Calculation of crystalline modulus of syndiotactic polystyrene using molecular modelling

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Mechanical properties of semicrystalline polymers are determined mainly by the proportion of crystalline phase and its ordered microstructure. Owing to its inherent planar zigzag backbone conformation, syndiotactic polystyrene (sPS) is expected to have a crystalline modulus exceeding that of many polymers, and with potential applications as a low-cost, high-performance material. Molecular modelling has been used to simulate the deformation behaviour of a perfect sPS crystal lattice with the molecular chains oriented parallel to the applied stress, thus deriving the tensile modulus. Intrachain interactions including bond stretching and bending, are found to be the primary forces influencing tensile modulus, whereas the interchain van der Waals contribution is not significant. The calculated crystal modulus for sPS is comparable with the literature value utilizing X-ray diffraction.

(Keywords: syndiotactic polystyrene; molecular modelling; crystalline modulus)

INTRODUCTION

In recent years, since the successful development of syndiotactic polystyrene (sPS)[1], the structure of this material has been studied extensively by different laboratories. The attractive physical characteristics of this polymer are (1) a relatively high melting temperature (270°C) and (2) a rapid crystallization rate *versus* isotactic polystyrene. It is anticipated that syndiotactic polystyrene will exhibit not only good solvent resistance but perhaps enhanced mechanical performance at elevated temperatures as well. Detailed structural studies using X-ray, i.r. and electron microscopy[2–4] have revealed that polymorphism (α- and β-form) coexists in the crystalline phase of sPS. However, the fully extended α-form with *trans–trans* conformation is frequently encountered, and reported to be the most stable phase of the two[5]. The *trans* planar zigzag conformation leads to an inherently stiff backbone and strong intramolecular interactions; the macroscopic properties such as modulus and strength are expected to exceed those of many polymers.

Mechanical properties of semicrystalline polymers are determined principally by crystallinity, crystallite size and the orientation of the molecular chain with respect to the direction of applied stress. In attempting to produce high-modulus polymers, it is essential to have information on the modulus at the microscopic level (i.e. the modulus of a perfect polymer crystal). Along with other scattering techniques, such as Raman and inelastic neutron scattering[6,7], the main method for determining the crystalline modulus is X-ray diffraction, where the position of the X-ray maximum is followed as the specimen is stressed. However, there can be problems in determining the local stress on the crystalline elements from the overall applied stress[8]. In this paper, using molecular modelling, we simulate the microdeformation behaviour of the crystalline lattice when tensile stress is applied, thus to predict the crystalline modulus of syndiotactic polystyrene.

METHOD

The molecular modelling program POLYGRAF[9] was used to simulate the stress–strain behaviour of crystalline sPS. The molecular geometry is adjusted corresponding to the associated stress in order to minimize the potential energy of the entire system. Periodic boundary conditions are used to carry out the simulation. This enables the study of an infinite system, which eliminates any perturbations from polymer chain ends and incorporates non-bonded intermolecular and intramolecular interactions. The unit cell is constructed just large enough to contain one molecular chain; its dimension is determined assuming van der Waals contact of the outer atoms. Covalent bonds can be formed across the unit-cell boundaries to create infinite chains. In our case the macromolecular repeat is chosen to be 5.1 Å and the chain set parallel to the c axis direction. Any disoriented arrangements of the crystallites are not considered here. Since there are a small number of atoms within the unit cell, the Fletcher–Powell[9] algorithm for minimization is preferred to obtain a faster convergence.

The Dreiding force field[9] is selected to predict geometries and conformational energies of the molecules. The energy of an arbitrary geometry for a molecule is written as a superposition of various two-body, three-body and four-body interactions. The bonded interactions consist of bond stretching, bond angle bending, dihedral angle torsion and inversion terms,

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while non-bonded interactions consist of only the van der Waals term for sPS. The potential energy is expressed as a sum of bonded and non-bonded interactions:

$$E = \tfrac{1}{2}k_{ij}(r - r_{ij})^2 + \tfrac{1}{2}K_{ijk}(\theta - \theta_{ijk})^2 + \tfrac{1}{2}V_\phi[1 + d\cos(n\phi)] + \tfrac{1}{2}k_\omega(\omega - \omega_0)^2 + D_{ij}[-2(x_{ij}/x)^6 + (x_{ij}/x)^{12}]$$

where k_{ij} is the force constant and r_{ij} is the standard bond length between the ith and jth atoms; θ_{ijk} is the natural angle between the bonds ij and jk; and K_{ijk} is the bending force constant. The torsional terms for two bonds ij and kl are connected via a common bond jk, where V_ϕ is one-half the rotational barrier, n is the periodicity of the potential and d is the phase factor. For atoms i bonded exactly to three other atoms j, k, l the inversion k_ω is the force constant and ω is the natural improper torsion angle. A Lennard-Jones type expression is used here for non-bonded interactions, where D_{ij} is the well depth and x_{ij} is the van der Waals bond length. Van der Waals interactions are not calculated between atoms bonded to each other (1,2 interactions) or between atoms that are involved in angle interactions (1,3 interactions). In addition, van der Waals interactions are calculated only for pairs of atoms within a cut-off distance of 9 Å.

RESULTS AND DISCUSSION

Lateral packing constructed according to the van der Waals contact has the dimensions $a = 6.95$ Å, $b = 10.7$ Å with one molecular chain in each unit cell. During the energy minimization γ is fixed to 90°, assuming an orthorhombic structure. However, this constraint was relaxed so the angle could be varied during the minimization. The results indicated that the angle deviates only slightly from 90°. The repeat in the c axis direction was set at 5.1 Å, when no stress was applied, consistent with the observed data for the planar zigzag conformation of α-form sPS. The β-form of sPS with *TTGG* conformation was not considered here, since its tensile modulus is expected to be less than that of the α-form due to lower energies required to distort the torsional angles.

The potential energy of the whole system was first minimized when no force was applied. Then, the stress was applied with its direction perpendicular to the *ab* plane of the unit cell and the system again minimized to reach the new equilibrium state. The stresses applied in the modelling calculation went from 0.25 to 2.0 GPa; associated strains were recorded by examining the change of unit-cell dimensions in the c axis direction. The calculated stress–strain curve of the crystalline syndiotactic polystyrene is shown in *Figure 1*, where the elastic modulus estimated from the slope is 83 GPa, which is comparable with that, 86 GPa, reported by Chatani[10] using X-ray diffraction analysis. This theoretical limit, however, has not been reported to be attained for sPS. In fact, the experimental modulus is about two orders of magnitude lower than the predicted value. The reason for the lower modulus is due to a series of folded-back chains in the crystalline domain and random entanglements in the amorphous region, leading to a low load-bearing capability.

In our calculation, it is assumed that there is only one residual in the asymmetric unit. This assumption implies that the neighbouring molecular chains all have the same conformation and orientation. This does not account for

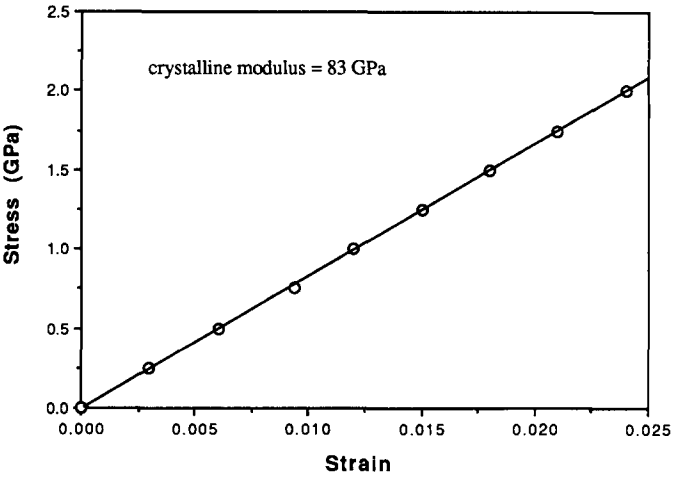

Figure 1 Calculated stress–strain curve for sPS

the possibility that a particular spatial correlation might exist between adjacent molecules. However, validity of this simplified assumption is assured in view of the absence of interchain electrostatic interactions and hydrogen bonding in the structure of sPS. The contribution of van der Waals interchain interaction to the tensile modulus is not significant. In fact, this energy term tends to decrease when the molecular chains are extended in the c axis direction (i.e. neighbouring chains tend to pack even closer together due to the mutual attraction generated by van der Waals interactions). One interesting consequence from doubling the unit-cell dimensions in both a and b axis directions is a new unit cell with dimensions $a = 14$ Å, $b = 21$ Å, and containing four molecular chains. This geometry approaches the results reported by Chatani[10], where his unit cell also consists of four molecular chains with cell dimensions $a = 12.9$ Å, $b = 19.8$ Å, $\gamma = 95°$. One conclusion could be that the van der Waals force, although exerting little influence on the tensile modulus, still plays an important role in determining the overall unit-cell size.

The inherent planar zigzag structure of sPS implies a negligible energy contribution from the rotational torsion in the calculation. The stiffness of crystalline sPS is mainly from intrachain interactions involving bond stretching and bending, of which the energy terms increase the most corresponding to the applied stress. The large benzene side group apparently prevents the close packing of the molecular chains and leads to the expanded *ab* cross sections for sPS. Comparatively, polyethylene (PE), having similar planar zigzag conformation, and without large side groups, tends to pack more densely. The orthorhombic polyethylene with lattice dimensions $a = 7.4$ Å, $b = 4.9$ Å accommodates two molecules in each unit cell. The average cross-sectional area for each molecule is approximately 18 Å^2 compared with 70 Å^2 for sPS. The resulting crystalline modulus of PE, with cited value 360 GPa[6] observed from Raman scattering, is almost four times higher than the value (83 GPa) obtained for sPS. This comparison demonstrates that the tensile modulus of a crystalline polymer, with planar zigzag chain conformation, is determined primarily by the basal area of an individual molecular chain. *Figure 2* shows the molecular packing in *ab* projection for the crystalline structure of sPS without any strain. The chain arrangement differs from that proposed by Chatani[10].

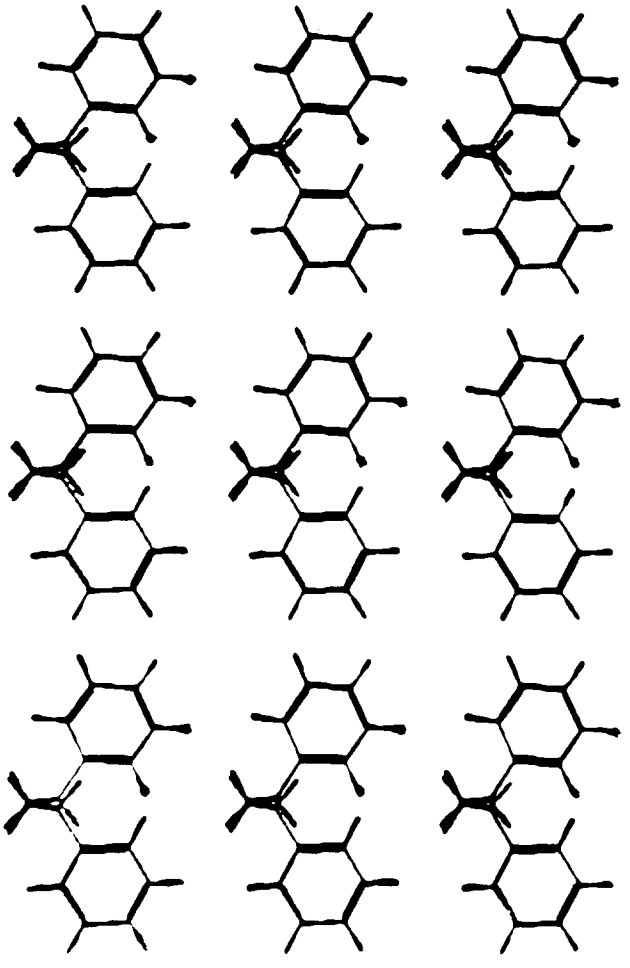

Figure 2 The *ab* projection of molecular conformation and chain packing for crystalline sPS

The preliminary model needs to be refined to consider more complicated spatial correlations between the neighbouring chains, especially when the deformations initiated by shear stresses are considered. A number of studies have been carried out to predict the conformation of a single molecular chain of sPS, but only limited data are available concerning the interchain packing, so the exact symmetry in the crystalline structure is still controversial. From transmission electron microscopy, Greis *et al.*[4] proposed a structure for sPS with the space group $P\bar{6}2c$, and postulated a model that three macromolecules form clusters through van der Waals contact. The other possible packings with space group $P2_12_12_1$ for an orthorhombic and $P2_1/a$ for a monoclinic unit cell were also reported[10]; nevertheless the exact arrangement is still not well understood. By examining these different packings, we observed that the average area of cross section (in *ab* plane) occupied by one molecular chain is almost identical. This suggests that there should be no significant difference in calculating tensile modulus, if different models are selected. In future work we plan to use molecular modelling combined with X-ray diffraction analysis to examine systematically the molecular conformation and chain packing in order to refine the existing model. Studies of the properties of crystalline sPS under compression and shear stress are also in progress and will be reported in a forthcoming paper.

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