

DIMENSIONS OF ATACTIC POLY(α -METHYLSTYRENE) CHAINS WITH SIDE GROUPS

Hai-zhu Ma^{a,b*} and Gao-xiang Ye^a

^aDepartment of Physics, Zhejiang University, Hangzhou 310027, China

^bDepartment of Physics, Zhejiang Education Institute, Hangzhou 310012, China

Abstract An improved configurational-conformational statistical method is developed and the mean-square radius of gyration for atactic poly(α -methylstyrene)(P α MS) chains is studied, in which the effect of large side groups is considered. The deduced formulas, based on the rotational isomer state theory, are used to investigate the configuration-dependent properties of the atactic polymer chain, and the statistical correlation of the unperturbed polymer chain dimension and structure parameters are calculated. For the fraction of meso dyads $w_m = 0.4$, the dependence of the radius of gyration R_g and the intrinsic viscosity $[\eta]$ on the molecule mass M are $R_g = 2.63 \times 10^{-2} M^{0.50}$ nm and $[\eta] = 7.36 \times 10^{-2} M^{0.497}$, respectively, which are in agreement with the previous experimental data for the P α MS samples. A small hump is detected in the curve of the characteristic ratio of the unperturbed mean-square radius of gyration versus the chain length for short P α MS chains. The R_g increases linearly with the temperature T , and the effects of the chain length and the tacticity on the temperature coefficient are remarkable. These are quite different from the results for P α MS chains not considering side groups or for the monosubstituted polystyrene chain.

Keywords: Side groups; Rotational isomeric state; Radius of gyration; Poly(α -methylstyrene) chain.

INTRODUCTION

The mean-square radius of gyration $\langle S^2 \rangle$, the radius of gyration $R_g = \langle S^2 \rangle^{1/2}$, the intrinsic viscosity $[\eta]$, the temperature coefficient K , and the dipole moment are characteristic parameters for describing the properties of polymers. On the experimental side, these quantities are measured by viscometry, laser light scattering, small angle neutron scattering and so on for the dilute solution or the bulk amorphous polymer^[1–6]. On the theoretical side, they are usually calculated based on Flory's rotational isomeric state (RIS) theory^[7–15], the Monte Carlo simulation of Yamakawa's helical wormlike chain (HW) model and so on^[16, 17]. The Lagrange relation of RIS approximation is an effective method to calculate $\langle S^2 \rangle$, in which the interaction of only neighbor beads and the size of skeletal bonds are taken into account and the effect of side groups is usually neglected^[7–9]. Therefore, the RIS calculation is approximate and the results for several polymers with large side groups, such as poly(methyl methacrylate) (PMMA) chains and polystyrene(PS) chains, are not in agreement with experimental data^[5, 10, 11]. In Yamakawa's HW model, the obtained values of $\langle S^2 \rangle$ fit the situation of freely rotating chain very well, but it cannot be used to consider the effect of side groups^[16]. In our previous RIS calculation of $\langle S^2 \rangle$, the effect of large side groups was introduced, in which method the substitutes of PMMA chain were divided into two parts, and a complicated derivation of $\langle S^2 \rangle$ was involved^[10]. Recently, a simplified method of calculating $\langle S^2 \rangle$ was developed for a lot of substituted polymers taking account of the effect of side groups or heteroatoms in the backbone^[13, 14], but the $\langle S^2 \rangle$ of poly(α -methylstyrene) (P α MS) was calculated only for isotactic chains and syndiotactic chains, and the difference of $\langle S^2 \rangle$ between substituted and unsubstituted polymer chains was not discussed. In this paper, the simplified consideration of side groups and the improved RIS derivation will be used

* Corresponding author: Hai-zhu Ma (马海珠), E-mail: Mahaizhu@126.com

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to investigate $\langle S^2 \rangle$ of atactic P α MS chains. The calculated model of atactic P α MS chains is determined by the comparison between the experimental data and the theoretical results. Therefore, the dimension and temperature feature, depended on the chain length, the temperature and the tacticity, will be investigated based on this model.

MODEL AND METHOD

A lot of substituted polymers possess large side groups. For example, the structural terminology of the geminal substituted P α MS is $\text{H} - [\text{CH}_2 - \text{C}^\alpha(\text{CH}_3)(\text{C}_6\text{H}_5)]_x - \text{CH}_3$, where x is the polymerization degree. The skeletal bonds $\text{C}^\alpha - \text{C}$ are f-type, and the bonds $\text{C} - \text{C}^\alpha$ are a-type. In the improved method, the equivalent center of the benzene ring C_6H_5 and methyl CH_3 is defined as b, the length of imaginary bond l_b is the distance between the center b and the asymmetric carbon C^α . Figure 1 shows a simplified model $-\text{[f-a(b)]}_x-$.

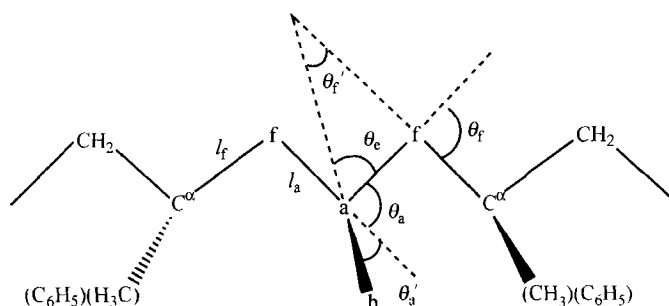


Fig. 1 Schematic diagram and model of an atactic P α MS chain

Following the developed RIS method, the square radius of gyration S^2 is determined from^[10]

$$S^2 = \frac{1}{M^2} \left[\sum_{0 \leq i < j \leq 2x} m_i m_j r_{ij}^2 + \sum_{i=0}^{2x} \sum_{j=1}^x m_i m_j r_{ij'}^2 + \sum_{0 \leq i' < j' \leq x} m_{i'} m_{j'} r_{i'j'}^2 \right] \quad (1)$$

where the number i or j is marked on the skeletal atoms, and i' or j' on side groups. The mass of atoms (or groups) is m_i , and the chain mass is M . If the spatial situation of side groups is considered, the expression of square end-to-end distance of atom pairs will be modified as follows

$$r_{ij}^2 = J_P g_i g_j g_{i+1}^{(j-i)} g_a g_b J_Q \quad (2)$$

where g_k is the generator matrix in the matrix algebra method^[7, 8].

$$g_k = \begin{bmatrix} 1 & 2L^T T & l^2 \\ 0 & T & L \\ 0 & 0 & 1 \end{bmatrix}_k \equiv G[2L^T T, l^2, T, L]_k \quad (3)$$

$$J_P = [1 \ 0 \ 0 \ 0 \ 0], \quad J_Q = [0 \ 0 \ 0 \ 0 \ 1]^T \quad (4)$$

where the transformation matrix of the racemic dyad T_k and the bond matrix L_k are

$$T_k = \begin{bmatrix} \cos \theta & \sin \theta & 0 \\ \sin \theta \cos(\phi + \phi') & -\cos \theta \cos(\phi + \phi') & \sin(\phi + \phi') \\ \sin \theta \sin(\phi + \phi') & -\cos \theta \sin(\phi + \phi') & -\cos(\phi + \phi') \end{bmatrix}_k \quad (5)$$

$$L_k^T = [l_k \ 0 \ 0] \quad (6)$$

where the subscript $k = A, F$ in the matrix of skeletal atoms, the additive angle of internal rotation $\phi' = 0$. The subscript $k = a, f, b, e$ in the terminal matrix of side groups, $\phi' \neq 0$. The additive angles are calculated by

$$\cos\phi'_a = -(\cos\theta_e + \cos\theta'_a \cos\theta_a) / \sin\theta'_a \sin\theta_a \quad (7)$$

$$\cos\phi'_f = -(\cos\theta'_f + \cos\theta_e \cos\theta_f) / \sin\theta_e \sin\theta_f \quad (8)$$

$$\cos\theta'_f = \cos\theta_e \sin(\theta_f / 2) / \sin(\theta_a / 2) \quad (9)$$

Following the generator matrix method, the square radius of gyration S^2 is given as

$$S^2 = M^{-2} \sum_{q=1}^6 m(q) \mathbf{J}_{P'} [\mathbf{F}(q) \mathbf{A}(q)]_i^x \mathbf{J}_{Q'} \quad (10)$$

$$\mathbf{J}_{P'} = \begin{bmatrix} 1 & 0 & \cdots & 0 \end{bmatrix}, \quad \mathbf{J}_{Q'} = \begin{bmatrix} 1 & 1 & \cdots & 1 \end{bmatrix} \quad (11)$$

where $m(q)$ is the sequence of atom-pair masses: $m(1) = 1$, $m(2) = m(3) = m_f m_b$, $m(4) = m(5) = m_a m_b$, $m(6) = m_b^2$. Obviously, the Lagrange relation can be deduced from Eqs.(1) and (10)^[8], let $m_j = m_b = 0$, $m_a = m_f$. The square end-to-end distance of atom pairs is expressed as $\mathbf{J}_{P'} [\mathbf{F}(q) \mathbf{A}(q)]_i^x \mathbf{J}_{Q'}$, where $\mathbf{F}(q)$ and $\mathbf{A}(q)$ are the super generator matrixes of f-type and a-type, respectively. For the distance of skeletal atom pair, the super matrixes are

$$\mathbf{F}(1) = \mathbf{G}[m_a \mathbf{J}_P \mathbf{g}_F, m_a m_f l_f^2, \mathbf{g}_F, m_f \mathbf{g}_F \mathbf{J}_Q] \quad (12)$$

$$\mathbf{A}(1) = \mathbf{G}[m_f \mathbf{J}_P \mathbf{g}_A, m_f m_a l_a^2, \mathbf{g}_A, m_a \mathbf{g}_A \mathbf{J}_Q] \quad (13)$$

For the distance between the skeletal atoms and side groups, the super matrixes are gained by

$$\mathbf{F}(2) = \mathbf{G}[0, 0, \mathbf{g}_F, 0] = \mathbf{F}(4), \quad \mathbf{A}(2) = \mathbf{G}[\mathbf{J}_P \mathbf{g}_A, r_{fb}^2, \mathbf{g}_A, \mathbf{g}_a \mathbf{g}_b \mathbf{J}_Q] \quad (14)$$

$$\mathbf{F}(3) = \mathbf{G}[\mathbf{J}_P \mathbf{g}_e \mathbf{g}_f, r_{bf}^2, \mathbf{g}_F, \mathbf{g}_F \mathbf{J}_Q], \quad \mathbf{A}(3) = \mathbf{G}[0, 0, \mathbf{g}_A, 0] = \mathbf{A}(5) \quad (15)$$

$$\mathbf{F}(5) = \mathbf{G}[\mathbf{J}_P \mathbf{g}_e \mathbf{g}_f, 0, \mathbf{g}_F, \mathbf{J}_Q], \quad \mathbf{A}(4) = \mathbf{G}[\mathbf{J}_P, l_b^2, \mathbf{g}_A, \mathbf{g}_a \mathbf{g}_b \mathbf{J}_Q] \quad (16)$$

For the distance among the atoms of side group, the super matrixes are

$$\mathbf{F}(6) = \mathbf{G}[\mathbf{J}_P \mathbf{g}_e \mathbf{g}_f, 0, \mathbf{g}_F, 0], \quad \mathbf{A}(6) = \mathbf{G}[0, 0, \mathbf{g}_A, \mathbf{g}_a \mathbf{g}_b \mathbf{J}_Q] \quad (17)$$

The RIS conformational-configurational statistics of S^2 is defined as $\langle S^2 \rangle$. Since the a-type atom is an asymmetric atom C^α with side groups, the weight matrix of meso dyads is taken as $\mathbf{u}_{am}$, and the matrix of racemic dyads is $\mathbf{u}_{ar}$ in conformational statistics, for instance, the 2-state statistical matrixes of the P α MS chain are^[9]

$$\mathbf{u}_f = \begin{bmatrix} 1 & 1 \\ 1 & 0 \end{bmatrix}, \quad \mathbf{u}_{am} = \begin{bmatrix} 1 & \alpha \\ \alpha & \alpha^2 / \beta \end{bmatrix}, \quad \mathbf{u}_{ar} = \begin{bmatrix} \beta & \alpha \\ \alpha & \alpha^2 / \beta \end{bmatrix} \quad (18)$$

where the weight factors α and β are determined by the interaction energy E_ξ of atom pairs and the temperature T . The dyads statistic matrixes $\mathbf{U}_m$ and $\mathbf{U}_r$ are

$$\mathbf{U}_m = \mathbf{u}_f \mathbf{u}_{am} \quad (19)$$

$$\mathbf{U}_r = \mathbf{u}_f \mathbf{u}_{ar} \quad (20)$$

Similarly, the super matrixes of meso dyads $F_m(q)$ and racemic dyads $F_r(q)$ for the f-type are determined by the transformation matrixes of meso dyads T_F^* or T_r^* and racemic dyads T_F or T_r , respectively. Therefore, after the matrix orders are uniformed between the statistical weight matrix and the generator matrix, the super matrixes of meso dyads S_m and of racemic dyads S_r are induced as follows

$$S_m(q) = [(u_f \otimes E_7) \| F_m(q) \|] [(u_{ar} \otimes E_7) \| A(q) \|] \quad (21)$$

$$S_r(q) = [(u_f \otimes E_7) \| F_r(q) \|] [(u_{ar} \otimes E_7) \| A(q) \|] \quad (22)$$

where E_7 is the unit matrix of 7×7 orders. The mean-square radius of gyration of i -th representative chain is defined $\langle S^2 \rangle_i$ in the configurational statistics. According to the method of the pseudostereochemical equilibrium and the periodicity condition method^[10], the microstructure of an asymmetric chain with the x-ads constitutions can be simulated by the repeating p-ads constitutions, and the number of repeating p-ads X is given by $(x-1)/p$. Theoretically, there are 2^p distinguishable configurations in the subensemble of representative chains, the occurrence probability P_i of the i -th sequence is determined by Bernoullian function^[10], where the occurrence probability of meso dyads for an asymmetric chain is defined as the fraction of meso dyads w_m , and the fraction of racemic dyads is $1 - w_m$. Therefore, the tacticity of polymers is described by w_m . Therefore, the unperturbed mean-square radius of gyration $\langle S^2 \rangle$ of stereoregular or stereoirregular polymer $\langle S^2 \rangle$ is deduced by the configurational statistic average of the matrix $S_i(q)$ and U_i for the i -th representative chain, and determined as follows.

$$\begin{aligned} \langle S^2 \rangle &= \sum_{i=1}^{2^p} P_i \langle S^2 \rangle_i \\ &= M^{-2} \sum_{i=1}^{2^p} P_i \sum_{q=1}^6 m(q) [J^* \otimes J_p \| A(q) \|] S_i(q)^X [\| F(q) \| J \otimes J_q \| J^* U_i^X J] \end{aligned} \quad (23)$$

$$J^* = [1 \quad 0 \quad \dots], \quad J = [1 \quad 1 \quad \dots]^T \quad (24)$$

When the dyad number $p \geq 4$ in a repetitive unit, the results calculated by RIS conformational-configurational statistics are in fair agreement with those by Monte Carlo simulation.

The temperature coefficient of $\langle S^2 \rangle$ is defined as

$$\kappa = \sum_{i=1}^{2^p} P_i \frac{d \ln \langle S^2 \rangle_i}{dT} \quad (25)$$

Similarly, the configurational parameter $\langle S^2 \rangle / M$ is easy to get from Eq. (23), and the intrinsic viscosity of polymer solution is determined by^[7, 12]

$$[\eta] = 6^{3/2} \Phi (\langle S^2 \rangle / M)^{3/2} M^\alpha \quad (26)$$

or

$$[\eta] = K M^\alpha \quad (27)$$

where K is a function of the viscosity factor Φ and the configurational parameter $\langle S^2 \rangle / M$. The scale α is relevant to the temperature T .

RESULTS AND DISCUSSION

Solution properties of near-monodispersed P α MS chains can be investigated by the light scattering and the intrinsic viscosity measurements. For example, the Mays' experimental values for various real P α MS samples in

the moderate solvent *n*-butyl chloride. The dependences of the radius of gyration and the intrinsic viscosity on the chain mass at 278 K^[2] are the following power laws.

$$R_g = 2.1 \times 10^{-2} M^{0.526} \text{ (nm)} \quad (28)$$

$$[\eta] = 3.36 \times 10^{-2} M^{0.87} \text{ (mL} \cdot \text{g}^{-1}) \quad (29)$$

The experimental values of Kato and Noda at 308 K^[3, 4] are

$$R_g = 2.89 \times 10^{-2} M^{0.50} \text{ (nm)} \quad (30)$$

$$[\eta] = 7.3 \times 10^{-2} M_w^{0.5} \text{ (mL} \cdot \text{g}^{-1}) \quad (31)$$

The R_g and $[\eta]$ are also calculated theoretically basing on the improved RIS method. The structure parameters of P α MS as follows^[9]: the length of C—C $^\alpha$ bond is 0.153 nm, the angle $\angle \text{CC}^\alpha\text{C}$ is 109.5° , $\angle \text{C}^\alpha\text{CC}^\alpha$ is 122° . The imaginary bond parameters are estimated $\theta_a' = \theta_c = 67.66^\circ$, $\theta_t' = 71.38^\circ$, $l_b = 0.232$ nm and $m_b = 92$ g/mol. The internal rotation angle of skeletal bond $\phi_t = 10^\circ$ in the *trans*, $\phi_g = 110^\circ$ in the *gauche*, and the additive angles are estimated $\phi_a' = 125.55^\circ$ and $\phi_t' = 131.59^\circ$ by Eqs. (7)–(9). The conformational statistical weight factor $\alpha = 0.6 \exp(-500/RT)$, and $\beta = 0.9 \exp(1200/RT)$ in Eq. (18), where the universal constant $R = 1.987 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. Therefore, taking the fraction of meso dyads $w_m = 0.4$, the dependence of R_g and $[\eta]$ on the M at the unperturbed temperature 308 K are calculated to be

$$R_g = 2.63 \times 10^{-2} M^{0.50} \text{ (nm)} \quad (32)$$

$$[\eta] = 7.36 \times 10^{-2} M^{0.497} \text{ (mL} \cdot \text{g}^{-1}) \quad (33)$$

where the viscosity factor $\Phi = 2.6 \times 10^{23} \text{ mol}^{-1}$. The theoretical result of intrinsic viscosity is compared with the experimental values which are shown in Fig. 2. It is visible that the $[\eta]$ in this work for the atactic P α MS chain with the occurrence probability of meso dyads 40% is in good accord with the experimental $[\eta]$ of Noda and Mays, which are the average values of real P α MS samples. Therefore, the dependence of the characteristic ratio $\langle S^2 \rangle / 2xl^2$ and the logarithm of chain length x in $w_m = 0.4$ is investigated further by Eq. (23), and the results are shown in Fig. 3. If the effect of side groups is considered in the calculation of ratio, a maximum value is detected in the ratio curve with square dots. The similar hump is found in Osa's experimental curve for the P α MS samples^[11]: the ratio as a function of x first increases steeply for $x \leq 20$, then passes through a hump at $x = 40$, and finally approaches its asymptotic value for $x \geq 1 \times 10^3$. The ratios without considering the size of side groups are also calculated, and compared with that of considering side groups, let the mass of $-\text{C}^\alpha(\text{CH}_3)(\text{C}_6\text{H}_5)-$ $m_a = 104$ g/mol, $m_t = 14$ g/mol, and $m_b = 0$. No hump is detected in the ratio curve with circle dots in Fig. 3. The ratios appear to be about 7% differences between $m_b \neq 0$ and $m_b = 0$ at $x = 40$. However, they tend to the uniform asymptotic value 1.76 for the large x . If the mass of skeletal atom is considered as identity $m_a = m_t = 1$ g/mol, and $m_b = 0$ in Eq. (23), the Lagrange relation of the RIS approximation is deduced, and no maximum value is also found in its numerical results for short chains.

A similar bump has been exhibited in the previous paper for the disubstituted PMMA chain^[10], but no hump is found in the result for the monosubstituted polymer, such as the PS chain^[11]. Therefore, it is concluded that the effect of side groups on chain dimension cannot be neglected, especially for the disubstituted polymer of short chain.

The ratios $\langle S^2 \rangle / 2xl^2$ as a function w_m are shown in Fig. 4, which represent the dimension of the stereoregular and the stereoirregular P α MS chains at 308 K. The ratio is only little difference with the chain length increase for atactic P α MS chains. A polymer chain with little ratio exhibit a compact structure. Therefore, the isotactic P α MS chain is the most compact and flexible one, and the syndiotactic P α MS chain is a relatively loose one. The up-bow curve of ratio is similar to the ratio curve of the mean-square end-to-end distance of Sundararajan for P α MS chains^[9], and also similar to that of the disubstituted PMMA chain^[10]. But the curve is different from that of the monosubstituted PS chain. Generally, the atactic chains of the monosubstituted polymer are relatively compact.

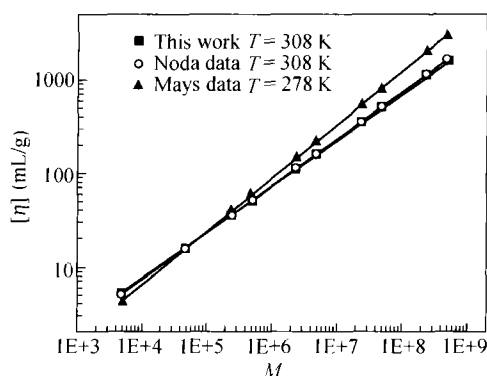


Fig. 2 The comparison of the logarithm of intrinsic viscosity $[\eta]$ versus the logarithm of chain mass M between the experimental data and the theoretical value for atactic $P\alpha MS$ chains

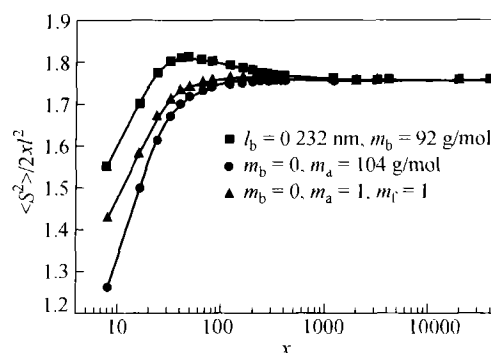


Fig. 3 A comparison of the characteristic ratios of mean-square radius of gyration $\langle S^2 \rangle / 2xl^2$ as a function of the logarithm of chain length x for atactic $P\alpha MS$ chains between considering side groups and not considering side groups

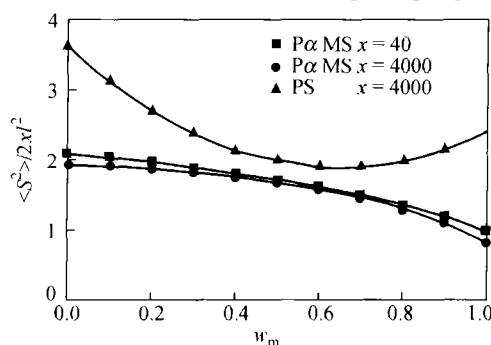


Fig. 4 The characteristic ratios of mean-square radius of gyration $\langle S^2 \rangle / 2xl^2$ against the fraction of meso dyads w_m for atactic $P\alpha MS$ chains and atactic PS chains

In Fig. 5, the dependence of R_g on T is a linear correlation. There is a large R_g difference between long chains and short chains. The temperature coefficients K as a function of the fraction of meso dyads w_m are given in Fig. 6. The dependence of K on w_m is different from that of PS chain^[11], the syndiotactic chain possess the largest temperature coefficient. Moreover, the large difference of K between long chains and short chains is found, especially in $x = 40$. Therefore, the behavior of short chains considering side groups is different from that of long chains.

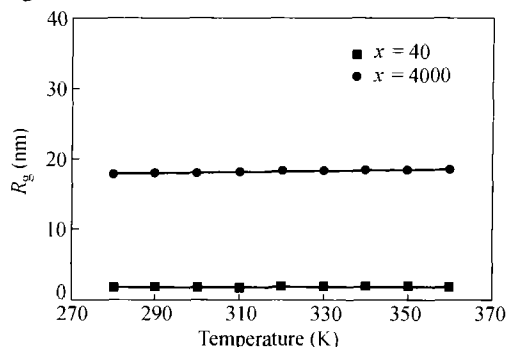


Fig. 5 The dependence of radius of gyration R_g on the temperature T for atactic $P\alpha MS$ chains

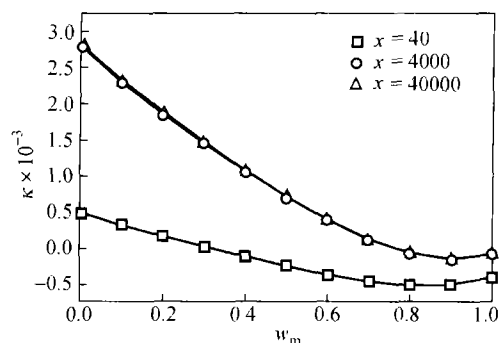


Fig. 6 A comparison of the temperature coefficient K of mean-square radius of gyration versus the fraction of meso dyads w_m between the long $P\alpha MS$ chain and the short $P\alpha MS$ chain

CONCLUSION

The contribution of the side groups to the unperturbed dimensions of polymer chains is investigated by the improved RIS method. The main conclusions are as follows:

(1) In the improved method, two side groups of the geminal substituted P α MS chain are considered as an imaginary bond. However, the effect of side groups on the configuration-dependent properties, such as the $\langle S^2 \rangle / 2xl^2$ versus $\log x$ or w_m and the K versus w_m , is calculated to be different from those of monosubstituted polymer chains. Especially, a small hump is found in the curve of $\langle S^2 \rangle / 2xl^2$ for the short P α MS chain, and it disappears if the side groups are neglected, or if the calculation is used to the $\langle S^2 \rangle / 2xl^2$ of PS chains.

(2) For the atactic P α MS chain with $w_m = 0.4$, the radius of gyration and the intrinsic viscosity are estimated theoretically $R_g = 2.63 \times 10^{-2} M^{0.50}$ nm and $[\eta] = 7.36 \times 10^{-2} M^{0.497}$, respectively, which are in agreement with the experimental values obtained for the real P α MS samples.

(3) The dimension of atactic P α MS chains increases proportionally with temperature. Therefore, their flexibility increases with the temperature. The temperature coefficient increases with the chain length increase for short P α MS chain, and decreases with the stereoirregularity increase for long P α MS chain.

The theoretical method developed in this paper can be used to calculate the unperturbed dimension of polymers with the flexible skeletal chain and the rigid side groups. With the development of polymer synthesis technology, and the increase of the polymers with the large side groups or side chains, the investigation of them in the theoretical method will be more significant.

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