

다분산 고분자의 점탄성에 대한 분자이론

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Molecular Theory on Viscoelasticity of Polydisperse Polymers

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요 약 : 분자량 분포가 고분자의 유변학적 물성에 미치는 영향을 설명하기 위하여 reptation과 local constraint release가 동시에 일어나는 각 성분사슬의 완화과정을 순수한 reptation에 의해 관을 빠져나가는 equivalent primitive chain의 완화과정으로 해석하였다. 각 equivalent chain의 특성변수들을 알므로써 다분산 고분자계에 대한 응력방정식을 얻는다. 제시된 이론을 검증하기 위하여, 분포도가 아주 낮은 선형 폴리스티렌 표준시료들의 2성분 및 3성분 혼합물의 전단응력 완화 함수 $G(t)$ 를 rheometer로 측정하였다. 실험적으로 얻은 $G(t)$ 의 마스터곡선은 이론적 예측결과와 잘 일치하였다.

Abstract : In order to describe the effects of molecular weight distribution on the rheological properties of linear polymeric liquids, the terminal relaxation process of each component chain including concurrent reptation and local constraint release is visualized as the pure reptational disengagement of an equivalent primitive chain. The stress equation for polydisperse polymers is also formulated by knowing the parameters of each equivalent chain. To test the proposed theory, the shear stress relaxation modulus $G(t)$ of binary and ternary blends of polystyrene fractions with narrow MWD are measured in a linear deformation regime. The master curves of $G(t)$ obtained experimentally are in good agreement with the predicted values.

INTRODUCTION

The effect of molecular weight distribution (MWD) on rheological properties of polymeric liquids is one of the most important problems not

only in polymer science but also in polymer processing of commercial polymers which contain a range of molecular sizes. Prediction of the viscoelastic response of these materials requires an understanding of the effect of each individual

molecular parameter and the interactions between parameters ultimately from a molecular viewpoint.

During the last few years promising investigations to represent the viscoelastic behavior of entangled linear polymers have been carried out by using de Gennes' reptation concept¹ which means the motion of a chain along the tube-like region restricted by surrounding chains. Doi and Edwards² applied the reptation idea to the viscoelasticity of polymers and showed that many characteristic features of their rheological properties are naturally explained by the tube model. Data from related experiments suggest that motions other than pure reptation are also important. The finite lifetime of tube constraints is conceivable in entangled polymer liquids,³ and the reptational diffusion of tube-forming chains that supply the topological constraints results in constraint release by tube renewal. Both reptation and constraint release are relaxation mechanisms that are associated with intermolecular interactions.

Thermal fluctuation in chain contour length is considered as another concurrent relaxation mechanism,⁴⁻⁶ which is related with intramolecular chain dynamics. Recent modified tube models incorporating the fluctuation effect into the reptational process explain well the relationship between the zero-shear viscosity η_0 and the molecular weight (MW), $\eta_0 \propto M$,^{3,4} experimentally observed.

The other fast intramolecular relaxation processes have been also proposed.^{6,7} One of them is the Rouse relaxation of monomeric subunits between two adjacent entanglement points. Another is the slippage of the chain segment through entanglement links to equilibrate the curvilinear monomer density along the chain contour.⁶ These short time relaxation processes are deeply related to the viscoelastic response not only in short time (or high frequency) region but also in high deformation-rate region.

Kim and Chung have proposed the equivalent primitive chain model⁸ to account for the behavior of binary blends by introducing the constraint release by local tube renewal which is very significant for the relaxation process of a high MW

model chain in the blend of two monodisperse species of the chemically identical polymers. The longest relaxation time of the model chain is related to the component relaxation time in its pure state, molecular weights of blend components and composition. From the knowledge of the longest relaxation times of the blend components, the stress equation has been formulated for the binary blend. The blending laws for terminal viscoelastic properties have been derived from this equation and fitted well experimental data over a wide range of the blend composition and component MW ratio. In this paper, the equivalent primitive chain model for the binary blend is extended to multicomponent blends with arbitrary distribution in chain length, and thus a constitutive stress equation can be formulated for the polydisperse polymers from the knowledge of the longest relaxation times of component chains. Besides the intermolecular interactions such as reptation and constraint release, the stress equation including intramolecular interactions, i.e., the shortest Rouse equilibration between two entanglements, the equilibration of monomer density along the chain and the chain ends fluctuation, is formulated by using recent modified tube model.

To test the theoretical prediction, we prepare the binary and ternary blends composed of two and three narrowly distributed polymer fractions which are desirable to explain clearly the effects of MWD on viscoelastic properties, and measure the stress relaxation modulus $G(t)$ of these samples by using parallel plate rheometer. Through the comparison between theory and experiment, the reasonability of the equivalent primitive chain model proposed here is reconfirmed for the polydisperse system.

Equivalent Primitive Chain Model for Binary Blends

The binary blend composed of two monodisperse linear polymers with different molecular weights is the most critical example describing the MWD effect on chain relaxation mechanism in polydisperse polymers.

To explain the relaxation process, the equivalent

primitive chain model has been proposed⁸ with the consideration of constraint release by local tube renewal. In the binary blend the short chain (designated hereafter as 1-chain) relaxes mainly by reptation, whereas the long chain (designated as 2-chain) shows somewhat complex behavior. That is, the 2-chain relaxes by reptation alone in the tube of diameter $a_2 = a$ and entanglement spacing M_e until the characteristic relaxation time τ_{c1} of the tube-forming 1-chains around the 2-chain. For time larger than τ_{c1} , the 2-chain renews its conformation by reptation and local constraint release. When such a tube renewal by 1-chains between two 2-2 entanglements is completed, the 2-chain disengages by reptation again in the expanded tube of diameter a_2' and the equivalent entanglement spacing $M_{e2}' (= M_e w_2^{-\nu})$ where w_2 is the weight(or volume) fraction of the 2-chain and changes from 1.0 at $M_1 / M_2 = 0$ to zero at $M_1 / M_2 = 1$. [refer to the reference (8) for the detail] The visualization of the relaxation process of the 2-chain is shown in Fig. 1.

As a result, including the contour length fluctuation effect in the chain relaxation, general expressions for the longest relaxation times of the binary blend components are summarized as follows :

(i) for the low MW 1-chain :

$$\tau_{d1} = \tau_{d1}^0 \quad (1)$$

(ii) for the high MW 2-chain :

$$\tau_{d2} = \begin{cases} w_2^\nu \tau_{d2}^0 & \text{if } w_2 > w_c \\ w_c^\nu \tau_{d2}^0 & \text{if } w_2 < w_c \end{cases} \quad (2)$$

where

$$\tau_{d1}^0 = K(M_1^3 / M_e) (1 - 1 / \sqrt{N_1})^2 \quad (3)$$

with $N_1 = M_1 / M_e$

The coefficient K is a function of temperature only and is independent of MW. The critical composition due to onset of entanglement between 2-chains, w_c , and the index ν are respectively given by

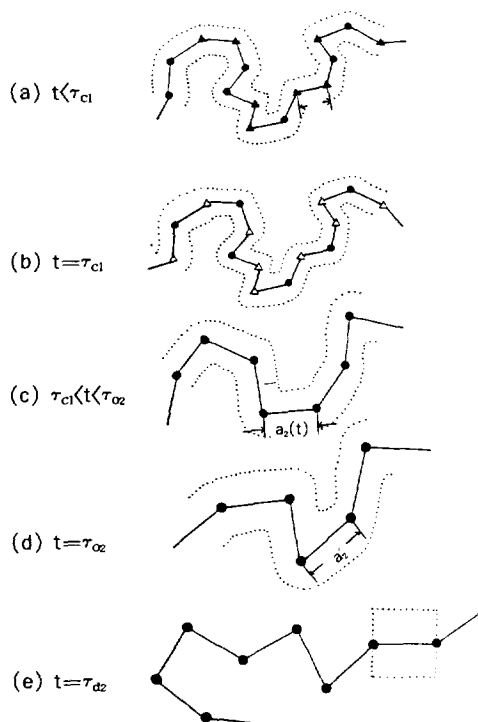


Fig. 1. Schematic illustration of the relaxation process for the 2-chain : (a)The 2-chain disengages the original tube by reptation at $t < \tau_{c1}$; (b)At $t = \tau_{c1}$ the constraints by 1-chains begin to evaporate (denoted by open triangle) ; (c)During the local tube renewal process the memory of the original tube conformation is represented by the equivalent survived tube(dotted line) and the distance $a_2(t)$ between two equivalent transient slinklinks (filled circles) increases with time ; (d)At the completion of local tube renewal the 2-chain is visualized as the equivalent one with the step length a_2' ; (e)The equivalent 2-chain completes the reptational disengagement at τ_{d2} .

$$w_c = \left(\frac{M_1}{M_2} \right)^{1/\nu} \quad (4)$$

$$\nu = 1 - M_1 / M_2 \quad (5)$$

The time for the completion of tube renewal is related with w_2 and the number of primitive steps between two 2-2 entanglements, N_t , and the characteristic relaxation time τ_{c1} of the 1-chain :

$$\tau_{02} = \tau_{c1}(1 + K_p N_t^2) \quad (6)$$

$$N_t = N_2 / [(N_2 - 1)w_2 + 1] \quad (7)$$

where K_p is a constant ($=1/6$)³ and τ_{c1} is the characteristic relaxation time of constraints by 1-chains. Klein⁹ argued that the release rate of the effective constraints defining a tube is considerably enhanced as a result of the nonindependence of constraints forming the tube. Following his argument, the constraint relaxation time is

$$\tau_{c1} = \tau_{d1}^0 / \sqrt{M_1 / m_0} \quad (8)$$

where m_0 is the molecular weight of a repeat unit.

According to eqs. (2) and (6), the ratio τ_{02} / τ_{d2} for any composition is predicted to be less than unity.

$$\begin{aligned} \frac{\tau_{02}(w_2)}{\tau_{d2}(w_2)} &< \frac{[\tau_{02}(w_c)]_{\max}}{[\tau_{d2}(w_c)]_{\min}} \\ &= \frac{e^2 / 6 \cdot \tau_{d1}^0}{(N_1 / N_2) \tau_{d2}^0} \ll 1 \end{aligned} \quad (9)$$

Therefore, it is conceivable that the 2-chain always finishes its terminal relaxation after the completion of local tube renewal process.

Relaxation Process in Multicomponent System

The theoretical consideration for the binary blends is now extended to a polydisperse blend with N_c monodisperse components whose MW's are $M_{Nc} > \dots > M_1 > \dots > M_2 > M_1$. Correspondingly, the terminal relaxation times in their respective pure states are expressed as $\tau_{dNc}^0 > \dots > \tau_{d1}^0 > \dots > \tau_{d2}^0 > \tau_{d1}^0$. The composition of the polydisperse blend is characterized by the weight fraction w_1 ($\langle i \rangle \langle N_c \rangle$).

If an i -th component chain is selected as a model chain, its entanglement couplings are composed of two types of slip-links. One is the interaction of the model chain with the same or higher MW component chain. This kind of slip-link is nearly fixed until the model chain passes through. It corresponds to the type-2 slip-link for the binary blend case. The other type of slip-link is formed by a shorter solvent k -chain of $1 \leq k \leq i-1$, which releases its effective constraints at τ_{ck} . The constraints of i -chain imposed by the solvent chains start to abandon their original conformations at τ_{c1} , τ_{c2} , \dots , and $\tau_{c(i-1)}$, and their respective local tube renewal processes are completed at τ_{02} , \dots , and τ_{0i} in a sequential manner. The local tube renewal processes for the model chain proceed from τ_{c1} to τ_{0i} in accordance with the superposed releases of the constraints by the tube-forming short chains. As mentioned in the binary blend case, after the completion of the superposed local tube renewal processes, the residual memory of the equivalent i -chain for its original conformation is maintained by the same or higher MW surrounding chains. That is to say, according to eq. (9), the reptational disengagement of the equivalent i -chain should be finished after the completion of local tube renewal, i.e., $\tau_{d1} > \tau_{0i}$, and thus the terminal relaxation time τ_{d1} is not related to the history of the local tube renewal process but to the chain parameters of the equivalent i -chain corrected at $t > \tau_{0i}$.

Thus the relaxation of the model i -chain can be interpreted as that of a 2-chain in a corresponding binary blend system. In other words, the solvent chains shorter than the i -chain behave like the 1-chains in the binary blend if the topological constraints imposed by neighboring solvent chains are visualized as a mean field composed of monodisperse chains with an average MW. There are several ways in defining the average MW of the solvent molecules in accordance with MWD; but the average MW should characterize the average terminal relaxation time of those molecules constructing the mean field. It is widely acknowledged that the zero-shear rate viscosity η_0 for both monodisperse and polydisperse linear polymers with high entanglements is expressed in terms of the weight average molecular weight (M_w), $\eta_0 \propto M_w^{3.4}$ and that the average terminal relaxation time for the polymers is directly proportional to η_0 , i.e., $\tau_{d(avs)} \propto \eta_0(M_w)^{10}$. Based on this understanding, the average MW of the solvent chains, \bar{M}_s , is chosen and defined as

$$\tilde{M}_i = \sum_{k=1}^{i-1} M_k w_k / (1 - \phi_i) \quad (10)$$

where

$$\phi_i = \sum_{j=1}^{N_c} w_j \quad (11)$$

That is to say, the ϕ_i means the weight fraction of the chains larger than or equal to the size of test chain, and the \tilde{M}_i designates the weight average molecular weight of the solvent molecules smaller than the model i -chain.

Since the interactions between the model i -chain and the high MW component chains are the same as those fixed slip-links between the same i -chains, the parameters for the equivalent i -chain are given as follows.

$$M_{ei}' = M_e \phi_i^{-\nu_i} \quad (12)$$

with

$$\nu_i = 1 - \frac{\tilde{M}_i}{M_i} \quad (13)$$

$$\phi_{ic} = \left(\frac{\tilde{M}_i}{M_i} \right)^{1/\nu_i} \quad (14)$$

Here M_{ei}' represent the entanglement spacing for the equivalent i -chain at time t , ν_i is the power index for i -component chain, and ϕ_{ic} is the critical weight fraction of polymers greater than or equal to the MW of i -component polymer in multicomponent blends because of the effect of entanglements between i -chain and j -chain with $M_j > M_i$. Then, the relaxation times τ_{di} 's in polydisperse polymers are expressed as follows:

$$\tau_{di} = \phi_i^{\nu_i} \tau_{di}^0 \quad \text{for } \phi_i > \phi_{ic} \quad (15)$$

$$\tau_{di} = \tau_{di}(\phi_{ic}) \quad \text{for } \phi_i < \phi_{ic} \quad (16)$$

where τ_{di}^0 is given by eq. (3).

It is apparent that the local tube renewal process for the relaxation of the i -chain should affect its stress decay at the short time region after a deformation, which will be discussed in the following section. Thus, the characteristics for the renewal process need to be given here. They can be obtained

directly from the analysis for the binary blend case following the above argument that the relaxation of a model chain in multicomponent blend can be interpreted as that in the corresponding binary system:

$$\tau_{oi} = \tilde{\tau}_{ci} (1 + K_p N_{ti}^2) \quad (17)$$

$$\tilde{\tau}_{ci} = \tilde{\tau}_{di}^0 / \sqrt{\tilde{M}_i / m_0} \quad (18)$$

$$N_{ti} = N_i / [(N_i - 1) \phi_i + 1] \quad (19)$$

where $\tilde{\tau}_{ci}$ and $\tilde{\tau}_{di}^0$ represent the average constraint lifetime and the relaxation time of averaged solvent chain with molecular weight \tilde{M}_i , respectively. Then, the sequential release occurrences of tube-forming constraints on the model i -chain by surrounding solvent chains are interpreted as the local tube renewal due to the constraint release of solvent chains in the corresponding binary blend composed of M_i - and M_i -chains. As a result, the time dependent entanglement spacing $M_{ei}(t)$ is

$$M_{ei}(t) = \begin{cases} M_e & \text{for } t < \tilde{\tau}_{ci} \\ \frac{M_e(\tau_{oi} - t) + M_{ei}'(t - \tilde{\tau}_{ci})}{\tau_{oi} - \tilde{\tau}_{ci}} & \text{for } \tilde{\tau}_{ci} < t < \tau_{oi} \\ M_{ei}' = M_e \phi_i^{-\nu_i} & \text{for } t > \tau_{oi} \end{cases} \quad (20)$$

Here M_{ei} for $\tilde{\tau}_{ci} < t < \tau_{oi}$ is for the transient state due to the local tube renewal. The time evolution of the chain parameters for the equivalent i -chain is summarized in Table 1.

Blending Law for Stress Equation

Following the single chain approximation of Doi and Edwards² that every molecule contributes independently to stress, the respective contribution of blend components sums to the stress tensor of the multicomponent blends:

$$\sigma(t) = \sum_{i=1}^{N_c} \sigma_i(t) \quad (21)$$

According to the equivalent primitive chain model proposed in the preceding sections, the deviatoric stress tensor $\sigma_i(t)$ attributed to i -component chains in the multicomponent blend is written as

$$\sigma_1(t) = 3n_1 k_B T [L_1(t) / a_1(t)] Q(E) \cdot \mu(t; \tau_{d1}(t)) \quad (22)$$

where n_1 is the number of i-chains per unit volume in the blended polymer system and E is a deformation gradient tensor: $Q(E)$ and $\mu(t; \tau)$ are respectively given by

$$Q(E) = \frac{1}{\langle E \cdot u \rangle_0} \langle \frac{(E \cdot u) \cdot (E \cdot u)}{E \cdot u} \rangle_0 \quad (23)$$

$$\mu(t; \tau) = \sum_{p, \text{odd}} \frac{8}{\pi^2 p^2} \exp(-tp^2 / \tau) \quad (24)$$

where $\langle \dots \rangle_0$ means an average over isotropic u vector u . The time dependent values of the overall contour length $L_1(t)$, the temporarily determined terminal relaxation time $\tau_{d1}(t)$, and the primitive step length $a_1(t)$ of the equivalent i-chain are visualized at a moment t as explained in Table 1.

On the other hand, the stress equation obtained in eq. (22) is related with only interchain interactions such as reptation and constraint release. This equation can be extended to a more completed form if modifications due to intrachain dynamics are incorporated. Recent Lin's modified tube model theory⁶ allows us to extend the current result to a constitutive stress equation. Although his assumption of the independence of short-time int-

ramolecular chain dynamics from the terminal relaxation process is still a disputable point, his theory describes the stress relaxation process in short time region fairly well. For a simple shear deformation with a sufficiently small step strain for linear response, the constitutive equation for multicomponent blends with intermolecular and intramolecular dynamics is finally obtained.

$$G(t) = G_N^0 \sum_{i=1}^{N_c} \{w_i [1 + \mu_{Ai}(t)] \{1 + \frac{1}{4} \exp(-t / \tau_{eai})\}\} \cdot F_i(t) \quad (25)$$

with

$$G_N^0 = \frac{4}{5} \frac{cRT}{M_e} \quad (26)$$

The $\mu_{Ai}(t)$ is first blanket of eq. (25) represents the decay function for the Rouse relaxation of the chain segment between two entanglement couplings:

$$\mu_{Ai}(t) = \sum_{p=1}^{N_e} \exp(-t / \tau_{Ai}^p) \quad (27)$$

$$\tau_{Ai}^p = \frac{K\pi^2}{24\sin^2(\pi p / 2N_e)} \frac{M_e^2}{N_e^2} \quad (28)$$

where N_e means the number of statistical segments between two entanglements. The second blanket

Table 1. Time Evolution of Chain Parameters for Equivalent i-chain

Parameters	* $t < \bar{\tau}_{cl}$	$\bar{\tau}_{cl} < t < \tau_{ol}$ time	$t > \tau_{ol}$
MW	M_1	M_1	M_1
Primitive Step Length	a	$a_1(t) = a [M_{ei}(t) / M_e]^{1/2}$	$a_1' = a \phi_1^{-\nu_1/2}$
Entanglement Spacing	M_e	$M_{ei}(t)$ by eq. 20	$M_{ei}' = M_e \phi_1^{-\nu_1}$
Square End-to-end Distance	$N_1 a^2$	$N_1 a^2$	$N_1 a^2$
No. of Primitive Steps	$N_1 = M_1 / M_e$	$N_1 M_e / M_{ei}(t)$	$N_1 M_e / M_{ei}'$
Longest Relaxation Time	τ_{d1}^0 [eq. 3]	$\tau_{d1}(t) = \tau_{d1}^0 M_e / M_{ei}(t)$	$\tau_{d1} = \tau_{d1}^0 M_e / M_{ei}'$
Overall Contour Length	$L_1^* = N_1 a$	$L_1^* [M_e / M_{ei}(t)]^{1/2}$	$L_1^* \cdot \phi_1^{\nu_1/2}$
Survived Tube Length	$\exp[-t / \tau_{d1}^0]$	$[M_e / M_{ei}(t)]^{1/2} \times$	$\phi_1^{\nu_1/2} \exp(-t / \tau_{d1})$
Divided by L_1^*		$\exp[-t / \tau_{d1}(t)]$	

*At $t < \bar{\tau}_{cl}$ the equivalent i-chain has the same chain parameters of the original i-chain.

means the segmental density equilibration process with characteristic relaxation time τ_{eq1} by monomer slips through the entanglement links. Lin obtained the τ_{eq1} which is closely proportional to MW from experimental data for $G(t)$ of polystyrene fractions.

$$\tau_{eq1} = K M_e M_l \quad (29)$$

The last term, $F_l(t)$, denotes the fraction of initial path steps still occupied at time t within the original tube including chain ends fluctuation by random thermal motion on a reptating chain :

$$F_l(t) = B_l \mu(t; \tau_{Bl}) + \frac{M_e}{M_{el}(t)} C_l \mu(t; \tau_{dl}(t)) \quad (30)$$

with

$$B_l = M_e / M_l = 1 / \sqrt{N_l} \text{ and } C_l = 1 - B_l \quad (31)$$

$$\tau_{Bl} = \frac{1}{3} K M_l^2 \quad (32)$$

$$\tau_{dl}(t) = \frac{M_e}{M_{el}(t)} \tau_{dl}^0 \quad (33)$$

The separate contributions of each term to the stress relaxation behavior were already demonstrated by Lin.⁶

While the intramolecular equilibration processes of a model chain are not influenced by the MWD of its tube-forming chains, the second term of $F_l(t)$ is relevant to intermolecular interactions and depends on the composition of the polydisperse blends.

EXPERIMENTAL

In order to compare the current theoretical results with experimental data for the representative time-dependent viscoelastic property $G(t)$, binary and ternary blends of narrowly distributed linear polymer fractions were prepared. The fractions used in this study are standard polystyrene (PS)

polymers manufactured by Pressure Chemical Co.

For quantitative analysis of the polydispersity effect for the polymer fractions used, details of MWD data were obtained by a gel permeation chromatography (GPC, Water Associates Model 150C) with four styragel column of porosity 10^3 , 10^4 , 10^5 , and 10^6 Å.

The shear stress relaxation modulus was measured using a Rheometric Dynamic Spectrometer (RDS) in the parallel plate mode. The relaxation modulus is measured in the transient mode. Step tests cause the servo to make a single step jump to a strain. The measured torque M_t (gr-cm) is related to $G(t)$ as

$$G(t) = \frac{2000 \times 980.7}{R_p^3} M_t \text{ dyn/cm}^2 \quad (34)$$

where R_p is the plate radius (12.5mm).

All samples, including the standard fractions and their blends, were prepared by dissolving weighed amounts of the individual components in a large excess of benzene used as solvent. One gram of polymers was added to 45ml benzene in a cleaned bottle specially made for freeze-drying. The polymer solutions were kept in the dark for 24 hours, and were swirled gently several times until complete dissolution. The solvent was then removed by freeze drying under a vacuum of about 0.1-0.2mmHg. The samples were further dried at least two days at about 60°C in a vacuum oven in order to remove any possible traces of the benzene. The dried samples were first shaped into disk form 25mm diameter and 2mm thickness at about 160-170°C under vacuum.

Samples used for the viscoelastic measurements were designated in accordance with blend type. The first letters M, B and T represent standard fraction, binary blend and ternary blend, respectively. The numbers followed these letter and separated by slash denote the apparent molecular weights of the fractions multiplied by 10^{-3} . Finally the digits in blend denotations separated by colon designate the weight ratio of the components. For example, T95 / 400 / 1600-6:3:1 is a ternary blend

composed of M95, M400 and M1600 fractions with the weight fractions, 0.6, 0.3 and 0.1, respectively.

Viscoelastic data for $G(t)$ were obtained over the largest range of time at which a reasonable torque value (>1 gr-cm) could be measured. The gap between the two parallel plates with diameter 25mm was less than or equal to 2.0mm. Data were taken at several temperatures from 140 to 250°C. The reference gap was set at 160°C, and the gap at every temperature was corrected due to the thermal expansion of the mixture used. The applied step shear strain was adjusted with test temperature to obtain the reasonable torque value during stress relaxation. Linear viscoelastic response was confirmed by measuring $G(t)$ at different strain values (0.005-0.1). In general, the strain was increased with temperature and decreased with the average MW of sample. The fraction sample M1600 was too rubbery to be measured by parallel plate rheometer.

The molecular and rheological characteristics of the sample are shown in Table 2, in which M_w and M_n represent the weight and number-averaged molecular weights, respectively.

RESULTS

Experimental Result

Fig. 2 shows the molecular weight distribution for the five standard fractions, where the norma-

lized weight fraction $f(M)$ is plotted against MW. In this figure symbols for each MWD curve represent the weight fractions of specific components. Although being nearly monodisperse, the fractions will be regarded as multicomponent blends composed of N_c specific components hereafter, especially in the quantitative calculation of their rheological properties by the presently proposed theory. The shear stress relaxation modulus $G(t)$ was measured for all polystyrene samples at several temperatures. Each set of the measured moduli data were then shifted to construct a master curve, which exhibits complete modulus versus time behavior at a constant temperature, in accordance

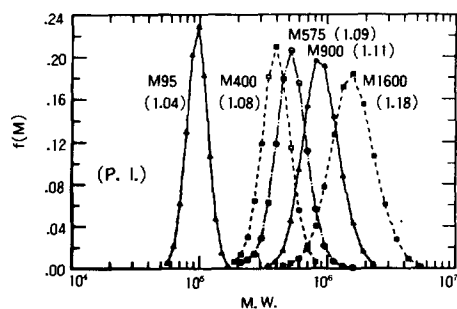


Fig. 2. Molecular weight distribution (MWD) of the polystyrene fraction samples used. Normalized weight fraction $f(M)$ is plotted against molecular weight. Symbols denote the specific components of the fractions.

Table 2. Molecular and Rheological Characteristics of Polystyrenes

Sample	M_w	M_w / M_n	η_0 (poise)	J_e^0 (cm ² / dyn)
M95	96,700	1.04	5.04×10^5	9.76×10^{-7}
M400	401,000	1.08	7.82×10^7	1.25×10^{-6}
M575	528,000	1.09	2.60×10^8	1.46×10^{-6}
M900	919,000	1.11	1.14×10^9	1.54×10^{-6}
M1600	1,649,000	1.18		
B400 / 900-6:4	478,900	1.27	2.52×10^8	3.19×10^{-6}
B95 / 575-8:2	181,100	1.65	5.66×10^6	2.60×10^{-5}
B95 / 575-6:4	137,900	1.96	2.02×10^7	6.98×10^{-6}
B95 / 575-4:6	111,300	1.97	4.60×10^7	4.79×10^{-6}
T95 / 400 / 1600-6:3:1	139,900	2.51	2.42×10^7	6.97×10^{-5}
T95 / 400 / 1600-1:1:1	212,800	3.36	4.04×10^8	1.67×10^{-5}
T95 / 400 / 900-5:4:1	152,700	1.97	1.84×10^7	1.28×10^{-5}

with the time-temperature superposition principle. In Fig. 3, values of horizontal shifting factor a_T with the reference temperature $T_R=160^\circ\text{C}$ are plotted against temperature and the empirical WLF equation (solid line) for undiluted polystyrenes with narrow distribution is obtained as $\log a_T = -6.5 + 715 / (T - 323^\circ\text{K})$. It is observed that both the fraction samples (filled circles) and blends (squares) have nearly the same values of a_T , and obey the time-temperature superposition principle represented by the WLF equation very well over a wide temperature-range.

In Fig. 4~8 the respective symbols represent the master curves of $G(t)$ reduced at 160°C for standard fractions, B97 / 530, B400 / 900, T97 / 400 / 1600, and T97 / 400 / 900 blends, respectively. Their characteristics will be discussed in the next chapter.

Theoretical Calculation

Basic parameters for the viscoelastic properties of the polystyrene samples tested at 160°C are selected as follows.

(i) Specific Components

Even the standard PS fraction samples are regarded as the multicomponent blends composed of $(N_c)_1$ specific components. As an example, Table 3 shows the dependence of the viscoelastic constants on the number of specific components for

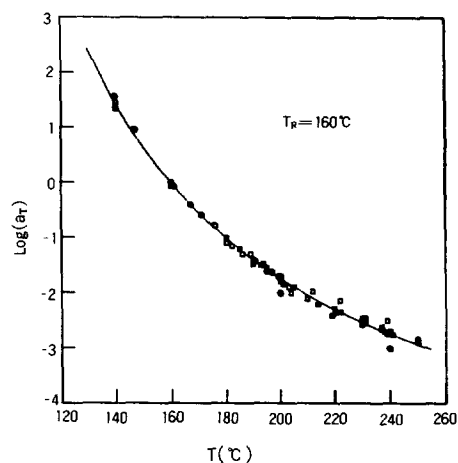


Fig. 3. Shifting factor a_T versus temperature. Symbols represent a_T for master curves of polystyrene fractions (filled circles) and blends (squares). Line denotes the empirical WLF equation.

the fractions. The steady state compliance J_e^0 is very sensitive to the molecular weight distribution than η_0 . Here we adjusted the number of specific components as the value when the theoretical viscoelastic properties, viscosity (η_0) and compliance (J_e^0), of the fractions and blends become nearly constant independently to N_c . Values of N_c for blends tested here are listed in Table 4 with two primary viscoelastic properties. The details

Table 3. Dependence of Viscoelastic Constants on the Number of Specific Components

Sample	N_c	$\eta_0(N_c)$	$\eta_0(N_c=1)$	$J_e^0(N_c)$	$J_e^0(N_c=1)$
M95	11	4.90×10^5	4.92×10^5	1.24×10^{-6}	8.27×10^{-7}
M400	12	8.30×10^7	1.10×10^8	1.33×10^{-6}	7.52×10^{-7}
M575	15	2.09×10^8	2.81×10^8	1.49×10^{-6}	7.30×10^{-7}
M900	13	1.21×10^9	1.75×10^9	1.54×10^{-6}	6.96×10^{-7}

Table 4. Specific Components and Theoretical Values of Viscoelastic Constants for Blends

Sample	N_c	$\eta_0(\text{poise})$	$J_e^0(\text{cm}^2/\text{dyn})$
B400 / 900-6:4	18	2.71×10^8	3.69×10^{-6}
B95 / 575-8:2	26	4.67×10^6	2.14×10^{-5}
B95 / 575-6:4	26	1.86×10^7	8.36×10^{-6}
B95 / 575-4:6	26	5.04×10^7	4.07×10^{-6}
T95 / 400 / 1600-6:3:1	33	3.73×10^7	7.02×10^{-5}
T95 / 400 / 1600-1:1:1	33	4.03×10^8	1.56×10^{-5}
T95 / 400 / 900-5:4:1	29	2.59×10^7	1.42×10^{-6}

have given elsewhere.¹¹

(ii) Characteristic Parameters for Monodisperse Polystyrenes

The number of statistical segments N_e between two successive entanglement points was taken to be 14, which was already discussed by Lin.⁶ Besides MW, characteristics of polymers are well represented by the MW-independent average entanglement spacing M_e and the plateau modulus G_N^0 . Earlier experimental works for PS melts show that $M_e=18,000$ and $G_N^0=2.0 \times 10^6$ dyn/cm².

(iii) Relaxation Times in Monodisperse Polymers

In order to estimate the longest relaxation times τ_{dl} 's of the specific components in the multicomponent blend, the corresponding values τ_{dl}^0 's in their respective pure, monodisperse states should be given, and they can be calculated by eq. (3). The MW-independent and only temperature-dependent coefficient K in the equation is of material characteristic. Based on the relationship that average relaxation times of linear polymers are proportional to η_0 , the temperature dependence of K can be deduced from the WLF equation and η_0 data measured at various temperatures for undiluted PS fractions with narrow MWD by Orbon and Plazek:¹²

$$\log K(T) = \log K_0 + \frac{887}{T - (T_g - 60)} \quad (35)$$

where T in $^{\circ}\text{C}$

where $T_g(^{\circ}\text{C}) = 98 - 1.02 \times 10^{-5} / M_w$. The proportionality constant K_0 is selected to be 2.1109×10^{-18} in this study, which fits well the terminal viscoelastic properties of all the tested PS fractions. Thus τ_{dl}^0 's (in sec) for all the specific components were calculated by the single equation (3) with K of eq. (35), which agrees fairly well with that given by Montfort et al.,¹³ $\tau_{dl}^0 = 5.25 \times 10^{-18} M_l^{3.4}$ at 160°C , for PS fractions with $M_l \geq 2M_e$.

From this value of K , relaxation times for intramolecular chain dynamics, τ_{Bi} , τ_{eqi} and τ_{Ai} , are calculated by eqs. (32), (29), and (28), respectively. Theoretical $G(t)$ curves are drawn in the same figures as the experimental data.

DISCUSSION

Standard Fractions

Master curves of the measured $G(t)$ for the tested standard fractions, as shown in Fig. 4, exhibit a typical viscoelastic response of highly entangled linear polymers with narrow MWD showing the three viscoelastic response regions.¹⁰ The terminal region at long time side is deeply related to polymer MW and exhibits a rapid stress relaxation. In the transition region, the stress relaxation is nearly independent of MW and is dominated by the short-time Rouse relaxation mode. The rubbery plateau region intervenes those two regions and becomes region at every $G(t)$ master curve supports that all the PS fraction samples are sufficiently entangled.

In addition, as shown in this figure, fairly good agreement of the theoretical predictions with data is achieved over a wide range of time and MW.

Binary Blends

Effects of MWD on the viscoelastic properties of polydisperse polymers are best represented by the binary blends of two nearly monodisperse component polymers.¹³⁻¹⁵ The relaxation modulus curves of the binary blends exhibit interesting differences from the standard fractions. Fig. 5, 6 show the observed master curves (symbols) of $G(t)$ for blends with low, medium, high blend ratio and theoretical predicted curves (solid lines).

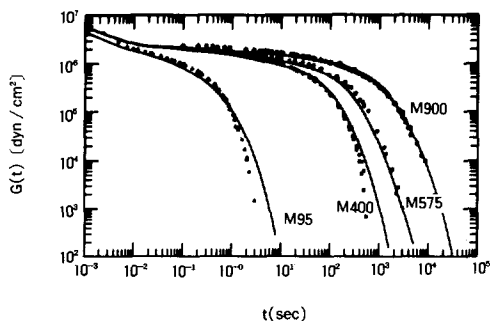


Fig. 4. Relaxation modulus versus time for polystyrene fraction samples. Symbols denote superposed data at 160°C . Solid lines represent theoretical predictions for fractions.

Firstly, Fig. 5 shows the results for B400/900 binary blend with low MW ratio. Quantitative agreement of theory and data is illustrated in this figure. The appearance of a shoulder or two-step rubbery plateau is not observed in this low-MW ratio blend. This figure shows that the relaxation mode shifts smoothly from that of M900 fraction (denoted by dashed lines) as time increases. On the other hand, M900 chains in the blend relax at the terminal region much faster than in pure states.

Secondly, Fig. 6 shows the results of B95/575 binary blends with medium MW ratio. Typical examples of the blending effects in polydisperse polymers with bimodal distribution are well represented by these blends as shown in this Figure. A shoulder appears in each master curve of $G(t)$

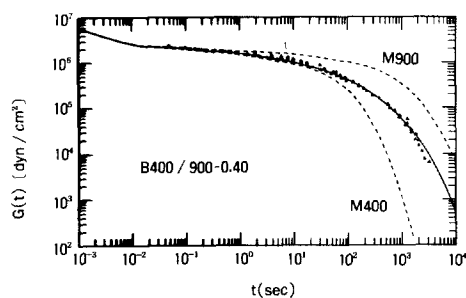


Fig. 5. Relaxation modulus versus time for polystyrene binary blend B400/900-6:4. Solid and dashed lines represent theoretical predictions for blend and fractions, respectively. Symbols denote superposed data at 160°C.

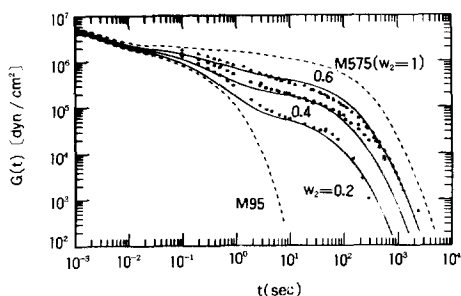


Fig. 6. Relaxation modulus versus time for polystyrene binary blends of M95 and M575. Symbols and curves are identified in Figure 5.

and its height increases and becomes the second plateau which extends to the long time side with increasing w_2 . The two-step rubbery plateau is well predicted by the present theory. From a molecular viewpoint, the second plateau is attributed to the contribution of the 2-component polymer to stress and is well described by the proposed blending law for stress, especially by the second term of eq. (32) associated with tube enlargement due to local constraint release.

Another remarkable observation is that the plateau at short times in $G(t)$ shift to longer time side with increasing w_2 . The shift may be explained by the reason that for the purely bimodal blend, i.e., $(N_c)_1 = (N_c)_2 = 1$, the terminal relaxation time of the M95 1-chains in blended state increases to some extent than in pure state, $\tau_{d1} > \tau_{d1}^0$. This means that the terminal relaxation process of the short chain approaches pure reptation process more closely when some of its tube-forming chains are long enough to impose more completely fixed obstacles upon the model 1-chain. Such interpretation has also been suggested by the observation that unattached chains relax slower in a network¹⁶ than in a melt of the same chains. It is thus predictable that the constraint release mechanism should still be effective to some extent and compete with reptation in pure, monodisperse polymers.

Ternary Blends

The blending algorithm proposed by the present theory for polydisperse polymers can be tested more generally for the multicomponent blends with trimodal MWD. The generalization of the theoretical interpretation for binary blends to polydisperse polymers with continuous distribution can be confirmed by examining that for the ternary blend cases.

Fig. 7 shows the master curves of $G(t)$ at 160°C (denoted as symbols) and theoretical curves (denoted as solid lines) for T95/400/1600 ternary blends which have a typical trimodal MWD. The master curves represent three separate rubbery plateaus contributed by the three respective component polymers. Especially, the second plateau region formed by the M400 chains apparently

intervenes between the upper and lower plateaus, and shows how the contribution of such intermediate MW chains to stress is modified in the ternary blend system. Theoretical curves also predict well such characteristic viscoelastic response in the blended system. For the two blends tested, the contribution of the M1600 chains to stress in the terminal region is somewhat overestimated as shown in the comparison of theory with data. This verifies again that the τ_{dl}^0 's of the specific components of the M1600 fraction in pure state are rather overestimated as in the B95 / 1600 binary blend cases.

Master curve of $G(t)$ and theoretical prediction for the ternary blend of T95 / 400 / 900-5:4:1 are respectively denoted as symbols and solid line in Fig. 8. As shown in this figure, three separate plateaus are not observed in the data due to the MWD of this blend which is intermediate between

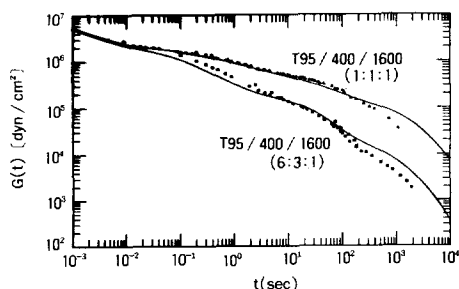


Fig. 7. Relaxation modulus versus time for polystyrene ternary blends of M95, M400 and M1600. Symbols and curves are identified in Figure 5.

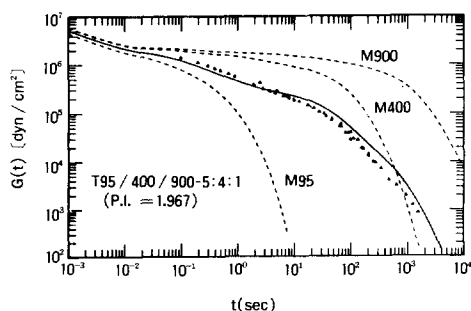


Fig. 8. Relaxation modulus versus time for polystyrene ternary blend T95 / 400 / 900-5:4:1. Symbols and curves are identified in Figure 5.

bimodal and trimodal distribution. Theoretical curve describes that the viscoelastic response of the M400 fraction is superposed on the plateau region of the M900 fraction and thus only two plateaus are appreciable. Such superposition is represented by the slanted shape of the theoretical $G(t)$ curve at about $t > 40$ sec. This is confirmed by the measured data at the time region.

CONCLUSION

The effect of MWD on the $G(t)$ of highly entangled linear polymers has been investigated from a molecular viewpoint. Presupposing the significant effect of the constraint release mechanism on the chain relaxation in polydisperse polymers, a modified tube model theory for monodisperse polymers was extended to polydisperse polymeric liquids. To examine the proposed theory the relaxation moduli of binary and ternary blends of well-characterized linear polystyrenes with very narrow distribution were measured with a parallel rheometer. A stress equation for multicomponent blends was formulated based on the time dependence of the equivalent chain parameters. It was then led to the shear stress relaxation modulus $G(t)$, the constitutive equation for the linear viscoelasticity of polydisperse linear polymers, including not only the intermolecular interactions but also the intramolecular chain dynamics argued by earlier Lin's molecular theory for monodisperse polymers.

In theoretical predictions of those properties even the standard fractions were regarded as the multicomponent blends composed of N_c monodisperse specific components. If the characteristic parameters for these monodisperse polymers were given, any additional adjusting parameters were not required in the predictions. The current theory predicted the measured $G(t)$ for both the tested fractions and their blends with various distribution modes fairly well over a wide range of time. From the time-dependent $G(t)$, the frequency-dependent dynamic moduli, $G'(\omega)$ and $G''(\omega)$, and the two primary viscoelastic properties, zero-shear

viscosity and recoverable compliance, can be obtained. Conclusively, the equivalent primitive chain model based on the reptation idea is a promising model for explaining quantitatively the rheological properties of arbitrary distributed linear polymers where the constraint release due to local tube renewal affects critically on their relaxation processes.

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