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Configuration energy calculation of single-chain polystyrene glass sphere by the RIS–Monte Carlo method

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Changes of the conformational energies of a single-chain polystyrene under and above T_g has been studied using the RIS–Monte Carlo method. This simulation is realistic for a chain length as long as 40 000 repeats. The energy change obtained was found to be close to a released energy that was observed as a d.s.c. exothermic peak appearing near T_g when the particles of the polymer were heated in the first run. The conformational feature and the conformational change for the glassy spheres of single-chain polystyrene were thereby predicted. The choice of conditional probability, sampling without biasing correction, and the critical chain length for the appearance of a d.s.c. exothermic peak we discussed. Copyright © 1996 Elsevier Science Ltd.

(Keywords: rotational isomeric state; Monte Carlo; conformational energy)

INTRODUCTION

A paucity of atoms or small molecules can make a cluster that has remarkably different properties from the same atoms or molecules in bulk. In polymer science, if a tiny particle consists of only one chain or a paucity of chains (or 'pauci-chain') of polymers does it have different properties from the same chains in bulk? Single- or pauci-chain polystyrene (SCPS) particles are generated by the free-radical polymerization of styrene in microemulsions. The microlatex particles contain only one or at most a few high molecular weight polymer chains[1]. Such a chain confined in a sphere at temperatures below T_g is in the state of a single-chain glass. In microparticles of 20–30 nm diameter containing only one or just a few chains, the polymer chains adopt a highly compact conformation that occupies only a few per cent of the random-coil volume. It is interesting to observe an exothermic peak appearing near T_g for the virgin SCPS samples in the first heating-up run of d.s.c., and the exothermic peak disappeared on the second scan. On the contrary, the ordinary polystyrene (OPS) does not show an exothermic peak on heating through T_g. The purpose of our simulation is to explore the origin of this difference.

Monte Carlo (MC) methods have proved to be very useful in the investigation of the statistics of free or confined polymer chains during the last two decades[2–8]. However, as shown in extensive works by Kremer[9,10], if one samples long chains by the procedure of generating random walks and then searching for self-avoiding walks (SAW), the procedure breaks down. As the length of the chain increases, the gain becomes exponentially small. Data results in this MC are thus restricted to a chain length of $N \approx 100$[9,10]. Obviously, this causes serious problems for simulation of a polymer system having more realistic chain lengths. In order to solve this problem, biased sampling methods were introduced[11,12] and developed[13]. With these methods one samples as for standard SAW, obtaining chains with various statistical weights or a modified distribution, and then corrects for this with the knowledge of the growing monomer's local environment. Although these modified methods are effective in sampling and very useful for some systems, for longer chains ($N > 200$), the relative error of both the partition function and the directly measurable physical quantities (mean square radius of gyration, structural function, etc.) increase exponentially with the degree of polymerization, and the results will lose reliability.

Our simulation primarily aims at reproducing an experimental process in a more realistic way. The energy measure of d.s.c. relates to a long chain containing thousands of bonds condensed into a glassy sphere on a nanometre scale. We found that the method of rotational isomeric states–Monte Carlo (RIS–MC)[14–16] meets our goal. The SCPS chains can be generated inside a small sphere with a rigid impermeable wall. During the generation, conformational states are selected according to Flory's RIS model[17]. The origin of the d.s.c. data difference might come from the cohesional entanglement of the chain as previously suggested[1], or from the difference in the conformational energy between OPS and SCP chains. The simulated results by RIS–MC will show statistical properties of the system regarding the energy of the chain conformations.

MODEL AND METHODS

SCPS is experimentally generated by polymerization of

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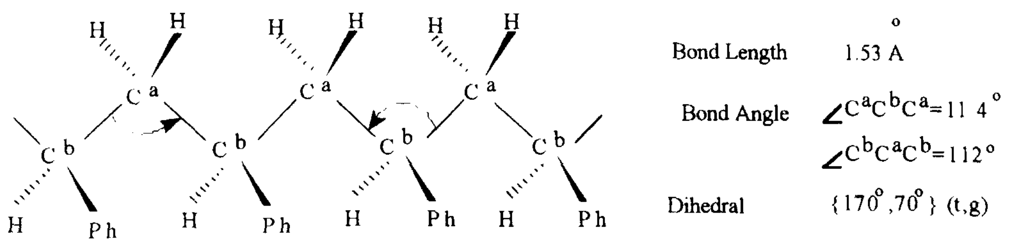

Figure 1 Portion of the atactic polystyrene chain in the all-*trans* conformation

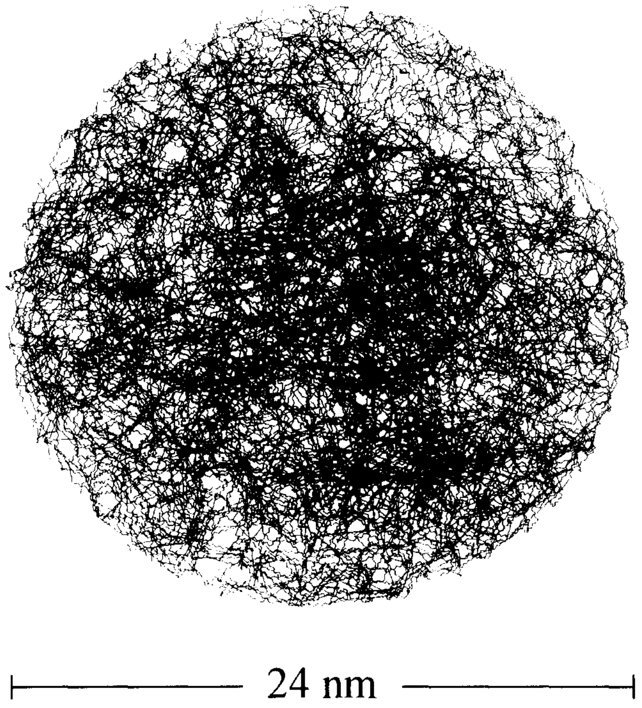

Figure 2 A simulated glassy sphere of SCPS (chain length is 10^4, radius is 120 Å)

its monomers confined in a water dispersed microemulsion droplet. The conformation of the chain will be different from that for chains in the bulk environment. In order to verify this, we choose the SCPS model confined in a small sphere of definite volume. According to the real system, we consider here a polystyrene (PS) chain containing 4×10^4 repeat units of styrene with molar mass 4.16×10^6. The chain needs to be confined in a sphere with a radius of 120 Å, so that the density will be 0.95 g cm^{-3}, close to the actual experimental value[1]. The skeleton of PS chain is treated as having definite bond lengths, bond angles and torsion angles[18] as shown in *Figure 1*. The SCPS chain is atactic, consisting of 30% *meso* dyads and 70% *racemic* dyads. *Figure 2* shows one of the SCPS glassy spheres obtained by computer.

The RIS–MC method does not consider the *exclude volume effect* of the polymer chains, that is the system belongs to a Θ condition. In the present study, the RIS model adopted consists of two rotational isomeric states, *t* and *g*, in terms of Flory's early work[19]. The g^- conformational state was ignored as having very high steric interactions involving the relatively large planar phenyl groups[19]. The generated chain travels inside the sphere without collision until reaching the wall. During the generation, *t* or *g* state for a bond are randomly selected according to their conditional probabilities calculated through the use of statistical weight matrices.

The statistical weight matrices $\mathbf{U}'$, $\mathbf{U}''_m$ and $\mathbf{U}''_r$ of the PS conformer are defined as follows[19]:

$$\mathbf{U}' = \begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix} \mathbf{U}''_m = \begin{pmatrix} \omega'' & 1/\eta \\ 1/\eta & \omega/\eta^2 \end{pmatrix}$$

$$\mathbf{U}''_r = \begin{pmatrix} 1 & \omega'/\eta \\ \omega'/\eta & 1/\eta^2 \end{pmatrix} \qquad (1)$$

where $\mathbf{U}'$ is the complementary matrix, $\mathbf{U}''_m$ and $\mathbf{U}''_r$ are statistical weight matrices for the pair of bonds within *meso* and *racemic* dyads. In accordance with Flory's definitions, η denotes the first-order interaction (E_η parameter, expressing the statistical weight of the *trans* relative to the *gauche* state.

$$\eta \approx 0.8\exp(-E_\eta/RT) \qquad (2)$$

The second-order interaction parameters between CH_2-CH_2, $CH_2-C_6H_5$, and $C_6H_5-C_6H_5$ are defined by ω, ω', ω'', with the energy $E\omega$, $E\omega'$, $E\omega''$ ($E\omega = E\omega' = 1000\,\text{cal mol}^{-1}$) being associated with the interactions between these units,

$$\omega \approx \omega' \approx 1.3\exp(-1000/T) \qquad (3)$$

$$\omega'' \approx 0.8\exp(-E\omega''/RT) \qquad (4)$$

then according to the values of η, ω, ω' and ω'' given in the literature[19], the statistical weight matrices (300 K) are obtained as follows:

$$\mathbf{U}' = \begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix} \mathbf{U}''_{meso} = \begin{pmatrix} 0.12 & 0.37 \\ 0.37 & 0.0062 \end{pmatrix}$$

$$\mathbf{U}''_{racemic} = \begin{pmatrix} 1.0 & 0.017 \\ 0.017 & 0.13 \end{pmatrix} \qquad (5)$$

With these matrices we obtain the dyad conditional probability matrices by the calculations carried out in the next section.

Rejections of some conformational states are performed during the generation procedure (*Figure 3*). At any step, if the choice of one of the conformational states makes the chain touch the wall, this conformational state is rejected. In the case of dealing with ν states of the RIS model, the remainder is $\nu - 1$ states. We thus continue a new trial by randomly selecting a state according to the renormalized conditional

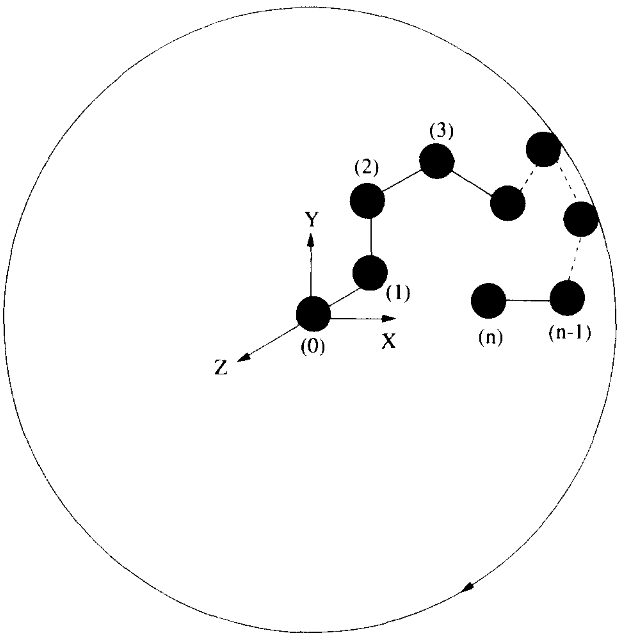

Figure 3 Diagram for showing generating process. The generated chain starts from the centre of the sphere

probabilities of the other $\nu - 1$ states. In general, if a new bond touches the wall τ times, a new trial can choose other $\nu - \tau$ states. When $\tau = \nu$, this bond is rejected, and the previous bond becomes the starting point again. For a generated bond, most of possible trials after the bond are searched in calculation. This is a procedure of sub-searching in the present work.

Reasons for using the model and method are threefold. First, in the glassy state of SCPS, the conformations of the SCPS chain are similar to those under the Θ condition. Second, in the simulation for long polymer chains, one has to deal with too many internal degrees of freedom which makes the computation very complex. The use of the RIS–MC model, however, makes the calculation much easier and faster. Third, the two rotational isomeric states of PS are the most probable among all of possible conformations. The PS chains thus generated are weighted by the Boltzmann factor. The distribution of states is specified by the Boltzmann partition function with given temperature and equilibrium energies.

RESULTS AND DISCUSSION

A priori *probabilities and conditional probabilities*

The implementation of RIS–MC needs to determine *a priori* probabilities and conditional probabilities of the bonds to be generated for polymer chains in the system. According to Flory's theory[17], when the $(i-1)$th bond is in the state ϕ', the conditional probability of the ith bond to be in the state ϕ is:

$$Q_{i-1,i}(\phi', \phi) = \frac{P_{i-1,i}(\phi', \phi)}{P_{i-1}(\phi')} \tag{6}$$

where $P_{i-1,i}(\phi', \phi)$ is the probability of the ith and the $(i-1)$th bonds being in the states ϕ, ϕ' respectively, and $P_{i-1}(\phi)$ is the probability of the $(i-1)$th bond being in the state ϕ. For atactic PS of $2n+1$ dyads, these two *a priori* probabilities are defined as:

$$P'(\phi) = Z^{-1}[1\ 0]\left[\prod_{i=1}^{n}(\mathbf{U}'\mathbf{U}_i'')\right]\left[\frac{\partial(\mathbf{U}')}{\partial \ln u(\phi)}\mathbf{U}''\right]\left[\prod_{j=1}^{n}(\mathbf{U}'\mathbf{U}_j'')\right]\begin{bmatrix}1\\1\end{bmatrix} \tag{7}$$

$$P''(\phi) = Z^{-1}[1\ 0]\left[\prod_{i=1}^{n}(\mathbf{U}'\mathbf{U}_i'')\right]\left[\mathbf{U}'\frac{\partial(\mathbf{U}'')}{\partial \ln u(\phi)}\right]\left[\prod_{j=1}^{n}(\mathbf{U}'\mathbf{U}_j'')\right]\begin{bmatrix}1\\1\end{bmatrix} \tag{8}$$

$$P'(\phi', \phi) = Z^{-1}[1\ 0]\left[\prod_{i=1}^{n}(\mathbf{U}'\mathbf{U}_i'')\right]\left[\frac{\partial(\mathbf{U}')}{\partial \ln u(\phi', \phi)}\mathbf{U}''\right]\left[\prod_{j=1}^{n}(\mathbf{U}'\mathbf{U}_j'')\right]\begin{bmatrix}1\\1\end{bmatrix} \tag{9}$$

$$P''(\phi', \phi) = Z^{-1}[1\ 0]\left[\prod_{i=1}^{n}(\mathbf{U}'\mathbf{U}_i'')\right]\left[\mathbf{U}'\frac{\partial \mathbf{U}''}{\partial \ln(u(\phi', \phi))}\right]\left[\prod_{j=1}^{n}(\mathbf{U}'\mathbf{U}_j'')\right]\begin{bmatrix}1\\1\end{bmatrix} \tag{10}$$

$$Z = [1\ 0]\left[\prod_{i=1}^{2n+1}(\mathbf{U}'\mathbf{U}_i'')\right]\begin{bmatrix}1\\1\end{bmatrix} \tag{11}$$

where $\mathbf{U}_{\mathrm{m}}''$ and $\mathbf{U}_r''$ are simply expressed as $\mathbf{U}_i''$, and Z is the partition function.

As discussed by Flory, the *a priori* probability of each state of the ith bond of a long chain tends to be constant when the chain length exceeds 5[17]. In our calculation, we used two PS chain segments, each segment consisting of 25 dyads (*Figure 4*). The two segments were generated individually as follows: first, the sequence of *meso* and *racemic* dyads were generated with the Monte Carlo method. The ratio of *meso* and *racemic* dyads (3:7) in every segment was the same as that of the SCPS model. Second, each atactic segment was generated at the Θ condition by the MC method with two rotational

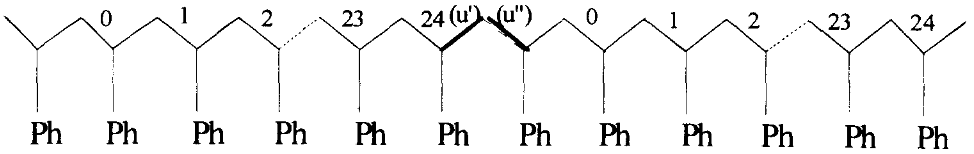

Figure 4 Two segments of atactic PS (each consists of 50 bonds with 30% *meso* and 70% *racemic* dyads) shown in all-*trans* conformation

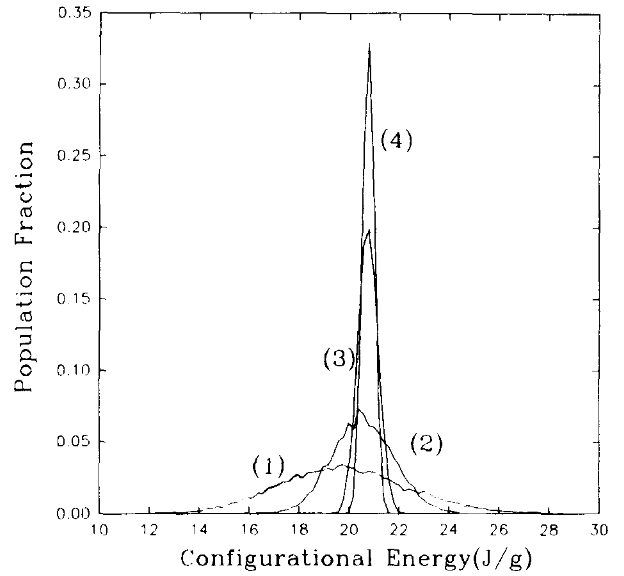

Figure 5 Chain conformational energy distributions. The chain length varies from: (1) $N = 2 \times 10^2$, (2) $N = 10^3$, (3) $N = 10^4$, (4) $N = 8 \times 10^4$. As N increases, the distributions roughly satisfy gaussian forms. But for long chains, the distribution is relatively narrow and the average values of configurational energy increase

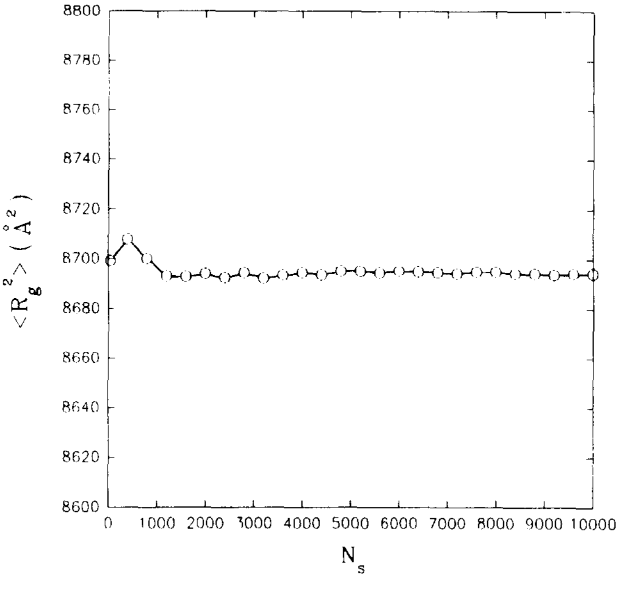

Figure 6 Contribution to the mean square radius of gyration ($< R_g^2 >$) as a function of sample of chains (N_s). Here, the length of SCPS is 8×10^4 and the radius of the sphere is 120 Å

isomeric states being randomly selected. After the procedure of generation, we used equations (5) and (7)–(11) ($n = 25$) to calculate the *a priori* probabilities of the bonds in a dyad linking either end of the two segments, then by equation (6) we calculated the dyad conditional probability matrices (300 K):

$$Q' = \begin{pmatrix} 0.781 & 0.219 \\ 1.0 & 0.0 \end{pmatrix} Q_{meco} = \begin{pmatrix} 0.314 & 0.686 \\ 0.987 & 0.013 \end{pmatrix}$$

$$Q_{racemic} = \begin{pmatrix} 0.987 & 0.013 \\ 0.158 & 0.842 \end{pmatrix} \qquad (12)$$

Sampling without biasing correction

During the procedure of RIS–MC simulation the chain is confined in a small sphere. Each sphere was built up from 4×10^4 repeat units of PS. In this case, how frequently the chain touched the wall is important to determine. Since one of the touches will bias the statistical weight of the chain, the bias will finally influence the statistical average of physical variables of the system. Our results indicate that the generation leads to many rejected walks (about 20% of total steps for generating a chain), where 93% or so of the rejected walks dissipated in sub-searching for generating a bond. Therefore, about 1.4% of the total steps finally leads to biased steps (1340 steps on average). However, for 8×10^4 bonds of a generated chain, the number of biased steps is only a small fraction (<2%), and the distribution of chain conformational energy does not deviate from the gaussian form (*Figure 5*). This indicates that in this simulation so small a bias could not make a significant error in the statistical average of all samples thus obtained.

The sampling size is very important in the present study. In order to obtain average quantities as accurately as possible for such long chains, it is important to determine how many samples we have to choose. For general lattice MC, if each bond has two possible walks, the total conformational states of a polymer chain containing 8×10^4 bonds will reach 2^{80000} at most. Theoretically, one has to sample more than 2^{80000} chains. In fact, such a huge number of samples is impossible for any simulation. However, in the present work the sampling obeys the RIS model; the polymer chains thus generated are simply around the most probable configurations. The number of samples are therefore much reduced. Examinations of the number were performed through the chain properties of mean square end-to-end distance ($< R^2 >$) and mean square radius of gyration ($< R_g^2 >$).

Figure 6 shows the average of $< R_g^2 >$ plotted against various sampling size. It is obvious that the average has no significant fluctuation when the number of successfully sampled chains reaches 10^4. The results seem to be reasonable. During the sampling procedure, every SCPS chain of 8×10^4 length was generated in a small sphere of 120 Å radius. The polymer chain fills almost all of the space in the sphere to form a compact structure. The distribution of $< R_g^2 >$ examined is very narrow compared with a free gaussian chain. The square value of $< R_g^2 >$ is close to the scale of radius of the sphere.

Conformational energy

It is our opinion that the conformational energy of the macromolecule increases when it changes from a gaussian coil (free state) to a compact glass (confined state). In order to verify this point, more details about this variance are given in this section, and the final simulation results are compared with d.s.c. data.

For a symmetric polymer with N bonds, the conformational energy can be calculated as follows[17]:

$$E_c = E_t + \sum_{i}^{N-2} E_{\mathrm{dyad}(i)} \qquad (13)$$

where E_c is the conformational energy of the chain, E_t is the energy of terminal bonds, and $E_{\mathrm{dyad}(i)}$ expresses the conformational energy of the ith dyad. In the case of an asymmetric polymer, for example, in the present work,

Table 1 Fraction of conformational dyad ($X_{\alpha\beta}$) OPS and SCPS

Fraction of conformational dyad	m_{tt}	m_{tg}	m_{gt}	m_{gg}	r_{tt}	r_{tg}	r_{gt}	r_{gg}
OPS	0.079	0.173	0.047	0.001	0.582	0.007	0.018	0.093
SCPS	0.084	0.167	0.048	0.001	0.575	0.008	0.022	0.096

m: *meso*; r: *racemic*

Table 2 Dyad conformational energies ($E_{\alpha\beta}$) of PS conformer

Dyad conformational energy	m_{tt}	m_{tg}	m_{gt}	m_{gg}	r_{tt}	r_{tg}	r_{gt}	r_{gg}
Cal mol^{-1}	1600.0	700.0	700.0	3300.0	0.0	2800.0	2800.0	1500.0

m: *meso*; r: *racemic*

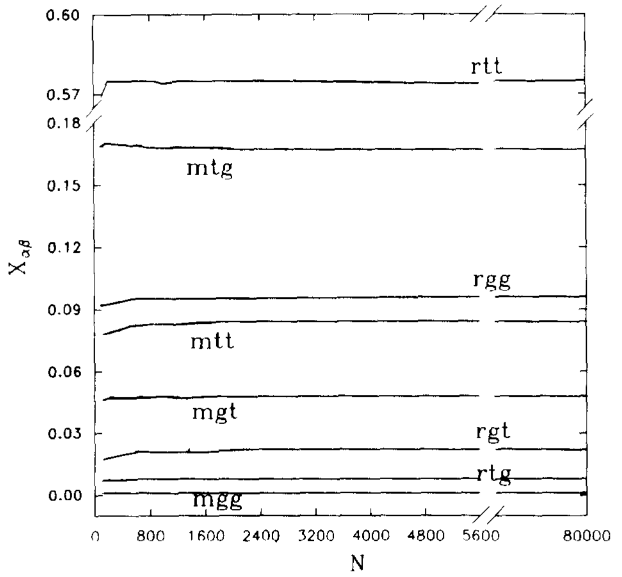

Figure 7 Dyad fractions ($X_{\alpha\beta}$) of SCPS as a function of chain length (N). m: *meso*; r: *racemic*. The radius of the sphere is 120 Å

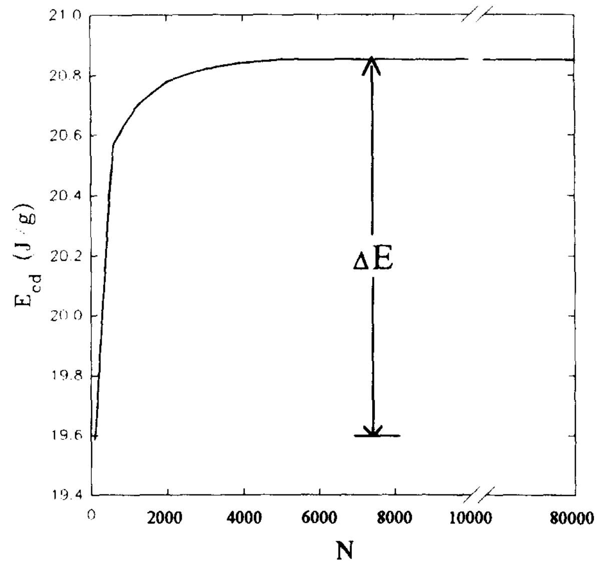

Figure 8 Conformational energy (E_{cd}) of SCPS as a function of chain length (N). The radius of the sphere is 120 Å

there are eight kinds of dyads for an atactic PS chain, tt, tg, gt, gg states for a *meso* dyad, designated as mtt, mtg, mgt, mgg; and tt, tg, gt, gg states for a *racemic* dyad, designated as rtt, rtg, rgt, rgg. If we use α to express a *meso* or *racemic* dyad and β to express the conformational state of a pair of bonds, then the conformational energy can be expressed as:

$$E_c = E_t + \frac{N-2}{2}\sum_{\alpha}\sum_{\beta} X_{\alpha\beta}E_{\alpha\beta} \qquad (14)$$

where E_t is the energy of the terminal bonds and $E_{\alpha\beta}$ is the conformational energy of a pair of bonds in the $\alpha\beta$ state. In the second term of the equation, $(N-2)/2$ indicates the number of the conformational dyads except the terminal bonds in a macromolecule of length N. $X_{\alpha\beta}$ expresses the fraction of the conformational dyad. For OPS, $X_{\alpha\beta}$ is the dyad conditional probability, but for SCPS it is calculated as follows, in which $N_{\alpha\beta}$ expresses the number of dyads in the $\alpha\beta$ state in a SCPS chain.

$$X_{\alpha\beta} = \frac{N_{\alpha\beta}}{\sum_{\alpha}\sum_{\beta} N_{\alpha\beta}} \qquad (15)$$

Since $X_{\alpha\beta}$'s are normalized for the eight kinds of dyads, the last term in equation (14) can be defined as conformational energy averaged on a single dyad (E_{cd}):

$$E_{cd} = \sum_{\alpha}\sum_{\beta} X_{\alpha\beta}E_{\alpha\beta} \qquad (16)$$

The conformational energy differences of SCPS and OPS can therefore be calculated. They both contained 8×10^4 bonds, and the former was confined in a sphere of 120 Å radius. Using the results (listed in *Table 1*) which were statistically averaged from the simulation and the conformational energies ($E_{\alpha\beta}$ for OPS) given by Flory[19] (*Table 2*), we obtained the conformational energy difference between SCPS and OPS:

$$\Delta E_{cd} = E_{SCPS} - E_{OPS} \approx 23.0 \text{ cal mol}^{-1} \approx 0.93 \text{ J g}^{-1}$$

This value is very close to the d.s.c. experimental data $(1 \sim 2 \text{ J g}^{-1})^1$.

Now, it is reasonable to draw the conclusion that the relaxation of the high conformational energy of SCPS during heating up to T_g contributes significantly to the exothermic peak observed in the d.s.c. experiment.

Critical chain length for the appearance of a d.s.c. exothermic peak

As was found in experiments[1,20] some glassy

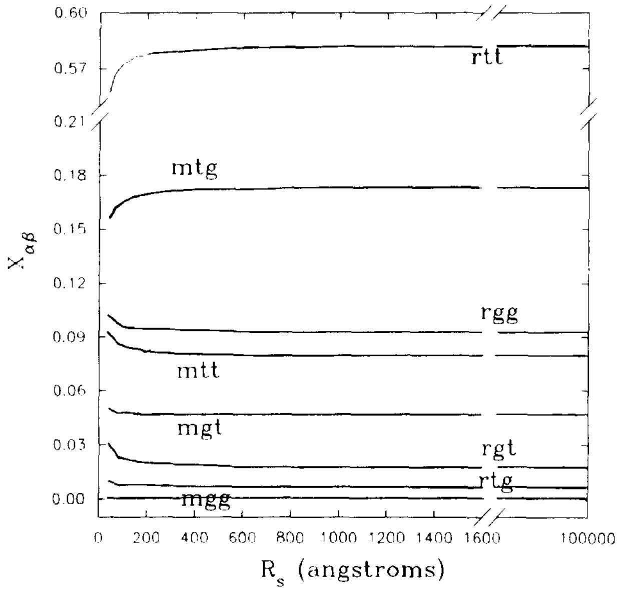

Figure 9 Changes of dyad fractions ($X_{\alpha\beta}$) following the expansion of SCPS glass sphere. m: *meso*; r: *racemic*. R_s is the radius of the sphere and the chain length is 10^4

microspheres may contain a few PS chains, therefore, we have to take pauci-chain systems into account in our simulation. For such a microsphere model, computations are followed with the chain length (N) changing from 10^2 to 8×10^4, whilst the radius of the sphere (120 Å) and the density (0.95 g cm^{-3}) are taken as the same as the SCPS ($N = 8 \times 10^4$).

Figure 7 shows the evolution of $X_{\alpha\beta}$ performed vs N. In a very large number of tests, or for large N, it is found that $X_{\alpha\beta}$ is completely unaffected. However, in the region $N < 4.8 \times 10^3$, the fractions of high conformational energy dyads (*meso*-tt; *race*-gg, *race*-gt, *race*-tg) decrease and those of low conformational energy dyads (*meso*-tg, *race*-tt) increase as N decreases. These trends become very rapid when $N < 2.0 \times 10^3$. This behaviour is also shown in the conformational energy (E_{cd}) as a function of N, in *Figure 8*, where ΔE is the difference of conformational energies between confined and free chains. It is observed that when $N > 4.8 \times 10^3$, the values of ΔE are constant. The fall of ΔE starts from $N = 4.8 \times 10^3$, and much faster drops happen when $N < 2.0 \times 10^3$. Reasons for this result can be attributed to the effect of restriction caused by the wall of the sphere. Because of this effect, local conformation of the chain segments near the surface is disturbed, this affects the conformational energy of the chain. For long chains, when $N > 4.8 \times 10^3$, the chains have to walk in a greatly distorted way in order to avoid intruding the wall. On the contrary, short chains grow more freely in the sphere.

The results show that there is a critical value of chain length $N_c = 4.8 \times 10^3$ for a confining sphere of 120 Å diameter, below which the conformational differences between a pauci-chain PS and a SCPS chain confined in the sphere decrease significantly with N. $N_c = 4.8 \times 10^3$ means that there are nearly 20 chains in the sphere, and for $N = 2.0 \times 10^3$, there are nearly 40 chains. If we use the number of chains (M) contained in the sphere to describe the variance of E_{cd}, it can be seen that ΔE does not vary until $M < 20$, it decreases slowly in the region $M = 20$–40, and for $M \geq 40$, it vanishes rapidly.

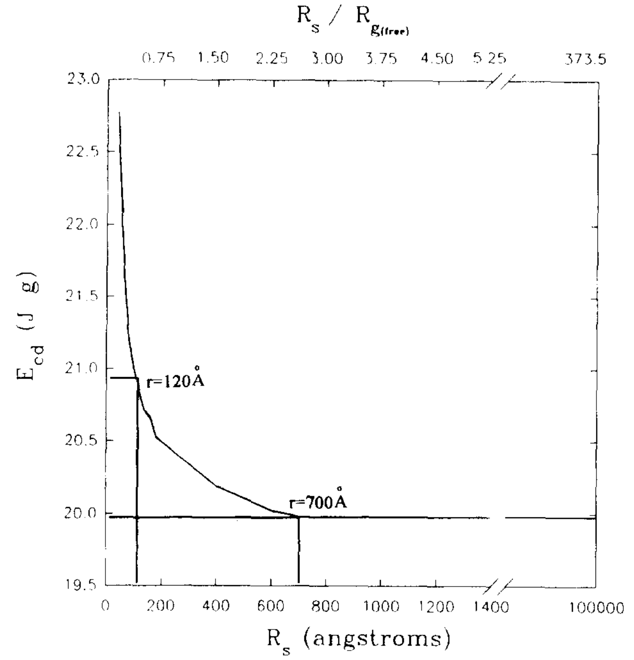

Figure 10 Changes of conformational energy (E_{cd}) following the expansion of the SCPS sphere. Here, R_s is the radius of the sphere and the chain length is 10^4. $R_{g(free)}$ is the radius of gyration of a free PS chain in the case of 10^4 chain length

Another way to express the results presented above is to observe the effect of changing the radius of confining spheres, for a SCPS chain of a given length 10^4.

The fractions of conformational dyad ($X_{\alpha\beta}$) and the conformational energy (E_{cd}) as functions of sphere radius (R_s) are shown. In *Figure 9*, the fractions of high conformational energy dyads (*meso*-tt; *race*-gg, *race*-tg, *race*-gt) increase while those of low conformational energy dyads (*meso*-tg; *race*-tt) decrease as R_s decreases. The changes of conformational states cause corresponding changes of E_{cd} (*Figure 10*). There appears a critical value $R_s = 700$ Å (or $R_s/R_{g(free)} = 2.63$, where $R_{g(free)}$ is the radius of gyration of a free PS chain), below which E_{cd} changes rapidly.

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