

MOLECULAR SIMULATION TECHNIQUE ON POLYMERIC MATERIALS*

YANG Xiaozhen (杨小震)

(Polymer Physics Laboratory, Institute of Chemistry,
Academia Sinica, Beijing 100080)

Molecular simulation, or molecular modeling, is recently fast emerging as an important technique of both the research in polymer science and the design of polymeric materials. Not only single chain behavior but also bulk properties of amorphous^[1-5], crystalline^[6-8], and liquid crystalline polymers^[8,9] can be investigated by this technique. In other fields of science such as biochemistry and pharmaceutical chemistry, molecular simulation has already been established itself as an extremely powerful tool. Although conformational properties of single chain of polymers have been studied since 1960's^[10,11], the importance of simulation in the polymer field is only around 1990 beginning to be recognized widely. Requirements for such investigations, such as powerful computers, valid force field, efficient algorithms and user—friendly software, are much more demanding. The appearance of these new comers in recent years, however, made it possible for problems in polymers to be investigated by molecular simulation techniques. The achievements in this area as will be mentioned below would make people believe that a door leading to the stage of designing new polymer materials without chemical synthesis is open.

Molecular simulation technique includes many methods such as quantum mechanics^[12], molecular mechanics (MM)^[13], molecular dynamics (MD)^[14], Brownian dynamics^[15], Monte Carlo (MC)^[16], etc. For a molecular system, we can express the positions and the momenta of all atoms, n , in the molecules

$$\mathbf{q} = (q_1, q_2, \dots, q_n)$$

$$\mathbf{p} = (p_1, p_2, \dots, p_n)$$

Then we have the Hamiltonian of the system

$$H(\mathbf{q}, \mathbf{p}) = K(\mathbf{p}) + V(\mathbf{q})$$

where the kinetic term

$$K(p) = \sum_{i=1}^n \frac{1}{2m_i} (p_{x,i}^2 + p_{y,i}^2 + p_{z,i}^2)$$

and the potential term describing an interaction of multi-body problem

$$V(q) = \sum_i V_1(q_i) + \sum_i \sum_j V_2(q_i, q_j) + \sum_i \sum_j \sum_k V_3(q_i, q_j, q_k) + \dots$$

To calculate various physical variables of the system, one can either optimize the geometry structure on one hand, or solve the equation of motion

$$\dot{p} = -\frac{\partial H}{\partial q} \quad ; \quad \dot{q} = \frac{\partial H}{\partial p}$$

numerically as a function of time on the other hand.

Ab-initio quantum chemical methods offer a reliable and nonempirical approach for the calculation of molecular geometry and conformational energies. MM is able to calculate a system consisted of thousands of atoms. MD provides more features on description of molecular system, such as with kinetic energy term, the temperature-dependence, and the time-dependence. Brownian dynamics is an alternative approach to MD when the behaviors of deformation of polymer chain at large time scale or transportation at large distance displacement need to be calculated. MC is convenient to generate long polymeric chains in certain thermodynamic state. Among these methods, as shown in Table 1, MD possesses remarkable advantages for molecular simulation. It is able to describe the kinetic energy of the system, and also to describe the spatial coordinate and the momentum at every moment for each atom in the system. As a result, one can describe a molecular system in the static and the dynamic state by using molecular simulation technique. One can describe the properties and the behaviors of the system as well.

Table 1 The methods and properties of molecular simulation technique

Method	Potential energy	Kinetic energy	Temperature	q, p as a function of time
Quantum mechanics	yes	no	no	no
Molecular mechanics	yes	no	no	no
Monte carlo	yes	no	yes	no
Molecular dynamics	yes	yes	yes	yes

Up to now in polymer science, molecular simulation technique has been extensively applied to crystalline structure^[6-8], amorphous structure^[1-5,17], mechanical properties^[7,18-20], the glass transition^[2,5,21], electrical and optical properties^[22,23], diffusion in polymers^[24,25], polymer blends^[26], liquid crystalline structure^[7,9], conformational state transition^[6,27,28], phase transition^[8,29], thermodynamic properties^[18] and other interesting fields. In this article, the simulation on the amorphous structure and the conformational state transition is dealing with at the beginning, and the crystalline structure and mechanical properties is focused on more intensively.

Amorphous structures

Detailed molecular structure in the amorphous phase used to be a thorny problem. There have recently been two ways to approach the structure by using molecular simulation technique. In general, a periodic box is needed to hold polymer chains inside. One way of the approach is a computationally more efficient technique proposed by Ludovice and Suter^[31], who used a rotational isomeric-state model for the unperturbed chain to make the initial chain structure. In the other way, a chain with random distribution of dihedral angles at the internal C—C bonds can also be used as the initial structure^[17], then a relaxed structure is obtained by application of cycles of energy minimization and molecular dynamics at a very high temperature. Calculated amorphous structure of atactic polypropylene^[5] was compared with observed X-ray structure factor in the low-Q region^[31]. Clearly, the agreement in peak positions and relative heights is excellent. Thus indicating that the model polymer reproduces the intermolecular structure of the actual material. Simulated volumetric expansion coefficients in the liquid state and in the glass state are $8.27 \times 10^{-4}/\text{K}$ and $3.16 \times 10^{-4}/\text{K}$, which are very close to the experimental value, $8.10 \times 10^{-4}/\text{K}$ and $2.7 \times 10^{-4}/\text{K}$, respectively.

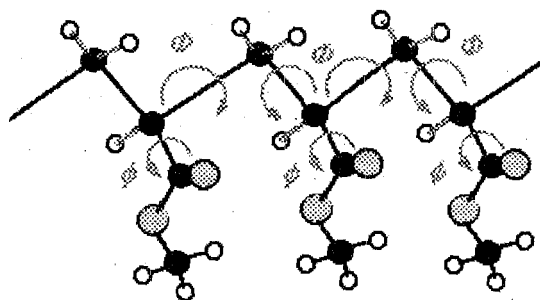


Fig. 1 The side-group reorientation during conformational state transition

Conformational state transition

The conformational state transition of polymer chains relates to crystallization processes, migration of the chains in solution, fluctuation of the end-to-end distance of random coils, and the relaxation and phase transitions of polymers. A description of the conformational state transition requires questions about how many stable conformational states for a specific σ bond; about the barriers between the states; about the mechanism of the conformational transition; and about any cooperative behavior during the transition. Flory and his coworkers made excellent works on statistical mechanics of polymer chains and determined some of the answers^[11]. A number of studies on transitions between rotational isomers in polymer chains were carried out by using MD^[6,27,29,32]. The time scale of the motion of conformational state transition is on the order of nanoseconds or less. It is well suited for investigation by simulation of MD. A run over 3.7 ns at 400 K for $C_{50}H_{102}$ reveals the transition occurs at all of the internal C—C bonds^[32]. It was found that transition correlations between rotational isomeric transitions at bond i and $i \pm 2$ are in much the same manner as in the Brownian dynamics simulations^[33]. On the other hand, the side-groups must reorient during conformational state transition along the backbone, which is an important cooperative behavior to be understood. In the early studies, with a rigid model, this could not be described. Recently, a full relaxation model was adopted to investigate this important behavior for polypropylene and poly(methyl acrylate) by using MM^[28]. The side group reorientations along the low energy pathways for both polymers were obtained. A 20° rotation was found for each methyl group of polypropylene. A large cooperative rotation, $\sim 130^\circ$, is needed for the two ester groups of poly(methyl acrylate) to climb over the energy barrier.

Crystalline structure and mechanical properties

The crystalline cells of polyethylene (PE)^[7], poly(butylene terephthalate) (PBT)^[8], poly(p-benzamide) (PBA)^[7], poly(p-phenylene terephthalamide) (PPTA)^[7,34], and poly(benzobisoxazole) (PBZO)^[30] were simulated and well coincided with the cell parameters obtained experimentally. X-ray diffraction patterns simulated for the unit-cells of those polymers appear very similar to the observations.

It would be a dream of chemists to design a polymer of mechanical material immediately from chemical structure. However, there are so many critical points in between to be understood. One of them is the crystalline cell. In general, molecular crystals possess anisotropic feature in inter-

molecular interaction. Specially, the feature is remarkably enhanced in polymer system. In polymer mechanics, the crystalline cell is once focused on as a basic unit to describe macroscopic mechanical behavior of whole polymeric materials, anisotropic elastic constants of crystals of the polymers have to be known at first. Generally, the number of the anisotropic elastic constants is 21 for the lowest symmetry case, the triclinic crystal; 13 for monoclinic symmetry; 9 for orthorhombic; 5 for hexagonal and 3 for cubic symmetry. Since difficulties lie in measuring these parameters experimentally so far, most of the features of these anisotropic variables are still remained unknown.

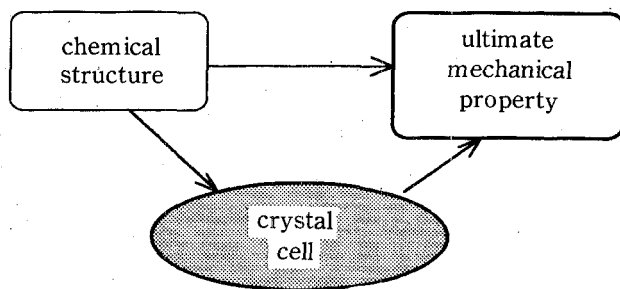


Fig. 2 The importance of the mechanical property of the unit cell in designing of new mechanical polymeric materials

Molecular simulation technique has nowadays been a challenge in solving this problem. Recently, the technique was used to three polymers, PE, PBA and PPTA with orthorhombic crystalline cell. POLYGRAF and CERIUS were used to perform the simulation analysis. Periodic boundary conditions were employed to model an infinite system, to eliminate the perturbations from polymer ends and to incorporate both non-bonded intermolecular and intramolecular interactions. In order to calculate elastic constants, either strain along a particular plane or applied stress to one of the planes associated with the unit cell was induced. The entire structure was then minimized with these constraints present. The values obtained from these theoretical stress strain experiments were then used to calculate the elastic constants.

In order to validate the simulation procedure, the unit cells for three polymers, PE, PPTA and PBA were simulated (Figure 3). For PE the repeat along the chain was calculated accurately (1.18% error). The maximum deviation was along the B axis at 4.04%. The setting angle is 42° . The unit cell parameters calculated for the strongly hydrogen bonded systems such as PPTA and PBA, were extremely accurate for the C axis repeat (0.6% and

1.25% error respectively) and least accurate for stacking distance of hydrogen bonded planes (the maximum error was 6.92% for PPTA). The repeat containing interchain hydrogen bonds was accurately simulated. The dihedral angle for the adjacent phenylene rings was $\sim 72^\circ$. The dihedral angle between the phenylene ring plane and the amide group were 32° and 37° , close to experimental values, 30° and 38° ^[35].

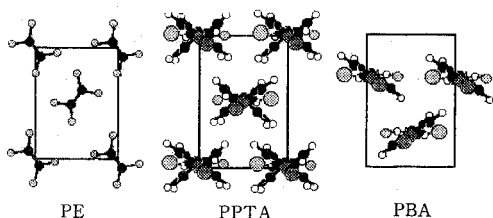


Fig. 3 Simulated unit cell for PE, PPTA and PBA

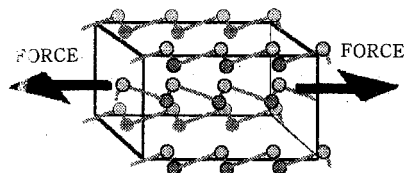


Fig. 4 Simulated deformation of the unit cell under external forces

The anisotropic elastic constants were calculated for the polymers. Features of these anisotropic elastic constants for various polymers were compared with the experimental data and the theoretical values done before, and discussed according to various interaction energies such as the bond stretching energy, the bond angle bending energy, the torsion energy, the van der Waals energy and the hydrogen bond energy, etc.

The longitudinal modulus calculated for PE was 280 GPa, slightly lower than the 290 GPa obtained from Raman or neutron scattering experiments. The transverse elastic constants were calculated to be ~ 10 GPa, somewhat lower than the values measured for n-alkanes (13–16 GPa). The shear moduli of PE, G_{yz} and G_{xz} were found to be 5.0 and 2.4 GPa respectively, as compared to the 3.7 and 1.5 GPa found in an earlier study^[36].

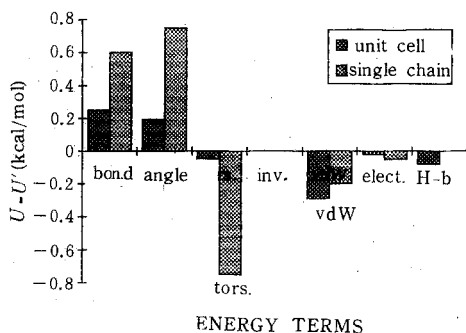
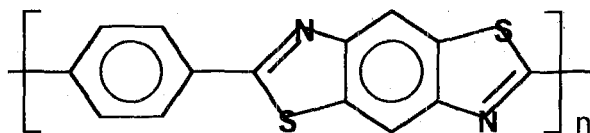


Fig. 5 Decomposition of the energy change $U - U'$ associated with PBA under longitudinal deformation in the case of the unit cell and in the case of the single chain. The energy terms: the bond, the angle, the torsion, the inversion, the van der Waals, the electrostatics and the hydrogen-bond

For the aromatic polyamides, authors found a value of 335 GPa for PPTA, whereas the experimental value is only 153 GPa. A number of

factors, including degree of crystallinity, segmental orientation, lattice distortion, and packing defects, can all lower the longitudinal modulus in experiments. What is surprising is that the values calculated were considerably higher than the ones calculated earlier using single chain approximation^[37].

For PE, the deformation behavior of the unit cell was not different from the single chain approximation. For PPTA which was deformed longitudinally, most of the strain was divided into contributions from the bonds and the valence angles. However, when PPTA crystals were sheared, strongly hydrogen bonded interactions dominated the restoring force. These calculated results generally reveal a different deformation mechanism. Very similar behavior occurred to the other aromatic polyamide, PBA. For the full unit cell calculation, the modulus was found to be 322 Gpa. The decomposition of the energy is shown in Figure 5; the intrachain interaction and the interchain interaction are all important. The energy from the bond stretching term is as large as that in the case of PE taking the top position in the bonded interactions. When eliminating the interchain interactions, a single chain approximation was used. A completely different deformation mechanism, therefore, turned out; the torsional term became the dominant one (Figure 5). Consequently, modulus of the PBA chain decreased to 207 Gpa. This result clearly illustrates the importance of intermolecular interactions. When these terms are included, the degree of freedom associated with valence angle bending and torsional motions becomes severely restricted. Most of the strain is taken up by bond deformation, thereby raising the longitudinal modulus so that it is considerably higher than the one would be predicted by using the single chain approximation.



Another very interesting new polymeric material is the wholly aromatic, heterocyclic rigid rod polymer, poly (p-phenylene benzobisthiazole) (PBZT), possessing high-modulus, high-strength and good thermal stability. As revealed in extensive studies^[38-42], the rigid chains of the polymer are likely to align to a very high extent but exist with irregularly axial shift of the chains along chain axis. No suitable crystals of PBZT have so far been obtained for a perfect structural observation of X-ray diffraction or Electron diffraction. One day, a new way may be found to make a perfect crystal of the polymer. However, the reason of difficulty in or the mechanism of forming very ordered crystals from PBZT chains, nowadays, remains unknown.

In recent study^[43], possibilities of the chains packing in crystal were examined by molecular simulation technique. The possible answer for the difficulty was thus proposed.

The conformation of the stiff chain drew more attention in the past twelve years. Molecular mechanics,^[40] and semi-empirical molecular orbital calculations, such as CNDO/2, MNDO, AM1,^[42,44] were used for the subject. The minimum energy torsion angle of the bond between the phenylene ring and the heterocyclic ring in the repeat of the polymer was obtained to be 20° from CNDO/2^[42] and 29° from AM1.^[44] Even though these values are very close to 23° that is experimentally measured from a model compound^[41] for the dihedral angle, the barrier of this torsion at 0° is markedly small, 0.5 kcal/mol^[42] or 0.11 kcal/mol,^[44] in comparison with the main barrier at 90°, 6.0 kcal/mol^[42] or 0.75 kcal/mol.^[44] In other words, there is an energy basin centered at 0° broadening to about $\pm 20^\circ$ for the torsion angle. Calculation in the work using a newly developed semi-empirical quantum mechanics method, PM3,^[45] for the model Φ -H gave a much similar stable torsion angle 20° (where Φ =phenylene ring, H=heterocyclic ring). For the model Φ -H- Φ , the two stable torsion angles calculated under the key word "PRECISE" are 20° and 16°. For the model H- Φ -H, they are 20° and 10°. These results support the early studies in two points, that is, the stable torsion angle is around 20°, and the energy well is broad especially at the side down to 0°.

Furthermore, interchain interaction of PBZT was studied with a model of two infinite chains, which is different from the model in the early study.^[46] This is to avoid interaction effect of the chain ends. Two of the models were designed in the simulation. The difference between the two is on the torsion angle that has been mentioned above. In the model 1, the torsion angle is 20°, and it is 0° in the model 2. The interaction behaviors of the two chains calculated from the two models are substantially different. As shown in Figure 6, the low energy contours that are under 1.0 kcal/mol are located around the shifts of 0.9–1.2 nm while the chains are 0.35–0.36 nm apart. Alternatively, the shifts of the contours can be read as 0–0.3 nm since it is a relative shift with the periodic length ~ 1.22 nm as PBZT repeat. The minimum of the interchain interaction is at the point of the 0.16 nm or 1.06 nm shift and the 0.35 nm apart. This minimum is even close to the one in the early study.^[46]

The different features of the model 2 is shown in Figure 7. A lot of low energy wells are located side by side as the two chains are 0.35–0.36 nm apart. In the view of the 1.0 kcal/mol energy contour, it likes a channel

towards the 0.35–0.36 nm in the abscissa and along the ordinate from 0.1 to 1.1 nm. The 0.5 kcal/mol energy contour makes another channel that is along the ordinate from 0.3 to 0.9 nm and towards the same range in the abscissa. In turn, three wells are made of the energy contours under 0.3 kcal/mol. Their shifts along the ordinate are around 0.18 nm, 0.56 nm and 0.7 nm.

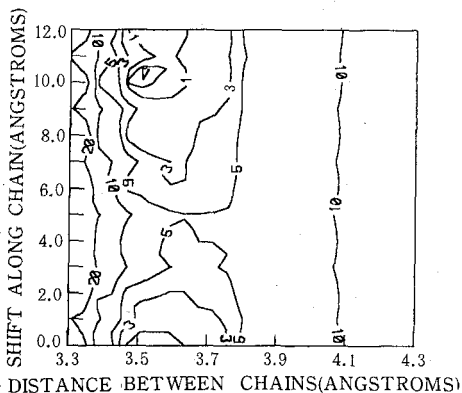
TWO PARALLEL INFINITE PBZT CHAINS^[20]

Fig. 6 Energy contour map of the interchain interaction of two parallel PBZT chains, the model 1, in which the torsion angle between the phenylene ring and the heterocyclic ring is 20°. The numbers along with the contour lines are in kcal. The contour levels from the minimum to the maximum are 0, 0.3, 0.5, 1, 3, 5, 10, 20.

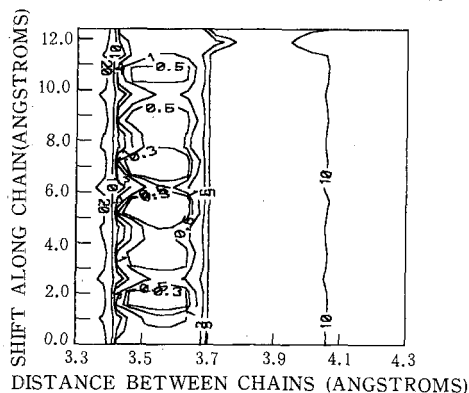
TWO PARALLEL INFINITE PBZT CHAINS^[20]

Fig. 7 Energy contour map of the interchain interaction of two parallel PBZT chains, the model 2, in which the torsion angle between the phenylene ring and the heterocyclic ring is 0°. The numbers along with the contour lines are in kcal. The contour levels from the minimum to the maximum are 0, 0.3, 0.5, 1, 3, 5, 10, 20.

Taking both the intrachain interaction and the interchain interaction into account, the packing difficulty of the chains was examined. Now, the PBZT chains are assumed to be fixed as the model 1 with a 20° torsion angle. Put them on the starting position in the contour map of Fig. 6 where the two chains shift from each other as far as 0.56 nm and located 0.35 nm apart. The potential force will make them slide along themselves down to the end position where their relative shift is 0.16 nm. As shown in the contour map, this move can make a ~ 5 kcal/mol energy decay. However, it was known in the study that in the conformational interaction of PBZT there is an energy basin centered at 0° broadening to about $\pm 20^\circ$ for the torsion angle. The obstacle in the basin, that is to be overcome for the torsion travelling down through, is under 0.5 kcal/mol. In reality, the two chains are able to undergo another path to reduce the packing energy. In the path, no shift occurs to the chains but the torsion angle turns to 0°. This change is

also a ~ 5 kcal/mol energy decay as shown in the above two Figures. With this suggestion, it is quite possible for the low energy channel to detain some chains in various positions and to impede the chain sliding. Combining the move of chain sliding and the move of torsion angle turning, there emerge so many energy stable positions that are much more than those revealed in the two models. The existence of such amount of stable positions obviously causes the difficulty of forming a unique perfect crystalline structure of PBZT.

Molecular simulation technique is nowadays able to reproduce the amorphous structures and the crystalline structures of polymers to a better extent, and to predict mechanical property of polymers quite reliable. This technique brings us to a new stage. This technique enables us to design a new polymeric material on the screen, and to select the better new candidates having the best physical property in computer, just before starting a huge of jobs to synthesize thousands of unknown polymers.

Keywords:

Molecular simulation; Molecular modelling; Polymers; Crystalline structure; Mechanical properties.

Acknowledgement This project has been supported by the National Basic Research Project—Macromolecular Condensed State, the National Natural Science Foundation of China and also supported by Polymer Physics Laboratory, Academia Sinica.

REFERENCES

- [1] Rigby, D. and Roe, R. J., *J. Chem. Phys.*, **1988**, 89, 5280.
- [2] Rigby, D. and Roe, R. J., *Macromolecules*, **1989**, 22, 2259.
- [3] Boyd, R. H. and Pant, P. V. K., *Macromolecules*, **1991**, 24, 4078.
- [4] Mansfield, K. F. and Theodorou, D. N., *Macromolecules*, **1991**, 24, 6283.
- [5] Sylvester, M. F.; Yip, S. and Argon, A. S. in "Computer Simulation of Polymers", Ed. by Roe, R. J., p105, Prentice Hall, New Jersey, **1991**.
- [6] Sumpter, B. G., Noid, D. W. and Wunderlich, B., *J. Chem. Phys.*, **1990**, 93, 6875.
- [7] Yang, X. and Hsu, S. L., *Macromolecules*, **1991**, 24, 6680.
- [8] Nitzsche, S. A.; Wang, Y. K.; Hsu, S. L., *Macromolecules*, **1992**, 25, 2397.
- [9] Pachter, R.; Bunning, T. J.; Adams, W. W., *Comput. Polym. Sci.*, **1991**, 1, 179.
- [10] Birshtein, T. M.; Ptitsyn, O. B., "Conformations of Macromolecules", Interscience, New York, **1966**.
- [11] P. J. Flory, "Statistical Mechanics of Chain Molecules", Interscience, New York, **1969**.
- [12] Pulay, P. in "Application of Electronic Structure Theory, Modern Theoretical Chemistry"; Schefer III, H. F., Ed.; Vol. 4, p153, Plenum Press, New York, **1977**.
- [13] S. Lifson and A. Warshel, *J. Chem. Phys.*, **1968**, 49, 5116.
- [14] Alder, B. J. and Wainwright, T. E. "Transport Processes in Statistical Mechanics", p97, New York: Interscience, **1958**.
- [15] Ermak, D. L.; McCammon, J. A., *J. Chem. Phys.*, **1978**, 69, 1352.
- [16] Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E., *J. Chem. Phys.*, **1953**, 21, 1089.
- [17] Lee, K-J; Mattice, W. L., *Comput. Polym. Sci.*, **1992**, 2, 55.

- [18] Fan, C. F. ; Hsu, S. L. , *Macromolecules*, **1992**, 25, 266.
- [19] Brown, D. ; Clarke, J. H. R. *J. Chem. Phys.* , **1986**, 84, 2858.
- [20] Brown, D. ; Clarke, J. H. R. *Macromolecules*, **1991**, 24, 2075.
- [21] Takeuchi, H. , *J. Chem. Phys.* , **1990**, 93, 2062.
- [22] Clough, S. B. ; Sun, X. F. and Tripathy, S. K. , *Macromolecules*, **1991**, 24, 4264.
- [23] Karasawa, N. ; Goddard III, W. A. , *Macromolecules*, to be published.
- [24] Sonnenburg, J. ; Gao, J. ; Weiner, J. H. , *Macromolecules*, **1990**, 23, 4653.
- [25] Takeuchi, H. ; Roe, R-J. ; Mark, J. E. , *J. Chem. Phys.* , **1990**, 93, 9042.
- [26] Fan, C. F. ; Olafson, B. D. ; Blanco, M. ; Hsu, S. L. , *Macromolecules*, **1992**, 25, 3667.
- [27] Doherty, D. C. ; Hopfinger, A. J. , *Macromolecules*, **1989**, 22, 2472.
- [28] Yang, X. ; He, L. ; An, B. ; Ma, D. , Proceedings of the Second International Conference Computer Applications to Materials and Molecular Science and Engineering, Pacifico, Yokohama, Japan, Sept. 22—25, **1992**.
- [29] Doherty, D. C. ; Hopfinger, A. J. , in "Computer Simulation of Polymers", Ed. by Roe, R. J. , p55, Prentice Hall, New Jersey, **1991**.
- [30] Yang, X. , Preprints of Third National Symposium on Molecular Mechanics and Pharmacy Designation, p7, Beijing, **1991**.
- [31] Ludovice, P. J. , Suter, U. W. , *Macromolecules*, **1985**, 18, 1467.
- [32] Zuniga, I. ; Bahar, I. ; Dodge, R. ; Mattice, W. L. , *J. Chem. Phys.* , **1991**, 95, 5348.
- [33] Helfand, E. ; Wasserman, Z. R. ; Weber, T. A. , *J. Chem. Phys.* , **1979**, 70, 2016.
- [34] Rutledge, G. C. ; Suter, U. W. ; Papasporides, C. D. , *Macromolecules*, **1991**, 24, 1934.
- [35] Northolt, M. G. , *Eur. Polym. J.* , **1974**, 10, 799.
- [36] McCullough, R. L. ; Peterson, J. M. , *J. Appl. Phys.* , **1973**, 44, 1224.
- [37] Tashiro, K. ; Kobayashi, M. ; Tadokoro, H. , *Macromolecules*, **1977**, 10, 413.
- [38] Minter, J. R. ; Shimamura, K. ; Thomas, E. L. , *J. Mater. Sci.* , **1981**, 16, 3303.
- [39] Odell, J. A. ; Keller, A. ; Atkins, E. D. T. ; Miles, M. J. , *J. Mater. Sci.* , **1981**, 16, 3309.
- [40] Welsh, W. J. ; Bhaumik, D. ; Mark, J. E. , *Macromolecules*, **1981**, 14, 947.
- [41] Wellman, M. W. ; Adams, W. W. ; Wolff, R. A. ; Dudis, D. S. ; Wiff, D. R. ; Fratini, A. V. , *Macromolecules*, **1981**, 14, 935.
- [42] Welsh, W. J. , *J. Mater. Sci.* , **1983**, 18, 1119.
- [43] Liu, Y. ; Yang, X. , *Chinese Chem. Lett.* , **1993** , 4, 779.
- [44] Farmer, B. L. ; Wierschke, S. G. ; Adams, W. W. , *Polymer*, **1990**, 31, 1637.
- [45] Dewar, M. J. S. , *J. Comput. Chem.* , **1990**, 11, 541.
- [46] Bhaumik, D. ; Welsh, W. J. ; Jaffe, H. H. ; Mark, J. E. , *Macromolecules*, **1981**, 14, 951.