

MEAN-SQUARE RADIUS OF GYRATION AND DIPOLE MOMENT OF POLY(METHYLPHENYLSILOXANE) CHAINS*

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Abstract The mean-square radius of gyration $\langle S^2 \rangle$, the mean-square dipole moment $\langle D^2 \rangle$, the mean-square end-to-end distance $\langle R^2 \rangle$ and their temperature coefficients of unsymmetrical disubstituted poly(methylphenylsiloxane) (PMPS) chains, as a function of stereochemical structure, conformational energies and length of polymers, were studied by using an improved configurational-conformational statistical method based on the rotational-isomeric-state theory. It is found that the increase in isotacticity of PMPS chains causes a significant decrease in the unperturbed dimensions and increase in their temperature coefficients. This correlation of the properties of PMPS and its stereochemical structure is different from that of vinyl monosubstituted polystyrene and disubstituted poly(α -methylstyrene) chains. Dependence of the characteristic ratio of $\langle S^2 \rangle$ on conformational energy $E_{\omega'}$ of $C_6H_5 \dots C_6H_5$ four-bond interactions increases markedly with the degree of isotacticity increasing, the dependence on the conformational energy E_{δ} and dE_{σ} decreases with increasing the degree of isotacticity. It is also found that the characteristic ratios of $\langle R^2 \rangle$ and its temperature coefficients are in agreement with corresponding experimental results in the degree of isotacticity of about 0–40%. Moreover, the $C_6H_5 \dots C_6H_5$ four-bond interactions play a dominant role in regard to the dimensions of high syndiotactic chains. In addition, the effect of large side groups on unperturbed dimensions is investigated further by the improved expressions of $\langle S^2 \rangle$.

Keywords: Poly(methylphenylsiloxane); Stereochemical structure; Mean-square radius of gyration; Mean-square dipole moment; Temperature coefficient.

INTRODUCTION

Silicone polymers are an important class of inorganic polymers, which are used in a variety of commercial applications including lubricants, defoamers, greases, resins and elastomers. Therefore, silicone polymers, in particularly silicone elastomer poly(dimethylsiloxane) (PDMS)^[1–8] have been widely investigated both theoretically and experimentally. Poly(methylphenylsiloxane) (PMPS) is an important member of the class of disubstituted siloxanes of general structure $[Si(C_6H_5)(CH_3)-O-]_x$, x is the polymerization degree, or $-[Si(b)(\beta)-O-]_x-$, in which b and β are defined as the equivalent centers of benzene ring C_6H_5 and methyl CH_3 , respectively. Since $b \neq \beta$, the PMPS chain has a stereochemical variability in that Si atoms are pseudoasymmetric. This variability makes PMPS a much more complicated chain molecule than PDMS with side groups $b = \beta = CH_3$ ^[8, 9]. The scheme for characterizing the stereochemical structure of PMPS chains is identical to that used for the extensively studied vinyl class of polymers, the monosubstituted vinyl chains $-[C(b)-CH_2-]_x-$ and the disubstituted chains $-[C(b)(\beta)-CH_2-]_x-$, such as polystyrene (PS) and poly(α -methylstyrene) (P α MS), respectively. Because of the wealth of information obtained on them, the effect of stereochemical composition on their statistical properties is quite well understood^[10–14]. In contrast, the

*This research was supported by the National Basic Research Program (973) of China (No. 10574109), the Zhejiang Provincial Science and Technology Department (No. 2007G60G1120019), National Science Foundation of Zhejiang Province (No. Y604064), and Zhejiang Gongshang University (No. 08-13), China.

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Received October 29, 2007; Revised December 24, 2007; Accepted January 8, 2008

correlation of stereochemical structure and statistical properties of disubstituted siloxanes is less known, therefore, comparison between structure-property relationships for these types of stereochemically variable polymers would obviously be of very great interest. Therefore, in the present investigation, an improved model of chain structure and configurational-conformational statistical method will be employed in regard of PMPS dimensions calculation, including the mean-square radius of gyration $\langle S^2 \rangle$, the mean-square dipole moment $\langle D^2 \rangle$ and their temperature coefficients.

MODEL AND METHOD

An unsymmetrical disubstituted PMPS chain is shown schematically in Fig. 1, where the chain is given in the planar all-*trans* conformation for facilitating definition of the required stereochemical characteristics. Considering the effect of spatial situations of substitutes, the skeletal atoms are defined as A-type and F-type in

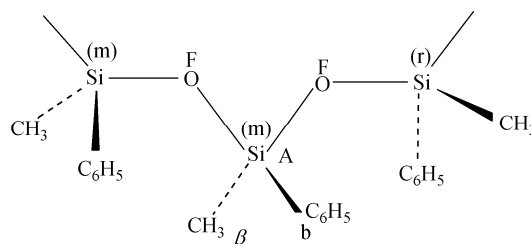


Fig. 1 A portion of the poly(methylphenylsiloxane) chain showing the variable stereochemistry

the improved model of $-[A(b)(\beta)-F]_x$ —^[15, 16], therefore, the expressions of end-to-end distance of atom pairs are modified as

$$r_{i'j'}^2 = J_P g_e g_f (g_A g_F)^{(j-i)} g_a g_b J_Q \quad (1)$$

$$g_i = \begin{bmatrix} 1 & 2L_i^T T_i & l_i^2 \\ 0 & T_i & L_i \\ 0 & 0 & 1 \end{bmatrix} \equiv G[2L_i^T T_i, l_i^2, T_i, L_i] \quad (2)$$

$$i, j \text{ or } A, F \quad \text{for skeletal atoms} \quad (3)$$

$$i', j' \text{ or } a, b, e, f \quad \text{for side group } b, \quad (4)$$

$$i'', j'' \text{ or } \alpha, \beta, \gamma, \delta \quad \text{for side group } \beta, \quad (5)$$

The present form of matrix T , L , J_P , J_Q , J_P , J_Q , J and J^* are identical to the definition of literature [14]. The length of skeletal bond is l in bond matrix L_i , the length of side group l_b or l_β is defined as the distance between b (or β) and asymmetric Si. The internal rotation angle φ has been replaced by $\varphi + \varphi'$ in the transformation matrix T_i , where the additive angle φ' has regard to effect of side groups, and the expressions of angles were introduced in literature [15]. Therefore, the square radius of gyration based on the rotational-isomeric-state theory is deduced from its definition^[1, 14], that is

$$S^2 = \frac{1}{M^2} \sum_{q=1}^{13} m(q) J_P [F(q) A(q)]_i^x J_Q \quad (6)$$

where M is the mass of a chain. $m(q)$ is the sequence of the atom-pair masses. Following the definition of Eq. (2), the main elements of matrix in super generator matrix $F(q)$ of F-type and $A(q)$ of A-type are listed in Table 1. Obviously, if the mass of side groups $m_b = m_\beta = 0$ and the mass of skeletal atoms $m_A = m_F$, Eq. (6) agrees with the Lagrange relation^[1]

$$S^2 = \frac{1}{(2x+1)^2} \mathbf{J}_P [\mathbf{F}(1) \mathbf{A}(1)]_1^x \mathbf{J}_Q \quad (7)$$

The mean-square radius of gyration $\langle S^2 \rangle$ of unsymmetrically disubstituted PMPS chains is treated by the configurational-conformational statistics of S^2 . Following the stereochemical structure of chains characterized in Fig. 1, the Si atom on which the attached phenyl (C_6H_5) group is in front of the plane of the chain backbone will be arbitrarily designated as m, and the Si atom with its phenyl group behind the plane will be designated as r. Thus, the sequence of chain shown in Fig. 1 corresponds to the stereochemical sequence mmr.... When all of the Si atoms of a chain are of the same configuration (mmmm... or rrrr...), the polymer is said to be isotactic. Other stereochemical forms are the syndiotactic, in which there is regular alternation (mrmmr...), and the atactic, in which the sequences are irregular stereochemically (mmrmr...). Therefore, in a replication unit, the statistical weight matrices on an asymmetric atom are divided into the meso dyad matrix $\mathbf{u}_{Am}$ and the racemic dyad matrix $\mathbf{u}_{Ar}$. Therefore, the matrices $\mathbf{U}_m, \mathbf{U}_r$ of replication unit are

$$\mathbf{U}_m = \mathbf{u}_F \mathbf{u}_{Am} \quad \text{for meso dyads} \quad (8)$$

$$\mathbf{U}_r = \mathbf{u}_F \mathbf{u}_{Ar} \quad \text{for racemic dyads} \quad (9)$$

Table 1. Sequence of $m(q)$ and the matrices $\mathbf{F}(q)$ and $\mathbf{A}(q)$ of PMPS

q	$m(q)$	$\mathbf{F}(q) = \mathbf{G}[f_{12}, f_{13}, f_{22}, f_{23}]$				$\mathbf{A}(q) = \mathbf{G}[a_{12}, a_{13}, a_{22}, a_{23}]$			
		f_{12}	f_{13}	f_{22}	f_{23}	a_{12}	a_{13}	a_{22}	a_{23}
1	1	$m_A \mathbf{J}_F \mathbf{g}_F$	$m_A m_F l_F^2$	$\mathbf{g}_F$	$m_F \mathbf{g}_F \mathbf{J}_Q$	$m_F \mathbf{J}_F \mathbf{g}_A$	$m_A m_F l_A^2$	$\mathbf{g}_A$	$m_A \mathbf{g}_A \mathbf{J}_Q$
2	$m_F m_b$	0	0	$\mathbf{g}_F$	0	$\mathbf{J}_F \mathbf{g}_A$	r_{Fb}^2	$\mathbf{g}_A$	$\mathbf{g}_A \mathbf{g}_b \mathbf{J}_Q$
3	$m_b m_F$	$\mathbf{J}_F \mathbf{g}_e \mathbf{g}_f$	r_{bF}^2	$\mathbf{g}_F$	$\mathbf{g}_F \mathbf{J}_Q$	0	0	$\mathbf{g}_A$	0
4	$m_A m_b$	0	0	$\mathbf{g}_F$	0	$\mathbf{J}_P$	l_b^2	$\mathbf{g}_A$	$\mathbf{g}_A \mathbf{g}_b \mathbf{J}_Q$
5	$m_b m_A$	$\mathbf{J}_F \mathbf{g}_e \mathbf{g}_f$	0	$\mathbf{g}_F$	$\mathbf{J}_Q$	0	0	$\mathbf{g}_A$	0
6	$m_F m_\beta$	0	0	$\mathbf{g}_F$	0	$\mathbf{J}_F \mathbf{g}_A$	$r_{F\beta}^2$	$\mathbf{g}_A$	$\mathbf{g}_A \mathbf{g}_\beta \mathbf{J}_Q$
7	$m_\beta m_F$	$\mathbf{J}_F \mathbf{g}_\gamma \mathbf{g}_\delta$	$r_{\beta F}^2$	$\mathbf{g}_F$	$\mathbf{g}_F \mathbf{J}_Q$	0	0	$\mathbf{g}_A$	0
8	$m_A m_\beta$	0	0	$\mathbf{g}_F$	0	$\mathbf{J}_P$	l_β^2	$\mathbf{g}_A$	$\mathbf{g}_A \mathbf{g}_\beta \mathbf{J}_Q$
9	$m_\beta m_A$	$\mathbf{J}_F \mathbf{g}_\gamma \mathbf{g}_\delta$	0	$\mathbf{g}_F$	$\mathbf{J}_Q$	0	0	$\mathbf{g}_A$	0
10	$m_b m_\beta$	$\mathbf{J}_F \mathbf{g}_e \mathbf{g}_f$	0	$\mathbf{g}_F$	0	0	0	$\mathbf{g}_A$	$\mathbf{g}_A \mathbf{g}_\beta \mathbf{J}_Q$
11	$m_\beta m_b$	$\mathbf{J}_F \mathbf{g}_\gamma \mathbf{g}_\delta$	0	$\mathbf{g}_F$	0	0	0	$\mathbf{g}_A$	$\mathbf{g}_A \mathbf{g}_b \mathbf{J}_Q$
12	$m_b m_b$	$\mathbf{J}_F \mathbf{g}_e \mathbf{g}_f$	0	$\mathbf{g}_F$	0	0	0	$\mathbf{g}_A$	$\mathbf{g}_A \mathbf{g}_b \mathbf{J}_Q$
13	$m_\beta m_\beta$	$\mathbf{J}_F \mathbf{g}_\gamma \mathbf{g}_\delta$	0	$\mathbf{g}_F$	0	0	0	$\mathbf{g}_A$	$\mathbf{g}_A \mathbf{g}_\beta \mathbf{J}_Q$

Similarly, the F-type super generator matrices are divided into the meso dyad $\mathbf{F}_m(q)$ and the racemic dyad $\mathbf{F}_r(q)$, related to the meso dyad transformation matrices $\mathbf{T}_F^*$ and $\mathbf{T}_r^*$ and the racemic dyad matrices $\mathbf{T}_F$ and $\mathbf{T}_r$, respectively. Therefore, the matrices $\mathbf{S}_m$ and $\mathbf{S}_r$ of replication unit are deduced as

$$\mathbf{S}_m(q) = [(\mathbf{u}_F \otimes \mathbf{E}_7) \|\mathbf{F}_m(q)\|] [(\mathbf{u}_{Am} \otimes \mathbf{E}_7) \|\mathbf{A}(q)\|] \quad \text{for meso dyads} \quad (10)$$

$$\mathbf{S}_r(q) = [(\mathbf{u}_F \otimes \mathbf{E}_7) \|\mathbf{F}_r(q)\|] [(\mathbf{u}_{Ar} \otimes \mathbf{E}_7) \|\mathbf{A}(q)\|] \quad \text{for racemic dyads} \quad (11)$$

Here $\mathbf{E}_7$ is the unit matrix of 7 orders. Theoretically, the microstructure of an asymmetric chain with the x -ads constitutions can be simulated by the repeating p -ads constitutions, then, there are 2^p distinguishable configurations in the subensemble of representative chains. In present calculation, the occurrence probability P_k

of the k -th sequence of the p -ads is a function of the fraction of meso dyad w_m following the Bernoullian function^[16]. The replication probability w_m will characterize the degree of isotacticity and tacticity of an asymmetric chain. Therefore, the unperturbed mean-square radius of gyration of stereoirregular polymers is carried out by the statistic treatment of matrix $S_k(q)$, the result is

$$\begin{aligned} \langle S^2 \rangle &= M^{-2} \sum_{k=1}^{2^p} P_k \langle S^2 \rangle_k \\ &= M^{-2} \sum_{k=1}^{2^p} \left\{ P_k \sum_{q=1}^{13} [m(q) [J^* \otimes J_P \| A(q) \|] S_k(q)^X [\| F(q) \| J \otimes J_Q] / J^* U_k^X J] \right\} \end{aligned} \quad (12)$$

where the p -ads repeating number $X = (x - 1)/p$. The expressions of mean-square end-to-end distance $\langle R^2 \rangle$ have been introduced in the literature [15]. Similarly, the mean-square dipole moments may be induced as

$$\begin{aligned} \langle D^2 \rangle &= \sum_{k=1}^{2^p} P_k \langle D^2 \rangle_k \\ &= \sum_{k=1}^{2^p} \{ P_k [J^* \otimes J_P \| g_A \| D_k^X \| g_F \| J \otimes J_Q] / J^* U_k^X J \} \end{aligned} \quad (13)$$

$$D_m = [(u_F \otimes E_5) \| g_{Fm} \|] [(u_{Am} \otimes E_5) \| g_A \|] \quad (14)$$

$$D_r = [(u_F \otimes E_5) \| g_{Fr} \|] [(u_{Ar} \otimes E_5) \| g_A \|] \quad (15)$$

The generator matrices above are also defined by Eq. (2), in which the bond matrices L_i are replaced by the matrix of dipole moment

$$\mu_i^T = [\mu_0 \quad 0 \quad 0]_i \quad (16)$$

where μ_0 is the dipole moment of i bond. The temperature coefficients are carried out by

$$\kappa_f = \sum_{k=1}^{2^p} P_k \frac{d \ln \langle f^2 \rangle_k}{dT} \quad (17)$$

The differential of ratios on conformational energy E_ξ is carried out by

$$\frac{df}{dE_\xi} = \sum_{k=1}^{2^p} P_k \frac{d \ln \langle f^2 \rangle_k}{dT} \quad (18)$$

$f = S, D$ or R corresponding to the radius of gyration, the end-to-end distance and the dipole moment, respectively. E_ξ is the conformational energy of pentane-type.

The expressions above can be also used to investigate the unperturbed dimension of other stereochemically variable polysiloxanes $-\text{[Si(CH}_3\text{)b-O-]}_x-$, where $b = \text{H, C}_6\text{H}_5, \text{CH}_2\text{CH}_3, \text{CH}_2\text{CH}_2\text{CH}_3$ or $\text{CH}_2\text{CH}_2\text{CF}_3$.

RESULTS AND DISCUSSION

In present calculation, the structure parameters used to characterize the PMPS repeat unit were adopted from the structural information reported in the literature for the related molecules PDMS^[3, 4] and P α MS^[10]. The length of skeletal bonds $l = 0.164$ nm. The lengths of imaginary bonds $l_b = 0.31$ nm, $l_\beta = 0.19$ nm. The dipole moment of skeletal bonds $\mu_0(\text{Si-O}) = 0.6D$, $\mu_0(\text{O-Si}) = -0.6D$. The angles of bonds $\angle\text{OSiO} = \angle\text{OSiC} = 110^\circ$, and

$\angle\text{SiOSi} = 143^\circ$. In the improved method, the additive angles are carried out by the expressions of the literature[15]. The internal rotation angle of skeletal bonds $\varphi_t = 0$ in the *trans*, $\varphi_{g+} = 120^\circ$ and $\varphi_{g-} = -120^\circ$ in the *gauche*. The statistical weight matrix for the pair of bonds O—Si and Si—O is thus^[9]

$$\mathbf{u}_F = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & 0 \\ 1 & 0 & \sigma \end{bmatrix} \quad (19)$$

The statistical weight matrices for the Si—O and O—Si bond pairs are

$$\mathbf{u}_{Am} = \begin{bmatrix} \omega' \omega'' & \sigma \omega' \delta & \sigma \omega' \\ \omega'' & \sigma \delta & \sigma \omega \omega'' \\ \omega' \delta & \sigma \omega \omega' & \sigma \delta \end{bmatrix} \quad \text{for meso dyads} \quad (20)$$

$$\mathbf{u}_{Ar} = \begin{bmatrix} (\omega'')^2 & \sigma \omega'' \delta & \sigma \omega' \\ \omega'' \delta & \sigma & \sigma \omega \omega'' \\ \omega' & \sigma \omega \omega' & \sigma \delta^2 \end{bmatrix} \quad \text{for racemic dyads} \quad (21)$$

The statistical weight factor for each intra-molecular interaction was assumed to be a simple Boltzmann function $\xi = \exp(-E_\xi/RT)$, which is associated with the conformational energy E_ξ , the factors of the pentane-type interactions are designated in Table 2^[9]. These statistical weight matrices may be used to calculate the unperturbed dimensions of PMPS chains, including their characteristic ratio of mean-square end-to-end distance $C_n = \langle R^2 \rangle / 2xl^2$, the ratio of mean-square dipole moment $D_n = \langle D^2 \rangle / 2x\mu_0^2$ and the ratio of mean-square radius of gyration $S_n = \langle S^2 \rangle / 2xl^2$.

Table 2. Statistical weight factor and conformational energies of PMPS at 298 K

Pentane-type interaction	Statistical weight factor ξ	Associated conformational energy E_ξ (kJ/mol)
	σ	1.465
	δ	-4.187
	ω	6.699
	ω'	-10.467
	ω''	-3.768
	ω'''	-2.093

The numerical calculation results of unperturbed dimension of PMPS chains are calculated by using the parameters of Table 2, the ratios C_n , S_n and D_n shown in Fig. 2 decrease with increasing the degree of isotacticity. The differential of ratios on conformational energy E_ξ is also presented as a function of the replication probability w_m in Fig. 3, there, df/dE_ω ($f = S_n$, D_n or R_n) increases markedly with the degree of isotacticity increasing, df/dE_δ and df/dE_σ decrease with increasing the degree of isotacticity. Moreover, in the case of high syndiotacticity (low w_m), C_n and S_n increase with increase of E_ω , only S_n increases markedly with increase of E_δ . This dependence is a direct consequence of the fact that the unequal bond angles in PMPS chains cause the all-*trans* form to approximate a closed figure^[2, 8]. Such a closed figure obviously corresponds to a

small molecular dimension. Although three-bond interactions in PMPS cause a preference for this *trans* conformation, the very favorable $C_6H_5...C_6H_5$ four-bond interactions (related to $E_{\omega'}$) play a dominant role with regard to the dimensions for this chain molecule. In the case of high syndiotacticity, the C_6H_5 groups are on opposite sides of the chain in the all-*trans* form. Therefore, the lowering of energy accompanying formation of the highly favorable $C_6H_5...C_6H_5$ interactions causes transitions away from the *trans* states. This tends to make the characteristic ratio relatively large at small values of w_m , as is shown in Fig. 2. On the other hand, at high isotacticity, the C_6H_5 groups are already on the same side of the chain in the all-*trans* conformation, and thus the favorable $C_6H_5...C_6H_5$ interactions stabilize the compact *trans* conformation.

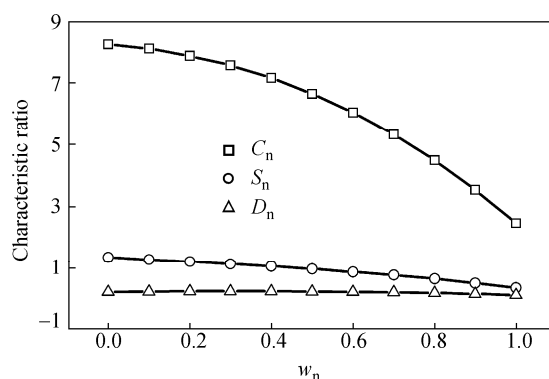


Fig. 2 Dependence of the characteristic ratios on the replication probability w_m for PMPS chain of $x = 40001$

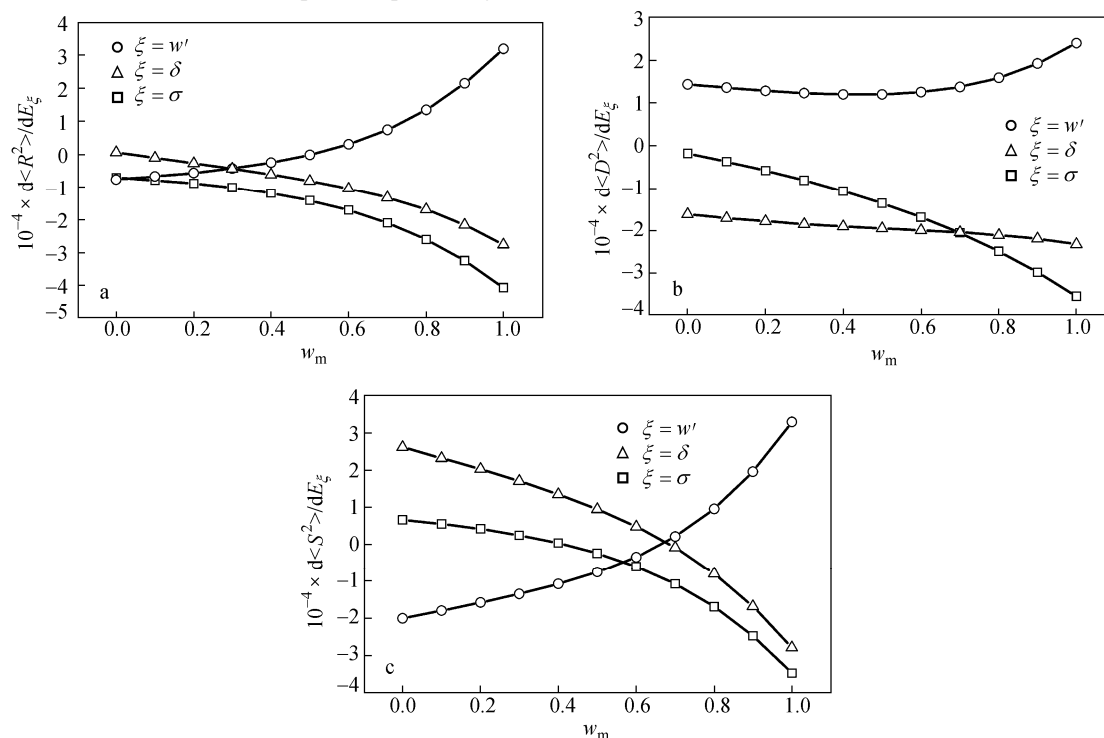


Fig. 3 Dependence of the characteristic ratios on their conformational energies $E_{\omega'}$, E_{δ} and E_{σ} at 298 K versus the replication probability w_m for PMPS chain of $x = 40001$
a) The mean-square end-to-end distance; b) The mean-square dipole moment; c) The mean-square radius of gyration

Comparison between PMPS and the related vinyl polymers PS and P α MS is presented in Fig. 4. Obviously, the characteristic ratios S_n of them show a very different dependence on stereochemical structure. The primary reason for this difference is the fact that the relatively long Si—O skeletal bonds and relatively large skeletal bonds angles $\angle\text{SiOSi}$ in PMPS increase the intra-molecular distances between interacting groups in pentane-type conformations, so that the interactions are attractive, rather than repulsive as they are in the more congested vinyl chains. The feature of monosubstituted polymer PS is the large S_n for the chains of syndiotacticity and isotacticity. This occurs because the C—C skeletal bonds are relatively short, and the $\angle\text{CCC}$ skeletal bond angles are relatively small, such as the distance of separation of the C_6H_5 groups in the pentane-type interaction in PS is only about 0.25 nm^[9]. (the distances of separation in PMPS is *ca.* 0.38 nm). Such repulsion interactions among side groups result in a helical conformation of chains, and thus correspond to large molecule dimensions. In the case of the disubstituted vinyl chain P α MS, the two pendant groups CH_3 and C_6H_5 are apparently somewhat similar in their intra-molecular interactions. Since changes in stereochemistry involve interchanges of these two groups around the disubstituted carbon atoms, their interactions are not very different accounts for the observed fact that the characteristic ratio of P α MS is not strongly dependent on the stereochemistry of the chain.

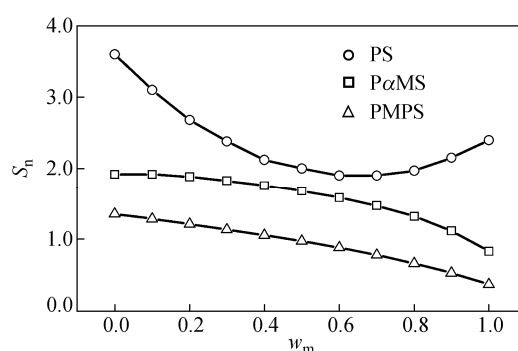


Fig. 4 Comparison of the ratios $S_n = \langle S^2 \rangle / 2xl^2$ of PMPS chain as a function of the replication probability w_m with that of PS and P α MS chain

Various temperature coefficients κ_r , κ_s and κ_μ of PMPS chains as a function of w_m with the illustrative three sets of conformational energies are presented in Fig. 5. These relations are rather identical, the coefficients increase markedly with increasing the degree of isotacticity, and are mainly positive values. The largest values correspond to highly isotactic PMPS chains, for which an increase in temperature causes transitions from the low energy, compact *trans* states to alternative states of higher spatial extension.

Theoretical values of C_n and κ_r are tentatively compared with the experimental results in Mark's works^[9]. The C_n of 8.7–8.8 was reported for two typical samples of stereochemically uncharacterized PMPS^[17, 18], these experimental results can be reproduced from the model only by assuming a relatively large fraction of syndiotactic placement. The temperature coefficients κ_r predicted for this degree of syndiotacticity is then also in good agreement with the experiment value $(0.61 \pm 0.09) \times 10^{-3} \text{K}^{-1}$ ^[19]. However, the experimental results of cyclization studies suggest that PMPS is essentially atactic and has large C_n for the short PMPS chain^[20]. The present theoretical values in Figs. 2 and 5(a), compared with the experimental data, suggest that the PMPS chains with the relatively small degree of isotacticity are of significant and have w_m values of about 0–0.4. In fact, the suitable resolution for the calculated theoretical results requires reliable experimental values, determined on samples of known stereochemical structure. Therefore, as a tentatively theoretical investigation, the dependence of S_n on the logarithm of chain length x is calculated by using the suggested parameters of PMPS in Table 1. The results, related to three typical stereochemical structures of polymers, syndiotacticity, isotacticity and atacticity (50% isotacticity), are presented in Fig. 6(a). It is found that the characteristic ratios of the PMPS chain as functions of x first decrease steeply, and finally approach the asymptotic values. Moreover, the consideration of side groups leads to the larger ratios in $x < 10^2$. The ratio of syndiotactic PMPS chain is

also calculated by taking $m_b = m_\beta = 0$ and $m_A = m_F$ in the Eq. (12), which approximate to Lagrange relation without considering the side groups [see the Eq. (7)]. This ratio increases with x increase and finally approaches an asymptotic value with considering the side groups. Another interesting fact is that the polymers of different tacticity have same ratio values at about $x = 10$, in fact, the skeletal bond number of a closed figure of PMPS chain in all-*trans* is also about 20. Therefore, these results may indicate that the consideration of side group effect is significant, particularly for short disubstituted polymers.

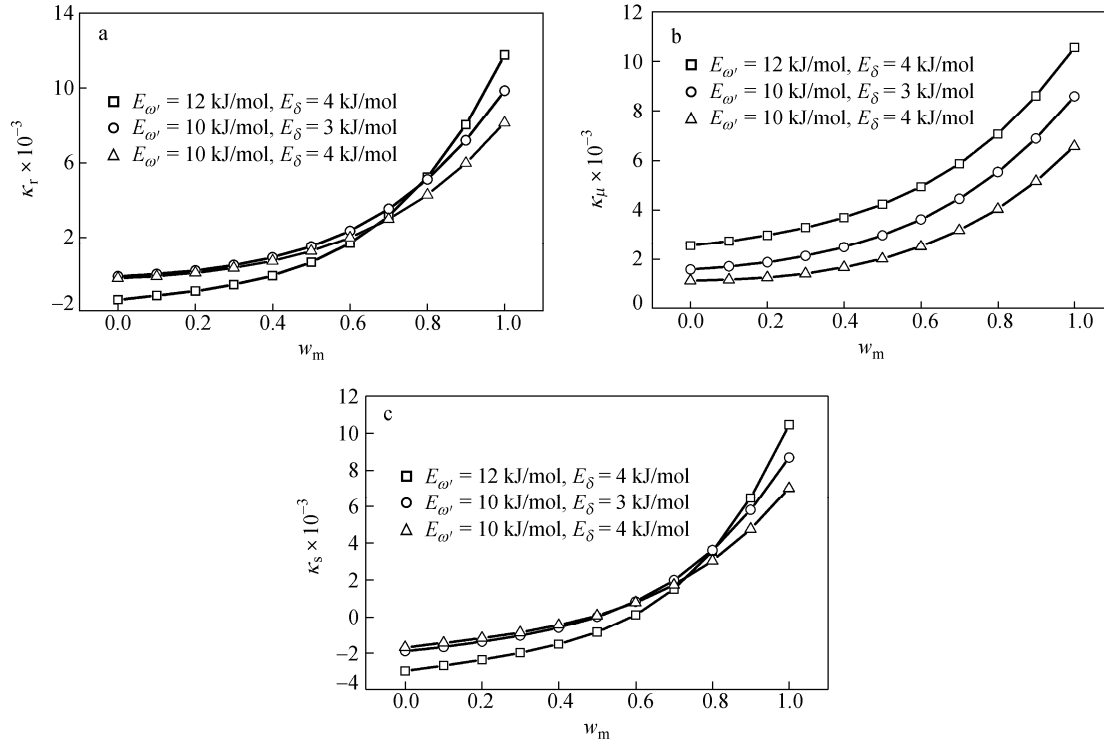


Fig. 5 Plots of the temperature coefficients versus the replication probability w_m for PMPS chain of $x = 40001$ at 298 K

a) κ_r for the mean-square end-to-end distance; b) κ_μ for the mean-square dipole moment; c) κ_s for the mean-square radius of gyration

Finally, the correlation of the characteristic ratio of mean-square dipole moment and the logarithm of chain length x is shown in Fig. 6(b), the results are similar to those of the PDMS chains reported in the literature [6].

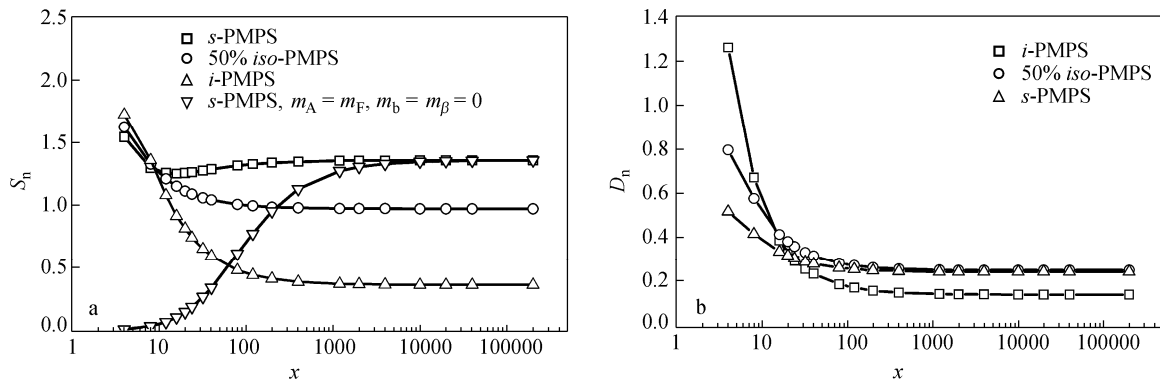


Fig. 6 Characteristic ratios of the mean-square radius of gyration S_n (a) and the mean-square dipole moment D_n (b) against the logarithm of chain length x at 298 K

CONCLUSIONS

An improved theoretical method is used to study the effect of the stereochemical structure of unsymmetrical disubstituted siloxane polymers on their unperturbed dimensions.

(1) It is found that the characteristic ratios S_n , D_n and C_n of PMPS chains are rather large at small values of the degree of isotacticity, and their temperature coefficients increase with increasing w_m . The effect of stereochemical structure on the unperturbed dimensions is rather different from the case for the closely related monosubstituted and disubstituted vinyl polymers.

(2) The theoretical values of C_n and κ_i are compared with the experimental data, the results suggest that the most PMPS chains have relatively small degree of isotacticity (about 0–40%). The conformational energies E_ω of $C_6H_5 \dots C_6H_5$ four-bond interactions give important effect on the unperturbed dimension and the temperature coefficients for the high syndiotactic PMPS chains. df/dE_ω ($f = S, D$ or R) increases markedly with the degree of isotacticity increasing.

(3) The behavior of PMPS chains with considering the effect of side groups is found to be quite different from that of not considering side groups. The difference of characteristic ratios S_n is mainly found when the length $x < 10^4$. Therefore, it may be not a good idea to calculate the unperturbed dimension of polymers with large side groups simply by using the mean-square end-to-end distance and the mean-square radius of gyration defined Lagrange relation.

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