

## 분자량 분포와 사슬구조가 엉킨 유연성 고분자의 점탄성에 미치는 영향

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### Effect of Large-scale Molecular Structure on the Viscoelastic Properties of Entangled Flexible Polymers

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#### 요 약

분자량이 큰 고분자의 구조가 점탄성에 미치는 영향을 설명하기 위해 선형-선형 고분자 블랜드에 적용되었던 equivalent primitive chain 모델을 블랜드의 긴 완화시간을 갖는 사슬이 엉킨이 중요한 star 고분자를 포함하는 고농도 용액에까지 확장한다. 긴 완화시간을 갖는 사슬의 완화현상에서 이 사슬의 국부에서 주의 사슬들의 제약이 해제되므로서 일어나는 현상을 고려하여 분자량과 사슬구조는 다르나 화학적 성질은 같은 이성분계 고분자 블랜드의 유변학적 거동을 설명한다.

**Abstract**—In order to describe the effects of large-scale molecular structure on viscoelastic properties, the equivalent primitive chain model previously suggested for linear-linear blends is extended to star-containing blends especially in concentrated region where the entanglements between higher relaxation-time components are prominent. Taking into account the significance of the tube renewal by the local constraint release for the relaxation process of a model chain with higher relaxation time, consider, the inhomogeneous binary blend composed of different chain structures on large-scale but chemically identical species as a homogeneous blend consisted of same structures with different effective molecular sizes.

**Keywords:** Melt rheology, Equivalent Primitive Chain model, Linear-Star blends, Relaxation process.

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## 1. Introduction

General purpose polymers universally consist of chains with different lengths and can include various forms of branched structures which remarkably control their processability. To understand the structural dependence of rheological properties, many investigations have been done for the effect of molecular parameters, i.e., molecular weight (MW), molecular weight distribution (MWD), and long chain branching, by using model polymers with narrow MWD's and well-defined branched samples instead of structurally more complicated commercial polymers. The simplest branched molecule is a star polymer with f-arms coupled together at a single branch point. Such star-branched model polymers show strikingly different behaviors from linear molecules in various rheological properties [1-5]:

The star polymer has the lower value of zero-shear viscosity  $\eta_0$  than the linear polymer of the same molecular weight in low range of molecular weights. As molecular weights increases,  $\eta_0$  for the star is enhanced rapidly relative to the linear.

The recoverable compliance  $J_e^0$  for branched polymers is directly proportional to the molecular weight over the experimentally accessible range, while for highly entangled linear polymer  $J_e^0$  is independent of molecular weight.

The concentration dependence of linear viscoelastic properties in small molecular solvents has been studied for the branched as well as for the linear polymers. At the concentrated regime, the concentration and molecular weight dependences can be summarized as follows:

$$\eta_0 \propto (cM)^{3.4}, J_e^0 \propto 1/G_N^0 \propto 1/c^{2.0 \sim 2.3} M^0, J_e^0 G_N^0 = (2 \sim 3)M^0 \quad (1)$$

For star-branched polymers,

$$\eta_0 \propto (cM)^d \exp(cM), J_e^0 \propto c^{-1} M^1, G_N^0 \propto c^2, J_e^0 G_N^0 \propto cM \quad (2)$$

where  $d$  is a constant,  $c$  concentration, and  $M$  molecular weight of the sample polymer. The plateau modulus  $G_N^0$  is commonly expressed in terms of the apparent average molecular weight  $M_e$  bet-

ween two successive entanglement couplings [1]. The  $G_N^0$  or  $M_e$  for star polymers has a larger uncertainty rather than linear polymers, especially for those of low molecular weight, but in the case of large molecular weight the  $G_N^0$  is independent of the branch structure and virtually identical with that for the linear polymers [3].

During the last few years notable advances have been made in understanding the rheological properties of highly entangled linear polymers using de Gennes' reptation idea [6]. But long branches would be expected to restrain highly such snake-like motion of the chain. De Gennes [7] suggested that translational diffusion of the star could take place only when a branch retraced without crossing any of the obstacles to the branch point. More recently, Bartels and his coworkers [8] have shown that, in contrast to monodisperse linear polymers which relaxes through mainly reptation, the relaxation of monodisperse stars are somewhat dominated by constraint release mechanism in addition to the retraction process.

Binary mixtures of each monodisperse component have been used in order to elucidate the polydispersity effect on viscoelastic properties. For linear polymers, various mixing rules have been proposed both theoretically and experimentally on the basis of the reptation and the tube renewal due to constraint release [9-14]. On the other hand, when the long branch are mixed with linear polymers the relaxation processes become more complicated than linear-linear system because of structural nonhomogeneity. Recently, Struglinski and his coworkers [15] have investigated the diversity effects of binary mixtures consisted of linear and 3-arm star polybutadiene, four linear-star and one star-star. In their work, storage and loss moduli were measured over a wide range of frequencies and the compositional dependence of  $\eta_0$  and  $J_e^0$  were analyzed by an experimental constant-architecture mixing rule. But the theoretical description for the star containing blends may be a very difficult problem. We have not found an unified theory for the star containing blends. For this reason, studies on the dynamics of the dynamics of the blends of branched polymers and li-

near polymers may give more direct information on the role of each polymer in the blended state.

In this paper, we propose a simple blending law based on tube models for mixtures consisted of different chain architectures such as linear-linear, linear-star, and star-star blends it is expected that the relaxation process of the star is very complex. So we focus our interest on the interaction between different chains disregarding the constraint release effect in each monodisperse state.

## 2. Theoretical background

In the tube model, the relaxation of stress following a step strain is affected by some modes of molecular dynamics [16]. During the first stage, the entanglement points are supposed to behave as strong crosslinks allowing only a wriggling motion of the monomer units in the transverse direction to the primitive chain segment. During the stage of equilibration across slip-links, the relaxation process is a longitudinal reequilibration of monomer density between parts of the chain which have been differently extended or compressed. Some authors [17, 18] suggested that the curvilinear monomer density along the chain contour could be equilibrated by monomer slips through the entanglement links. These relaxation processes on a short time scale are nearly independent of the chain structures, but in the terminal region associated with chain orientations imposed by the distorted tube conformations, the relaxation process is strongly dependent on polymer structure.

### 2.1 Monodisperse Linear Polymers

Even after the primitive chain recovers its equilibrium arc length, the conformation of the primitive chain is still in a non-equilibrium state. The chain disengages from the deformed tube by the reptation, i.e., the crawling motion of the random coil chain along its own contour through highly entangled surrounding chains. Assuming the lifetimes of constraints that confine the chain are long enough and the stored energy is distributed uniformly along the chains on average, the stress relaxation function  $G_i^o(t)$  for monodisperse linear

polymer system is proportional to the abandonment of primitive path steps [19]:

$$G_i^o(t) = G_N^o \mu(t; T_d^o) \quad (3)$$

with

$$\mu(t; T_d^o) = \sum_{p, \text{odd}} \frac{8}{\pi^2 p^2} \exp(-tp^2/T_d^o) \quad (4)$$

$$T_d^o = K \left( \frac{M_i^3}{M_e} \right) \quad (5)$$

$$K = \frac{\xi_0 b^2 N_e^2}{kT \pi^2 M_e^2} \quad (6)$$

where  $\xi_0$  denotes the friction coefficient associated with each statistical segment (Kuhn's segment) of the length  $b$ ,  $k$  the Boltzmann constant,  $T$  the temperature, and  $N_e$  is the number of Kuhn's segments per one step of the primitive path. It is notable that the coefficient  $K$  is independent of MW and dependent on temperature.  $M_i$  represents the molecular weight of the linear polymer. The plateau modulus  $G_N^o$  is given by

$$G_N^o = \frac{4 \rho RT}{5 M_e} \quad (7)$$

where  $\rho$  is the density of a polymer and  $R$  is the universal gas constant.

### 2.2 Monodisperse Star-branched Polymers

The polymer considered here is a simple and symmetric star-branched polymer molecule with  $f$ -arms of equal length. We designate the MW of star molecule as  $M_s$  and the MW of one arm as  $M_a (= M_s/f)$ . For such nonlinear molecule the relaxation process is dominated by the retraction along its own contour [20-21]. It is assumed as in the system of linear polymers that each arm of the star is composed of  $N_a$  primitive steps and each step contains  $N_e$  statistical Kuhn's segments, which are connected by bonds of mean length  $b$  and have friction coefficient  $\xi_0$  per segment. It is also assumed that the monomeric friction coefficient  $\xi_0$  for branched molecules is equal to that for linear molecules. Due to the branching, the central segment is considered not to move along the tube in the sense of time scale.

Pearson and Helfand [21], treating the arm retraction as a dynamic process in a potential well similar to that proposed by Doi and Kuzuu [20], obtained a longest relaxation time for the arm:

$$T_b^o = T_A N_a^{3/2} \exp(\beta N_a) \quad (8)$$

where  $\beta$  is a constant and  $T_A$  represents the maximum Rouse relaxation time for a single subunit of  $N_e$  monomer as

$$T_A = \frac{\xi_0 b^2 N_e^2}{2\beta kT} \left(\frac{\pi}{\beta}\right)^{1/2} = 2K\pi^2 M_e^2 \quad (9)$$

The last term of eq. (9) can be obtained from eq. (6) by giving  $\beta=0.6$  which is another parameter in addition to  $\xi_0$  and  $M_e$ .

They estimated the fraction  $\mu_b(t; T_b^o)$  of the tube not visited by the end of arm chain having  $N_a$  segments in the form

$$\mu_b(t; T_b^o) = \int_0^1 \exp\left[-\frac{t}{T_b^o} \exp\{\beta N_a (1-\xi^2)\}\right] d\xi \quad (10)$$

For a simple shear strain  $\gamma$  which is small enough to evoke only a linear response, the relaxation modulus  $G_b^o(t)$  of branched polymer in pure state can be written as

$$G_b^o(t) = G_N^o \cdot \mu^b(t; T_b^o) \quad (11)$$

which is obtained by assuming that the remaining stress at time  $t$  is proportional to the average length of the tube unreleased. The plateau modulus for star polymer is equal to that for the linear molecule as elucidated experimentally.

### 3. Blending laws for mixtures

In mixtures with different chain architectures, linear-linear (L-L), linear-star (L-S or S-L), and star-star (S-S) blends, let 2-chain and 1-chain represent the chains (in the case of star polymer the chain designates one arm chain) with longer relaxation time and shorter one in their pure states, respectively. Both  $T_{d1}$  (or  $T_{b1}$ ) and  $T_{d2}$  (or  $T_{b2}$ ) in a blend state can be related with their pure state values,  $T_{d1}^o$  (or  $T_{b1}^o$ ) and  $T_{d2}^o$  (or  $T_{b2}^o$ ), and

the volume fraction  $\phi_2$  of the 2-chain by describing how the relaxation process of model chain is affected by its surrounding chains. Our primary interest is the interpretation of the intermolecular interactions between 1-chain and 2-chain by introducing the constraint release mechanism. It is assumed that each pure component relaxes only by reptation (or retraction) and does not experience the constraint release of the surrounding chains with the same architecture during its relaxation.

#### 3.1 Linear-Linear Blends

According to the tube model theories, the MWD effects are well described by constraint release mechanism in addition to reptation [9-14]. Kim and Chung [14] have extended the tube model to explain the terminal viscoelastic properties of binary blends in the highly entangled state of two linear monodisperse polymers. In the L-L blend the short chain, 1-chain, relaxes mainly by reptation, whereas the long chain, 2-chain, shows somewhat complex behavior: after tube-forming short chains around 2-chain are released, the tube enlargement and thereafter the long-chain disengages the enlarged tube by reptation. The relaxation of 2-chain by both reptation and tube renewal is visualized as the relaxation by pure reptation an equivalent primitive chain. The details about the effects of chain length distribution was already reported [14].

#### 3.2 Star-containing Blends

In the binary blends, linear-star and star-star blends as well as linear-linear blends, the constraint release is an important mechanism. the linear-star blends may be divided into two kinds of blends: the relaxation time of the star component is (a) greater than that of the linear component, and (b) smaller than that of the linear component. For the sake of convenience, the former case will be hereafter called the "L-S blends" and the latter case called the "S-L blend". The second letter followed the dash designates the component with longer relaxation time.

Firstly, in the system of case (a) the tube renewal of a branched molecule in a linear matrix

has been explored theoretically by Klein [12] and studied experimentally by Roovers [22] at the dilute concentration of a star polybutadiene in the low molecular weight linear ones. But their studies have been limited in the low concentration region with no branch-branch interaction, so that we propose relaxation mechanisms and blending laws for binary blends where the branch-branch interactions, i.e., 2-2 entanglements, become noticeable.

If a linear chain selected as a labeled chain (1-chain) in the L-S blend where the relaxation time of an arm of the star component is greater than that of the linear component, the constraints, the constraints provided by neighboring linear and branch chains are not changed until  $T_{c1} (\approx \pi^2/12 \cdot T_d^1)$ , the average lifetime of slip-links imposed by a tube-forming linear chains. Therefore, the linear chain relaxes by reptation along with terminal re-

laxation time  $T_{d1}^0$  by eq. (5).

On the other hand, an arm of a star polymer labeled as a 2-chain relaxes by retraction alone until  $T_{c1}$  because there is no change in the topology of constraints. The arm 2-chain evaporates its original conformation by retracting along its axis pushing out unentangled loops into the surrounding matrix as shown in Fig. 1b.

Then at the time  $T_{c1}$  the arm chain begins to be subjected to the rearrangements of the constraints by tube-forming linear chains. For  $t > T_{c1}$ , the chain renews its conformation mainly by the local tube renewal related with the slip-links formed by 1-chains. Whereas, most of the branch-type slip-links keep their original locations until one end of the model chain passes through them (filled circles of Fig. 1c).

When  $T_o$  is supposed to be a tube renewal time between two branch-type slip-links, the time  $(T_o - T_{c1})$  corresponds to the longest relaxation time of the Rouse-like local tube segment as [9-10]

$$T_o - T_{c1} = K_p N_l^2 T_{c1} \quad (12)$$

The value of proportionality constant  $K_p$ , less than unity is still disputable and will be discussed later. The number of primitive steps between two branch-type slip-links,  $N_l$ , is given by [14]

$$N_l = N_{a2} / [(N_{a2} - 1)\phi_2 + 1] \quad (13)$$

where  $N_{a2}$  is the number of primitive steps per arm 2-chain.

After such a tube renewal between two branch slip-links is completed the linear 1-chains behave as somewhat solvent-like molecules and the virtual tube diameter is expanded from  $a$  to  $a_2$ . It is expected for the branch chain to relax by retraction alone in the enlarged tube for the time larger than  $T_o$ .

The arm chain at  $T_o$  can be envisaged as a homogenized primitive chain constrained effectively only by some imaginary fixed slip-links equally separated by the distance  $a_2$ . This remodeled chain is called as an "equivalent primitive chain", which is denoted by thick line in Fig. 1d. The equivalent average molecular weight  $M_{e2}$  between two slip-links with the distance  $a_2$  is expressed

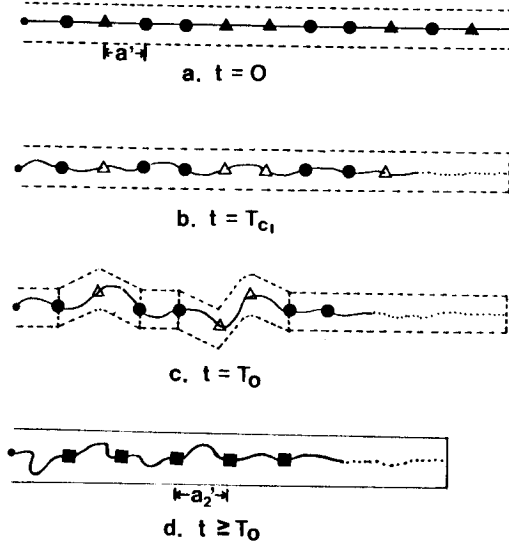


Fig. 1. Schematic illustration of the relaxation process of 2-chain with higher relaxation time: (a) Original 2-chain is shown in a straightened form; (b) Primitive 2-chain begins to be subjected to the tube renewal at  $t = T_{c1}$  (denoted by open triangle); (c) At  $t = T_o$  tube renewal between two type-2 slip-links is completed; (d) The model chain can be visualized as the equivalent 2-chain and equivalent survived tube (thin line).

as

$$M_{e2'} = M_e \phi_2^v \quad (14)$$

where  $v$  is a parameter that represents the degree of departure from the pure solvent-like dependence varying from unity to zero. The  $M_{e2'}$  is deduced from the relation between the entanglement spacing and the concentration of polymers in low molecular solvent.

The index  $v$  must be a parameter related to each effective molecular size in the binary mixture. Thus in order to find the value of  $v$ , we regard the linear 1-chain as a branch-type 1-chain of the star polymer with the same characteristic lifetime as that of linear polymer. That is, the structurally nonhomogeneous binary mixture is considered as a constant-architecture mixture toward higher relaxation-time component. In general, the average lifetime of the tube-forming type-1 constraints on the 2-chain is defined by [10]

$$T_c = \int_0^\infty \mu(t) dt \quad (15)$$

where  $\mu(t)$  means the fraction of primitive steps which are still occupied at time  $t$  and is given by eq. (4) for linear polymers and by eq. (10) for branched ones. Let us consider the linear constraint as a branched constraint with same lifetime:

$$\frac{\pi^2}{12} T_{d1} = \frac{(T_{b1'})^*}{2\beta N_{a1}^*} \quad (16)$$

where the superscript\* means the effective 1-chain having the same structure with 2-chain. The  $N_{a1}^*$  means the number of primitive steps of a branch-equivalent constraint. When  $N_{a1}^*$  approaches  $N_{a2}$ , the 2-chain hardly experiences the local tube renewal before it completely abandons original memory. In another extreme case for  $N_{a1}^*/N_{a2} \rightarrow 0$ , the short chain behaves as solvent-like one. Apparently, the index  $v$  in eq. (14) must be a function of  $N_{a1}^*/N_{a2}$  satisfying two limiting conditions that varies from unity at  $N_{a1}^*/N_{a2} = 0$  to zero at  $N_{a1}^*/N_{a2} = 1$ .

On the other hands, the fraction of the equivalent tube survived at  $t > T_e$  is equal to the fraction for a certain purely retracting chain with the arm molecular weight  $M_{a2}$ , entanglement spacing  $M_{e2'}$ ,

and number of primitive steps  $N_{a2'} = M_{a2}/M_{e2'}$ . Thus the disengagement time  $T_{b2}$  can be written as

$$T_{b2} = \phi_2^{v/2} T_{b2'} \exp\{-\beta N_{a2}(1-\phi_2^v)\} \quad (17)$$

Therefore, the fraction of the equivalent survived tube maintaining the original conformation,  $\mu_b [t; T_{b2}(t)]$ , over all range of time is written as

$$\mu_b [t; T_{b2}(t)] = \int_0^1 \exp\left[-\frac{t}{T_{b2}(t)} \exp\{\beta N_{a2}(t)(1-\xi^2)\}\right] d\xi \quad (18)$$

where  $N_{a2}(t) [=M_{a2}/M_{e2}(t)]$  is the number of equivalent primitive steps. Here  $M_{e2}(t)$  and  $T_{b2}(t)$  are equal to  $M_e$  and  $T_{b2'}$  for  $t > T_{c1}$ , respectively. For  $t > T_e$  they are given as  $M_{e2'}$  and  $T_{b2}$  in eqs. (14) and (17), respectively. During the local tube renewal process,  $T_{c1} < t < T_e$ , it is roughly expected for  $M_{e2}(t)$  to increase linearly from its lower limit  $M_e$  to upper limit  $M_{e2'}$  and for  $T_{b2}(t)$  to be equivalent to the relaxation time of an arm chain with the corresponding transient  $M_{e2}(t)$  and  $N_{a2}(t)$ .

The time evolution of the chain parameters of the equivalent 2-chain for each case of blends is summarized in Table I.

On the basis of the blending law in which every molecule contributes independently to the stress [23], various viscoelastic properties of binary blends can be predicted. For example, the stress relaxation function of binary blends,  $G_B(t)$ , is calculated as the sum of the respective contribution of blend components. The  $G_i(t)$  attributed to  $i$ -component chains in the blend is written as

$$G_i(t) = \frac{4}{5} n_i kTN_i(t) \cdot \mu_i(t) \quad (19)$$

where  $n_i$  is the number of 1-chains in the blend, and  $\mu_i(t)$  is equal to  $\mu_i(t; T_{d1})$  for linear 1-chain and  $\mu_b [t; T_{b2}(t)]$  for arm 2-chain. thus

$$G_B(t) = G_N^0 [\phi_1 \mu_1(t; T_{d1}) + \phi_2 \frac{M_e}{M_{e2}(t)} \mu_b \{t; T_{b2}(t)\}] \quad (20)$$

which is obtained by replacing  $4/5 n_i kTN_i(t) = \phi_i G_N^0 M_i/M_{e_i}(t)$ .

**Table I.** Time Evolution of Chain Parameters of The Equivalent 2-chain

Parameters	Time		
	$t < \tau_{c1}$	$\tau_{c1} < t < \tau_o$	$t < \tau_o$
Molecular weight	$M_2$	$M_2$	$M_2$
Entanlement spacing	$M_e$	$M_{e2}(t) = \frac{M_e(\tau_o - t) + M_{e2}'(t - \tau_{c1})}{\tau_o - \tau_{c1}}$	$+ M_{e2}' = M_e \phi_2^{-\nu}$
Primitive step length	$a$	$a_2(t) = a [M_{e2}(t)/M_e]^{1/2}$	$a_2 = a \phi_2^{-\nu/2}$
Number of primitive paths	$N_2$	$N_2(t) = N_2 M_e / M_{e2}(t)$	$N_2 = N_2 \phi_2^\nu$
L-L(or S-L) blend	$\tau_{d2}^o$	$\tau_{d2}(t) = \tau_{d2}^o M_e / M_{e2}(t)$	$\tau_{d2} = \phi_2^\nu \tau_{d2}^o$
L-S(or S-S) blend	$T_{b2}^o$	$T_{b2}(t)$	$T_{b2} = \phi_2^{-\nu/2} \exp[\beta N_{d2}(1 - \phi_2)]$
Fraction of stress remained :			
L-L(or S-L) blend	$F_2(t; \tau_{B2}; \tau_{d2}^o)$	$B_2 \mu(t; \tau_{B2}) + \frac{M_e}{M_{e2}(t)} \mu[t; \tau_{d2}(t)]$	$B_2 \mu(t; \tau_{B2}) + C_2 \frac{M_e}{M_{e2}'} \mu[t; \tau_{d2}]$
L-S(or S-S) blend	$F_b(t; T_{b2}^o)$	$\frac{M_e}{M_{e2}(t)} F_b[t; T_{b2}(t)]$	$\frac{M_e}{M_{e2}'} F_b[t; T_{b2}]$

\*At  $t < \tau_{c1}$  the equivalent 2-chain has the same chain parameters with the original 2-chain.

$\tau_{c1}$  and  $\tau_o$  are equal to  $T_{c1}$  and  $T_o$ , respectively, if the 1-chain is the branch.

<sup>†</sup> $N_1$  and  $N_2$  in the index  $\nu$  are given as their effective values corresponding to the blend.

Secondly, in the case (b) of the S-L blend with the star component of smaller relaxation time than linear component, where the 1-chain is an arm chain which relaxes by retraction only and the 2-chain is the linear chain which experiences the local constraint release by the branch 1-chains, the linear component of the same relaxation time can be substituted for the star component. The relaxation process of the linear 2-chain in the S-L blend is equivalent to that in the L-L blend replacing  $T_{c1}$  with

$$T_{c1} = \frac{T_{b1}^o}{2\beta N_{d1}} \quad (21)$$

Thus the relaxation modulus of this blend is represented by

$$G_B(t) = G_N^o [\phi_1 \mu_b(t; T_{b1}^o) + \phi_2 \frac{M_e}{M_{e2}(t)} \mu[t; T_{d2}(t)]] \quad (22)$$

where all parameters for the linear 2-chain in the S-L blend are the same with those for the 2-chain in the L-L blend as noted in Table I. That is to say, the binary blend consisted of different molecular structures on large-scale is considered as the homogeneous binary composed of same struc-

tures with different chain lengths.

Finally, in the binary blends composed of two monodisperse star components with different molecular weights, the branch chain in lower molecular weight star relaxes only by retraction with terminal relaxation time  $T_{b1}^o$ . The relaxation process of branch 2-chain is equivalent to that in the L-S blend replacing  $T_{c1}$  in eq. (21). Then the relaxation function  $G_B(t)$  of the S-S blend can be written as

$$G_B(t) = G_N^o [\phi_1 \mu_b(t; T_{b1}^o) + \phi_2 \frac{M_e}{M_{e2}(t)} \mu_b\{t; T_{b2}(t)\}] \quad (23)$$

Hitherto, we visualized the relaxations of each component in binary mixtures as pure disentanglement processes with time-dependent entanglement network in order to describe the effect of chain architectures on viscoelasticity of polymers, which is called equivalent primitive chain model. From these relaxation mechanisms, the blending laws were proposed for several mixtures. We will discuss the qualitative features between the theory and some experimental data from literature.

#### 4. Discussion

We have extended the local constraint release mechanism from linear-linear blends to linear-star and star-star blends. The 2-chain with the longer relaxation time in the binary blend relaxes by three successive mechanisms, i.e., reptation (or retraction), local tube renewal between two slip-links formed by 2-chains, and finally reptation (or retraction) again. After 1-chain relaxed by reptation (or retraction) alone, the 1-chains behave like solvent and thus the effective entanglement spacing of 2-chain is aggrandized.

Klein [9] and Grassley [10] have considered the tube renewal as a Rouse-like random jumping motion of a tube constraints on the primitive paths. Extending the treatments by those to the current case, the local tube segment is pictured as a virtual Rouse chain. The 2-chain experiences the constraint release by surrounding 1-chains and 2-chains, i.e., the short-range or local tube renewal of  $N_l$  local tube segment by neighboring 1-chains and the long-range tube renewal of a single virtual Rouse chain with  $N_2\phi_2^v (=M_2/M_{e2})$  submolecules where  $N_2$  means the number of primitive steps of the effective 2-chain. The  $N_2$  is equal to  $N_{l2}$  for linear 2-chain or  $N_{a2}$  for arm 2-chain. Attention given here is restricted to such a local tube renewal between two adjacent entanglements with 2-chains which are assumed to be distributed uniformly. As shown in eq. (12), the importance of local tube renewal is alleviated with increasing  $\phi_2$  while the long-range tube renewal time increase with  $\phi_2$ .

In binary blends, the relaxation of 1-chain is mainly dominated by reptation (or retraction) independent of its volume (or weight) fraction, while the behavior of 2-chain possibly shows different aspects with its composition. That is, in infinite dilute region where the 2-chain is isolated in the 1-chain matrix, the 2-chain renews its conformation only by tube renewal with the equivalent Rouse chain with  $N_2$  submolecules after the relaxation of 1-chains. As  $\phi_2$  increases to a concentrated region where the entanglements among 2-chains are prominent the short-range tube rene-

wal can occur between two entanglements with 2-2 couplings immediately after the occurrence of constraint release. The rheological properties are very important in this concentrated region. Thus in order to make the model applicable even in dilute region  $\phi_2 < \phi_c$ , where the interactions among the 2-chains are not effective, we can identify the behavior of the 2-chain at  $\phi_2 < \phi_c$  with the behavior at  $\phi_c$  where the entanglements among 2-chains begin. The critical 2-chain content dependent on the effective molecular sizes of each component chain can be scaled as [14]

$$\phi_c = \left[ \frac{N_1^*}{N_2} \right]^{1/v} \quad (24)$$

where  $N_1^*$  represents the number of primitive steps of effective 1-chain. This criterion for the onset of entanglement between 2-chains is universal for all kinds of blends discussed currently.

On the other hands, in addition to reptation the path length fluctuation affects the stress relaxation for monodisperse linear polymers. It has been considered that the discrepancy of  $\eta_0$  for linear polymers between experimental observations,  $\eta_0 \propto M^{3.4}$  and the reptational predication,  $\eta_0 \propto M^3$ , is mainly caused by the thermal fluctuation of the primitive chains. We can adopt the Lin's treatment [10] in order to include the fluctuation effect in the present equivalent chain model for binary blends. The contour length fluctuation effect reduces the terminal relaxation time of the linear component in pure state.

$$\tau_d^0 = T_d^0 (1 - 1/\sqrt{N_l})^2 \quad (25)$$

##### 4.1 Linear-Linear Blends

Effects of chain size distribution on the viscoelastic properties of polydisperse linear polymers are well represented by the binary mixtures consisted of two nearly monodisperse components [11, 24-25]. Experimental observation for the relaxation modulus curves of binary blends show interesting differences from the nearly monodisperse fractions depending on their blending ratio,  $M_2/M_1$ . The experimental work for binary blends are divided into two classes with the value of



$C^* = T_{c1} N_2^2 / T_{d2}^0 = M_1^3 / M_2 M_c^2$ . If  $C^* > 1$ , the longest relaxation time of 2-chain is independent of  $\phi_2$  as was noted by Struglinski and Graessley [11]. Otherwise, the constraint release effects become very important. In this case, the conformation of 2-chain reaches a local equilibrium state with enlarged tube diameter after tube-forming short chains released and thereafter the 2-chain reptates the tube dilated. The longest relaxation time depends on  $\phi_2$ . Fig. 2a shows the shape of the relaxation modulus curve, as an example, of a blend consisting of two monodisperse linear polymers. The qualitative feature is matched by the several experimental data on polystyrene blends. The second plateau region appears after local tube renewal was completed. Then the level of intermediate plateau is given by the value of  $G_{plat} / G_N^0 = \phi_2^{1+\nu}$  which varies with its blend ratio from  $\phi_2$  at  $M_1 / M_2 = 1$  to  $\phi_2^2$  at  $M_1 / M_2 = 0$ . The dependence of the

index  $\nu$  on the blend ratio has been well covered by first-order approximation for explaining viscoelastic properties [14].

#### 4.2 Star-Containing Blends

In earlier chapter, we regarded the 1-component in a mixture consisted of different chain structures as an effective 1-component having same architecture with 2-component. The effective molecular weight is not affected by its composition because the relaxation of 1-chains have the same behavior in its pure state. Struglinski and his co-workers [15] have obtained the star-equivalent molecular weight for the linear polymer from  $\eta_0$  by using the relationship for the star polymers and succeeded obtaining a star polymer mixing rule. In Fig. 3, the effective number of primitive steps of 1-chain including the contour length fluctuation for linear component are compared with

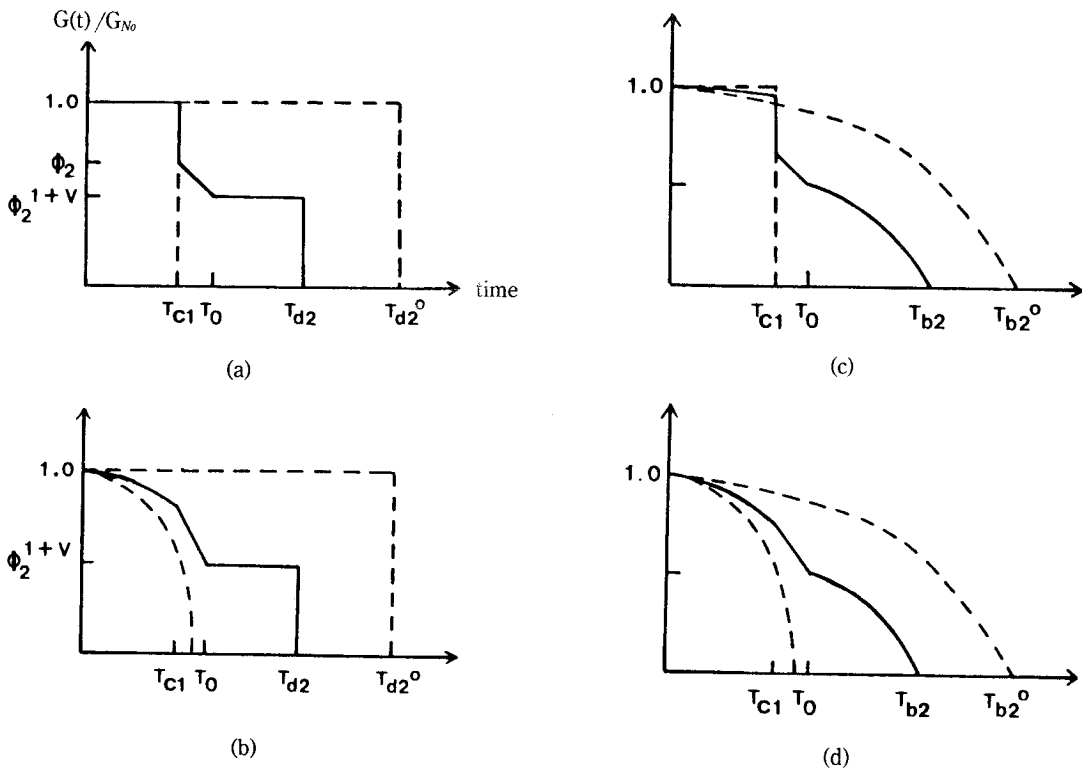


Fig. 2. Relaxation modulus for several types of blends; (a) L-L blend, (b) S-L blend, (c) L-S blend, and (d) S-S blend. The dashed lines represent moduli for each monodisperse component in blends.

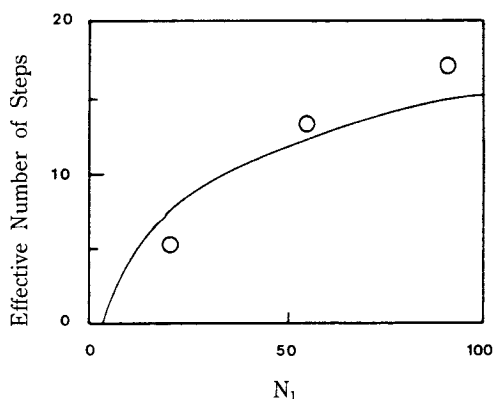


Fig. 3. Number of primitive steps of effective 1-chain having same structure with branched 2-chain in L-S blends.

the empared with the empirical calculation by them which is denoted by open circles. As shown in this figure, their qualitative features are substantially the same. That is, the effective molecular weight increases logarithmically as the molecular weight of linear 1-chain increases.

The rheological properties of the star-containing blends are well characterized by shear relaxation modulus which is shown in Fig. 2b, c, d. In the nearly monodisperse star, the longest relaxation times cannot be defined from experimental modulus curves owing to the broad relaxation spectra of star components. The relaxation of stars, in contrast to that of monodisperse linear polymers, has not a clear plateau, which may be caused by mainly retraction, i.e., chain ends fluctuation of kind [20-21], and partly constraint release [8]. However, we have obtained the blending laws of rheological properties by assuming that the constraint release is not effective in pure states. This assumption can cause an overestimation of the blending effect in the star-containing blends. But it is expected that the interaction between two different chains is well explained by the present model.

For  $t < T_{c1}$ , all chains participate in entanglement network and thus the stress relaxation takes place only by reptation or retraction. For transient region  $T_{c1} < t < T_n$ , the entanglement spacing is enlarged to average spacing between 2-2 entangle-

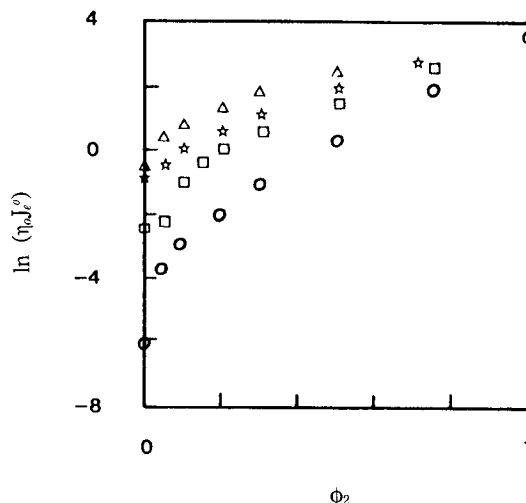


Fig. 4. Variations of weight-average relaxation time with volume fraction of 2-components for star containing blends, three L-S and one S-S blend. In all cases the higher molecules are the star polymer with molecular weight 127,000. The lower molecules in the mixtures are linear polymers with molecular weight 36,800 ( $\circ$ ), weight 100,000 ( $\square$ ), weight 168,000 ( $\triangle$ ), and one star polymer having molecular weight 74,600 ( $\star$ ).

ments. If the 1-chain is a branch type as shown in Fig. 2b and d, the  $T_{b1}^0$  may be greater or smaller than the  $T_{c1}$ . In these systems, we designate the stress relaxation curve as a simple line although it is somewhat complicate. Finally for  $t > T_n$ , the contribution of 1-chain to stress becomes very weak. The stress relaxation occurs almostly by 2-chains with the expanded entanglement spacing.

It is known that the longest relaxation time for a Rouse chain fixed at a point is four times larger than that for a free Rouse chain of the same length [10]. Thus the proportionality constant  $K_p$  in eq. (12) can be replaced by 1/6 for linear virtual Rouse chain and by 4/6 for branched one. And also, the product of viscosity and compliance,  $\eta_w J_e^0$ , defines a characteristic time of the mixture weighted toward the longest times, i.e., weight average relaxation time of the terminal region which may be a function of  $\phi_2$  and blend ratio. Fig. 4 shows the variation of  $\ln(\eta_w J_e^0)$  with volume frac-

tion of 2-chain for star containing blend, three linear-star and one star-star. In this figure we argue, using data from Struglinski and his coworkers, that the weight average relaxation times are exponentially dependent on  $\phi_2$ , which is qualitatively predicated by eq. (17). As  $\phi_2$  increases, the 2-2 entanglements increase and thus the fraction of the 2-chain experiencing constraint release decreases. Owing to the increase of the interaction among 2-chains, the terminal relaxation time of 2-chain increases with  $\phi_2$ . And also the  $\phi_2$ -dependence of the relaxation time weakens as the blend ratio  $M_2/M_1^*$  increases, which is deeply related to the value of the index  $\nu$  in eq. (17).

Additionally, the criterion for the significance of tube enlargement in linear-linear blends which was proposed by Doi, et al. can be extended to the star containing blends with the value of  $C^* = T_{c1}N_{a2}^2/T_{b2}^0$ . The present theory indicates that the relaxation of 2-chain is accelerated by the release of constraint formed by neighboring 1-chains, which is realized when  $C^* < 1$ .

### 5. Concluding remarks

In order to account for the side-chain effects on the dynamical behavior and rheological of polymers, we considered the tube enlargement due to local constraint release and remodeled the relaxation mechanism by adopting the idea of disengagement by pure reptation (or retraction) of an equivalent primitive chain after the completion of the tube renewal.

Here we ignored the constraint relaxation process of a model chain. In monodisperse polymer system consisted of all same chains the overall lifetime  $T_c$  of tube for a model chain is given by  $T_c = T_d^0$  for linear system and given by  $T_c = T_b^0/N_a$  for an arm chain in star polymer system and thus the rate of constraint release is enhanced by a factor  $N_a$  for the star. Hence it is understood that the effect of constraint release in monodisperse state is more important in branched system than in linear system. In blended states, the interaction between 1-chain and 2-chain is more dominant than the interaction between same chains. Thus

it is expected that the present theory captures the essential features for relaxation process of the star containing blends.

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