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Unperturbed dimensions of atactic poly(dibenzyl itaconate)s*

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Abstract: The unperturbed dimension and temperature character of poly(dibenzyl itaconate)s (PDBzI) are studied by a revised rotational isomeric state (RIS) method. The improved formulas of the mean-square radius of gyration, deduced by the pseudo-stereochemical equilibrium approach, may be used to investigate the configurational-conformational properties of atactic polymers with large side groups [poly(itaconates) for instance]. The calculated results showed that poly(itaconates) have larger dimension of the molecule than other vinyl polymers. Comparison of the dimension between considering and without considering side groups showed that the effect of large side groups on the unperturbed dimension for short-chain polymers is more obvious than that of long-chain polymers and, if the dimension of side groups increases, the effect also increases. The dimension differences of PDBzI between short-chain and long-chain polymers are investigated by the relation of characteristic ratios and temperature coefficients with temperature. Moreover, the dependence between the temperature coefficients and the tacticity of chains shows that the temperature characters of the isotactic, syndiotactic and atactic PDBzI chains have remarkable difference.

Key words: Poly(dibenzyl itaconate)s, Mean-square radius of gyration, Temperature coefficient, Tacticity
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INTRODUCTION

With properties of poly(itaconic acid) derivatives (e.g. poly(itaconates)) being similar to those of the structurally related poly(acrylates)s and poly(methacrylates)s (PMMA), interest for these products is increasing as the aicd and several other reactants for the production of monomers can be obtained by fermentation processes of agricultural wastes (Saiz *et al.*, 1988). The poly(itaconates) have been studied from both a fundamental and a practical point of view, such as the mechanical properties and thermal transitions in bulk samples and their dilute solution properties (Velickovic and Filipovic, 1984; Saiz *et al.*, 1988). The unperturbed dimension and chain stiffness parameter for a few poly(itaconates) have been determined from the intrinsic viscosity. In theoretical side, the configurational-conformational properties of poly(dibenzyl itaconate)s (PDBzI) and several vinyl polymers have been studied by calculating the unperturbed dimensions (Saiz *et al.*, 1988; Zhou and Yan, 1995; Yan and Zhou, 1999; Osa *et al.*, 2000; Zhou and Yan, 2001; Yamakawa and Yoshizaki, 2004; Ma and Ye, 2006) and dipole moments (Zhou and Abe, 2003; 2004), however, the unperturbed dimensions for the PDBzI chains are only described by the mean-square end-to-end distance (Saiz *et al.*, 1988). In this work, attention is focused on the mean-square radius of gyration $<S^2>$ of the polymers, considering the effect of large side groups. As an example for the PDBzI chains, the characteristic ratio and the temperature coefficient of $<S^2>$ are calculated theoretically. The unperturbed dimensions of other poly(itaconates) can also be inferred by the improved calculations.

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THEORETICAL FRAMEWORK

Structure terminology of poly(itaconates) in following investigation is

$$CH_3\text{-}[C^{\alpha}(COOR)(CH_2COOR)\text{-}CH_2]_x\text{-}H,$$

where the group $R=(CH_2)_nC_6H_5$ [e.g. n=0 for poly(diphenyl itaconate) (PDFI) chains; n=1 for PDBzI chains and n=2 for PDEFI chains]. A monomer of the PDBzI chains is represented in Fig.1a. The consideration of the structure and chiral character leads to different skeletal bonds, which are divided into F-type bond (C^{α}-C) and A-type bond (C-C^{α}) shown in Fig.1b. The equivalent centers of ester groups (COOR) and (CH_2COOR) are defined as b and β, respectively, the distances between the center b (or β) and the asymmetric carbon C^{α} is l_b (or l_{β}), i.e., the length of imaginary bond. Therefore, a simplified model of polymers is introduced as -[A(b)(β)-F]$_x$- in improved calculation of $\langle S^2 \rangle$, where x is the number of monomeric unit. Following the model given in Fig.1b (Ma *et al.*, 1997) and the generator matrix method of the rotational isomeric state (RIS) approximation, the square of end-to-end distance is revised as

$$r_{i'j'}^{\ 2} = \boldsymbol{J}_P \boldsymbol{g}_e \boldsymbol{g}_f \boldsymbol{g}_{i+1}^{\ (j-i)} \boldsymbol{g}_a \boldsymbol{g}_b \boldsymbol{J}_Q, \tag{1}$$

where i (or j) is the serial index of the skeletal atoms along the chain. The consideration of side groups leads to the introduction of generator matrices with the index a, b, e and f corresponding to index of bond. Moreover, the matrix of b-side group is divided into $\boldsymbol{g}_b$ (the right terminal matrix of a-atom) and $\boldsymbol{g}_e$ (the left terminal matrices of a-atom); similarly, the matrix of β-side group is divided into $\boldsymbol{g}_{\beta}$ and $\boldsymbol{g}_{\gamma}$. The generator matrix of the skeletal bonds in RIS scheme is (Flory and Sundararajan, 1974; Flory and Yoon, 1974):

$$\boldsymbol{g}_k = \begin{bmatrix} 1 & 2\boldsymbol{L}_k^{\mathrm{T}}\boldsymbol{T}_k & l_k^2 \\ 0 & \boldsymbol{T}_k & \boldsymbol{L}_k \\ 0 & 0 & 1 \end{bmatrix} = \boldsymbol{G}[2\boldsymbol{L}_k^{\mathrm{T}}\boldsymbol{T}_k, l_k^2, \boldsymbol{T}_k, \boldsymbol{L}_k], \tag{2}$$
$$k = A, F; a, b, e, f; \alpha, \beta, \gamma, \delta,$$

where the transformation matrix is defined as $\boldsymbol{T}(\theta_k, \phi_k + \phi_k')$ in our previous paper (Ma and Ye, 2006), and the additive angles of internal rotation ϕ_k' in the terminal matrix (k=a,f) are estimated by

$$\cos\phi_a' = -(\cos\theta_e + \cos\theta_a \cos\theta_A)/(\sin\theta_a \sin\theta_A), \tag{3}$$

$$\cos\phi_f' = -(\cos\theta_f + \cos\theta_e \cos\theta_F)/(\sin\theta_e \sin\theta_F), \tag{4}$$

where

$$\cos\theta_a = \cos(\delta \pm \alpha)\sin(\theta_A/2), \tag{5}$$

$$\cos\delta = \cos\theta_e / \sin(\theta_A/2), \tag{6}$$

$$\cos\theta_f = \cos\theta_e \sin(\theta_F/2)/\sin(\theta_A/2). \tag{7}$$

The formulas above are also used in terminal matrix of the β-side groups. Therefore, the square radius of gyration S^2 is revised as (Ma and Zhang, 1997; Ma *et al.*, 2001)

$$S^2 = \frac{1}{M^2}\left(\sum_{0\le i<j\le 2x} m_i m_j r_{ij}^2 + \sum_{i=0}^{2x}\sum_{j'=1}^{x} m_i m_{j'} r_{ij'}^2 + \sum_{0\le i'<j'\le x} m_{i'} m_{j'} r_{i'j'}^2 \right)$$
$$= \frac{1}{M^2}\sum_{q=1}^{2^p} m(q)\boldsymbol{J}_{P'}[\boldsymbol{F}(q)\boldsymbol{A}(q)]_1^x \boldsymbol{J}_{Q'}, \tag{8}$$

where M and m_i are the masses of chain and groups,

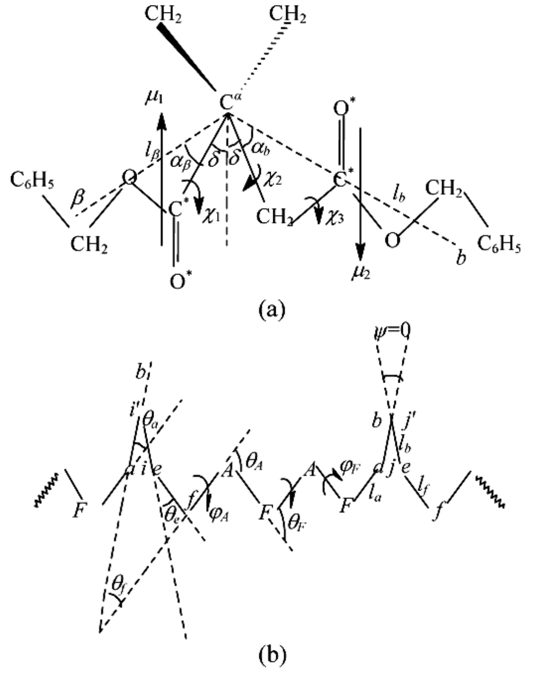


Fig.1 (a) The equivalent center *b* (or *β*) of the disubstituent $CH_2COO(CH_2)C_6H_5$ [or $COO(CH_2)C_6H_5$] with $\chi_1=\chi_2=\chi_3=0$ in a monomer of PDBzI; (b) A simplified model of polymer with the repeat unit -[A(b)-F]- to illustrate the method of considering side groups

respectively. The sequence $m(q)$ of pair-group mass, the super generator matrixes $\boldsymbol{F}(q)$ and $\boldsymbol{A}(q)$ of F-type and A-type bonds are given respectively and listed in Table 1. Obviously, after taking m_b=0, m_β=0, m_A=m_F=1, Eq.(8) is simplified to Lagrange relation used to estimate unperturbed dimensions of polymers (Flory and Yoon, 1974).

To according for the chiral order of groups attached to the skeletal atom C$^\alpha$ of an asymmetric chain, the skeletal bonds C-C$^\alpha$ and C$^\alpha$-C may be identified as l- or d-type bond. The transformation matrixes for the adjacent frames of the same senses (either ll or dd) are defined as the racemic dyads $\boldsymbol{T}_F$ (or $\boldsymbol{T}_f$), whose opposite senses (either ld or dl) are named as the meso dyads $\boldsymbol{T}_F^*$ (or $\boldsymbol{T}_f^*$). Accordingly, the super matrixes of F-type bonds are distinguished as the racemic dyads $\boldsymbol{F}_r(q)$ and the meso dyads $\boldsymbol{F}_m(q)$, respectively. According to the conformational analysis, the statistic weight matrices of PMMA have been suggested for use in the treatment of PDBzI (Sundararajan and Flory, 1974). The statistic weight matrixes on an asymmetric atom C$^\alpha$ are also distinguished as $\boldsymbol{u}_{Am}$ and $\boldsymbol{u}_{Ar}$. Then, the 3-state weight matrices adopted in the conformational statistics of poly(itaconates) are

$$\boldsymbol{u}_F=\begin{bmatrix}1 & 1 & 1\\ 1 & 0 & \psi\\ 1 & \psi & 0\end{bmatrix}, \tag{9}$$

$$\boldsymbol{u}_{Am}=\begin{bmatrix}1 & \alpha & \beta\rho\\ \alpha & \alpha^2/\beta & \alpha\rho\\ \beta\rho & \alpha\rho & \rho^2\end{bmatrix} \text{ for meso dyads,} \tag{10}$$

$$\boldsymbol{u}_{Ar}=\begin{bmatrix}\beta & \alpha & \rho\\ \alpha & \alpha^2/\beta & \alpha\rho\\ \rho & \alpha\rho & \beta\rho^2\end{bmatrix} \text{ for racemic dyads.} \tag{11}$$

Their weight factors are (Sundararajan, 1986):

$$\alpha=0.85\exp(-E_\alpha/(RT)), \tag{12}$$

$$\beta=0.77\exp(-E_\beta/(RT)), \tag{13}$$

$$\rho=0.87\exp(-E_\rho/(RT)), \tag{14}$$

$$\psi=1.00\exp(-E_\psi/(RT)), \tag{15}$$

where the conformational energies E_ψ=10.467 kJ/mol. Then, the statistic matrixes of dyads are given as

$$\boldsymbol{U}_m=\boldsymbol{u}_F\boldsymbol{u}_{Am} \text{ for meso dyads,} \tag{16}$$

$$\boldsymbol{U}_r=\boldsymbol{u}_F\boldsymbol{u}_{Ar} \text{ for racemic dyads.} \tag{17}$$

The super generator matrixes of dyads are introduced by the conformational statistics of $[\boldsymbol{F}(q)\boldsymbol{A}(q)]$ (Ma and Zhang, 1997). For meso dyads

$$\boldsymbol{S}_m(q)=[(\boldsymbol{u}_F\otimes\boldsymbol{E}_7)\|\boldsymbol{F}_m(q)\|][(\boldsymbol{u}_{Am}\otimes\boldsymbol{E}_7)\|\boldsymbol{A}(q)\|], \tag{18}$$

Table 1 Sequence of $m(q)$ and the matrices $F(q)$ and $A(q)$ for PDBzI

q	$m(q)$	$\boldsymbol{F}(q)=\boldsymbol{G}[f_{12},f_{13},f_{22},f_{23}]$				$\boldsymbol{A}(q)=\boldsymbol{G}[a_{12},a_{13},a_{22},a_{23}]$			
		f_{12}	f_{13}	f_{22}	f_{23}	a_{12}	a_{13}	a_{22}	a_{23}
1	1	$m_A\boldsymbol{J}_P\boldsymbol{g}_F$	$m_Am_Fl_F^2$	$\boldsymbol{g}_F$	$m_F\boldsymbol{g}_F\boldsymbol{J}_Q$	$m_F\boldsymbol{J}_P\boldsymbol{g}_A$	$m_Fm_Al_A^2$	$\boldsymbol{g}_A$	$m_A\boldsymbol{g}_A\boldsymbol{J}_Q$
2	m_Fm_b	0	0	$\boldsymbol{g}_F$	0	$\boldsymbol{J}_P\boldsymbol{g}_A$	r_{Fb}^2	$\boldsymbol{g}_A$	$\boldsymbol{g}_a\boldsymbol{g}_b\boldsymbol{J}_Q$
3	m_bm_F	$\boldsymbol{J}_P\boldsymbol{g}_e\boldsymbol{g}_f$	r_{bF}^2	$\boldsymbol{g}_F$	$\boldsymbol{g}_F\boldsymbol{J}_Q$	0	0	$\boldsymbol{g}_A$	0
4	m_Am_b	0	0	$\boldsymbol{g}_F$	0	$\boldsymbol{J}_P$	l_b^2	$\boldsymbol{g}_A$	$\boldsymbol{g}_a\boldsymbol{g}_b\boldsymbol{J}_Q$
5	m_bm_A	$\boldsymbol{J}_P\boldsymbol{g}_e\boldsymbol{g}_f$	0	$\boldsymbol{g}_F$	$\boldsymbol{J}_Q$	0	0	$\boldsymbol{g}_A$	0
6	m_Fm_β	0	0	$\boldsymbol{g}_F$	0	$\boldsymbol{J}_P\boldsymbol{g}_A$	$r_{F\beta}^2$	$\boldsymbol{g}_A$	$\boldsymbol{g}_\alpha\boldsymbol{g}_\beta\boldsymbol{J}_Q$
7	$m_\beta m_F$	$\boldsymbol{J}_P\boldsymbol{g}_\gamma\boldsymbol{g}_\delta$	$r_{\beta F}^2$	$\boldsymbol{g}_F$	$\boldsymbol{g}_F\boldsymbol{J}_Q$	0	0	$\boldsymbol{g}_A$	0
8	m_Am_β	0	0	$\boldsymbol{g}_F$	0	$\boldsymbol{J}_P$	l_β^2	$\boldsymbol{g}_A$	$\boldsymbol{g}_\alpha\boldsymbol{g}_\beta\boldsymbol{J}_Q$
9	$m_\beta m_A$	$\boldsymbol{J}_P\boldsymbol{g}_\gamma\boldsymbol{g}_\delta$	0	$\boldsymbol{g}_F$	$\boldsymbol{J}_Q$	0	0	$\boldsymbol{g}_A$	0
10	m_bm_β	$\boldsymbol{J}_P\boldsymbol{g}_e\boldsymbol{g}_f$	0	$\boldsymbol{g}_F$	0	0	0	$\boldsymbol{g}_A$	$\boldsymbol{g}_\alpha\boldsymbol{g}_\beta\boldsymbol{J}_Q$
11	$m_\beta m_b$	$\boldsymbol{J}_P\boldsymbol{g}_\gamma\boldsymbol{g}_\delta$	0	$\boldsymbol{g}_F$	0	0	0	$\boldsymbol{g}_A$	$\boldsymbol{g}_a\boldsymbol{g}_b\boldsymbol{J}_Q$
12	m_bm_b	$\boldsymbol{J}_P\boldsymbol{g}_e\boldsymbol{g}_f$	0	$\boldsymbol{g}_F$	0	0	0	$\boldsymbol{g}_A$	$\boldsymbol{g}_a\boldsymbol{g}_b\boldsymbol{J}_Q$
13	$m_\beta m_\beta$	$\boldsymbol{J}_P\boldsymbol{g}_\gamma\boldsymbol{g}_\delta$	0	$\boldsymbol{g}_F$	0	0	0	$\boldsymbol{g}_A$	$\boldsymbol{g}_\alpha\boldsymbol{g}_\beta\boldsymbol{J}_Q$

and for racemic dyads

$$\boldsymbol{S}_r(q)=[(\boldsymbol{u}_F\otimes \boldsymbol{E}_7)\|\boldsymbol{F}_r(q)\|][(\boldsymbol{u}_{Ar}\otimes \boldsymbol{E}_7)\|\boldsymbol{A}(q)\|]. \quad (19)$$

Similarly, the matrixes of dyads in calculation of the mean-square end-to-end distance are deduced by the conformational statistics of [$\boldsymbol{g}_F\boldsymbol{g}_A$], they are, for meso dyads

$$\boldsymbol{R}_m=[(\boldsymbol{u}_F\otimes \boldsymbol{E}_5)\|\boldsymbol{g}_{Fm}\|][(\boldsymbol{u}_{Am}\otimes \boldsymbol{E}_5)\|\boldsymbol{g}_A\|]; \quad (20)$$

for racemic dyads

$$\boldsymbol{R}_r=[(\boldsymbol{u}_F\otimes \boldsymbol{E}_5)\|\boldsymbol{g}_{Fr}\|][(\boldsymbol{u}_{Ar}\otimes \boldsymbol{E}_5)\|\boldsymbol{g}_A\|]. \quad (21)$$

In configurational statistics, following the pseudo-stereochemical equilibrium approach for an asymmetric chain (Alfonso *et al.*, 1993), the microstructure of an asymmetric chain with x-ads constitutions can be simulated by the repeating p-ads constitutions. 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 mean-square radius of gyration $<S^2>_k$ of the kth representative chain is a sequence of successive multiplication of $\boldsymbol{S}_m(q)$ and $\boldsymbol{S}_r(q)$ in accordance with the kth configuration of chain, its occurrence probability P_k as function of the fraction of meso dyads w_m is determined by Bernoullian statistics (Ma and Zhang, 1997). Therefore, the tacticity of polymers may be described by w_m, e.g. the fraction of isotactic polymers $w_m=1$.

If the configurational-conformational statistics of S^2 is defined as $<S^2>$, the unperturbed mean-square radius of gyration for the stereoirregular polymer is deduced as

$$<S^2>=\sum_{k=1}^{2^p}P_k<S^2>_k=M^{-2}\sum_{k=1}^{2^p}\left\{P_k\sum_{q=1}^{6}\Big[m(q)\right.$$
$$\left.\cdot[\boldsymbol{J}^*\otimes\boldsymbol{J}_{P'}\|\boldsymbol{A}(q)\|]\boldsymbol{S}_k(q)^X[\|\boldsymbol{F}(q)\|\boldsymbol{J}\otimes\boldsymbol{J}_{Q'}]\Big]/\left(\boldsymbol{J}^*\boldsymbol{U}_k^X\boldsymbol{J}\right)\right\}.$$
$$(22)$$

Similarly, the unperturbed mean-square end-to-end distance is formulated

$$<r^2>=\sum_{k=1}^{2^p}P_k\boldsymbol{J}^*\otimes\boldsymbol{J}_p\|\boldsymbol{g}_A\|\boldsymbol{R}_k{}^X\|\boldsymbol{g}_F\|\boldsymbol{J}\otimes\boldsymbol{J}_Q/\left(\boldsymbol{J}^*\boldsymbol{U}_k{}^X\boldsymbol{J}\right). \quad (23)$$

The corresponding temperature coefficients are respectively calculated by

$$\kappa_r=\sum_{k=1}^{2^p}P_k\frac{\mathrm{d}\ln<r^2>_k}{\mathrm{d}T}, \quad (24)$$

$$\kappa_s=\sum_{k=1}^{2^p}P_k\frac{\mathrm{d}\ln<S^2>_k}{\mathrm{d}T}. \quad (25)$$

RESULTS AND DISCUSSION

Poly(itaconates) carry highly crowded side groups. According to the depiction of ester groups (Zhou and Abe, 2003), in addition to the steric exclusions inherent to $\alpha.\alpha$-disubstituted vinyl polymers, the dipole-dipole interaction due to the pendant carbonyl groups has to be considered. However, PDBzI for instance, has two ester groups $COO(CH_2)C_6H_5$ and $CH_2COO(CH_2)C_6H_5$) in a monomer approach symmetry, the effects of side-chain conformations on the interactions of neighboring groups decrease in some cases. The torsion angles χ_1, χ_2 and χ_3 take preferably the four cases in Table 2, in which the dipole-dipole interactions may be canceled out partially, therefore, the interactions are neglected in the present calculation. However, the effect of side-chain conformations on dimension of polymers is investigated by the geometric parameters of $\alpha.\alpha$-disubstituted vinyl polymers (Sundararajan and Flory, 1974). Structure parameters of imaginary bonds for PDBzI are listed in Table 2, where the angle δ and α_β are 54.66° and 32.78°, respectively, and the length l_β is 0.438 nm. Moreover, Table 3 lists the structure parameters of other poly(itaconates) in $\chi_1=\chi_2=\chi_3=0$. Then, the angles of the imaginary bond can be calculated by Eqs.(4)~(8).

Using the deduced equations and parameters above, the characteristic ratios of mean-square end-to-end distance $<r^2>/(2xl^2)$ are calculated theore-

Table 2 Structure parameters of imaginary bonds for PDBzI

Torsion angles	l_b (nm)	α_b (°)	$\delta\pm\alpha_b$	$\delta\pm\alpha_\beta$
$\chi_1=\chi_2=\chi_3=0$	0.538	18.31	$\delta+\alpha_b$	$\delta+\alpha_\beta$
$\chi_1=\chi_2=180°$, $\chi_3=0$	0.538	18.31	$\delta-\alpha_b$	$\delta-\alpha_\beta$
$\chi_1=\chi_3=180°$, $\chi_2=0$	0.423	69.73	$\delta+\alpha_b$	$\delta-\alpha_\beta$
$\chi_2=\chi_3=180°$, $\chi_1=0$	0.423	69.73	$\delta-\alpha_b$	$\delta+\alpha_\beta$

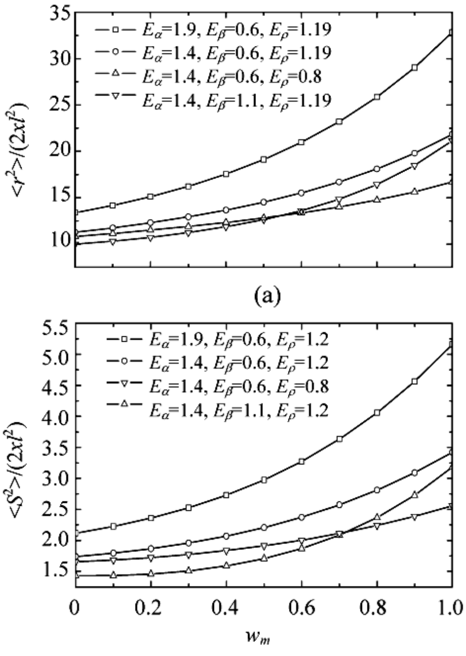
Table 3 Chain structure parameters for poly(itaconates) in $\chi_1=\chi_2=\chi_3=0$

Polymer addrev.	m_b (g/mol)	m_β (g/mol)	l_b (nm)	l_β (nm)	α_b (°)	α_β (°)
PDFI	135	121	0.473	0.369	32.71	11.91
PDBzI	149	135	0.538	0.438	18.31	32.78
PDEFI	163	149	0.605	0.523	29.52	19.47

tically, the correlations of the ratios with the fraction w_m of meso dyads for several conformational energies are presented in Fig.2a. We found that the value 12.6 of ratio is obtained by the following parameters: E_α=5861.5 J/mol, E_β=2512.1 J/mol and E_ρ=4982.3 J/mol at the unperturbed temperature T=298 K, the number of monomeric unit x=4001, and w_m=0.25. This value is in agreement with the experimental data in theta solvent (Yazdani-Pedram *et al.*, 1985a; 1985b), and also in accordance with previous theoretical results (Saiz *et al.*, 1988).

Therefore, using these parameters, we also calculate the dependence of characteristic ratio $<S^2>/(2xl^2)$ on the fraction w_m by Eq.(22), the results are shown in Fig.2b. Obviously, the ratio $<S^2>/(2xl^2)$ with the conformation energies and w_m is similar to that of $<r^2>/(2xl^2)$: the unperturbed dimensions depend mainly on the conformation of chain, and also relate to configuration of chain. As the conformation energies E_α and E_ρ increase, the dimensions increase, and the dimensions decrease as E_β increases. The phenomenon shown in Fig.2 can be explained in terms of Eqs.(9)~(15). The preferred conformation for the meso as well as for the racemic diads is *tt*, which results in the extension of chains. This gives the explanation for the high molecular dimensions of the PDBzI in the following results of calculation, especially for short-chain dimensions. However, the preference for the *trans* is higher in the meso diad than that in the racemic since β (or ρ)<1; consequently, the ratio is much higher for isotactic polymers than that of syndiotactic ones. With increase of E_α, the preference for *trans* increases and the dimensions thus go up. Conversely, as E_β increases, the statistical weight of the *trans* is diminished, and the higher weight to the conformation *gg* states acts as interruption in-between chain segments having *tt* or *tg* conformation, which results in much more molecule coils.

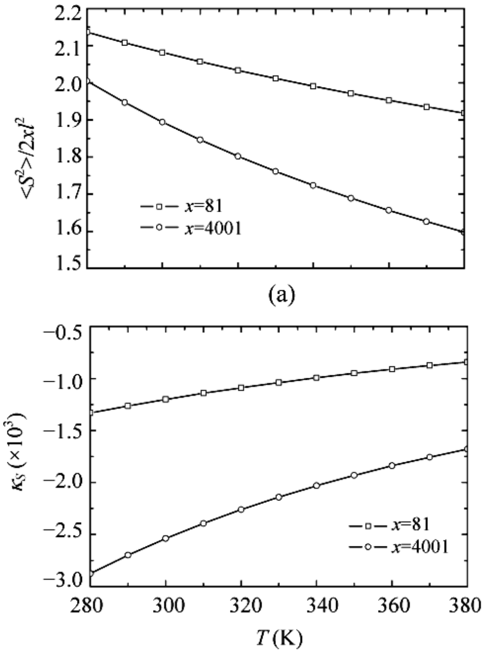
The temperature character of PDBzI is investigated and shown in Fig.3a. The ratio of $<S^2>$ exhibits



(a)

(b)

Fig.2 Characteristic ratio of mean-square end-to-end distance (a) and mean-square radius of gyration (b) vs the fraction of meso diads and conformational energies at 298 K, the monomeric unit x=4001 for PDBzI, the energy unit is kcal/mol (1 cal/mol=4.1868 J/mol)



(a)

(b)

Fig.3 The characteristic ratio of mean-square radius of gyration (a) and temperature coefficient (b) as functions of temperature for atactic PDBzI chains of w_m=0.25, contrasting the results of the long chain with that of short chain

a roughly linear correlation with temperature, moreover, the ratios decrease as temperature increases as long polymers are more obvious than short chains. Fig.3b exhibits the temperature coefficients κ_S as a function of temperature. Temperature coefficients κ_S as a function of w_m are studied by Eq.(25), the calculated results for several sets of the conformational energies E_α, E_β and E_ρ at T=298 K are shown in Fig.4: the increase of w_m results in the decrease of κ_S tremendously. That is to say, the temperature characters of the isotactic, syndiotactic and atactic polymers are quite different. The plots of Fig.4 contrasted with those of Fig.2 show that the temperature coefficients depend on w_m more obviously than that of the characteristic ratios. Therefore, it is suggested that temperature character of the stereoregular or stereoirregular PDBzI polymers is mainly determined by the tacticity of chains.

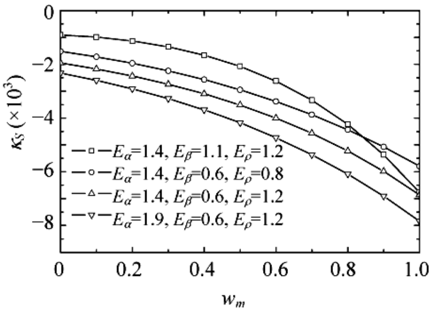
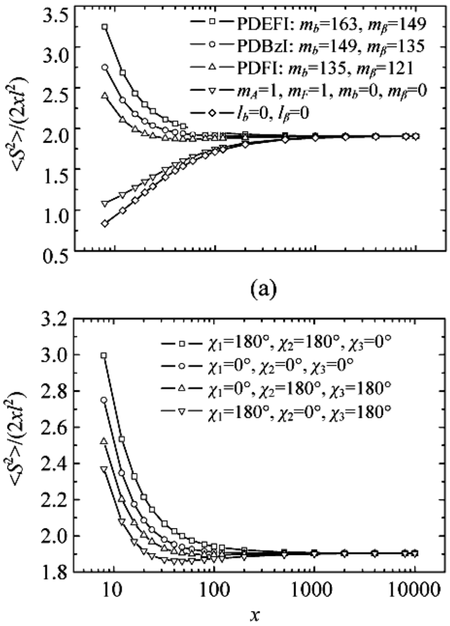


Fig.4 Dependence of temperature coefficient of mean-square radius of gyration on the fraction of meso diads and the conformational energies at *T*=298 K, the monomeric unit *x*=4001, the energy unit is kcal/mol (1 cal/mol=4.1868 J/mol)

The ratios $<S^2>/(2xl^2)$ depending on the logarithm of x monomeric units are also investigated by the energy parameters above. The results of considering and without considering the side groups are compared and shown in Fig.5a. Two ways of not considering the side groups are: the Lagrange relation, i.e. taking $m_b=m_\beta=0$ and $m_A=m_F=1$ in Eq.(22); the neglect of imaginary bond, i.e. taking $l_b=l_\beta=0$. Both ratios as functions of x first steeply increase, and finally approach an asymptotic value. However, it is interesting that the consideration of side groups leads to the larger ratios for $x<10^3$, and the ratios decrease steeply as x increases, although they approach the same asymptotic value for larger x. The ratios of PDFI, PDBzI and PDEFI considering the effect of side groups are also investigated in Fig.5a, using the structure parameters estimated in Table 2. The results showed that the larger side groups of PDEFI lead to the higher chain dimensions than those of PDBzI chain, similarly, the small side groups of PDFI lead to lower dimensions of chain when $x<10^3$. Obviously, the consideration of the side group for the polymers dimension is quite significant. Fig.5b shows the influence of side-chain conformations on the ratios of PDBzI, including four cases described in Table 2. It was also found that the larger size of side-chain structure leads to larger chain dimension of the short polymers. Therefore, these results explain that the consideration of side-chain structures is more important for short polymers.



(a)

(b)

Fig.5 (a) Dependence of characteristic ratios of mean-square radius of gyration with the logarithm of chain length for poly(itaconates) at *T*=298 K, w_m=0.25, and the contrasted results between considering side groups and not considering side groups; (b) Effect of the torsion angles χ_1, χ_2, χ_3 of side chains on the unperturbed dimension of PDBzI

The dependence of the temperature coefficients on the logarithm of x monomeric units, including κ_S of the mean-square radius of gyration and κ_r of mean-square end-to-end distance for the PDEFI, PDBzI and PDFI, was studied, with the results being shown in Fig.6. The coefficients κ_S is larger than κ_r for $x<10^3$, although the coefficients approach the same asymptotic value for $x\geq10^3$. Therefore, the consideration of the side groups also leads to the difference of the temperature coefficients, this result again indicates that the influence of the side groups on molecule dimension cannot be neglected for short polymers.

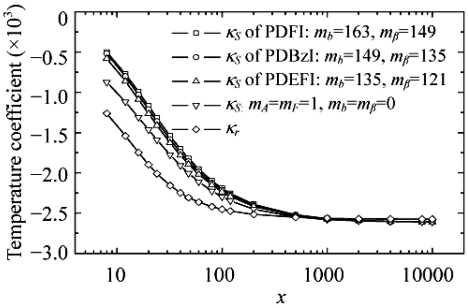


Fig.6 Effect of side groups of poly(itaconates) on temperature coefficient at T=298 K, the fraction of meso diads w_m=0.25, and the monomeric unit x=4001, including the temperature coefficient κ_S of mean-square radius of gyration and the temperature coefficient κ_r of mean-square end-to-end distance

CONCLUSION

The configuration and conformation-dependent properties of PDBzI were investigated by a revised RIS method, with the results being as follows:

PDBzI polymers have highly crowded chains. The consideration of steric exclusions inherent to $\alpha.\alpha$-disubstituted vinyl polymer and the structure of side groups leads to larger dimension of molecule. Moreover, the dependences of the unperturbed dimension and temperature coefficients on the conformation energies, temperature and the tacticity of chain are all obvious. Therefore, the effect of the chain configuration and conformation on the properties of PDBzI is quite important.

The physical behaviors of the short poly(itaconates) chains are quite different from those of the long chains if the side groups are considered, and the differences of both the unperturbed dimension and temperature character are mainly found when the length $x<10^3$. Moreover, the dimension of the polymers may go up as the dimensions of side group increase. Therefore, we suggest that it is not a good idea to calculate the unperturbed dimension of poly(itaconates) simply by Lagrange relation. In fact, the consideration of the excluded volume interaction for long-chain polymers will lead to the unperturbed dimension increase; therefore, the revised asymptotic values of long-chain dimension should be larger than the values in this calculation.

References

Alfonso, G.C., Yan, D.Y., Zhou, Z.P., 1993. Configurational-conformational statistics of atactic polypropylene. *Polymer*, **34**(13):2830-2835. [doi:10.1016/0032-3861(93)90128-W]

Flory, P.J., Sundararajan, P.R., 1974. Configurational statistics of vinyl polymer chains. *J. Am. Chem. Soc.*, **96**(16): 5015-5024. [doi:10.1021/ja00823a001]

Flory, P.J., Yoon, D.Y., 1974. Moments and distribution function for polymer chains of finite length. 1. theory. *Macromolecule*, **61**(12):5358-5365.

Ma, H.Z., Zhang, L.X., 1997. Effect of side group on mean-square radius of gyration of atactic poly(methyl methacrylate) chain. *Polymer Journal*, **29**(12):1012-1015. [doi:10.1295/polymj.29.1012]

Ma, H.Z., Ye, G.X., 2006. Dimensions of atactic poly(α-methylstyrene) chain with side groups. *Chinese Journal of Polymer Science*, **24**(1):87-93. [doi:10.1142/S0256767906001072]

Ma, H.Z., Wu, J.F., Xu, J.M., 1997. Unperturbed mean-square radius of gyration of atactic polystyrene chain with side groups. *European Polymer Journal*, **33**(10-12):1813-1815. [doi:10.1016/S0014-3057(97)00032-3]

Ma, H.Z., Zhang, L.X., Xu, J.M., 2001. Dependence of intrinsic viscosity on tacticity of polystyrene. *Acta Polymerica Sinica*, **6**:769-771 (in Chinese).

Osa, M., Yoshizaki, T., Yamakawa, H., 2000. Mean-square radius of gyration of oligo- and poly(α-methylstyrene)s. *Macromolecules*, **33**(13):4828-4835. [doi:10.1021/ma000353i]

Saiz, E., Horta, A., Gargallo, L., Hernández-Fuentes, I., Radic, D., 1988. Dipole moment and conformational analysis of itaconate. *Macromolecules*, **21**(6):1736-1740. [doi:10.1021/ma00184a034]

Sundararajan, P.R., 1986. Conformational analysis of poly(methyl methacrylate). *Macromolecules*, **19**(2):415-421. [doi:10.1021/ma00156a031]

Sundararajan, P.R., Flory, P.J., 1974. Configurational characteristics of poly(methyl methacrylate). *J. Am. Chem. Soc.*, **96**(16):5025-5031. [doi:10.1021/ja00823a002]

Velickovic, J., Filipovic, J., 1984. Unperturbed dimensions of poly{bis(phenyl-n-alkyl) itaconates}. *Macromolecules*, **17**(4):611-614. [doi:10.1021/ma00134a016]

Yamakawa, H., Yoshizaki, T., 2004. Contributions of short-rang and excluded-volume interactions to unperturbed polymer chain dimensions. *J. Chem. Phys.*, **121**(7):3295-3298. [doi:10.1063/1.1774155]

Yan, D.Y., Zhou, Z.P., 1999. Configurational-conformational statistics of stereoirregular poly(methyl methacrylate)s. *Joural of Macromolecular Science-Physics*, **B38**(3): 217-225.

Yazdani-Pedram, M., Gargallo, L., Radić, D., 1985a. Polymer conformation and viscometric behaviour—4. Characterization and conformational studies for poly(dibenzyl itaconate). *European Polymer Journal*, **21**(5):461-465. [doi:10.1016/0014-3057(85)90125-9]

Yazdani-Pedram, M., Gargallo, L., Radić, D., 1985b. Polymer conformation and viscometric behaviour—5: Synthesis, characterization and conformational studies for poly(monobenzyl itaconate). *European Polymer Journal*, **21**(8):707-710. [doi:10.1016/0014-3057(85)90110-7]

Zhou, Z.P., Abe, A., 2003. Effect of the pendany ester group orientations on the dipole moment of poly(alkyl acrylate)s. *Macromolecules*, **36**(19):7366-7371. [doi:10.1021/ma0302863]

Zhou, Z.P., Abe, A., 2004. A RIS treatment of the mean-square dipole moment of PMMA chains in consideration of the pendany ester group orientations. *Polymer*, **45**(4):1313-1320. [doi:10.1016/j.polymer.2003.03.001]

Zhou, Z.P., Yan, D.Y., 1995. Improved expression of the mean-square radius of gyration, 2 poly(1,1-disubstituted ethylene)s. *Macromolecular Theory and Simulations*, **4**(1):155-164. [doi:10.1002/mats.1995.040040111]

Zhou, Z.P., Yan, D.Y., 2001. Configurational-conformational statistics of poly(ethylene-propylene)s. *Journal of Macromolecular Science Part B-Physics*, **40**(2):231-237. [doi:10.1081/MB-100001808]