers"; Wiley-Interscience: New York, 1979. In the crystal, *inter*molecular energies play an important role, and the molecules may adopt conformation leading to better packing (lower lattice energy) which differ from the most stable conformation of an isolated chain. However, in dilute PMA solutions at Θ conditions only *intra*molecular energies are relevant. Under such conditions the differences in D_∞ caused by considering only two values of χ (0 and 180°) rather than all six local minima are smaller than those produced by an uncertainty of 0.1 kcal mol^{-1} in the value of E_ρ.
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Swelling of Model Poly(dimethylsiloxane) Networks

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ABSTRACT: Thermodynamically measured sorption data for the swelling of three poly(dimethylsiloxane) networks with cyclohexane at 30 °C are reported. The networks are end linked, with the junction functionalities ϕ and primary-chain molecular weights M_c being as follows (ϕ; M_c): (3; 11 300), (4; 11 300), and (4; 18 500). The swelling function $\lambda\mu_{1,el}$ displays a maximum, where λ^3 is the swelling ratio and $\mu_{1,el}$ the elastic contribution to the solvent chemical potential. These data provide quantitative information on the dependence of swelling upon controlled network structure variations. Results are compared with the theory of Flory and Erman.

Introduction

In previous papers of this series[1,2] we have explored the swelling of elastomers in a variety of solvents by the method of Gee, Herbert, and Roberts.[3] These results uniformly show that the swelling function

$$(\lambda/V_1)\ln(a_{1,c}/a_{1,u}) = f(\lambda^2) \qquad (1)$$

exhibits a maximum, contrary to the predictions of the Wall–Flory,[4] James–Guth,[5,6] or Mooney–Rivlin[7,8] theories. Here $\lambda^3 = V/V^\circ$ is the isotropic volume dilation, $a_{1,c}$ is the activity of solvent of molar volume V_1 over a swollen cross-linked polymer, and $a_{1,u}$ is the corresponding activity over an un-cross-linked, but otherwise identical, polymer at the same concentration of solvent.

We have further found evidence that the swelling function $f(\lambda^2)$ is dependent upon the nature of the diluent, contrary to the assumption of Flory and Rehner.[4,9] This observation implies that the elastic and mixing free energies are not strictly separable; there is a cross-term that has not yet been encompassed by theory.

Apart from this anomaly, the recently developed theory of Flory and Erman[10,11] succeeds in predicting the maximum in the swelling function found by Gee et al.[3] and by us. It is the only theory known to us that does so. Now, to further test their predictions, we report measurements on a series of end-linked and well-characterized poly(dimethylsiloxane) (PDMS) networks that have been swollen with cyclohexane at 30 °C. The results allow comparisons of (1) functionality dependence (three and four) for fixed-chain molecule weight (11 300 amu) between junctions and of (2) molecular weight dependence (11 300 amu and 18 500 amu) of the chains for fixed functionality (four). The results will be intercompared with stress–strain isotherms for the same samples obtained by Mark and co-workers and with the Flory–Erman theory.

Experimental Section

The PDMS used for this study was kindly supplied by Professor J. E. Mark. Two networks of functionality ϕ (designated EL1 and EL2) were prepared by reacting vinyl-terminated PDMS chains of known molecular weight with siloxane molecules having ϕ (relatively closely spaced) active hydrogens.[12-18] Another network (designated EL3) was prepared by end-linking hydroxyl-terminated PDMS chains of known molecular weight by means of a tetralkoxysilane.[19-26] The network characteristics of these unimodal samples are given in Table I. At equilibrium swelling in cyclohexane at 30 °C the polymer volume fraction in EL1, EL2, and EL3 are respectively 0.219, 0.223, and 0.146. Prior to the equilibrium swelling measurements, each sample was extracted for 6 days in cyclohexane to remove the soluble impurities. The un-cross-linked PDMS and cyclohexane used were described in a previous paper.[1]

Table I
Summary of Network Characteristics[18,19]

sample	M_c[a]	ϕ[b]
EL1	11 300	3
EL2	11 300	4
EL3	18 500	4

[a] Network chain molecular weight. [b] Junction functionality.

The vapor sorption apparatus[27] and experimental technique[1] have been previously described.

Results and Discussion

Integral sorption and activity measurements yield the Flory–Huggins interaction parameter, $\chi(v_2)$, as a smoothed function of the un-cross-linked polymer volume fraction, v_2. Results for the PDMS + cyclohexane system are shown in Figure 1. The solid line is a least-squares fit through our data at high concentrations and Kuwahara's[28] at low concentrations. The equation for the solid line is

$$\chi = 0.433 - 0.11v_2 \qquad (2)$$

The representative osmotic results of Kuwahara, Okazawa, and Kaneko[28] at 20 °C that are represented in Figure 1 as circles have not been corrected to 30 °C because the enthalpy of mixing for this system is not large.[1] Our data consist of results from five separate runs[1,2] using different un-cross-linked PDMS samples from the same lot; there is good agreement between the five data sets.

The differences in solvent mass absorbed by the un-cross-linked and cross-linked PDMS at equal solvent activities were converted into Δv, defined as $v_{1,u} - v_{1,c}$, where subscripts u and c refer respectively to un-cross-linked and cross-linked polymer, from specific volumes given previ-

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