A Review on Transport Phenomena of Entangled Polymeric Liquids

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This review article focuses on the transport phenomena of entangled polymeric liquids. The study of transport phenomena is one of the fundamental fields in chemical engineering, which addresses the transport of mass, momentum, and energy. For simple transport cases, such as the flow of a Newtonian fluid, the methodology of transport phenomena has been established. However, for an entangled polymeric liquid, which is an example of a viscoelastic liquid, various problems remain due to the various time and length scales involved. In this review article, we summarize studies of entangled polymeric liquids for problems on different time and length scales and multiscale problems that connect different scales.

Key Words: Transport phenomena / Polymer rheology / Multi-scale simulation

1. INTRODUCTION

Polymeric materials are widely used in our daily life, from daily necessities to automobiles and aircraft. Therefore, producing high-performance polymer products is an essential issue in the polymer industry. To obtain desirable physical properties in polymer products, a variety of techniques are employed, such as incorporating low molecular additives or blending different types of polymers. Due to the high frequency of use and usefulness of polymers, the twentieth century is referred to as the “Polymer Age” by Rubinstein and Colby.1)

The manufacturing process of polymer products typically consists of the following procedures: flow, shaping, cooling and solidification. Therefore, when manufacturing polymer products, it is necessary to address polymeric liquids, which are complex fluids. Thus, predicting and controlling the flow behavior of polymeric liquids is important for the polymer industry. However, the gap between basic polymer science and the polymer industry is still quite large, mainly for the following reasons: First, polymeric liquids themselves are complex fluids, and it is generally difficult to predict their flow properties. Second, many types of polymeric materials, such as polymer blends, are employed, and the interaction between different components have not been fully elucidated.

Addressing the flow properties of polymeric liquids can be regarded as a transport phenomenon problem in chemical engineering.2) The study of transport phenomena involves the transport of mass, momentum, and energy in the system under consideration. These three phenomena frequently occur simultaneously in industrial problems. An important aspect is the fact that the basic equations that describe the three phenomena are very similar, which means that the three problems can be solved using similar mathematical tools. As shown in Fig. 1, the fundamental equations can be derived from conservation laws (in other words, balance equations). For example, from the mass balance equation, the equation of continuity can be obtained as

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{v}), \quad (1)$$

where \(\rho\) is the density, \(t\) is time, and \(\mathbf{v}\) is the velocity. In particular, for a fluid with a constant density, a so-called incompressible fluid, Eq. (1) can be rewritten as

$$\nabla \cdot \mathbf{v} = 0. \quad (2)$$

Furthermore, from the momentum balance equation, the equation of motion can be obtained as

$$\frac{\partial}{\partial t}(\rho \mathbf{v}) = -\nabla \cdot (\rho \mathbf{v} \mathbf{v}) + \nabla \cdot \mathbf{\sigma} - \nabla \cdot (P \mathbf{I}) + \mathbf{F}, \quad (3)$$

where \(\mathbf{\sigma}\) is the stress tensor, \(P\) is the pressure, and \(\mathbf{F}\) is an external force. If we combine Eq. (1) with Eq. (3), then the equation of motion can be rewritten as

$$\rho \left( \frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) = \nabla \cdot \mathbf{\sigma} - \nabla \cdot (P \mathbf{I}) + \mathbf{F}. \quad (4)$$

This equation of motion is used to solve transport problems.
The remaining problem is to obtain an expression for the stress tensor $\sigma$. Any equation that relates deformation and stress is called a constitutive equation. In the simplest case, the constitutive equation can be expressed as

$$\sigma = 2\eta D,$$

(5)

where $\eta$ is the viscosity, and $D$ is the deformation rate tensor, defined as $D \equiv (\nabla v + \nabla v^T)/2$. Eq. (5) is referred to as Newton’s law of viscosity, and a fluid that follows Eq. (5) is a Newtonian fluid. Here, Eq. (5) can be regarded as a simple constitutive equation. By combining Eqs. (2), (4), and (5) with material constants and appropriate boundary conditions, we can solve any isothermal flow problem for a Newtonian fluid.

When dealing with flow problems of polymeric liquids, which are a type of viscoelastic fluid, viscoelastic constitutive equations should be employed. A viscoelastic constitutive equation is generally written as

$$\dot{\sigma}_{\alpha\beta} = f(\sigma, D, t) \quad \alpha, \beta \in \{x, y, z\},$$

(6)

where $\dot{\sigma}_{\alpha\beta}$ is the time derivative of the stress tensor. As shown in Eq. (6), a viscoelastic constitutive equation may depend on the deformation history. To solve flow problems involving polymeric liquids, we have to know the viscoelastic constitutive relation. Studies on viscoelastic constitutive equations have actively been performed in the field of “rheology”, a discipline that relates flow and deformation. In principle, with the help of rheology, we can solve the transport problems of polymeric liquids.

Figure 1 Schematic illustration of the background of transport phenomena.

Since the stress tensor of polymeric liquids is tightly related to the microscopic states of the polymer chains, in principle, the viscoelastic constitutive equations of polymeric liquids should be derived from microscopic scale dynamics, with the assistance of statistical theories. However, it is generally very difficult to derive constitutive equations for polymeric liquids, such as Eq. (6), because the stress caused by the polymer chains depends on their deformation history.\(^{3}\) While considerable efforts have been made in developing molecular-based constitutive equations, phenomenological constitutive equations are often employed for most polymer industry simulations. Here, “phenomenological” constitutive equations refer to equations that lack a solid molecular basis. Phenomenological constitutive equations, such as the Kaye-BKZ constitutive equation (for more details, please see Sec. 2.5), can give reasonably accurate linear and nonlinear viscoelastic predictions for practical flow problems in the polymer industry. However, as mentioned above, phenomenological constitutive equations do not allow us to obtain molecular insights into the configuration of the polymer chains. These microscopic molecular insights are necessary to design polymer products with specific physical properties.

It is important for transport problems of polymeric liquids to obtain the polymeric stress without losing microscopic molecular insights. From a simulation point of view, a molecular dynamics (MD) simulation is the promising technique to obtain the polymeric stress, as well as microscopic molecular insights. However, MD simulations do not allow us to probe the large length- and time-scale phenomena of polymeric liquids, which are important for polymer processing, mainly due to the large computational cost. Thus, designing polymer products with specific physical properties based on the microscopic states of polymer chains is still one of the great challenges, not only in chemical engineering but also in the field of materials science.

The content of this paper is organized as follows. In Sec. 2, we provide a short review of the theoretical and numerical studies on entangled polymeric liquids from microscopic to macroscopic scales. In Sec. 3, we present a review of multiscale simulations of polymer flows. Finally, we present future outlooks in Sec. 4.

### 2. ENTANGLED POLYMER DYNAMICS

Polymeric liquids in an entangled state are important for the polymer industry because many polymeric liquids are used in the entangled state. In this review, we limit ourselves mainly...
to entangled polymer dynamics. The “entangled state” in a polymeric liquid is universal, which means that the polymer dynamics in the entangled state does not depend on the polymer species. Here, we explain the entangled state by the molecular weight dependence of the zero shear viscosity. Experimentally, the zero shear viscosity $\eta_0$ depends on the molecular weight $M$ as

$$\eta_0 \propto M (M < M_c); \quad \eta_0 \propto M^{3.4} (M > M_c),$$  \tag{7}

where $M_c$ is the critical molecular weight. The dynamics of polymeric liquids qualitatively changes when $M$ is larger or smaller than $M_c$, and the region that corresponds to $M > M_c$ is called the “entangled state”. Moreover, the dependences of other physical quantities are experimentally observed to be

$$\langle \tau \rangle \propto M^{2} (M < M_c); \quad \langle \tau \rangle \propto M^{3.4} (M > M_c),$$  \tag{8}

$$D \propto M^{-1} (M < M_c); \quad D \propto M^{-2.3} (M > M_c),$$  \tag{9}

$$J_c \propto M (M < M'_c); \quad J_c \propto M^{0} (M > M'_c),$$  \tag{10}

where $\langle \tau \rangle$ is the average relaxation time, $D$ is the diffusion constant, $J_c$ is the steady-state shear compliance, and $M'_c$ is the critical molecular weight for the steady-state shear compliance.

There are several different theoretical and numerical methods for each characteristic scale because entangled polymer melts have a spatiotemporal hierarchical structure. A schematic representation of the theoretical and numerical methods for each time and length scale is shown in Fig. 2. In the following, I briefly review previous studies on entangled polymers, mainly from the theoretical and simulation points of view, from the microscopic level to the macroscopic level.

2.1 Molecular Dynamics Simulations

The most microscopic and detailed method shown in Fig. 2 is coarse-grained molecular dynamics (CGMD) simulation. Here, the term “coarse-grained” means that several monomers are represented by one bead in the CGMD simulations. In a pioneering study on CGMD simulations of entangled polymer melts, Kremer and Grest developed the Kremer-Grest (KG) model. In the KG model, a polymer chain is expressed by a number of beads connected by springs, and each bead moves according to an equation of motion. To address the effect of entanglements, the repulsive Lennard-Jones (LJ) potential is employed. Using the KG model, static and dynamic properties for unentangled to entangled polymer melts in the equilibrium state were extensively studied.

Linear viscoelastic properties, such as the relaxation modulus $G(t)$, were examined by Likhtman and coworkers using the KG model. Likhtman and coworkers enabled the calculation of $G(t)$ from stress-stress autocorrelation functions by using an efficient on-the-fly calculation method called the multiple tau correlator. The nonlinear rheological properties of the KG model have also been studied by many researchers. One of the important problems for nonlinear flow predictions using the KG model is how to set an appropriate boundary condition. When considering shear flows, the Leeds-Edwards boundary condition can provide a solution to this problem. By employing the Leeds-Edwards boundary condition, shear rheological properties, including the steady shear viscosity, transient shear viscosity, and shear banding, for mildly entangled polymer melts were studied. For the case of uniaxial elongational flows, the uniform extensional flow (UEF) algorithm was recently developed. The UEF algorithm enables one to investigate the uniaxial elongational properties of entangled polymer melts until a steady state is reached. Since investigations of the uniaxial elongational properties of entangled polymer melts using the KG model have only been possible recently, further studies are expected. For now, the nonlinear rheological properties of the KG model have been examined for specific flow types for which appropriate boundary conditions can be set. However, flows in polymer processing are generally combinations of the abovementioned flow types. It is still technically difficult to investigate the rheological properties of general flows using the KG model.

In addition to studies focusing on the rheological properties, there are also various studies that have examined the microscopic structure obtained from KG simulations, such as topological constraints in entangled polymer melts. The method that extracts topological constraints from the entangled network formed by KG polymer chains is referred to as primitive path analysis (PPA). Although there are some variations of the PPA method, the aims of these methods are almost the same. PPA is important not only as a technique for ex-
amining the microscopic structure of entangled polymers but also as a foundation of the mesoscale theories mentioned in the next section. Using PPA methods, the statistical properties of entangled polymer melts in the equilibrium state have been extensively examined. More recently, statistical properties in the nonequilibrium state were examined using PPA, and further developments are expected.

2.2 Tube Theory

The most successful mesoscale theory for entangled polymer melts is the tube model, which was first introduced by de Gennes. The basic idea of the tube model is that a polymer chain in an entangled polymer melt can be considered to be confined in a tube-like region formed by other polymer chains. While the lateral motion of the chain confined to the tube is highly suppressed by other chains, the confined chain can move along the tube. This curvilinear diffusion along the tube was called "reptation motion" by de Gennes. After this pioneering work performed by de Gennes, Doi and Edwards developed the famous Doi-Edwards (DE) model based on the reptation picture. In the DE model, a polymer chain is confined to a tube of constant length fixed in space. By analyzing the diffusion along the tube, the longest relaxation time \( \tau_{\text{d}}^{(\text{DE})} \), which is called the reptation time, can be evaluated as \( \tau_{\text{d}}^{(\text{DE})} \propto M^3 \). This prediction is close to the experimentally observed relaxation time shown in Eq. (8).

In addition to reptation motion, it is important to consider the following two relaxation mechanisms when predicting the rheological properties of entangled polymer melts in the linear region. One mechanism is the contour length fluctuation (CLF), which is the fluctuation of the polymer chain confined in the tube. By combining the CLF with the DE model, the rheological properties of entangled polymer melts can be better explained. For example, the molecular weight dependence of the zero shear viscosity is correctly predicted \( \eta_0 \propto M^{1.4} \). The other mechanism is the constraint release (CR), which is caused by the motion of other chains forming the tube. Most of the current variations of the tube model include these three relaxation mechanisms (reptation, CLF, and CR).

For linear rheological properties, there are many types of tube models, such as the Milner-McLeish (MM) model, the Likhtman-McLeish (LM) model, the time-marching algorithm (TMA), the hierarchical model, and the branch-on-branch (BoB) model. Although these models have a common theoretical background, these models differ in some assumptions, such as the method of introducing the CLF and CR. Specifically, there are several different methods to introduce the CR. In the LM model, which describes the linear rheology of entangled linear polymer melts, the CR is modeled as a Rouse-like motion of the chain with different mobilities. For entangled polymers that have broad relaxation time distribution, such as entangled star polymer melts, the dynamic tube dilation (DTD) is effective to model the CR. In the DTD picture, a tube diameter is dilated with time by the CR. Therefore, the DTD can be considered as a spatiotemporal coarse-graining process of the tube. The difference between these tube models has been examined for entangled linear polymer melts, symmetric star polymer melts, and branched polymer melts.

To predict nonlinear rheological properties, two mechanisms not addressed in the linear region need to be considered. One mechanism is the convective constraint release (CCR), which is important mainly for \( \dot{\gamma}, \dot{\varepsilon} > \tau_{\text{R}}^{-1} \), where \( \dot{\gamma} \) is the shear rate, \( \dot{\varepsilon} \) is the elongation rate, and \( \tau_{\text{d}} \) is the reptation time. In the CCR picture, entangled polymer chains are transiently stretched under flows, and subsequent retraction of polymer chains induces the CR in the strain rate region \( \dot{\gamma}, \dot{\varepsilon} > \tau_{\text{d}}^{-1} \). The other mechanism is the chain stretch, which becomes significant when \( \dot{\gamma}, \dot{\varepsilon} > \tau_{\text{R}}^{-1} \), where \( \tau_{\text{R}} \) is the Rouse relaxation time. There are various tube-model-based constitutive models, and these models are explained in the next section.

2.3 Tube-model-based Constitutive Models

One of the tube-based molecular theories for nonlinear rheological properties is the Mead-Larson-Doi (MLD) model. The MLD model, which includes the reptation, chain stretch, and the CCR mechanisms, can explain the nonlinear rheological responses of entangled linear polymer melts not only for the steady state, but also for transient phenomena at strain rates \( \dot{\gamma} > \tau_{\text{d}}^{-1} \). The Graham, Likhtman and Milner, McLeish (GLaMM) model was developed by Graham and coworkers. In the GLaMM model, the CCR mechanism is considered local Rouse-like tube motion, and the chain stretch is modeled based on the Rouse motion of a chain confined in the tube. Using the GLaMM model, nonlinear rheological properties of monodisperse entangled linear polymer melts can be predicted even under strong flow, including in the strain rate region \( \dot{\gamma}, \dot{\varepsilon} > \tau_{\text{R}}^{-1} \). Based on the GLaMM model, Likhtman and Graham derived a simple constitutive equation for fast flows of entangled linear polymer melts, which is called the Rouse linear entangled polymers (Rolie-Poly) constitutive equation. The Rolie-Poly constitutive equation can capture nonlinear rheological properties of entangled linear polymer melts with a lower computational cost than that of the GLaMM model.
The abovementioned nonlinear constitutive models are limited to monodisperse linear polymer melts. Industrially, sourced polymers generally have a molecular weight distribution or a branched structure to ensure rheological properties suitable for processing. In the Rolie-Double-Poly (RDP) model, the double reptation theory is combined with the Rolie-Poly model. The RDP model can capture nonlinear shear and elongational rheology for bispanser and polydispersor entangled linear polymers. However, it should be noted that the linear viscoelasticity predicted by the RDP model is not perfectly in agreement with experimental data.

For the polymer melts having two branch points and long-chain side branches, McLeish and Larson developed a molecular-based constitutive equation called the pom-pom constitutive equation. The key idea of the pom-pom constitutive equation is to include branch point withdrawal, which allows free arms to move into the tube originally occupied by the backbone. This motion is induced by the backbone stretch relaxation. The pom-pom model can qualitatively predict nonlinear rheology under both shear and elongational flows of branched polymer melts. Moreover, the multimode pom-pom model can quantitatively predict nonlinear rheological properties for commercial polymer melts, such as low density polyethylene (LDPE) melts.

Despite considerable efforts, it is still difficult to develop nonlinear constitutive models for polymer melts that have a molecular weight distribution or a branched structure from a molecular point of view. Alternatively, the following molecular-based coarse-grained simulation models are useful for predicting the linear and nonlinear rheology of entangled polymer melts.

### 2.4 Mesoscale Simulation Models

One of the successful mesoscale simulation models that can describe polymer dynamics in the entangled state is the slip-link (SL) model, in which entanglements are considered as “slip links”. A short review on the SL models can be found in Ref. 45. Here, a more extensive review on mesoscale simulation models is given. The concept of the SL model was first introduced by Doi and Edwards. This original SL model only considered a single chain confined by slip links, and the effect of the motion of other chains, such as the CR, was not addressed.

Since then, many types of SL models have been developed based on the pioneering work of Doi and Edwards. Hua and Schieber proposed an SL model that considers the effect of the CR. In the Hua-Schieber SL model, 1D Rouse chains that can slide along slip links are considered, and the slip links can be renewed and destroyed by the CR. After that, Schieber and coworkers developed a more mathematically rigorous SL model called the discrete SL model (DSM). In addition to quantitative predictions of the linear rheology of monodisperse linear melts, the DSM can successfully predict the linear rheology of bispanser and linear and star blends. Nonlinear rheological properties under both shear and elongational flows have also been examined using the DSM. For shear viscosities, predictions obtained by the DSM are in good agreement with experimental results. However, the DSM shows strain-softening behavior in transient elongational viscosities. This behavior is not seen in experiments of entangled polystyrene melts. Furthermore, the DSM was investigated from a thermodynamic point of view. For example, the DSM is consistent with the nonequilibrium thermodynamics formalism known as the GENERIC framework.

More recently, a more coarse-grained version of the DSM, called the clustered fixed SL model (CFSM), was developed by clustering several Kuhn steps of the DSM into a blob. The CFSM can give rheological predictions equivalent to those of the DSM with a lower computational cost.

Masubuchi and coworkers developed the primitive chain network (PCN) model. The PCN model can be considered as a real space model since a 3D entangled network of coarse grained polymer chains is described. Using the PCN model, various properties of entangled polymer melts and solutions have been examined, such as the linear rheology of monodisperse entangled polymer melts and bispanser blends, the linear and nonlinear rheology of branched polymer melts, and the nonlinear properties of entangled linear polymers under strong uniaxial elongational flows including chain stretch. In addition to rheological properties, fundamental aspects of the PCN model, such as the detailed balance condition and entanglement structure, have also been examined.

A more coarse-grained SL model than the above SL models was developed by Doi and Takimoto, which is schematically shown in Fig. 3 (b-i). The original Doi-Takimoto (DT) model can give good predictions for the linear rheology of monodisperse linear, polydispersor linear, and symmetric star polymer melt systems and for the nonlinear viscoelastic properties in the strain rate region \( \gamma > \dot{\varepsilon} < \gamma_{\text{R}}^{-1} \). Furthermore, nonlinear rheological properties, including chain stretch \( \gamma > \dot{\varepsilon} > \gamma_{\text{R}}^{-1} \), were recently examined.

A simple SL model based on the SL model for branched polymers was proposed by Shanbhag, which is called ecoSLM. Using ecoSLM, the linear rheological properties of monodisperse and bispanser linear polymer melts were
examined, and the results were in good agreement with the experimental data. However, the nonlinear viscoelastic properties under flows have not been investigated using ecoSLM.

Another type of coarse-grained model in which entanglements are modeled a priori is called the slip-spring (SS) model. Likhtman developed the single-chain SS model,\(^{71,72}\) in which a polymer chain is described by a Rouse chain, and entanglements are modeled as additional springs that impose constraints on the main Rouse chain (Fig. 3 (b-ii)). Likhtman’s SS model can predict experimental neutron scattering, linear rheology and diffusion data of unentangled and entangled monodisperse linear polymer melts. Furthermore, Likhtman’s SS model is well defined from a thermodynamic point of view since this model satisfies the Gaussian statistics on all length scales of main Rouse chains and slip springs. The nonlinear rheological responses under steady shear flows were also investigated by the single-chain SS models similar to Likhtman’s SS model.\(^{73,74}\)

A multichain SS model was developed by Uneyama and Masubuchi.\(^{75}\) This multichain SS model employs the total free energy of polymer chains and slip-springs\(^{49}\) and satisfies the detailed balance condition. Using the multichain SS model, Masubuchi examined the nonlinear rheological properties of entangled linear polymer melts\(^{76}\) and the linear rheological properties of branched polymer melts.\(^{77}\) Furthermore, Likhtman’s SS model is well defined from a thermodynamic point of view since this model satisfies the Gaussian statistics on all length scales of main Rouse chains and slip springs. The nonlinear rheological responses under steady shear flows were also investigated by the single-chain SS models similar to Likhtman’s SS model.\(^{73,74}\)

2.5 Phenomenological Constitutive Equations

Despite the considerable success of the SL and SS models, phenomenological constitutive equations are frequently employed for industrial simulations mainly for the following two reasons:\(^{3}\) First, phenomenological constitutive equations usually have a lower computational cost than more rigorous molecular-based models. Second, technically, there is less room for complexity in constitutive equations because industrial processing flow geometries are too complex.

Industrially, if the shear-rate-dependence of the viscosity is the most important aspect, and normal stress or elastic effects are negligible, the generalized Newtonian viscosity models, such as the power low model and the Carreau-Yasuda model, are employed to calculate the polymeric stress.\(^{83}\) When the shear-rate-dependence of the viscosity, as well as normal stress or elastic effects play an important role in industrial flow problems, viscoelastic constitutive equations should be employed.

In this section, a brief review of viscoelastic phenomenological constitutive equations is given. Phenomenological constitutive equations can be roughly divided into the following two types: integral equations and differential equations. In practical simulations, phenomenological constitutive equations that can well describe experimental results are employed. Moreover, to give accurate predictions of nonlinear rheological properties using phenomenological constitutive equations, there are many parameters that should be determined by comparing with experiments.

One of the important integral constitutive equations was developed independently by Kaye\(^{84}\) and Bernstein, Kearsley, and Zapas,\(^{85}\) which is called the Kaye-BKZ model. The Kaye-BKZ model is based on rubber elasticity theory, and the stress tensor can be derived from a free energy that depends on the invariants of the strain tensor. Since the elastic energy and the stress are allowed to relax in viscoelastic liquids, the elastic energy (and therefore the stress) can be expressed as a history integral. By comparing the model with step shear experiments, a specific functional form of the elastic energy for shear flows can be determined. After determining the elastic energy, the Kaye-BKZ model can be used to predict the non-
linear rheological properties under shear flows. However, it should be noted that step uniaxial elongation experiments are needed to determine the elastic energy for predicting the rheological properties under uniaxial elongational flows. This means that it is difficult to accurately predict polymer processing flows, which are mixtures of flow types, using the Kaye-BKZ model.

There are various differential constitutive equations. One of the simplest differential constitutive equations for polymeric liquids is the Maxwell equation. The Maxwell equation is expressed as

\[ \frac{\delta}{\delta t} \sigma + \alpha = 2\eta D, \]  \hspace{1cm} (11)\]

where \( \delta/\delta t \) is the time derivative, \( \lambda \) is the relaxation time, and \( \eta \) is the viscosity. If we simply employ Eq. (11), then the stress tensor depends on rotation, which means that rotations induce stresses. There is a basic principle that states constitutive equations should not depend on rotation, which is called the principle of “frame invariance”. To recover frame invariance, the time derivative on the left-hand side of Eq. (11) should be modified. The upper convected derivative is one of the candidates for this modification. The model that the upper convected derivative is incorporated into the Maxwell model is called the upper convected Maxwell (UCM) model. In addition to the polymeric stress evaluated by the UCM model, if we consider the solvent stress, then the model is referred to as the Oldroyd-B model, which is frequently employed in simulations of polymer processing. Although the Oldroyd-B model is frequently employed as a model for expressing the viscoelasticity of polymeric liquids, the Oldroyd-B model cannot reproduce some important rheological properties of polymeric liquids. For example, linear differential equations, such as those in the UCM and Oldroyd-B models, cannot reproduce the thinning behavior in shear flows.

There are mainly two ways to solve the above problem. One is to consider nonaffine motion, and the other is to include higher order terms in constitutive equations. A more realistic rheological constitutive model can be obtained by removing the assumption of affine deformation, which is used in the UCM and Oldroyd-B models. One of the constitutive equations that allows nonaffine motion is the Larson model. To address nonaffine motion, Larson proposed the partially extending convected derivative by introducing a parameter that represents the extent of strand retraction. The Larson model can capture the nonlinear rheological properties under shear and elongational flows better than the UCM and Oldroyd-B models. The Giesekus and Leonov models have a quadratic term in the stress, which can be interpreted as an accelerated relaxation. Including the quadratic term allows one to obtain good rheological predictions under shear flows. However, the Giesekus and Leonov models give less accurate predictions under elongational flows than temporary network models, such as the PTT model mentioned below.

To present the PTT model, we explain temporary network models. Green and Tobolsky proposed a constitutive equation based on rubber elasticity theory, which is called the Green-Tobolsky (GT) model. The GT model can be regarded as a type of temporary network model, since polymer chains in the GT model are considered to form a transient network that can break and reform. It should be noted that the GT model is equivalent to the UCM model. Therefore, the same problems as for the UCM model arise when employing the GT model. Generalized models based on the GT approach have been proposed. One of these generalized models is the Phan-Thien/Tanner (PTT) model, which allows non-Gaussian chains and a dependence of the breakage probability on polymer chain extension. The PTT model can give better predictions under elongational flows than the Giesekus and Leonov models.

### 2.6 Computer Simulations in the Polymer Industry

For industrial purposes, macroscopic flow simulations are performed to predict the flow properties of polymeric liquids in complex flow geometries. In this section, a review of a polymer melt spinning process and an injection molding process, which are typical processes in the polymer industry, is given.

The polymer melt spinning process schematically shown in Fig. 4 (a) is a common process for manufacturing polymeric fibers. One of the pioneering studies on this process was performed by Kase and Matsuo. They developed a mathematical model for this process using a Newtonian fluid. After these pioneering studies were performed by Kase and Matsuo for a Newtonian fluid, constitutive equations, such as those in the Maxwell model and the PTT model, were employed to address viscoelastic properties. Furthermore,
microscopic structures, such as the molecular orientation and crystallization induced by uniaxial elongational flows, were examined by many researchers. Mathematical models for the spinning process, including thermally and flow-induced crystallization, were developed using the Giesekus model,\(^{95–97}\) or the multimode PTT model.\(^{98}\)

Since the injection molding process is one of the major production techniques in the polymer industry, there are many related studies from both experimental and numerical aspects. Injection molding is composed of many different process elements such as mixing, flow, filling, and shaping.\(^{99}\) For the mixing process, Nakayama and coworkers analyzed this process using a shear thinning fluid.\(^{100,101}\) For flow properties, since the contraction-expansion channel (schematically shown in Fig. 4 (b)) can be considered one of the model geometries in the injection molding process, flows in this geometry have been extensively examined using phenomenological or molecular-based constitutive equations, including the Oldroyd-B model,\(^{102}\) the pom-pom model,\(^{103–105}\) and the Rolie-Poly model.\(^{106–110}\) For the filling process schematically shown in Fig. 4 (c), free surface flows should be addressed. Numerically, using mesh-based methods, such as the finite element method (FEM), to address free surface flows is generally difficult due to the meshing problem. Lagrangian fluid particle methods are some of the effective methods for addressing flows including a free surface.\(^{111,112}\)

The macroscopic flow properties (and the subsequent physical properties of polymer products) are determined by the microscopic states of polymer chains, including the molecular orientation and entanglements. Therefore, it is important to investigate the microscopic states of polymer chains in processing flows. Using tube-model-based constitutive models, such as the Rolie-Poly model or the pom-pom model, the molecular orientation and stretch can be obtained. However, when comparing with scattering experiments under flows, information on the molecular orientation and stretch is not sufficient to calculate structure factors, and a more detailed model such as the GLaMM model is required.\(^{106,108,110}\) On the other hand, using the phenomenological constitutive equations, molecular information cannot be directly obtained. To obtain both macroscopic flow properties and microscopic molecular insights, other simulation techniques are needed.

### 3. MULTI-SCALE SIMULATION METHODS

Conventional fluid dynamics approaches with phenomenological viscoelastic constitutive equations can access length and time scales suitable for polymer processing. However, it is generally difficult to uniquely choose a proper constitutive equation that can fit experimental rheological data on a targeting polymer melt. Moreover, phenomenological constitutive equations are too coarse grained to directly obtain molecular insights that would be useful for designing polymer products. For these problems, the Multi-Scale Simulation (MSS) approach, in which a microscopic (or mesoscopic) model is connected to macroscopic balance equations, is one promising method. Using the MSS technique, both macroscopic flow properties and microscopic polymer dynamics can be evaluated. A short review on the MSS approaches can be found in Ref. 113. Here, a more detailed review on transport problems using the MSS approaches is given.

A pioneering work on an MSS technique was performed by Laso and Öttinger, which was known as the Calculation of Non-Newtonian Flow: Finite Element and Stochastic Simulation Technique (CONNFFESSIT).\(^{114}\) In the original CONNFFESSIT approach, instead of employing phenomenological constitutive equations, the Hookean dumbbell model is employed to calculate the polymeric stress. Microscopic systems described by the Hookean dumbbell model are connected to macroscopic balance equations. These balance equations are solved by the FEM. The CONNFFESSIT technique was applied to the start-up Couette flow problem, and validated by comparing with solutions obtained from constitutive equations.\(^{114}\) After that, various flow problems have been investigated using the CONNFFESSIT approach, such as flows in an abrupt contraction,\(^{115}\) start-up Couette flows for liquid crystals and polymer melts,\(^{116}\) time-dependent flows,\(^{117}\) and free surface flows.\(^{118}\) Although the CONNFFESSIT is successful as a pioneering work, it has the following two main problems: the convection of microscopic components and the subsequent remeshing process in the FEM are calculation heavy, and microscopic information is limited since the simple Hookean dumbbell model is employed (except for the work of Hua and Schieber).\(^{116}\) Based on the CONNFFESSIT approach, many variations of the MSS method have been developed. As shown in Fig. 5, we can roughly classify MSS methods into the following two categories: (1) MSS methods that combine macroscopic balance equations with an MD simulation, and (2) MSS methods that employ more coarse-grained models than MD and address the convection of microscopic systems.

#### 3.1 MSS Methods using MD Simulations

As an MSS method using the MD simulation, the heterogeneous multiscale method (HMM) proposed by E and coworkers is one of the successful methods.\(^{119,120}\) In the HMM, macroscopic balance equations are combined with
MD simulations for Lennard-Jones (LJ) and dumbbell fluids. Macroscopic equations are solved using the finite volume method, and boundary conditions for MD simulations are obtained from macroscopic simulation. Using the HMM, typical flow problems such as a Poiseuille flow and a cavity flow were examined. De and coworkers developed a scale-bridging method that combines macroscopic balance equations with the KG model. In this MSS method, the memory effect of a weakly entangled linear polymer melt for flows between parallel plates and flows within a cylinder can be accurately evaluated. Yasuda and Yamamoto proposed a hybrid simulation method of the macroscopic balance equation and MD simulations for LJ liquids based on the HMM. In their hybrid simulation method, to properly employ the Lees-Edwards periodic boundary condition for MD simulations, the strain rate tensor calculated at the macroscopic level is transformed using a rotation matrix. Using their hybrid simulation method, the pressure-driven channel flow and the cavity flow of the LJ fluid were examined. Subsequently, the hybrid simulation method was extended to a polymer melt using the KG model, and various flow problems were examined. More recently, Yasuda and Yamamoto developed the synchronized molecular dynamics (SMD) method that can address flow problems of complex fluids with temperature changes. In the SMD, the KG simulations of local fluid elements are synchronized to satisfy the macroscopic momentum and energy equations at a macroscopic time interval. Using the SMD method, lubrication problems of unentangled and weakly entangled polymer melts were investigated.

In all MSS methods using MD simulations mentioned above, although detailed microscopic information can be obtained, there are mainly two limitations. First, the flow channel geometries are restricted to simple ones, such as flow between parallel plates, since it is impossible to set appropriate boundary conditions in MD simulations for general processing flows in which various types of flows are mixed, as mentioned in Sec. 2.1. Second, the polymer chains used in these MSS methods are relatively short or have few entanglements due to the large computational cost, which are not sufficient for most polymer processing flows.

3.2 MSS Methods using Coarse-grained Models

As an MSS method using a more coarse-grained model than MD, Hulsen and coworkers developed the Brownian configuration field (BCF) method, which can easily take the convection of microscopic systems into account. In the BCF method, a time evolution equation of a configuration field of dumbbells is employed instead of individual polymer molecules, and the configuration field description is incorporated into the FEM. After confirming the validity of the BCF method by investigating flows around a cylinder using this method, various problems have been considered, including fibre suspension flows in contraction and expansion channels, free surface flows, 3D contraction flows, and nonequilibrium phase transitions of polymer solutions under shear flows. Another variation of this type of the MSS method was developed by Halin and coworkers, which is called the Lagrangian particle method (LPM). In the LPM, the FEM for solving macroscopic balance equations is combined with the dumbbell model through a number of Lagrangian fluid particles on which the polymeric stress is calculated. Therefore, the deformation history of the polymers can be correctly addressed in the LPM. Using the LPM, the start-up flow between slightly eccentric rotating cylinders was examined. In all the MSS methods using coarse-grained models mentioned above, since the dumbbell model is employed to calculate the polymeric stress, the effect of entanglements is not addressed.

One of the MSS methods that addresses the effect of entanglements is the deformation field method. In the deformation field method, the deformation gradient fields are introduced to calculate the polymeric stress. Another approach was proposed by Masubuchi and coworkers. They developed a parameter-based bridging MSS method using the PCN model. In their parameter-based bridging MSS method, the parameters of the viscoelastic constitutive equation (the multimode Leonov equation) were obtained from the PCN model, and simulations of the filling process were performed. An MSS method that employs the smoothed particle hydrodynamics (SPH) method as a macroscopic model and the dumbbell model was developed by Murashima and Taniguchi. After that, they extended their MSS method to flows of an entangled linear polymer melt using the DT model, as schematically shown in Fig. 6 (a) and (b). Using this MSS method, both macroscopic (Fig. 6 (c-i)) and microscopic (Fig. 6 (c-ii)) information of the entangled polymer melt can be obtained without using phenomenological constitutive equa-
ions. Using an approach similar to the LPM, the author developed an MSS method that can calculate flows of a polymer melt spinning process using the dumbbell model\textsuperscript{145} and the DT model.\textsuperscript{146} More recently, flows of an entangled polymer melt in a contraction-expansion channel were examined using the MSS method by the author.\textsuperscript{113} Moreover, it is fair to note that a similar MSS method was developed by Schieber and coworkers by employing the DSM as a microscopic level model.\textsuperscript{147}

In the MSS methods using more coarse-grained models than MD, microscopic details are limited because of coarse-graining. However, this type of MSS methods can access various processing flow problems of well-entangled polymer melts.

### 4. FUTURE OUTLOOK

In this article, various numerical and theoretical approaches for studying entangled polymeric liquids are explained, ranging from the microscopic level to the macroscopic level. There are many remaining problems that should be solved at each scale, as briefly described in Sec. 2. Moreover, the Multi-Scale Simulation (MSS) methods that connect a microscopic model to a macroscopic model are also presented in Sec. 3. In this section, we present future outlooks, mainly MSS methods for flows of polymeric liquids. As described before, MSS is a promising method to analyze flow problems in the polymer industry. In addition to fundamental studies of MSS methods, some studies on the flows in polymer processing using MSS methods have also been performed. However, there are many remaining problems that should be addressed before MSS methods can be applied to industrial processes. Here, we summarize some of the remaining problems.

- In industrial processes, the polymeric liquids undergo temperature changes, which can result in crystallization or solidification. Macroscopically, there are many simulation studies that have addressed flows of polymeric liquids with temperature changes.\textsuperscript{95–98, 112, 139} In macroscopic approaches with crystallization, the crystallization kinetics is modeled in a phenomenological manner.\textsuperscript{95–98} Microscopically, although MD simulations would be effective in tackling problems related to polymer crystallization or solidification (for more details, please see Ref. 148 and references therein), the correlation between the macroscopic properties and microscopic states of polymer chains has not been investigated. Therefore, studies that include the role of temperature changes should be performed at both macroscopic and microscopic scales.

- Industrially, polydisperse polymer melts are used to obtain desirable properties. Namely, sourced polymers have various primary structures, such as linear and branched polymers, and additionally, they are often mixed. While such polymeric liquids are difficult to handle with present constitutive equations, some mesoscale molecular models that can address linear and branched polymers and mixtures thereof have been developed.\textsuperscript{51, 61, 62, 77} Using these molecular-based models, polydisperse polymer melts should be considered under processing conditions in the MSS method.

- Polymeric materials containing solid particles have been used in the polymer industry because the combination of polymers and solid particles can provide specific properties that cannot be obtained from a single polymer species. However, the interaction between polymeric liquids and solid particles is not fully understood. One of the reasons for this is that the flow near solid particles is complex because it is a mixture of shear and elongational flows. Characterizing this interaction is important to accurately predict the rheological properties of suspensions, such as
shear thickening in viscoelastic suspending fluids. Numerically, suspensions in a viscoelastic fluid are examined using phenomenological constitutive equations, such as the Oldroyd-B model.\textsuperscript{149,150} Although rheological properties can be qualitatively captured by macroscopic approaches, microscopic insights are limited depending on the employed constitutive equations. MSS approaches might be one of the candidates for unraveling the physics behind the rheological properties of suspensions. In addition, if the size of the solid particles is comparable to the characteristic length of the polymer chain, then development of a new mesoscale model is required. However, studies on developing such models have not been performed.

- MSS methods might be useful for understanding the microscopic origin of macroscopic phenomena, such as shear banding. Shear banding is observed in various complex fluids, including polymer melts, polymer solutions, and wormlike micellar solutions, and has been extensively examined from experimental, theoretical, and simulation points of view.\textsuperscript{151,152} In addition to accurately predicting a constitutive relation between shear stress and shear rate, one of the important aspects to predict shear banding is to incorporate the effect of the spatial concentration differences. The effect of such concentration difference has not yet been addressed in current MSS approaches, and should be considered in the future. Regarding wormlike micellar solutions, constitutive models that can capture rheological properties are not yet fully developed. Therefore, studies from a microscopic viewpoint are required.

- Recently, informatics and data-driven approaches have been applied in many fields, including materials science and chemical engineering. Combining data and statistical algorithms can be useful for developing complex predictive models. However, in the field of polymer science, the application of this information strategy is not as advanced as that in other fields. This is obviously because the characteristics of polymeric liquids are determined by complex combinations of properties at various time and length scales. Zhao and coworkers developed a data-driven MSS method using Gaussian processes (GP).\textsuperscript{153,154} In their data-driven approach, a GP regression technique is used to “learn” the constitutive relation from a small number of microscopic simulations. However, the deformation history of the polymers and the memory effects, which are important for flow problems of polymeric liquids, have not been addressed.

After solving the abovementioned problems, MSS methods can be employed for engineering applications. In the field of chemical engineering, process design has been performed using only macroscopic parameters, such as the viscosity. In the future, it will be important to design industrial processes using microscopic molecular structures as process design parameters. Regarding this point, MSS methods can provide a new perspective on transport phenomena in chemical engineering.

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