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Dipole Moment and Conformational Analysis of Itaconate Polymers

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ABSTRACT: The dipole moments (μ) of poly(monobenzyl itaconate) (PMBzI), and of poly(dibenzyl itaconate) (PDBzI), of known tacticity (w_m), have been determined in dioxane at 25 °C: $\mu = 1.96$ D, $w_m = 0.50$ (PMBzI); and $\mu = 1.52$ D, $w_m = 0.25$ (PDBzI). The dipole moment and the unperturbed dimensions (characteristic ratio, C_∞) of polyitaconate chains are calculated theoretically, as a function of polymer tacticity, by matrix multiplication methods. A two-state scheme (t, g^+) is used, with backbone bond angles close to each other. The C_∞ calculated increases with w_m from 15.7 (syndiotactic) to 23.0 (isotactic). These high values reflect the preference for the tt conformation, and the increase with w_m shows that the preference is higher for the meso diads. Although the comparison with the experimental C_∞'s shows good agreement with those calculated, the tacticity is not enough to explain the differences between PMBzI and PDBzI, and it must be admitted that the tt conformation is favored to a greater degree in PMBzI than in PDBzI. 2,2-Dimethylsuccinate is used as model compound to obtain the modulus and orientation of the dipole moment of the repeat unit. The polymer μ calculated is scarcely sensitive to tacticity. Comparison with experimental μ shows excellent agreement in the case of PDBzI. For PMBzI, the experimental μ is higher than calculated, and agreement requires modification of the conformational parameters (but within the precision limits of the calculation).

Poly(itaconic acid) derivatives have been studied widely: mechanical properties and thermal transitions in bulk[1-7] and dilute solution properties, mainly intrinsic viscosity,[8-17] from which unperturbed dimensions and chain stiffness parameters have been determined for a few monoesters and diesters of poly(itaconic acid).[8-17] But no direct analysis of the conformations of these polymers has been performed. Here, we make such analysis by mapping their conformational energy and calculating theoretically two observable properties that typically dependent on conformation: unperturbed dimensions and dipole moment, both as a function of tacticity. The values thus calculated theoretically are then contrasted with experiment.

Data can be found in the literature about unperturbed dimensions, presumably of atactic polymers, although the precise tacticity of the samples studied has never been investigated. With regard to dipole moment, no previous report of this property for the polyitaconates could be found in the literature. The dipole moment of a poly(dibenzyl itaconate) of well-characterized tacticity[18] has been determined very recently in our laboratory.[19] We decided to measure also the dipole moment of poly(monobenzyl itaconate) in order to have a complete set of experimental results of unperturbed dimensions and dipole moment of poly(mono and poly(di itaconates) with which to compare the results of our conformational analysis.

This paper contains first the report of the experimental determination of dipole moments and then the theoretical analysis of conformational energy, unperturbed dimensions, and dipole moment, as a function of tacticity.

Experimental Section

(a) Materials. Two samples of polymer, previously synthesized,[15,16] were selected for the present work, one of poly(monobenzyl itaconate), PMBzI, and the other of poly(dibenzyl itaconate), PDBzI. Molecular weights, determined by size-exclusion chromatography, were 0.93×10^5 and 1.19×10^5, respectively. The tacticities of these samples, as determined from their ^{13}C NMR spectra, have been reported before[18] as being $w_m = 0.50$ (PMBzI) and $w_m = 0.25$ (PDBzI).

Table I
Experimental Values of the Dielectric Constant Increment, $(\partial\epsilon/\partial w_2)$, the Refractive Index Increment, $(\partial n/\partial w_2)$, and the Dipole Moment, μ, of PMBzI and PDBzI, in 1,4-Dioxane, at 25 °C

polymer	$(\partial\epsilon/\partial w_2)$	$(\partial n/\partial w_2)$	μ, D
PMBzI	2.573	0.1187	1.96
PDBzI	1.304[a]	0.1428	1.52[a]

[a] From ref 19.

1,4-Dioxane used as solvent in refractometry and dielectric measurements was Carlo Erba of RPE quality. It had been dried over Merck 4-Å molecular sieves. The density (ρ) and dielectric constant (ϵ) measured after drying over molecular sieves were (25 °C) $\rho = 1.027\,99$ g·cm^{-3} and $\epsilon = 2.207$, in good agreement with literature values:[20] $\rho = 1.027\,97$ g·cm^{-3}; $\epsilon = 2.209$.

(b) Dielectric Measurements. The dielectric measurements were performed on a WTW Model DK-06 Multidekameter, at a frequency of 2.0 MHz. The cell used was made of silvered Pyrex glass and was calibrated at the working temperature, 25.05 ± 0.01 °C, using liquids with well-known dielectric constants (i.e., benzene, toluene, cyclohexane).[21] Polymer solutions in dioxane were preserved over molecular sieves before using. The concentration range of polymer solutions was $1 \times 10^{-3} < w_2 < 11 \times 10^{-3}$ (w_2 = polymer weight fraction).

In Figure 1 the measured dielectric constant, ϵ, for both polymer solutions in dioxane is plotted against w_2. Good linearity is observed. In Table I we give the values of $(\partial\epsilon/\partial w_2)$, determined as the slope of this plot by a least-squares fit.

(c) Refractometry. The difference in refractive index, n, of solutions and solvent was measured at 546 nm in a Brice-Phoenix 2000V differential refractometer, calibrated with aqueous KCl. Solvent and range of concentrations were the same as for dielectric measurements. In Table I we give the values of $(\partial n/\partial w_2)$ thus determined at 25 °C.

(d) Dipole Moment. The dipole moment per repeat unit of PMBzI and PDBzI has been determined with the Guggenheim–Smith equation:[22,23]

$$\mu^2 = \frac{27kTM_2v_1}{4\pi N_A(\epsilon_1+2)^2}\left[\left(\frac{\partial\epsilon}{\partial w_2}\right) - 2n_1\left(\frac{\partial n}{\partial w_2}\right)\right] \qquad (1)$$

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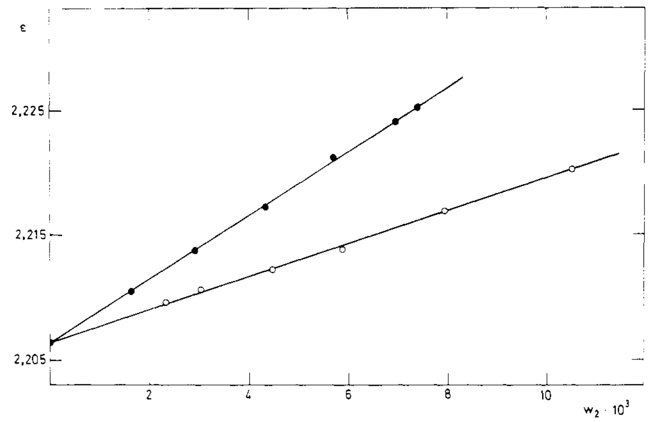

Figure 1. Dependence of dielectric constant, ε, on weight fraction of polymer, w_2, for (●) PMBzI and (○) PDBzI, in 1,4-dioxane, at 25 °C. (Data for PDBzI from ref 19.)

where k = Boltzmann's constant, N_A = Avogadro's constant, T = temperature, M_2 = molecular weight of repeat unit, v_1 = solvent specific volume, and ϵ_1, n_1 = solvent, ε, n. The method of Halverstadt–Kumler for the molar polarization and molar refraction[24] has also been used. Differences between μ values calculated by both methods is ≃3%. The results of μ thus determined experimentally for PMBzI and PDBzI in dioxane at 25 °C are shown on Table I.

Conformational Energy

The polymer repeat unit is similar, from the point of view of conformational analysis, to that of PMMA. Despite the differences between the group in α of PMMA (α-CH_3) and that of the itaconate polymers (α-CH_2COOR), it seems reasonable to use the statistical model of PMMA as a starting point for the polyitaconates. Sundararajan and Flory[25] proposed a very simple model for PMMA chains allowing only two rotational states (t, g^+) for each skeletal bond; the statistical weight matrices can then be written as

$$\mathbf{U}' = \begin{vmatrix} 1 & 1 \\ 1 & 0 \end{vmatrix} \qquad \mathbf{U}''_{\mathrm{m}} = \begin{vmatrix} 1 & \alpha \\ \alpha & \alpha^2/\beta \end{vmatrix} \qquad \mathbf{U}''_{\mathrm{r}} = \begin{vmatrix} \beta & \alpha \\ \alpha & \alpha^2/\beta \end{vmatrix} \tag{2}$$

Both authors have independently improved this scheme, proposing models with three[26] or six[27] states, which give a better account of the properties of PMMA. However, in this paper we have prefered to use the simplier old scheme as a first approach to the itaconate polymers. Hopefully, this model could be improved when more experimental data become available and the precision of the energy calculation for their oligomers is increased.

One of the differences between PMMA and the polyitaconates lies in the dimension of the chain, which in the latter is very high, with values of C_∞ (characteristic ratio) ranging[9-11,14-16] from 12 to 30, while in PMMA the experimental values of C_∞ are in the range[28-30] 7–11. It is not possible to obtain high values of C_∞ by modifying the energetic parameters α and β while keeping the difference in bond angles of the backbone equal to that used for PMMA[25] (θ' = 122°, θ'' = 110°; see Figure 2), since then even the all-trans conformation gives dimensions which are too low. Therefore, in the polyitaconates the bond angles of the backbone should have values closer to each other.

The calculation of conformational energies in itaconate polymers is complex because eight rotations have to be considered for every diad (three rotational angles, χ, for the lateral groups attached to each repeat unit, plus two angles in the backbone, ϕ; see Figures 2 and 3). This not only lengthens tremendously the time of calculation but, what is worse, lowers the precision of results, which have then to be taken only as semiquantitative.

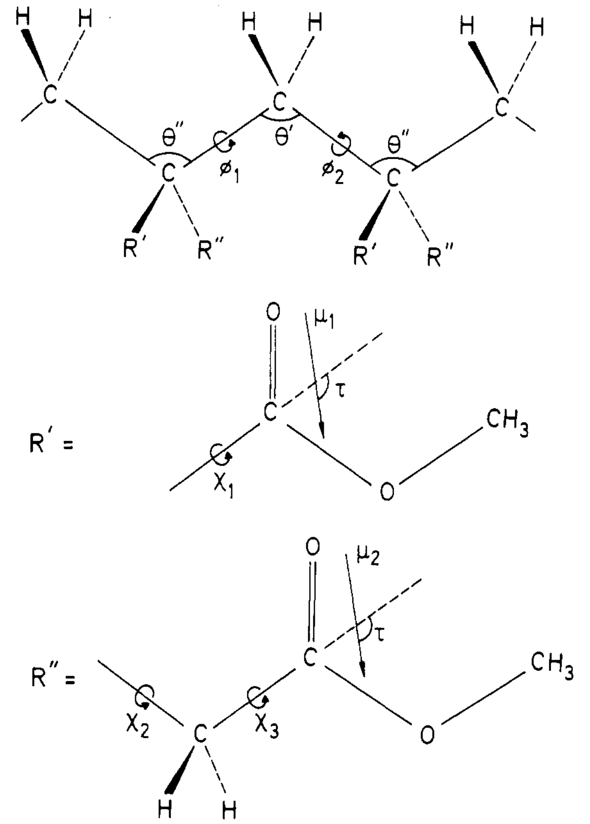

Figure 2. Structure of an isotactic diad of poly(dimethyl itaconate) in its all-trans conformation (taken as origin for the backbone rotational angles: $\phi_1 = \phi_2 = 0$). Angles χ define the three rotational freedoms of side groups. Vectors μ_1 and μ_2 represent the orientation (from negative to positive charges) of the two ester group dipoles.

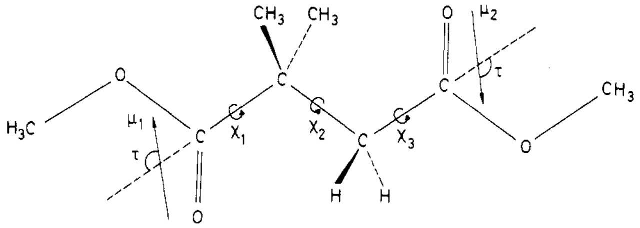

Figure 3. Structure of the dimethyl ester of 2,2-dimethylsuccinic acid which is used as a model molecule for the side groups of poly(dimethyl itaconate). The molecule is shown in its all-trans conformation (taken as the origin of the rotational angles: $\chi_1 = \chi_2 = \chi_3 = 0°$).

The calculations of conformational energies have been performed varying ϕ_1 and ϕ_2 with increments of 10° in the range of ±40° around the perfectly staggered states ϕ = 0, 120°. For each pair of values ϕ_1, ϕ_2, the angles χ have been varied, the energy calculated for each one of the orientations obtained, and the Boltzmann's factors (calculated at 25 °C) corresponding to those energies summed, in order to obtain the partition function, Z, the free energy, $A = -RT \ln Z$, and the mean energy of such conformation of the backbone (pair of values ϕ_1, ϕ_2). For the angles χ_1 only positions 0° and 180° have been considered, taking into account that any other orientation would give severe steric repulsions, since groups contiguous along the chain are very close to each other.[25] On the other hand, the angles χ_2 and χ_3 have been sampled with increments of 60° from 0° to 360°, since by coupling the rotations defined by these two angles it is possible to minimize the interactions with neighboring groups along the chain.

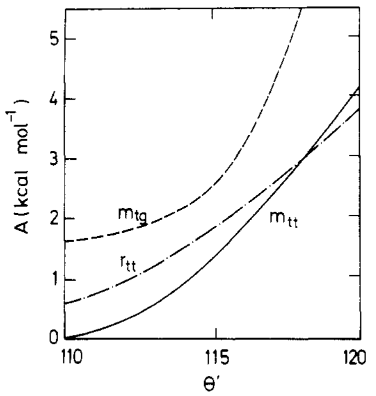

Figure 4. Values of free energy ($A = -RT \ln Z$) as a function of the bond angle, θ', for three conformations of poly(dimethyl itaconate) (T = 25 °C). See text for details of evaluation of the partition function, Z.

The procedure followed for the calculation is detailed elsewhere.[31] The geometrical parameters (bond lengths and valence angles) and the parameters to define the energy functions (Lennard-Jones potential for nonbonded interactions, partial charges for dipolar interactions, and intrinsic rotational barriers) were all taken from previous work.[25,32-36] Details about the numerical values used for these parameters can be found in ref 31. The energy of deformation of the valence angle θ' was taken as[25] $E_{\theta'} = A'(\Delta\theta')^2$, with A' = 80 kcal·mol^{-1} and $\Delta\theta'$ in radians.

The calculations of energy were carried out for diads of the polymer and for a low molecular weight model molecule (see later). In both cases the calculations were done for the dimethyl esters. Modifications produced in the location of minima and in their relative energies when the methyl group is substituted by a benzyl group or by the hydrogen of an acid are below the error margin affecting this type of calculations with molecules which have so many rotational freedoms as the ones studied here.

The values obtained, either from free energies or from mean energies, are very similar. Summarized in Figure 4 are the results for the free energies, as a function of the bond angle θ' (keeping θ'' = 110° constant), for the conformations meso tt (m_{tt}), meso tg (m_{tg}), and racemic tt (r_{tt}), taking arbitrarily $A = 0$ for m_{tt} at θ' = 110°. As can be seen in Figure 4, the values of A grow steadily with the backbone valence angle θ' without a minimum being clearly defined. The explanation for this behavior is simple. It is possible to decrease the repulsions between lateral groups by moving the rotational angles ϕ out of their perfectly staggered positions; then an adjustment of χ_2 and χ_3 rotations allows the second ester group to give attractive interactions with its neighbors. The energy can then be minimized with very small deformations of the backbone angle; as this deformation is increased, the energy of deformation increases the value of A.

Although no minimum exists for the energy as a function of θ', it can be seen in Figure 4 that around 114°, A starts a faster increase with θ', especially for the case of m_{tg}. This behavior suggests that θ' should lie in the range 110°–114°. For this reason, all the calculations have been done takin θ' = 112°, checking afterward the sensitivity of the chain properties calculated to the precise value of this angle.

Table II
Average Values of the Backbone Rotational Angles for the Different Conformational States of a Diad

	$\langle\phi_1\rangle$	$\langle\phi_2\rangle$		$\langle\phi_1\rangle$	$\langle\phi_2\rangle$
m_{tt}	2°	-25°	r_{tt}	2°	26°
$m_{tg}{}^a$	2°	114°	$r_{tg}{}^a$	-1°	120°
m_{gg}	114°	114°	r_{gg}	120°	120°

[a] Includes the gt conformation with reversal of $\langle\phi_1\rangle$ and $\langle\phi_2\rangle$.

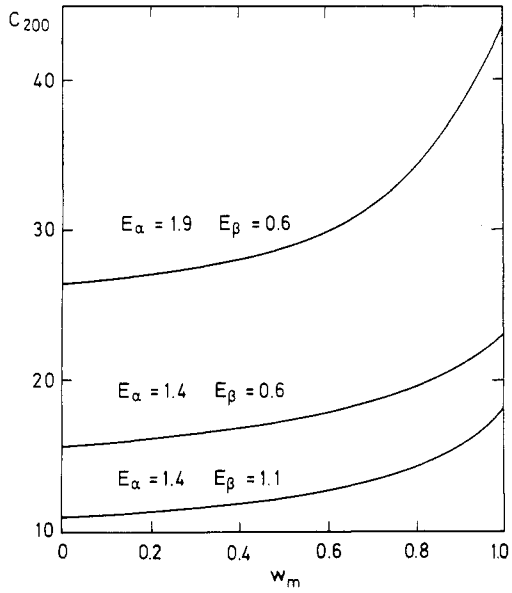

Figure 5. Characteristic ratio for chains having x = 200 repeat units, as a function of meso diads fraction, w_m, for three sets of values of the conformational energies E_α and E_β (T = 25 °C). The results for $0 < w_m < 1$ are averages over 20 Monte Carlo chains; the standard error of such averages are smaller than the thickness of the lines drawn.

Once the value of angle for the skeleton is fixed, the energetic parameters needed to define the matrices of statistical weights can be obtained. That is $E_\alpha = A(m_{tg}) - A(m_{tt})$; $E_\beta = A(r_{tt}) - A(m_{tt})$. The statistical weights α and β were evaluated as Boltzmann's exponentials of their corresponding energies. With the results of Figure 4 it is found that E_α = 1.4, and E_β = 0.6 kcal/mol, which have been used as a standard set of values in all calculations. The computation scheme which allows the utilization of average locations for each state of the bond pair of the diad[37,38] was used for all the calculations. Average values of the skeletal rotation angles were computed with θ' = 112°. The results are shown on Table II.

Unperturbed Dimensions

The usual matrix multiplication scheme[39,40] was employed to generate chains containing x repeat units; the unperturbed dimensions, $\langle r^2\rangle_0$, of such chains were then computed and converted into characteristic ratios: $C_x = \langle r^2\rangle_0/xl^2$. All the results presented are averages over 20 independently generated Monte Carlo chains, each of them having a Bernouillian distribution of meso and racemic centers. Some exploratory calculations were performed in order to check the variation of C_x with x. At low degrees of polymerization, C_x increases with x. For the range of C_∞ values of interest to compare with experimental results (C_∞ = 13–20), C_x reaches an almost asymptotic limit at x = 150–200, and differences between C_{200} and C_∞ (obtained by linear extrapolation of C_x versus x^{-1}) are 3–4% in this range. Therefore, all the results shown below were computed at x = 200 as representative of the limit value for $x \rightarrow \infty$.

The results obtained are summarized in Figure 5, where the values of C_{200} are plotted as a function of polymer tacticity (characterized by its meso diad fraction, w_m), for three sets of conformational energies, E_α and E_β. As can be seen in Figure 5, C_{200} increases with w_m for the three sets of conformational energy values. Taking E_α = 1.4 and E_β = 0.6 kcal/mol (the values obtained in the calculation of energies), one gets C_{200} = 15.7 and 23.0 for the syndiotactic and isotactic polymers, respectively. An increase in the value of E_α makes the dimensions increase tremendously, while an increase in E_β makes them decrease. This behavior can be explained in terms of the statistical weights matrices. The preferred conformation for the meso as well as for the racemic diads is tt, which gives rise to extended chains. This is why the polyitaconates have such high molecular dimensions. However, the preference for trans is higher in the meso diad than in the racemic since $\beta < 1$; consequently, C_{200} is much higher for the isotactic polymer than it is for the syndiotactic one. On increasing E_α (that is to say, on decreasing α), the preference for trans increases and the dimensions thus grow. Conversely, on increasing E_β (decreasing β), the statistical weight of trans is diminished, giving higher weight to the conformation gg which acts as interruption in between chain segments having tt or tg conformation, and much more coiled chains result.

The geometry of the chain has much less importance. For instance, a variation of 2° in θ or of 10° in any of the rotational angles ϕ produces a change of the order 2% in the values of C_{200}.

As already explained, the calculation of conformational energies is of low accuracy in the case of these polymers; the values obtained should be considered only as semiquantitative and they should be optimized by comparison between theory and experiment for some conformational properties of the polymer studied. In view of the results shown on Figure 5, it is concluded that the values of E_α and E_β estimated in the calculation of conformational energies require modifications of only 0.5 kcal/mol in order to span the range of experimental values of C_∞ obtained for this type of polymer.[9-11,14-16] For example, in the case of PMBzI, the experimental value[15] for a sample with w_m = 0.5[18] is 19.2, slightly above the theoretical result 17.2. On the other hand, in the case of PDBzI with w_m = 0.25,[18] the experimental value[16] 12.6 is below the theoretical result 16.4. But it suffices to modify any one of the two energies by approximately 0.2 kcal/mol (for instance, increasing E_α for PMBzI and decreasing it for PDBzI, or making the opposite variations of E_β) to reproduce exactly the experimental results of these two polymers. Therefore, the difference in tacticity between these two samples is not enough to explain their different molecular dimensions; it must be admitted that in the case of PMBzI the tt conformation is favored to a greater extent than in PDBzI, probably because of small repulsions between the additional benzyl groups in PDBzI. However, these differences are too small to be detected in the calculation of energies, since they are below the precision limit in such calculations.

Dipole Moments

The same scheme of calculation summarized above was applied to compute mean-square dipole moments of chains containing x repeat units; the results were converted into "effective dipole moments", defined as $\mu_{\text{eff}} = [\langle\mu^2\rangle/x]^{1/2}$, which are directly comparable to the results of experimental determinations. All the values of μ_{eff} shown below are expressed in debyes and were computed for x = 200, which is a good approximation for infinitely long chains (i.e.: differences between values computed with x = 150 and 200 are smaller than 1%).

In order to obtain the modulus and orientation of the dipole moment of the repeat unit, we have calculated the conformational energy for the dimethyl ester of the 2,2-dimethylsuccinic acid (see Figure 3), which can be considered as a reasonable approximation to such a repeat unit of this type of polymers. The fact that this molecule is not isolated but forms part of a polymer chain was taken into account in the calculation by imposing the restriction that χ_1 could take only the values 0° and 180° (see above). The dipole moment of each one of the two ester groups was represented by a vector,[31,32] μ, of modulus 1.83 D with orientation defined by an angle τ = 123°.

Table III
Summary of Results Obtained for the Dimethyl Esters of 2,2-Dimethylsuccinic Acid[a]

χ_1	χ_2	χ_3	E	μ	μ_x	μ_y	μ_z
0	0	290	0.0	1.76	0.00	−1.01	1.42
0	0	70	0.0	1.76	0.00	−1.01	−1.42
0	120	60	0.0	2.06	0.61	−0.99	1.70
0	240	300	0.0	2.06	0.61	−0.99	−1.70
180	0	290	1.0	2.51	0.00	2.06	1.44
180	0	70	1.0	2.51	0.00	2.06	−1.44

[a] χ = rotational angles defining conformation (Figure 3); E = relative energy (kcal/mol); μ = dipole moment (D); μ_x, μ_y, μ_z = components of μ.

The results obtained in this calculation are summarized in Table III, where in the first four columns are shown the position and relative energy of the principal minima. As can be seen, there are four minima that are practically equivalent when χ_1 = 0, and another two minima approximately 1.0 kcal/mol above the previous ones, when χ_1 = 180°. All other local minima have much higher energies and have not been included in Table III. The last four columns of Table III contain the dipole moment of each one of those conformations and its components μ_x, μ_y and μ_z.

It is important to point out that any of the conformations gathered in Table III, if taken alone, gives dipole moment of at least 5 D for the polymer chain, clearly above the experimental results. The explanation is simple: any of such conformations has an important μ_z component whose direction is coincident with that of chain propagation in space when in the all-trans conformation (the prefered conformation, as already mentioned). These components add up along the chain giving rise to a very high dipole moment. But, since in the actual chain several conformations of the repeat unit have practically the same energy, there is a very high probability that a repeat unit in a given conformation be followed by a neighboring unit in a conformation having μ_z of opposite sign and that these components cancel out. A rigorous way of taking into account these conformations of the repeat unit would be to split into six each rotational state of the backbone. It would then result in a model containing a cumbersome 12 rotational states. An alternative method[41] is to consider that the rotations around the backbone (rotational angles ϕ) are not coupled with the rotations around the degrees of freedom of the lateral groups (rotational angles χ), so that each repeat unit contributes to the chain with a value $\langle\mu\rangle$ averaged over its angles χ. Although this procedure is obviously an approximation, it seems to work reasonably well.[41-43]

With the data of Table III, $\langle\mu_x\rangle$ = 0.28, $\langle\mu_y\rangle$ = −0.74, and $\langle\mu_z\rangle$ = 0 were obtained. Using these average values as the dipole moment of the repeat unit[44] gave the results summarized in Figure 6, where μ_{eff} versus w_m is plotted, for three sets of conformational energies. As can be seen in Figure 6, the value of μ_{eff} is scarcely sensitive to the tacticity of the polymer, while it changes notably with the conformational energies E_α and E_β. As in the case of dimensions, μ_{eff} increases with increasing E_α and decreases with increasing E_β.

The values of μ_{eff} are more sensitive to the geometry of the chain than are the dimensions. Thus, μ_{eff} decreases

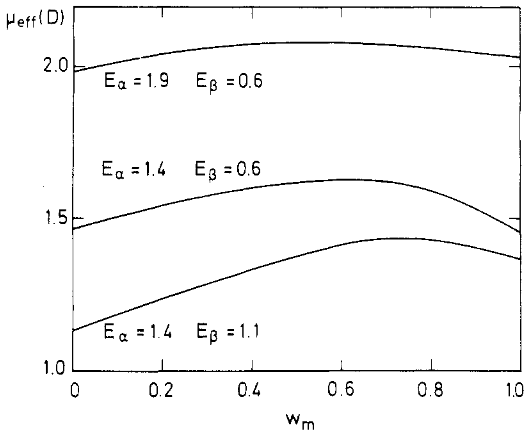

Figure 6. Effective dipole moment, μ_{eff}, for chains having x = 200 repeat units, as a function of meso diad fraction, w_m. See legend for Figure 5.

on increasing the bond angle θ'; the effect is almost identical for any tacticity and the variation is 2–3% per degree. μ_{eff} increases when the positions of the rotational isomers are forced to approach the staggered states; the largest effect is reached when modifying the position of tt, which is the prefered conformation, especially in the case of the meso diads. Thus, taking (ϕ_1, ϕ_2) = (2, −15) and (2, 16) for m_{tt} and r_{tt}, respectively (a variation of 10° in ϕ_2 from the values of Table II), increases in μ_{eff} of approximately 6, 10, and 17%, respectively, for w_m = 0, 0.5, and 1.0, were obtained. The values of μ_{eff} also change if the contributions $\langle\mu_x\rangle$, $\langle\mu_y\rangle$, or $\langle\mu_z\rangle$ of the repeat unit are modified; the variation goes in the sense of increasing μ_{eff} when any of those contributions is increased.

According to the results shown on Figure 6, the result of conformational energy calculations, namely, E_α = 1.4 and E_β = 0.6 leads to μ_{eff} = 1.54 and 1.62, for w_m = 0.25 and 0.5, respectively. The first of these values is in perfect agreement with the experimental result of 1.52 D measured for PDBzI in dioxane.

The value calculated for w_m = 0.5 is slightly lower than the experimental result 1.96 D measured for PMBzI in dioxane. On increasing E_α by approximately 0.2 kcal/mol, as suggested by the analysis of the dimensions of the polymer, the theoretical value of μ_{eff} goes up to 1.80 D, approaching the experimental value. It is possible to reproduce the experimental value by modifying slightly the positions of the rotational angles ϕ or the contributions $\langle\mu\rangle$ of the repeat unit. In order to reach 1.96 D, it would be necessary to change either ϕ_2 by approximately 10° for the trans isomer or any of the components of $\langle\mu\rangle$ by 0.1 D (which could be achieved by changing the energies of Table III in about 0.1 kcal/mol), or, obviously, an equivalent combination of these two effects. Any one of these modifications is within the error limits of the present calculation.

Conclusion

The unperturbed dimensions and the dipole moments of PMBzI and PDBzI can be reproduced theoretically with a two rotational isomeric state model analogous to that used for PMMA and with values for the conformational energies of E_α = 1.4 ± 0.2 and E_β = 0.6 ± 0.2 kcal/mol.

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Registry No. PMBzI, 113793-33-2; PDBzI, 58991-68-7; H_3C-$O_2C(CH_2)_2CO_2CH_3$, 597-43-3.

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(44) Note that these components are expressed in the coordinate system of the lateral group. They have to be transformed to the coordinate system of the bond C–CH_2 in the chain, before being included into the computational scheme. These three components give $\langle\mu\rangle$ = 0.79 D, clearly below the value $\langle\mu^2\rangle^{1/2}$ = 1.97 D that would be measured for an isolated molecule having these same conformational characteristics.