

Research
ReportHierarchical Procedure Bridging the Gap between Mesoscopic
and Atomistic Simulations for Materials Design

Satoru Yamamoto

材料設計のためのメソとミクロをつなぐ階層的シミュレーション

山本智

Abstract

A hierarchical procedure bridging the gap between atomistic and mesoscopic simulations for materials design is presented. A dissipative particle dynamics (DPD) is adopted for a mesoscopic simulation technique. In this method, a molecular structure is represented using a coarse-grained model, connecting soft spherical particles that correspond to a group of several atoms. The interaction parameters of the mesoscopic model, which are related to Flory-Huggins χ -parameters, are estimated by calculating the energy of mixing for each pair of components in the atomistic simulation. Mesoscopic structures of the binary polymer blend are simulated with realistic χ -parameters using DPD. This bridging method from the atomistic to the mesoscopic level is applied to prediction of the mesoscopic structure of a hydrated polyelectrolyte membrane for fuel cells.

The simulated structure of the membrane and its dependence on water content are in good agreement with experimental reports. For a reverse bridging method for different scale simulations, the molecular structure at the interface is extracted from the simulated mesoscopic structure by mapping atoms to the concentration profile of each component using a Monte Carlo technique. The complicated morphology of the binary polymer blend is successfully generated using this procedure. In the case of a hydrated polyelectrolyte membrane, an atomistic structure of a water channel is generated based on the mesoscopic structure. It is confirmed that the number of water molecules in the first coordination shell around the sulfonic acid group is of the same magnitude as the experimental study.

Keywords

Multiscale simulation, Mesoscopic simulation, Atomistic simulation, Dissipative particle dynamics, Molecular mechanics, Molecular dynamics, Polymer blend, Polyelectrolyte membrane, χ -parameter

要 旨

材料設計を目的としてミクロとメソ領域の計算を階層的に結合する手続きを提案した。メソ領域の計算法として散逸粒子動力学法を用いる。この方法では数個の原子集団を一つの粒子で表した粗視化モデルを用いて分子を表現する。粒子間の相互作用はFlory-Hugginsの χ パラメータに対応し、各粒子が表す化学種間の混合エネルギーを分子シミュレーションにより求めて用いる。このように決めた χ パラメータを使って、2成分ポリマーブレンドのメソ構造の計算を行った。このミクロからメソへつなぐ手続きを含水した燃料電池用高分子電解質膜のメソ構造予測に適用し、その結果得

られた構造は含水率依存性を含めてこれまでに報告されている実験と一致することを確認した。一方、メソからミクロへつなぐ方法として、計算したメソ構造の界面における濃度プロファイルに対応する分子モデルをモンテカルロ法を使って抽出することを試みた。2成分ポリマーブレンドの系ではこの方法により複雑なモルフォロジーを持ったメソ構造に対しても分子モデルを作成することができた。高分子電解質膜についてもメソ構造に基づいて分子モデルを作成し、スルホン基に配位する水分子の数が実験と一致することを確認した。

キーワード

マルチスケールシミュレーション, メソスケールシミュレーション, 原子論的シミュレーション, 散逸粒子動力学法, 分子力学法, 分子動力学法, ポリマーブレンド, 高分子電解質膜, χ パラメータ

1. Introduction

Atom-based simulations such as molecular dynamics (MD) and molecular mechanics (MM) methods have come into wide use for materials design. Using these atomistic simulation tools, we can analyze molecular structure on the scale of 0.1–10 nm. However, difficulty arises concerning limitations of the time- and length-scale involved in the simulation. Although a possible molecular structure can be simulated by the atom-based simulation, it is less realistic to predict the mesoscopic structure defined on the scale of 0.1–10 μm , for example the morphology of polymer blend and composite, which often dominates actual material properties. For the morphology on these scales, mesoscopic simulations such as dynamic mean field theory (MF)^{1, 2)} and dissipative particle dynamics (DPD)^{3–6)} are available as an alternative to atomistic simulation. It is therefore inevitable to adopt a mesoscopic simulation technique and bridge the gap between atomistic and mesoscopic simulations for an effective materials design.

In this study, we present a hierarchical procedure for bridging the gap between atomistic and mesoscopic simulations. In this procedure, Flory-Huggins χ -parameters between two components of the coarse-grained molecular models in the mesoscopic simulation are estimated through the atomistic simulation, and a mesoscopic structure is predicted using these χ -parameters. Then, an atomistic model is extracted from a density profile of the mesoscopic simulation results using a Monte Carlo technique. We demonstrate a series of procedures for immiscible polymer blend systems and a polyelectrolyte membrane for fuel cells.

2. Method

There are various simulation methods by which to study a mesoscopic structure, e.g. the time-dependent Ginsburg-Landau theory, the dynamic density functional theory, lattice-gas automata, and the lattice Boltzmann equation.^{7–10)} Some of these simulation methods, such as the dynamic mean field theory (MF) and dissipative particle dynamics (DPD) utilize coarse-grained molecular models to study the morphology of inhomogeneous materials

using Flory-Huggins χ -parameters between components. In this study, we adopt DPD as the mesoscopic simulation technique because of its convenience regarding a bridging procedure to the atomistic system, the simplicity of the simulation model and algorithm, and the simulation performance. In this case, estimating the χ -parameter using an atomistic simulation provides one method by which to bridge from atomistic to mesoscopic simulation. Then, we can predict mesoscopic structure more reliably using realistic χ -parameters based on the atomistic simulation. Next, as a way of bridging in the opposite direction from mesoscopic to atomistic simulation, an atom-based molecular model is extracted so as to be consistent with the concentration profile obtained by the mesoscopic simulation. This cooperative procedure is illustrated in **Fig. 1**, and shall be described in the following sections.

2.1 From atomistic to mesoscopic simulation

Mesoscopic simulations such as the mean field theory (MF)^{1, 2)} and dissipative particle dynamics (DPD)^{3–6)} are performed using a coarse-grained molecular model as shown in **Fig. 2** with the solubility parameters, that is the χ -parameter. The particle in mesoscopic simulation is related to a

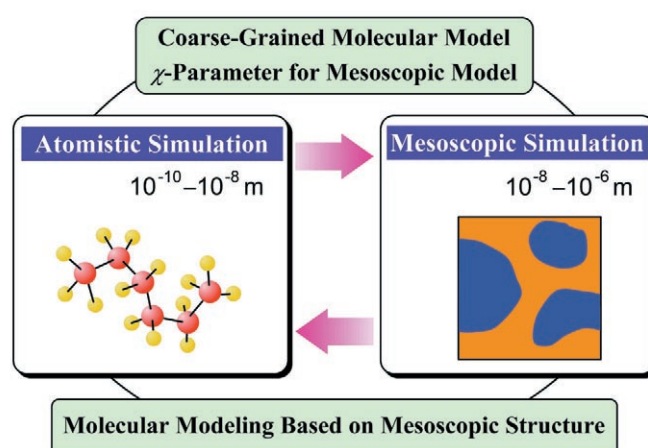


Fig. 1 Conceptual illustration of cooperation between atomistic and mesoscopic simulations.

group of several atoms in the atomistic simulation. In this study, we adopt DPD as a mesoscopic simulation technique and describe herein an outline of this method.

In the DPD simulation, the time evolution of interacting particles, the set of positions and velocities $\{\mathbf{r}_i, \mathbf{v}_i\}$, is governed by Newton's equation of motion (**Fig. 3**). The force acting on a particle is given by a conservative force $\mathbf{F}_{ij}^C$, a dissipative force $\mathbf{F}_{ij}^D$, a pair-wise random force $\mathbf{F}_{ij}^R$ and an extra spring force for binding the particles together $\mathbf{F}_{ij}^S$.

$$\mathbf{f}_i = \sum_{j \neq i} (\mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R + \mathbf{F}_{ij}^S) \quad \text{.....(1)}$$

Mutual solubility is considered in the conservative

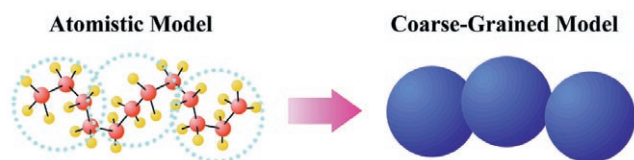


Fig. 2 Coarse-grained modeling from atomistic model.

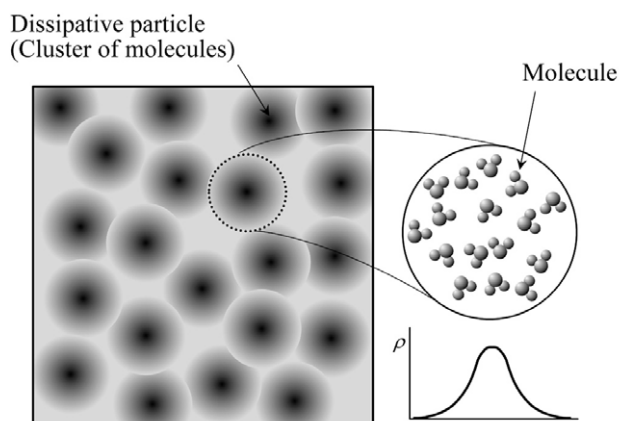


Fig. 3 Schematic illustration of the DPD system.

interaction, which is represented by

$$\mathbf{F}_{ij}^C = \begin{cases} -a_{ij} \left(1 - \frac{|\mathbf{r}_{ij}|}{r_c}\right) \mathbf{n}_{ij} & |\mathbf{r}_{ij}| < r_c \\ 0 & |\mathbf{r}_{ij}| \geq r_c \end{cases} \quad \text{.....(2)}$$

where a_{ij} is the maximum repulsion between particles i and j , $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$, $\mathbf{n}_{ij} = \mathbf{r}_{ij} / |\mathbf{r}_{ij}|$, and r_c is the interaction range. The repulsion parameters between particles in the conservative forces are related to the χ -parameters. For the case in which the reduced density ρ is 3, this relation is as follows:

$$a_{ij} = a_{ii} + 3.27\chi_{ij} \quad \text{.....(3)}$$

Several different computational methods are available for the estimation of χ -parameters between polymer-polymer, polymer-solvent, or solvent-solvent systems.¹¹⁻¹⁶⁾ In this study, we estimate χ -parameters from analysis of bulk atomistic simulations of blends and single component systems. The cohesive energies are calculated for pure components 1 and 2, and their mixture using a molecular mechanics technique (**Fig. 4**). Then, we can estimate the mixing energy and χ -parameter between components 1 and 2 from the energy of mixing ΔE_{mix} using an atomistic simulation,

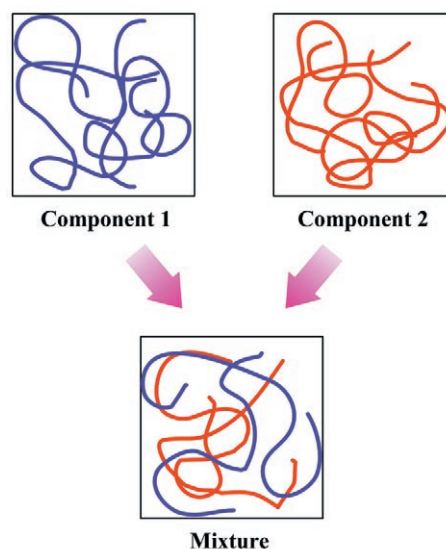


Fig. 4 Procedure of calculation of the mixing energy of two components.

$$\chi = V_{\text{seg}} \left(\frac{\Delta E_{\text{mix}}}{RT} \right) \quad \dots\dots\dots(4)$$

where V_{seg} is the volume of one polymer segment corresponding to the particles size in the DPD. Here, ΔE_{mix} is defined by the cohesive energy densities E_{coh}/V for pure components and their blends, calculated from the cohesive energy E_{coh} per volume V .

$$\Delta E_{\text{mix}} = \frac{1}{2} \left(\frac{E_{\text{coh}}}{V} \right)_1 + \frac{1}{2} \left(\frac{E_{\text{coh}}}{V} \right)_2 - \left(\frac{E_{\text{coh}}}{V} \right)_{12} \quad \dots\dots\dots(5)$$

To perform an atomistic calculation on the cohesive energy, we used molecular mechanics (MM) and molecular dynamics (MD) simulations. First, for each system of pure components and their blends, the amorphous state is generated in a periodic cell. For each system, MD calculation is performed and the energy of the system is equilibrated. Then, the energies of the system with and without periodic boundaries are calculated by MM simulation, and the cohesive energy is estimated using the following equation:

$$E_{\text{coh}} = E_{\text{non-periodic}} - E_{\text{periodic}} \quad \dots\dots\dots(6)$$

The quality of this atomistic study, of course, depends on the adopted forcefield. In order to assure reliable calculation, the use of a high quality forcefield and the validation of the cohesive energy by comparison with known experimental values are indispensable. By using realistic χ -parameters in cooperating an atomistic simulation, a reliable mesoscopic structure is predicted by the DPD simulation.

2.2 Molecular modeling based on mesoscopic structure

According to the simulated mesoscopic structure obtained by the DPD, a molecular structure is generated by a Monte Carlo technique (**Fig. 5**). This procedure is as follows:

1. Consider the concentration profile ϕ for the specific composition.
2. Generate an atom of desired molecule at a random position.
3. Acceptance or rejection for adoption of the generated atom is decided based on the concentration profile of the composition.

4. By repeating steps 2 and 3 for connecting atoms to the latest accepted atom, molecular structure is generated.

The above operation is continued until the concentration of the specific component reach the desired concentration.

After generating atom-based molecular models, we perform molecular mechanics (MM) and molecular dynamics (MD) simulations to obtain the stable structure without stress.

3. Application

3.1 Mesoscopic simulation

We demonstrate DPD simulation coupling with realistic χ -parameters for binary polymer blends of (a)PE(polyethylene)-PP(polypropylene), (b)PE-PS(polystyrene), and (c)PP-PS. The estimated χ -parameters for these mixtures by atomistic simulations with Dreiding force field¹⁷⁾ are listed in **Table 1**. These values allow the miscibility to be predicted as being on the (a)>(c)>(b) order. Then, mesoscopic structures are calculated for each polymer blend using the DPD simulation. **Figure 6** shows the concentration profiles and the density of each polymer for these mixtures. The thickness of the interface corresponds well to the miscibility

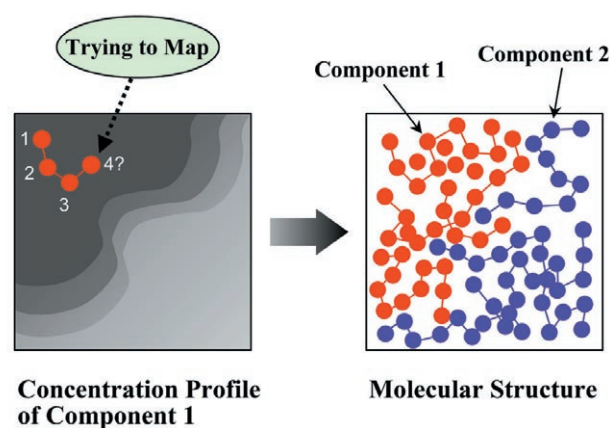


Fig. 5 Mapping of the molecular structure based on the concentration profile of mesoscopic structure.

order. Namely, in the case of the most miscible system of PE-PP, the thickness of the interface is the largest. On the other hand, the PE-PS system has a very thin interface because of the immiscibility PE and PP.

For more practical application of this procedure, the mesoscopic structure of a hydrated poly-electrolyte Nafion membrane is simulated.^{18, 19)} Nafion is a perfluorinated sulfonic acid membrane and is used in the polymer electrolyte fuel cell.²⁰⁾ There are several models for the structure of the membrane, however, which remains under discussion. A coarse-grained Nafion model is

Table 1 χ -parameter of binary polymer blends.

mixture	PE-PP	PE-PS	PP-PS
χ -parameter	0.09	0.71	0.21

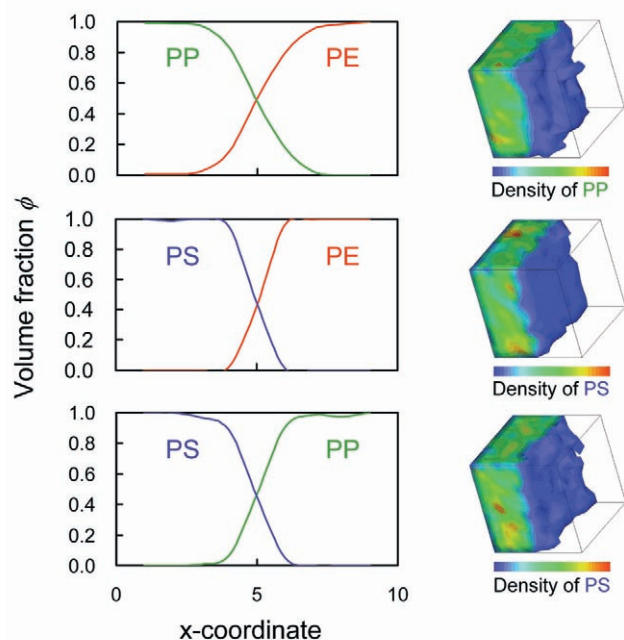


Fig. 6 Concentration profiles at an interface of binary polymer blend.

constructed, the χ -parameters of which are calculated using an atomistic simulation. DPD simulation reveals a sponge-like structure, as shown in **Fig. 7**. Water particles and hydrophilic particles of Nafion side chain form aggregates or clusters and are embedded in the hydrophobic phase of the Nafion backbone. Magnitudes of water clusters and their dependences on the water content are in good agreement with experimental reports. Although this sponge-like structure is essentially identical to the cluster-network model in previous experimental studies, the shape of water clusters is not spherical but irregular, and the water regions are indistinguishable structures of water clusters and their channels.

3.2 Molecular modeling

Molecular structures are generated by a Monte Carlo technique so as to be consistent with the concentration profile at the interface for binary polymer blends discussed in previous section (Fig. 6). **Figure 8** shows the carbon atoms of each polymer backbone and their connected bonds. Molecular structures are successfully obtained using this procedure, namely in the case of the most miscible system of PE-PP two components are most entangled at the interface. In this way, we can extract an atom-based molecular model from the mesoscopic structure.

Next, we applied this procedure to the complicated

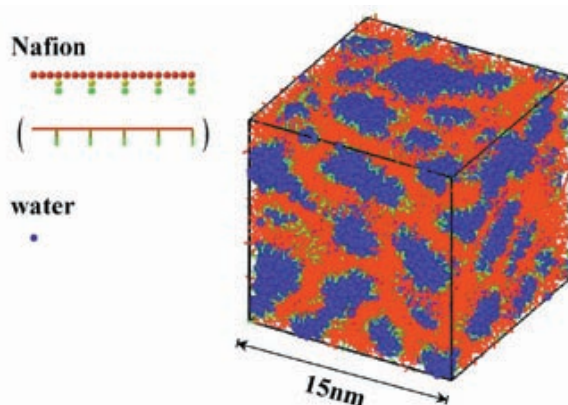


Fig. 7 Mesoscopic structure of a hydrated Nafion membrane simulated by DPD.

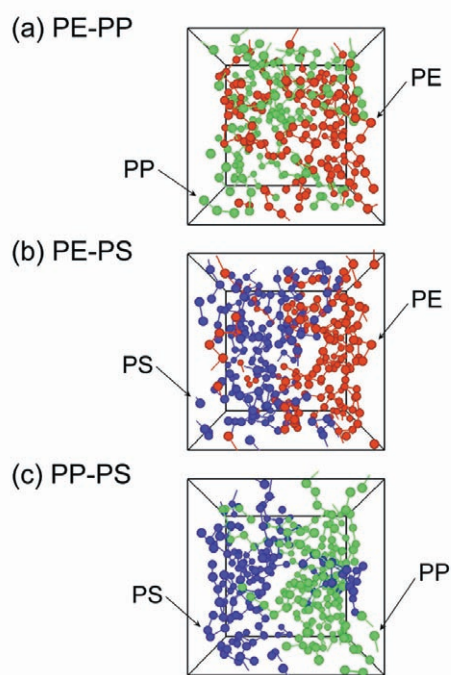


Fig. 8 Molecular structure at an interface of the binary polymer blend based on the mesoscopic structure in Fig. 6.

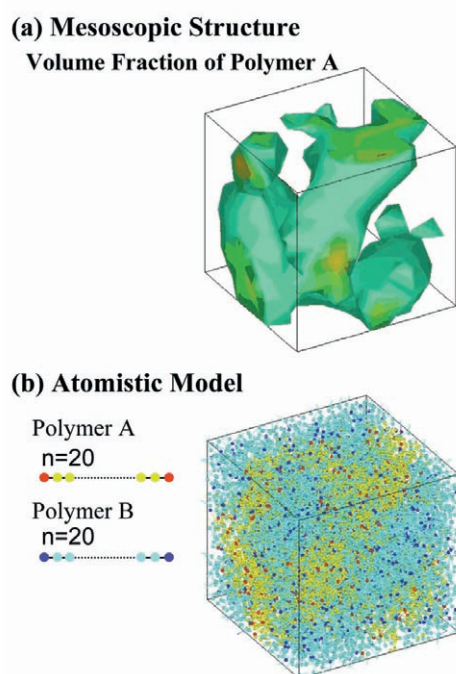


Fig. 9 Atomistic modeling of a complicated morphology of the binary polymer blend.

morphology of the binary polymer blend as shown in **Fig. 9**. In this system, two types of polymers (A and B) constructed from 20 monomer units are randomly mixed for the initial condition and then phase separation is calculated via the DPD simulation. Figure 9(a) shows the density profile of polymer A at a certain simulation step. An atomistic structure which corresponds well to the density profile of the mesoscopic structure is generated, as shown in Fig. 9(b). By using this atomistic model, we can perform a molecular dynamics simulation to study more realistic material properties such as gas diffusion at the interface.

Finally, in the case of a hydrated Nafion membrane, an atomistic structure of the water channel is generated based on the obtained mesoscopic structure (**Fig. 10**). After generating an atom-based molecular model, the model is optimized by MM simulations to obtain the stable structure without stress. It is observed that the sulfonic acid group is coordinated by water molecules within 0.5 nm. The number of water molecules in the first

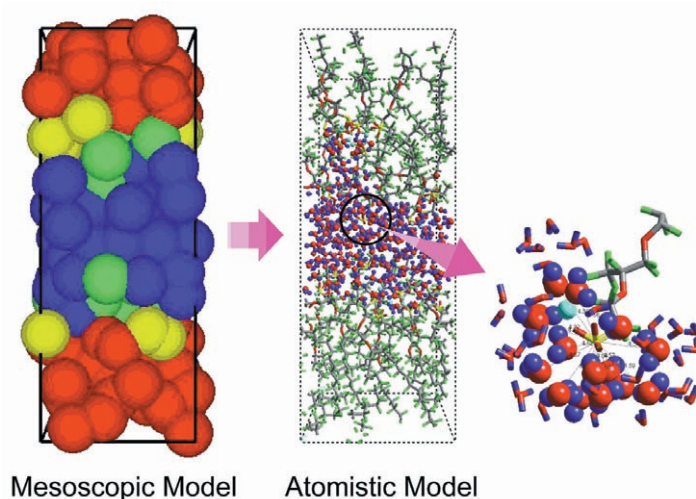


Fig. 10 Atomistic modeling of water channel based on the mesoscopic structure. Water molecules coordinating to the sulfonic acid group are rendered as spheres with radii related to the van der Waals radii at the right figure.

coordination shell around the sulfonic acid group is approximately nine (rendered as spheres, right-hand side of Fig. 10), the magnitude of which is identical to that of the experimental study.

4. Conclusion

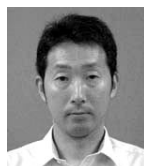
We have proposed a cooperative procedure to bridge the gap between atomistic and mesoscopic simulations, and have successfully demonstrated a method for binary polymer blends. For application of the bridging method from the atomistic level to the mesoscopic level, the mesoscopic structure of a hydrated Nafion membrane was simulated using the DPD with realistic χ -parameters. The predicted structure of the membrane was in good agreement with previous experimental reports. For a bridging method for different scales in the opposite direction, mapping of molecular structure was applied to the complicated interface of the binary polymer blend, and the molecular structure was successfully generated. In the case of a hydrated Nafion membrane, the atomistic structure of a water channel is generated based on the mesoscopic structure and the number of water molecules in the first coordination shell around the sulfonic acid group is of the same magnitude as that in experimental study.

References

- 1) Fraaije, J. G. E. M., et al. : J. Chem. Phys., **106**(1997), 4260
- 2) Hasegawa, R. and Doi, M. : Macromolecules, **30**(1997), 3086
- 3) Hoogerbrugge, P. J. and Koelman, J. M. V. A. : Europhys. Lett., **19**(1992), 155
- 4) Groot, R. D. and Warren, P. B. : J. Chem. Phys.,

- 107**(1997), 4423
- 5) Groot, R. D. and Madden, T. J. : J. Chem. Phys., **108**(1998), 8713
- 6) Yamamoto, S., et al. : J. Chem. Phys., **116**(2002), 5842
- 7) Fraaije, J. G. E. M. : J. Chem. Phys., **99**(1993), 9202
- 8) Valenko, S., et al. : J. Chem. Phys., **106**(1997), 3412
- 9) Benzi, R., et al. : Phys. Rep., **222**(1992), 145
- 10) Chen, S. and Doolen, G. D. : Ann. Rev. Fluid Mech., **30**(1998), 329
- 11) Eichinger, B. E., et al. : Comp. Polym. Sci., **5**(1995), 147
- 12) Honeycutt, J. D. : Macromolecules, **27**(1994), 5377
- 13) Fan, C. F., et al. : Macromolecules, **25**(1992), 3667
- 14) Mumby, S. J., et al. : Polymer, **34**(1993), 2540
- 15) Tiller, A. R. and Gorella, B. : Polymer, **35**(1994), 3251
- 16) Case, F. H. and Honeycutt, J. D. : TRIP, **2**(1994), 259
- 17) Mayo, S. L., et al. : J. Phys. Chem., **94**(1990), 8897
- 18) Yamamoto, S. and Hyodo, S. : Proc. 7th Jpn. Int. SAMPE Symp. Exhib., (2001), 861
- 19) Yamamoto, S. and Hyodo, S. : Prep. IUPAC Polym. Conf., (2002), 117
- 20) Gierke, T. D., et al. : J. Polym. Sci. Polym. Phys. Ed., **19**(1981), 1687

(Report received on Dec. 24, 2002)



Satoru Yamamoto 山本智

Year of birth : 1963

Division : Frontier Research Group V

Research fields : Computational suspension rheology, Computational chemistry

Academic degree : Dr. Engng.

Academic society : The Soc. of Polym. Sci., Jpn., The Soc. of Rheol. Jpn.

Awards : R&D 100 Award, 1999.

The Soc. of Rheol. Jpn. Res. Award, 2001.