

COMPUTER SIMULATIONS ON UNPERTURBED CONFIGURATIONAL DIMENSIONS OF POLY(METHYL ACRYLATE)*

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ABSTRACT

A full-relaxation optimization of molecule and the popular MM2 force field are employed to obtain the geometry parameters and the conformational energy surface of a meso or a racemic dyad of poly(methyl acrylate) (PMA) with a specified carbonyl-bond orientation in side-groups. It is found that the conformational energy maps calculated here considerably differ from those calculated with the rigid molecular model as reported in the earlier studies. The g^- state cannot be omitted in the obtained contour maps. Two important conformers tg^- and g^{-t} with energy minima were newly detected for a racemic dyad. The analysis on the conformations with energy minima confirmed that the ester groups are not always perpendicular to the plane defined by the two adjacent skeletal bonds and may change their relative orientations to meet the requirement of lower energies during the conformational state transition. Instead of the early way of adjusting the interaction energy parameters to fit the experimental data, we attempt to predict unperturbed chain dimensions via the reliable force field and the configurational statistical mechanics. The proposed scheme with three rotational states identified from the contour maps allowed us to satisfactorily reproduce the experimental dimensions of random PMA chains.

INTRODUCTION

The combination of the rotational isomeric-state (RIS) approximation and the matrix generator procedure has extensively proved to be more powerful means of evaluating the structural characteristics of vinyl polymer chains^[1]. The unperturbed chain dimension depends on (i) geometric structure of the chain such as the bond

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lengths and the bond angles; (ii) the conformational energy differences among various rotational states; and (iii) the averaged dihedral angle of each isomeric state. A suitable choice of both the molecular model and the potential functions is very important to construct the energy contour surface and to predict the chain dimensions. Using a rigid model and a threefold intrinsic potential, Yoon and Flory^[2] and Tarazona and Saiz^[3] analysed PMA conformationally and configurationally with energy contour maps consisted of two states, trans (t) and gauche (g). Additional state g^- was ignored because of its higher energy. However, their studies showed that the unperturbed characteristic ratio C_n calculated for the polymer was larger than that from the experiments, and the chain was more rigid than the real chain at θ condition. Agreements with the experimental data of chain dimension^[4-5] and dipole moment^[6] should be achieved by adjusting the interaction energy parameters. Following the same rigid model of molecule and the same potential function^[2], Ojalvo and Saiz^[7] presented a four-states scheme by splitting each rotational isomer into two different states according to the position of the lateral ester group. Although the carbonyl-bond orientations of side-groups were considered in the initial dyad model, the cooperative motion in side-groups and the re-orientations of carbonyl bonds were neglected during the conformational state transitions. This means that the use of rigid model may lead to the neglect of some conformers lay down the lower potential wells. In this case, it is argued that the short-range interactions thus obtained was not perfection. As a consequence, the calculation of chain configurations could not give numerical values consistent with the experimental data.

From a microscopic viewpoint of material design, it is essential to predict the averaged spatial chain configurations using a reliable force field and statistical mechanics. To do this generally requires a better evaluation of conformation energies. It should be noted from our recent study that a full-relaxation-model was positively able to avoid unreasonable high energies occurring when two unbonded atoms of a molecule go towards each other too close to be accepted^[8], and that the re-orientation of carbonyl bonds has a considerable influence on both the conformational energy surfaces and the chain dimensions^[8,9]. Therefore, the purpose of the present contribution is to carry out the conformational characteristics of PMA using a full-relaxation optimization of molecule and the configuration statistical mechanics. We here disregard the method of adjusting the energy parameters to fit the experimental chain dimensions at unperturbed state. Alternatively, we try to report some results of predicting the configurational dimensions of the isotactic, the syndiotactic and the atactic PMA chains with the full-relaxation-model and thereby with the side-group re-orientations. In addition, our attention is also placed on

the understanding of the interactions and the analysis of conformations with lower energies.

COMPUTATIONAL METHOD

In Fig. 1 shown is a molecular model of a meso dyad of PMA in all-trans conformation. Two carbonyls in the two side-groups are trans to C^α -H. We defined the dihedral angle χ between $C^* = O$ and C^α -H as 180° . A full-relaxation optimization of the model and the popular MM2 force field^[10] were used in the calculation of the conformational energy surfaces of PMA. Geometry parameters such as bond length, bond angle and torsion angle, are all not fixed during the minimization but varied under the confinement of the force field. Therefore, the component that contributes from the re-orientation of side-groups in the potential surface calculation was taken into account. In the energy expression, the bonded and the non-bonded terms consist of several potential interaction terms including bond stretching, bond angle bending, dihedral angle torsion, van der Waals, and dipole-dipole, etc. The Lennard-Jones 6—12 potential was employed for measuring van der Waals interaction. Conformational energy maps calculated as functions of the skeletal bond rotational angles Φ_i and Φ_{i+1} . The effective cut-off value of a distance between two arbitrary non-bonded atoms is defaulted as infinite. The data points in the energy contour maps computed were at intervals of 10° in Φ_i and Φ_{i+1} .

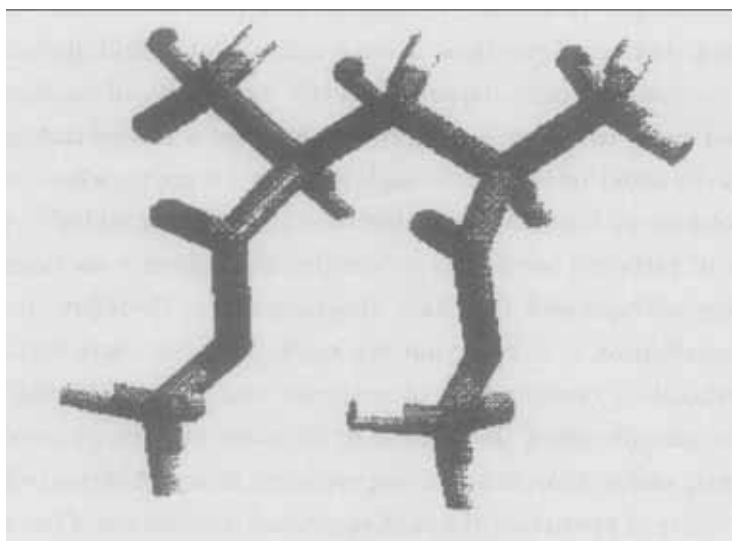


Fig. 1 A model of a meso dyad of PMA in an all-trans conformation (two carbonyls in the two side-groups trans to C^α -H)

For nine different conformers identified in the energy contour maps for a meso or a racemic dyad, the partitional function Z_η , average energy $\langle E \rangle_\eta$ and averaged rotation angle $\langle \Phi_k \rangle_\eta$ for each rotational state η were evaluated according to [9,11]

$$Z_\eta = \iint_\eta \exp(-E_\eta\{\varphi_i, \varphi_{i+1}\}/RT) d\varphi_i d\varphi_{i+1} \quad (1)$$

$$\langle E \rangle_\eta = Z_\eta^{-1} \iint_\eta E_\eta\{\varphi_i, \varphi_{i+1}\} \exp(-E_\eta\{\varphi_i, \varphi_{i+1}\}/RT) d\varphi_i d\varphi_{i+1} \quad (2)$$

$$\langle \varphi_k \rangle_\eta = Z_\eta^{-1} \iint_\eta \varphi_k \exp(-E_\eta\{\varphi_i, \varphi_{i+1}\}/RT) d\varphi_i d\varphi_{i+1} \quad (k = i \text{ or } i + 1). \quad (3)$$

With the resulting statistical weight matrices and the reasonable geometry parameters, one can easily calculate the unperturbed chain dimensions by the generator matrix procedure^[1]. The mean square end-to-end displacement is quoted as

$$\langle \gamma^2 \rangle_0 = Z^{-1} G_0 \left(\prod_{k=1}^{x-1} G'_k G''_k \right) G_x. \quad (4)$$

Then, we have the expression of the characteristic ratio by

$$C_n = \frac{\langle \gamma^2 \rangle_0}{nl^2}.$$

with

$$Z = U_0 \left(\prod_{k=1}^{x-1} U'_k U''_k \right) U_x \quad U'_i = \begin{bmatrix} V''_{tt} & V''_{tg} & V''_{tg^-} \\ V''_{gt} & V''_{gg} & V''_{gg^-} \\ V''_{g^-t} & V''_{g^-g} & V''_{g^-g^-} \end{bmatrix}$$

$$U''_{i+1} = \begin{bmatrix} Z_{tt} & Z_{tg} & Z_{tg^-} \\ Z_{gt} & Z_{gg} & Z_{gg^-} \\ Z_{g^-t} & Z_{g^-g} & Z_{g^-g^-} \end{bmatrix}$$

and G_i is supermatrix for each bond as defined by Flory^[1]. Here, the statistical weight matrix U''_{i+1} (U''_m or U''_r), comprehends all first-order interactions and the second-order or higher-order interactions dependent upon the rotations for the pair of skeletal bonds within a dyad. U''_{i+1} can be directly determined from the partitional functions of nine domains. The statistical weight matrix U'_i for the pair of bonds flanking a side-group represents the second order interactions only^[11,12]. Simplifying approximately the third-order interaction into the second-order, one can simply have^[12]

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

RESULTS AND DISCUSSIONS

Conformational energies

The energy contour maps showed that there existed five new stable conformers for the meso or the racemic dyad as we reported before^[8] besides the four conformers

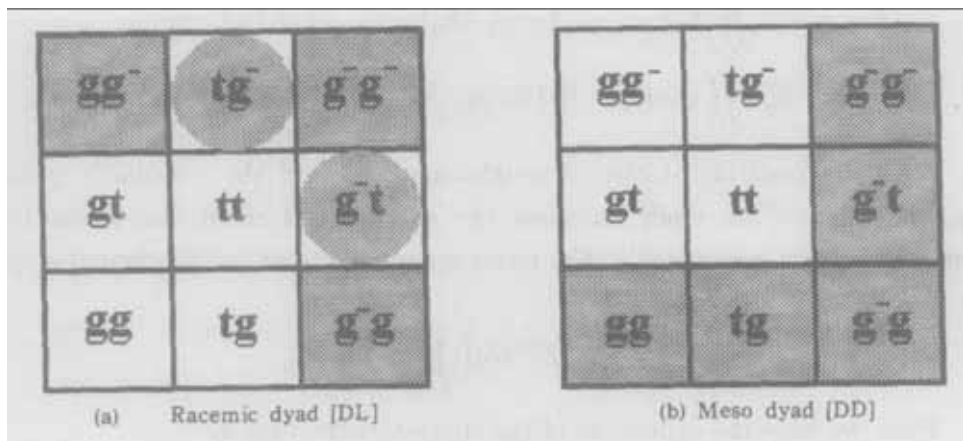


Fig. 2 Representation of elements in the statistical weight matrices with the two-state and the three-state schemes used for the calculation of unperturbed chain dimensions. The conformations in the white blocks are generally obtained from the rigid molecular model, while those in black blocks should be additionally detected by the full-relaxation of minimization

identified by Flory et al.^[2]. Fig. 2 showed a comparison between contour maps obtained from the rigid model of molecule and the full-relaxation optimization. The four states presented in the white blocks are those by Flory et al.. Exception for these four states, additional five states in black blocks are also obtained by our full-relaxation minimization of molecule. The improvement of the molecular mechanics program used in the present work has made it possible to obtain a potential contour surface for a polymer with complicated side-group more reasonable than that in the early study^[8]. This program has up to now been modified in two aspects. One is that the root-mean-square of the force on each atom was limited less than 0.01 for the runs to meet the criterion of convergence. Another is, the same conformer that was optimized with the backbone in all-trans was applied as the initial co-ordinates for calculating each point in the contour maps. These two modifications allow us to avoid effectively those conformations with unreasonably higher energies resulting from the conflicts between groups during the grid search of potential. Nevertheless, more or fewer points with such higher energies in the contour maps remain due to the limit of convergence method provided in the force field. The geometrical structures

corresponding to such points have been distorted. To correct such energy points, we only have to minor adjust bond angle and torsional angle in the side-groups for

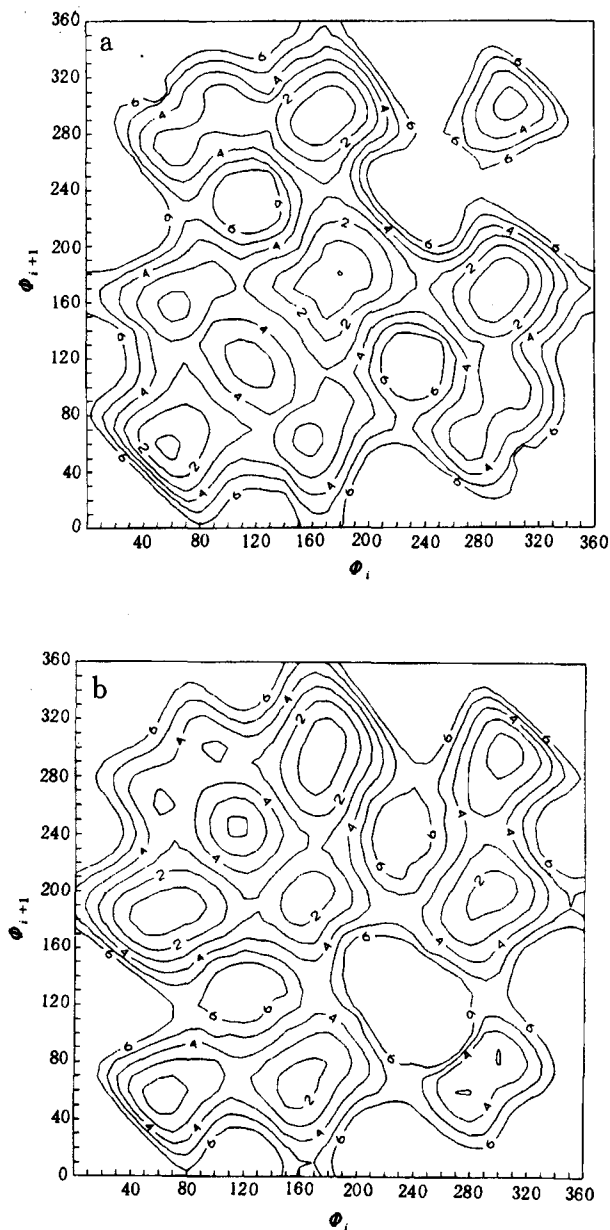


Fig. 3 Conformational energy contours for the racemic and the meso dyads of the specified PMA chain calculated as a function of bond rotations Φ_i and Φ_{i+1} . The energy contours are labelled in kcal/mol relative to the energy minimum of the racemic; tt conformer. The cut-off energy is selected as 6 kcal/mol, and the normalized energy is 5.0kcal/mol. (a) Racemic dyad; (b) Meso dyad

the corresponding conformers. An interface between the molecular graphical display and the modified MM2 program was thus developed in our laboratory in order to make conveniently a change of structure and the energy minimization. This interface has an advantage of convenience than the ALCHEMYTM software.

Table 1 Averaged dihedral angles and average energies calculated according to eqs.(1—3) for nine conformers with the energy minima less than 2.0kcal/mol for meso or racemic dyad

	gg	gt	gg ⁻	tg	tt	tg ⁻	g ⁻ g	g ⁻ t	g ⁻
Meso	60°, 60°, 70°, 190°, 1.553	0.4189		160°, 60°, 160°, 190°, 1.568	160°, 190°, 170°, 290°, 1.504	170°, 290°, 0.4189	300°, 160°, 1.568	300°, 300°, 1.553	
Racemic	60°, 60°, 60°, 160°, 0.8031	1.669		160°, 60°, 170°, 180°, 0. 1.669	170°, 180°, 0. 0.1447	170°, 290°, 0.1447	290°, 170°, 0.1447		

All energies have the same unit of kcal/mol relative to the racemic; tt conformer. The normalized energy is 5.0kcal/mol

However, it should be noted that the maps as directly obtained were not yet as symmetrical as shown in Fig. 3. There are a few distortions that broke the perfect symmetry of the shape of the contours along the axis through (0°, 360°) and (360°, 0°) for the meso dyad or (0°, 0°) and (360°, 360°) for the racemic dyad. This distortion of the contours occurred here did not take place in the case of a polymer with simple side-groups such as polypropylene^[8], or in the case of PMA with an interval of 30° between data points^[8] when the full-relaxation-model was adopted. The symmetrical data pair on the maps usually obtained in the case of the simply polymer sometimes did not occur in the present study where the unsymmetrical data pair result from two conformers having a few of different geometry. Obviously, the procedure of the full-relaxation minimization did not even make the molecular model undergo every thermodynamically stabilized conformational state with a complicated side-group. This means that a conformer with two specified rotational dihedral angles have a relatively fixed or lower value of energy after optimizing the geometric structure. Owing to the complex of large side-groups, the somewhat changes in position or angles of side-groups may probably make the energy of conformations vary from a minimum to another minimum. From a statistical viewpoint, these minima are all significant and have contributions to the chain configurations. In this situation, the corrected energy contours in both sides of the diagonal axis are all significant and can be treated in calculating the individual contour maps of each model. To include contributions from all possible conformations, we only simply carry out a superposition of energy data of the two sides of contour maps by Boltzmann factors for the meso or the racemic dyad. Thus, we have the two finally conformational energy surfaces as shown in Fig. 3. Of course, this is only an approxi-

mated way accessible to the real situation. It can be seen from this figure that the racemic tt conformer has the lowest energy among all conformers with energy minima. Table 1 gives these averaged dihedral angles and the average energies for nine conformers with the energy minima less than 2.0kcal/mol for meso or racemic dyad.

Table 2 Energy components for several conformers corresponding to the potential wells in the contour maps which have not performed the superposition of energy data

For a meso dyad:

State	Angles(°)	E_{total}	E_c	E_b	E_s	E_{vdwl-4}	E_{other}	$E_{torsion}$	E_{dip}	$M_{dip}(D)$
tt	170, 160	6.3722	.5981	3.6828	.2612	8.4808	-2.3177	-2.0369	-2.2962	5.357
gt	60, 180	5.2681	.5691	3.4878	.2594	8.4363	-1.5595	-2.4519	-3.4830	3.124
tg ⁻	180, -60	6.1729	.5752	3.4815	.2603	8.4567	-1.8042	-2.0709	-2.7246	4.173
gg ₁ ⁻	100, -60	7.7427	.6391	3.5382	.2920	8.9399	-1.4520	-1.4113	-2.8032	4.808
gg ₂ ⁻	60, -100	7.8883	.6671	3.6092	.2867	8.9197	-1.2332	-1.2987	-3.0627	3.630
g ⁻ t	-70, -160	6.4621	.5858	3.7534	.2857	8.5334	-1.8952	-1.5983	-3.2028	3.020
tg	160, 60	6.6133	.6194	3.9498	.3093	8.5149	-1.5346	-1.6900	-3.5556	1.964
g ⁻ g	-80, 60	7.8026	.6221	5.3740	.3817	8.6291	-1.7448	-1.1810	-4.2781	2.120
g ⁻ g ⁻	-50, -60	6.4277	.6018	4.1864	.3221	8.4574	-1.5302	-2.4151	-3.1846	1.050
gg ₁	70, 70	7.1071	.5592	4.4756	.3102	8.5022	-1.8550	-1.9846	-2.9006	2.589
gg ₂	60, 50	7.6063	.5965	4.5823	.3387	8.4744	-1.3114	-2.3880	-2.6862	5.356

For a racemic dyad:

State	Angles(°)	E_{total}	E_c	E_b	E_s	E_{vdwl-4}	E_{other}	$E_{torsion}$	E_{dip}	$M_{dip}(D)$
tt	170, 180	4.8293	.6079	3.4104	.2661	8.2367	-1.2279	-2.6738	-3.7901	.962
gg	60, 60	5.7981	.5994	3.5775	.2804	8.4263	-1.2665	-2.7971	-3.0219	3.865
gt	60, 160	6.6642	.6437	3.7205	.2876	8.4706	-1.3065	-2.2455	-2.9062	4.618
tg	160, 60	6.6642	.6438	3.7343	.2876	8.4739	-1.2996	-2.2639	-2.9118	4.608
g ⁻ t	-70, 170	5.1390	.5798	3.7021	.2737	8.4916	-2.4792	-1.4102	-4.0188	2.262
tg ⁻ 1	170, -70	5.1489	.5952	3.7191	.2734	8.4831	-2.4941	-1.4007	-4.0270	2.251
g ⁻ g ⁻	-60, -60	7.6102	.5886	5.1214	.3812	8.2524	-2.0252	-2.3911	-2.3171	5.213
g ⁻ g ₁	-90, 60	7.4171	.6253	4.3972	.3347	8.6289	-1.6082	-1.9345	-3.0263	1.678
g ⁻ g ₂	-60, 100	7.3284	.6075	3.7030	.3041	8.8174	-2.3297	-1.0810	-2.6928	2.800
gg ₁ ⁻	60, -90	7.4187	.6259	4.4076	.3352	8.6263	-1.6245	-1.9248	-3.0269	1.684
gg ₂ ⁻	110, -70	7.2298	.5820	3.6496	.2908	8.9297	-2.8163	-.7741	-2.6320	2.734

All energies have the same unit of kcal/mol relative to the racemic tt conformer. The top energy is 5.0 kcal/mol in a calculation of statistical average for each specific conformation area in contour maps. In order to analyse the interactions and geometry of conformers with energy minima, we also presented the energy compo-

nents and the two orientational dihedral angles (χ_1 and χ_2) for every conformer in Table 2 and 3, respectively. Each conformer corresponds to the conformation with energy minimum in the contour maps which have not performed the superposition of energy data.

Table 3 Orientational dihedral angles of carbonyl-bonds for several conformers with energy minima referred to Table 2

Model	State	E_{total} (kcal/mol)	$\phi_1, \phi_2(^{\circ})$	$\chi_1(^{\circ})$	$\chi_2(^{\circ})$
Racemic	tt	0.0	170, 180	-129.90(168.2)	-138.60(160.1)
	tg	1.83	160, 60	-142.5 (156.1)	-125.3 (168.8)
	tg ⁻	0.31	170, -70	-161.9 (137.6)	133.7 (73.8)
	gg	0.97	60, 60	126.8 (67.4)	-129.6 (166.3)
	gt	1.83	60, 160	-125.0 (169.2)	-143.4 (155.1)
	gg ₁ ⁻	2.59	60, -90	-128.7 (166.2)	123.4 (61.8)
	gg ₂ ⁻	2.40	110, -70	128.7 (69.9)	122.3 (60.6)
	g ⁻ g ₁	2.59	-90, 60	123.2 (61.5)	-128.4 (166.6)
	g ⁻ g ₂	2.50	-60, 100	123.1 (60.6)	129.2 (69.3)
	g ⁻ t	0.31	-70, 170	133.1 (73.1)	-161.8 (137.5)
	g ⁻ g ⁻	2.79	-60, -60	114.4 (51.7)	114.4 (51.7)
Meso	tt	1.54	170, -160	140.0 (85.2)	138.9 (-159.0)
	tg	1.78	160, 60	-152.7 (-145.8)	118.5 (-175.1)
	tg ⁻	1.34	180, -60	152.7 (95.0)	133.7 (-162.1)
	gg ₁	2.28	70, 70	140.2 (80.2)	-119.8 (-58.2)
	gg ₂	2.79	60, 50	131.0 (71.3)	104.4 (171.8)
	gt	0.44	60, 190	135.0 (76.2)	139.4 (-159.3)
	gg ₁ ⁻	2.91	100, -60	137.0 (71.8)	128.3 (-166.7)
	gg ₂ ⁻	3.06	60, -100	133.7 (74.2)	132.9 (-163.4)
	g ⁻ g	2.97	-80, 60	142.9 (83.0)	90.5 (157.4)
	g ⁻ t	1.63	-70, -160	130.7 (69.0)	148.8 (-150.3)
	g ⁻ g ⁻	1.60	-50, -60	199.2 (57.5)	130.8 (-164.8)

The total energies are labelled in kcal/mol relative to the energy minimum of racemic; tt conformer. ϕ and χ are the dihedral angles along the main chain and the side-group, respectively. The subscripts "1" and "2" of ϕ and χ refer to the first and the second dihedral angles when we view the dyad molecule from the lower to higher atom number. The data in brackets represent the dihedral angles between C^α-C[#] and C^{*}=O. C[#] is the skeletal carbon atom located between two carbon atoms flanking the ester group

One can find that two new important conformers tg⁻ and g⁻t with lower energies were detected here for the racemic dyad but not reported in the previous studies^[2,3,7]. In view of molecular structure of g⁻t and tg⁻ conformers shown in Fig. 4, two ester groups are parallel to each other and the directions of the two are opposite. It can

be seen from Table 2 that the two conformers possess the most negative value of the dipole-dipole interaction energy among all the conformers. This demonstrates that the electrostatic potential played a very important role in stabilizing the two conformers.

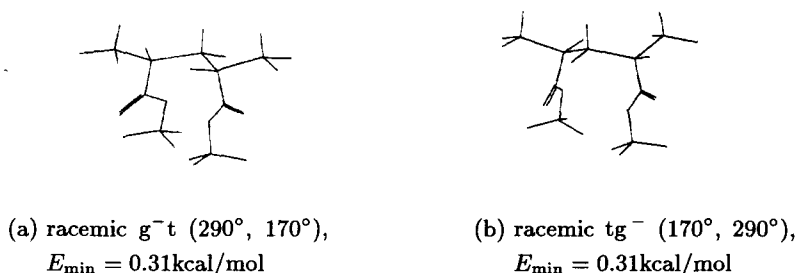


Fig. 4 Two important conformations g^-t and tg^- with energy minima of 0.31kcal/mol for a racemic dyad of PMA chain

As stated by Smith et al.^[13], two side-groups of the meso and racemic dyad of PMA have existed a severe interference and electrostatic interactions. Two dihedral angles χ_1 and χ_2 may fairly depart from their initial values. Table 3 showed these deviation from the initial angles. The data in brackets represent the dihedral angles between $C^\alpha-C^\#$ and $C^*=O$. $C^\#$ is the skeletal carbon atom located between two carbon atoms flanking the ester group. These values vary with the different conformers and different models and is not always nearly 90° . Three angle "60", "90" or "150" seem to be designated as reported by Smith et al.^[13]. This calculation once again supports that the side-groups are not perpendicular to the plane defined by two adjoining backbone bonds and the g^- state cannot be ignored during the conformational state transitions.

Statistical weight matrices

To determine the statistical weight matrix of $i-1$ and i bond pair is very difficult and generally needs a reasonable consideration of much higher-order interactions. As an approximation, we use the simplified matrix for this calculation^[12]. The statistical weight matrices of i and $i+1$ bond pair can be obtained for the partitional function quoted in eq.(1) and the energy contours for the meso and racemic dyads. They are

$$U''_{\text{meso}} = \begin{matrix} & \begin{matrix} t & g & g^- \end{matrix} \\ \begin{matrix} t \\ g \\ g^- \end{matrix} & \begin{bmatrix} .9232 & .07966 & .5928 \\ .5929 & .06356 & .01452 \\ .07962 & .008498 & .06362 \end{bmatrix} \end{matrix}$$

t

g

g⁻

t

g

g⁻

$$U''_{\text{racemic}} = \begin{bmatrix} 1.0 & .05509 & .6992 \\ .0550 & .2172 & .02861 \\ .6996 & .02847 & .008042 \end{bmatrix}$$

Unperturbed configurational dimensions

The three-state scheme is applicable with states at $\varphi_t = -7.80^\circ$, $\varphi_g = 116.37^\circ$ and $\varphi_g = -113.57^\circ$ for the meso dyad and at $\varphi_t = -7.79^\circ$, $\varphi_g = 112.56^\circ$ and $\varphi_g = -115.95^\circ$ for the racemic dyad. The configurational dimensions (such as characteristic ratio, radii of gyration and persistence length) of regularly stereochemical chains and atactic chains with the Bernoullian distribution generated by Monte Carlo method were primarily characterized by using the procedure mentioned above [1].

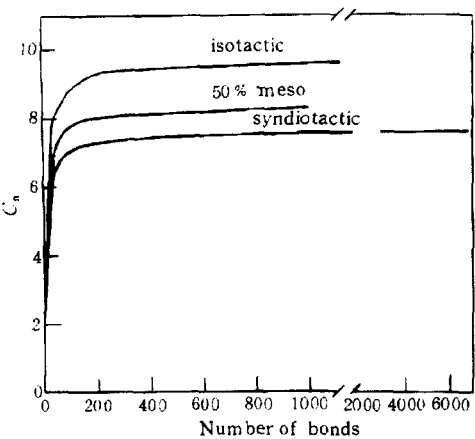


Fig. 5 The dependence of characteristic ratio on chain length for three kinds of stereoregularity of PMA chain at 300K

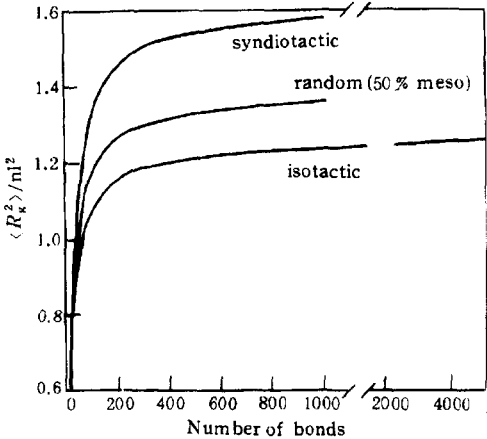


Fig. 6 The unperturbed mean-square radii of gyration for three kinds of stereoregularity of PMA chain at 300K

(1) Length of chain

To approach the equilibrium C_∞ or $\langle R_g^2 \rangle / nl^2$, several hundreds of bonds are at least required in the calculation for both of stereoregular and random chains. The computational results in Fig. 5 show that the C_∞ is about 7.5 for an isotactic chain or 9.6 for a syndiotactic chain. The persistence length is correspondingly 6.6 for an isotactic chain or 8.2 for a syndiotactic chain. The syndiotactic chain is slight more rigid than the isotactic one. The difference among the three kinds of stereochemical chains can be further confirmed by the dependence of unperturbed radius of gyration on chain length referred to Fig.6. The correlation between the mean-square radius

of gyration and the mean-square end-to-end distance follows the $1/6$ relation when the chain is enough long.

(2) Fraction of meso dyad

PMA prepared by radical polymerization is reported about $50(\pm 10)\%$ isotactic

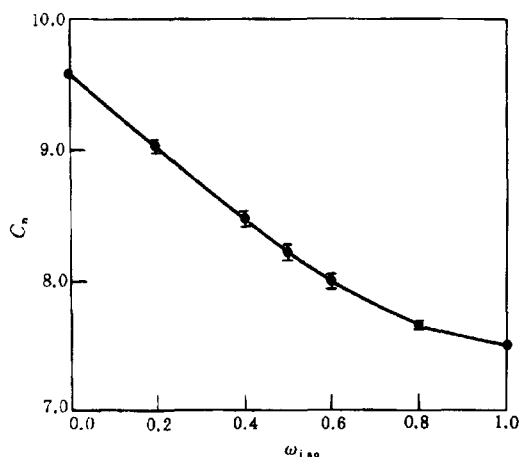


Fig. 7 Characteristic ratio C_n of PMA for Monte Carlo chains of 1,000 bonds at 300K. Each point in the range $0 < \omega_{iso} < 1$ represents average for more than 10,000 Monte Carlo chains

according to the NMR studies of Matsuzaki et al.^[14], Flory et al.^[2] concluded in their study that the adjustment of the statistical weight parameters must be required to fit the experimental range^[4-5] of $C_\infty \approx 8.4 \pm 0.5$ for such prepared PMA chain. Our numerical calculation of the unperturbed dimensions gives averaged $C_\infty \approx 8.2 \pm 0.3$ in Fig.7 for more than 10,000 atactic PMA chains with $\omega_m = 0.5 \pm 0.1$. The C_n of chain with 40% meso dyad has a maximum deviation of 6.266%. Though the statistical weight matrix U'_i adopted here is under the second-order interaction approximation^[12], this result is significant and found to be a good agreement with the experiments. Finally, the validity of Flory's approximation of the matrix U'_i for polymers with complex side-groups may remain to be further verified by using numerical calculation with high-order interferences. Since the side-group of PMA is not of a spherical symmetry, the two carbonyls in the meso or the racemic dyad obviously have three orientation combinations as is the case for polyacrylamide^[9]. Another two different combination of the two carbonyls of the meso or the racemic dyad may result in differences. These will be presented in a subsequent paper.

(3) Comparison with the results from the two-state approximation

When simplifying the three-state scheme into two states, we can obtain larger

values of characteristic ratio at 300K. For an isotactic chain, $C_\infty \rightarrow 11.22$, while a syndiotactic chain, $C_\infty \rightarrow 11.36$. This illustrates that the chain so examined is more rigid than from the three-state approximation and the minus gauche state may not be ignored in the chain statistics.

CONCLUSIONS

The present calculation indicates that the conformational energy contours obtained from the full-relaxation optimization of molecule are different from those calculated with the rigid molecular model. The minus gauche state and the orientational effect of ester group on chain configuration cannot be neglected during the conformational state transitions. The unperturbed chain dimensions calculated with the three-state RIS model are in good agreement with the experimental data for random chains.

Keywords:

Poly(methyl acrylate); Configurational statistics; Conformational energy

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