

다분산성이 선형고분자의 점탄성에 미치는 영향 I. 이성분 블랜드의 분자모델

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Effects of Polydispersity in Viscoelasticity of Linear Polymers I. Molecular Model for Binary Blends

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Abstract: The tube model theory of Doi and Edwards based on de Gennes' reptation idea is extended to explain the viscoelastic properties of binary blends in highly entangled state composed of two linear monodisperse species with different molecular weights M_1 and M_2 . A modified tube model theory is proposed in order to incorporate the relaxation mechanism of constraint release by tube renewal in the polydisperse polymers. The relaxation of the high MW component chain by the concurrent reptation and constraint release is remodeled as the disengagement by pure reptation of an equivalent primitive chain. This equivalent primitive chain model enables us to obtain the longest relaxation times of blend components and to formulate a general stress equation. In addition to those intermolecular interactions, the stress equation incorporates other modes of intermolecular chain dynamics such as chain length fluctuation and fast Rouse motions. Blending laws for viscoelastic properties can then be derived from the stress equation. The current theory is critically tested by comparing predicted values of the zero-shear viscosity and steady-state shear compliance with available experimental data on undiluted polybutadienes and polystyrenes. The comparison shows that the theory agrees well with the data over a wide range of blend composition and M_2/M_1 ratio.

INTRODUCTION

A molecular theory for polymeric fluids relates chain dynamics to viscoelasticity. In 1971, de Gennes¹ proposed the reptation model describing topological constraints upon the motion of polymer chain or the so called entanglement coupling. According to his idea, a polymer chain can move by curvilinear diffusion along its contour as if it is confined in a "tube" which re-

presents the constraints imposed by surrounding chains. Such a snake-like diffusional motion was called "reptation". In 1978, Doi and Edwards related the reptational motion and the mechanical properties of highly entangled polymers². Although their theory describes many viscoelastic features of the polymers, there still remain some discrepancies between the theory and experimental results.³ They can be accounted for by introducing several additional modes of chain

dynamics : constraint release by tube renewal,^{4,5} contour length fluctuation of the reptating chain^{6,7} and short-time(Rouse) relaxations.⁷⁻⁹

Since the viscoelasticity determines the relaxation of polymer stress and orientation in processing, it plays an essential role in linking molecular structures, such as molecular weight(MW) and MW distribution(MWD), and polymer processing.¹⁰ The MW-dependence of viscoelasticity is well understood by experiments or by the tube model theory. However, understanding its relation with MWD has been lacking even for the simplest case such as linear flexible polymers. Furthermore, while the original tube model theory dealt with monodisperse systems, industrially used polymers are broadly distributed in MW. It is therefore conceivable that difficulties in applying the molecular theory to predicting rheological properties or to computationally simulating polymer processing are mainly attributed to the effect of polydispersity on viscoelasticity.

Binary mixture(or blend) of two monodisperse homopolymers with different MW's is the simplest model system for examining the MWD effect. Very recently, a blending law for the relaxation spectrum $H_B(\tau)$ of the binary blend has been extensively studied by various authors on the basis of the tube model.¹¹⁻¹⁴ The blending law in the form of $H_B(\tau)$ can be the basis for linear viscoelasticity and verifies relaxation time distribution.¹⁰ But, nonlinear rheological properties important in processing cannot be determined from it. In addition, such a law inevitably possesses too many shift factors, intensity factors and cross terms to be decided empirically. Therefore, a blending law for stress equation need to be established in order to predict both linear and nonlinear viscoelastic responses of polymer to mechanical deformation.

In this study, we propose a modified tube model to obtain the longest relaxation time of blend components in the light of the significance of the constraint release mechanism in blended system. A stress equation for binary blends is also formulated, including the stress attributed to rep-

tation, constraint release, contour length fluctuation and short-time relaxation processes. The proposed blending laws are then tested by available literature data. The system under consideration is a binary blend in liquid state composed of two components with the MW M_1 and M_2 both of which are sufficiently greater than the MW between two entanglement points, M_e : i.e., $M_2 > M_1 \gg M_e$.

THEORY

Tube Model for Monodisperse Polymers

In advance to discussing binary blend cases, we need to mention the major results of tube model theories for monodisperse polymers. The original tube model theory dealt with chain entanglement as an intermolecular interaction and its relaxation by the reptational diffusion of a polymer molecule. Doi and Edwards predicted that the disengagement time τ_d^0 required for a chain to completely disengage out of its original tube by pure reptation at equilibrium should be equal to the longest relaxation time in a mechanically deformed state. Then the longest relaxation time is given as^{1,2}

$$\tau_d^0 = L^2 / \pi^2 D = KM^3 / M_e \quad (1)$$

where L is the contour length of a tube or its primitive path(center line of the tube) and D is the curvilinear diffusion coefficient of the primitive chain. The proportionality constant K at a temperature T is related to molecular structure and the friction coefficient of chain segment, and is independent of concentration and MW. Their theory then yields a stress equation in reptational regime :²

$$\sigma(t) = 3nkT(L/a) Q(E) F(t; \tau_d^0) \quad (2)$$

with

$$Q(E) = \frac{\langle (\mathbf{E} \cdot \mathbf{u})(\mathbf{E} \cdot \mathbf{u}) \rangle_0}{\langle |\mathbf{E} \cdot \mathbf{u}|^2 \rangle_0} \quad (3)$$

and

$$F(t; \tau) = \sum_{p, \text{odd}} 8 \exp(-p^2 t / \tau) / p^2 \pi^2 \quad (4)$$

where σ is the extra (deviatoric) stress tensor, E the deformation gradient tensor, n the number of chains per unit volume, k the Boltzmann constant, a the average distance between two entanglement points (or "slip-links"), and $\langle \cdots \rangle_0$ denotes an average over the isotropic unit vector u .

Including contour length fluctuation (Process-F), the Rouse relaxation between two slip-links (Process-A) and the equilibration of segment density along chain contour (Process-B), additional versions of the tube model can be summarized in an explicit form:⁵⁻⁹

$$\sigma(t) = 3nkT(L/a) Q(E) m_A(t) m_B(t) m_C(t) \quad (5)$$

Here, $m_C(t)$ is the relaxation function due to the simultaneously and independently occurring reptation and the Process-F, whose characteristic relaxation times are T_d and T_F , respectively:⁷

$$m_C(t) = F(t; T_F) / \sqrt{N} + (1 - 1/\sqrt{N}) F(t; T_d) \quad (6)$$

with

$$T_d = KM^3(1 - 1/\sqrt{N})^2 / M_e \text{ and } T_F = KM^2/3 \quad (7)$$

where $N (= M/M_e)$ is the number of the primitive steps per chain with $(N-1)$ slip-links. The function $m_B(t)$ is reduced to the time dependent one in a linear deformation region:

$$m_B(t) = 1 + \exp(-t/T_B)/4 \quad (8)$$

where the characteristic time for the process-B, T_B , is equal to T_F according to Doi⁸ and Thirion and Tassin,⁹ while Lin⁷ argues $T_B \approx KM^2/N$. The characteristic time T_A for the fast Process-A is approximated to be $KM_e^2/6$ ($\propto T_F/N^2$), and $m_A(t) = 1$ for $t > T_A$. As $T_d > T_F \geq T_B > T_A$, both $m_A(t)$ and $m_B(t)$ of eq. (5) become unity of $t > T_B$. It is notable that eq. (5) does not incorporate the contribution of constraint release, whose effect on chain relaxation is not significant in purely monodisperse polymers.^{3,4}

The Relaxation Times of Component Chains

It is conceivable that the three relaxation processes, Process-A, -B and -F, of a singled out chain ("model chain") are attributed to intramolecular chain dynamics and thus are not affected by the MWD of its surrounding tube-forming chains. In the sense that every chain in a polymer diffuses by reptational motion in a self-consistent manner, topological constraints imposed by tube-forming chains upon a model chain are not fixed ones and can be released in parallel with local tube renewal.^{4,5} We now visualize that the polydispersity affects chain relaxation mainly through the constraint release mechanism. On the other hand, we assume that the mechanism can be neglected in pure monodisperse state, as Graessley pointed out.⁵ Thus, the longest relaxation time T_{di}^0 of a blend component chain in pure state is expressed by eq. (7) if reptation and the Process-F occur simultaneously and independent:

$$T_{di}^0 = KM_i^3(1 - 1/\sqrt{N_i})^2 / M_e \quad (i=1 \text{ or } 2) \quad (9)$$

with

$$N_i = M_i / M_e \quad (10)$$

Let T_{d1} and T_{d2} be the longest relaxation times of the low MW chain ("1-chain") and the high MW chain ("2-chain") in a binary blend, respectively. Then, T_{d1} and T_{d2} are expected to be related to T_{d1}^0 , T_{d2}^0 , the entanglement spacing M_e , the component MW's, and the weight fraction of the high MW component w_2 :

$$T_{di} = f(T_{d1}^0, T_{d2}^0, M_e, M_1, M_2, w_2) \quad (11)$$

Relaxation of the 1-chain : If a 1-chain is selected as a model chain, it is subjected to two types of constraints: the 1-1 and 1-2 entanglements with its surrounding 1-chain and 2-chain, respectively. These constraints are not changed at least until $t \approx T_{c1}$, the average lifetime of the 1-1 entanglement; i.e., at every T_{c1} , it changes its location (or jumps). According to earlier derivations of the T_c required for such local jump in monodisperse polymers,^{4,5} T_{c1} for the current binary blend is nearly equal to T_{d1}^0 :

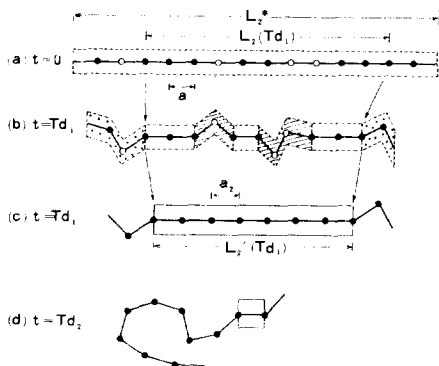


Fig. 1.: Schematic illustration of the relaxation process of the high MW chain. (a) Straightened original tube. (b) Primitive chain and tube at T_{d1} : filled and unfilled circles denote the type-2 and -1 sliplinks, respectively, (c) Equivalent primitive chain (thick line), equivalent fixed slip-links (filled circles), and equivalent survived tube (thin line). (d) Completed disengagement of the equivalent chain.

$$T_{c1} = (\pi^2/12) T_{d1}^0 = T_{d1}^0 \quad (12)$$

Therefore, constraint release affects the 1-chain's relaxation little, and pure reptation is the dominating mechanism:

$$T_{d1} = T_{d1}^0 \quad (13)$$

Relaxation Process of the 2-chain: First we consider a case where the MW difference between two components is very large, $M_1/M_2 \rightarrow 0$. The high MW 2-chain selected as a model chain relaxes by pure reptation for $t < T_{c1}$; the model chain reptates back and forth along its contour so that the original tube (broken line of Fig. 1-a) "evaporates" at its both ends (dotted area of Fig. 1-b) due to random directions chosen by the chain ends. The contour length of the survived tube at $T_{c1} (\approx T_{d1})$ except for the evaporated part is²

$$L_2(T_{d1}) \approx L_2^* \exp(-T_{d1}/T_{d2}^0) \quad (14)$$

where L_2^* is the average contour length of the 2-chain or the original tube at equilibrium. Due to the reptational diffusion of a tube-forming

1-chain, a 2-1 entanglement ("type-1" slip-link) renews its location and its corresponding tube segment is rearranged locally (Fig. 1-b). Such a local jump of the type-1 slip-link occurs at every T_{d1} , while each 2-2 entanglement ("type-2" slip-link) keeps its original location until either end of the model chain passes through it. Therefore, the survived tube part at T_{d1} is separated into two sections: one maintaining original conformation and the other experiencing periodical local tube renewal.

Let the type-1 and 2 slip-links be distributed uniformly along the chain. Considering T_{d1}^0 is much smaller than T_{d2}^0 by the ratio $(M_1/M_2)^3$ and that the orientations of periodically fluctuating primitive steps are isotropic, we are led to envisage the model chain as a homogenized "equivalent primitive chain" constrained effectively until T_{d2} only by some imaginary slip-links which are equally spaced by the distance a_2 . we call them the "equivalent fixed slip-links". For blends with $M_1/M_2 \rightarrow 0$, they correspond to the type-2 slip-links. Then, the isotropically fluctuating steps are assumed to be uniformly distributed over the equivalent chain and to behave like parts of wriggling Gaussian submolecules between two successive equivalent slip-links. The survived tube at T_{d1} is also remodeled by an equivalent one with original conformation (thin line of fig.1-c) the diameter of which is comparable to a_2 . With these treatments we can predict that T_{d2} should be equal to the time when the equivalent chain completely disengages by pure reptation out of the equivalent survived tube (Fig. 1-c and -d). The existence of neighboring short 1-chain would then affect the parameters for the equivalent chain and tube.

Now, in order to derive the residual disengagement time, $T_{d2} - T_{d1}$, parameters for the equivalent 2-chain should be obtained. The average MW between two equivalent slip-links, M_{e2} , can be deduced from the relation^{10,12}

$$c^\alpha M_e = \text{constant} \quad (15)$$

where c is the polymer mass per unit volume,

and the index α is unity for melts and highly concentrated solutions. The M_{e2} is then related to M_e and w_2 as

$$M_{e2}/M_e = (c/c_2)^\nu = w_2^{-\nu} \quad (16)$$

where ν is equal to α if $M_1/M_2 \rightarrow 0$ when 1-chains behave like solvent molecules against the 2-chain. Thus the contour length $L_2'(T_{d1})$ of the equivalent survived tube for residual disengagement of the remodeled reptating chain is

$$L_2'(T_{d1}) = w_2^{\nu/2} L_2(T_{d1}) \quad (17)$$

Then, the definition in eq. (1) enables us to write

$$T_{d2} - T_{d1} = L_2'^2 / \pi^2 D_2 \quad (18)$$

where the coefficient D_2 is remained constant throughout the whole disengagement process on the basis of the Einstein relation.^{2,5} Substituting eqs. (13) and (17) into eq. (18), we get

$$T_{d2} = T_{d1}^0 + w_2^{-\nu} T_{d2}^0 \exp(-2T_{d1}^0/T_{d2}^0) \quad (19)$$

Let us now extend above discussions to another extreme case of $M_1/M_2 \rightarrow 1$. In this case M_{e2} must tend to M_e . Thus, eq. (19) can be generalized to be used for blends with arbitrary M_1/M_2 ratios if the index ν is expressed as a function of the MW ratio. We do not know the functional form of $\nu(M_1/M_2)$ at this stage. If we simply take the first-order approximation for the MW ratio dependence, that function should be expressed as

$$\nu = \alpha \{1 - (M_1/M_2)\} \quad 0 < M_1/M_2 < 1 \quad (20)$$

in order to satisfy two limiting conditions: $\nu = \alpha$ for $M_1/M_2 \rightarrow 0$ and $M_{e2} = M_e$ (or $\nu = 0$) for $M_2 \rightarrow M_1$. Then, eqs. (19) and (20) can be used for blends with intermediate MW ratio.

So far, we have mentioned the relaxation process where the two component chains entangle with each other at least once. However, we can imagine two critical contents: one is w_c' where

each 2-chain entangles the 1-chain only once on average; the other is w_c'' where M_{e2} from eq. (16) is nearly equal to $M_2/2$, corresponding to the onset of entanglement among 2-chains. Thus, strictly speaking, eq. (19) is valid for a content range $w_c' < w_2 \leq w_c''$. The critical contents can be expressed in terms of $N_1 (= M_1/M_e)$ as

$$w_c' = \frac{N_1 - 1}{N_1 - 1 + (N_1/N_2)} \quad \text{and} \quad w_c'' = (2/N_2)^{1/\nu} \quad (21)$$

Considering N_1 and $N_2 \gg 1$, we need to note that w_c' and w_c'' are nearly equal to 1 and 0, respectively.

Although we have considered the relaxation process at equilibrium to estimate the T_{d2} , it is notable that there exists an equilibration stage for uniform segment density along contour (the Process-B) immediately after an instantaneous deformation. Putting T_0 be the time when the equivalent chain model begins to be applied, following two cases are conceivable:

$$T_0 = \begin{cases} T_{d1} & \text{if } T_{d1} > T_B \\ T_B & \text{if } T_{d1} \leq T_B \end{cases} \quad (22)$$

Finally, the general expression for the T_{d2} is summarized as

$$T_{d2}(w_2) = \begin{cases} T_0(w_c') & \text{for } 0 < w_2 \leq w_c' \\ T_0 + w_2^\nu T_{d2} \exp(-2T_{d1}^0/T_{d2}^0) & \text{for } w_c' < w_2 \leq w_c'' \\ T_{d2}^0 \text{ or } T_{d2}(w_c') & \text{for } w_c'' < w_2 \leq 1 \end{cases} \quad (23)$$

Blending Laws

Following the single chain approximation of Doi and Edwards⁷ that every molecule contributes independently to stress, the respective contribution of blend components sums to the total stress of binary blends:

$$\sigma_B(t) = \sigma_1(t) + \sigma_2(t) \quad (24)$$

where $\sigma_i(t)$ is estimate by eq. (5). Since eq. (5) does not incorporate effects due to constraint release mechanism, we have to modify the second

term of eq.(6). Let us consider the terminal time regime corresponding to the term. The 1-chain relaxes by reptation alone and

$$F_1(t) = F(t; T_{d1}^0) \quad (25)$$

On the other hand, in case of the 2-chain, we have to consider two time regions separately as discussed in the previous section. At first, it relaxes by pure reptation :

$$F_2(t) = F(t; T_{d2}^0) \text{ for } 0 \leq t \leq T_0 \quad (26)$$

After $t=T_0$, the concurrence of reptation and local constraint release leads us to apply the equivalent primitive chain model :

$$F_2(t) = T_{d2} F(t; T_{d2}^0) / T_{d2}^0 \text{ for } t > T_0 \quad (27)$$

which means the 2-chain relaxes in the same manner as a chain with the MW M_2 and the relaxation time T_{d2} (not T_{d2}^0) does by pure reptation in a monodisperse mean field with the entanglement spacing $M_e' = M_e T_{d2} / T_{d2}^0$ according to eq.(1). Therefore, the stress equation for binary blends is expressed as

$$\sigma_B(t) = G_0 Q(E) \sum_{i=1}^2 \{w_i m_{A_i}(t; T_{A_i}) m_{B_i}(t; T_{B_i}) m_{c_i}(t)\} \quad (28)$$

with

$$G_0 = 3cRT / M_e = 15G_N^0 / 4 \quad (29)$$

and

$$m_{c_i}(t) = F(t; T_{F_i}) / \sqrt{N_i} + (1 - 1/\sqrt{N_i}) F_i(t) \quad (30)$$

where R is the gas constant, and $F_i(t)$ ($i=1$ and 2) is given by eqs.(25~27).

COMPARISON OF THE THEORY WITH EXPERIMENTAL DATA

A critical test of the present theory is made by comparing the theoretical w_2 -dependences of the two principal viscoelastic constants, the zero-shear viscosity $(\eta_0)_B$ and steady-state shear compliance $(J_e^0)_B$, with available literature data.

Theoretical predictions of the constants are numerically calculated on the basis of the shear stress relaxation modulus $G_B(t)$ derived from the stress equation. For a simple shear deformation with a small step strain γ , eqs.(3) and (28) yield

$$Q_{yx}(E) = 4\gamma / 15 \quad (31)$$

$$G_B(t) = \lim_{\gamma \rightarrow 0} \frac{\sigma_{yx}(t)}{\gamma} \quad (32)$$

$$\begin{aligned} (\eta_0)_B &= \lim_{\omega \rightarrow 0} \omega \int_0^\infty G_B(s) \cos(\omega s) ds \\ &= \lim_{\omega \rightarrow 0} G'(\omega) / \omega \end{aligned} \quad (33)$$

$$\begin{aligned} (J_e^0)_B &= \lim_{\omega \rightarrow 0} \omega \int_0^\infty \frac{G_B(s) \sin(\omega s)}{\omega (\eta_0)_B^2} ds \\ &= \lim_{\omega \rightarrow 0} G_B'(\omega) / G_B^*(\omega)^2 \end{aligned} \quad (34)$$

A computer program calculating the storage and loss moduli $G_B'(\omega)$ and $G_B''(\omega)$ was prepared to estimate $(\eta_0)_B$ and $(J_e^0)_B$. This is a more accurate and efficient way than a direct numerical Fourier transformation of calculated values of $G_B(t)$ whose calculation extends over several decades of times. The infinite integrations in eqs.(33) and (34) are separated into two time regions : $0 \leq t \leq T_0$ and $T_0 < t < \infty$.

Fig.2 compares our theory (solid curves) with data (circles) on the binary blends of linear, narrowly distributed polybutadiene¹⁵ with a large blend ratio $M_2/M_1=10.7$. The solid lines are calculated by eqs. (33) and (34) with T_{d1}^0 calculated from the data of $(\eta_0)_B$ at $w_2=0$ and 1, and the plateau modulus $G_N^0=1.2 \times 10^7$ dyne/cm² and $M_e=1,880$.¹⁵ For comparison purposes, the predicted curve for $(J_e^0)_B$ is fit to coincide with the data at $w_2=1$. In the same manner, the comparison for polystyrene blends¹⁶ ($G_N^0=2 \times 10^6$ dyne/cm²; $M_e=13,000$)⁷ with a small blend ratio ($M_2/M_1=2$) is shown in Fig.3.

Blending laws for $H_B(\tau)$ proposed by others on the basis of the tube model are also compared in the figures : dashed lines denote the predictions

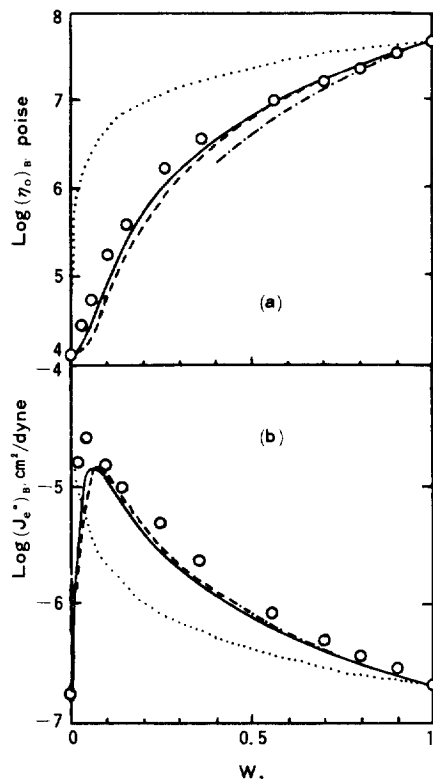


Fig.2. : (a) Zero-shear viscosity $(\eta_0)_B$ vs. composition w_2 for binary blends of undiluted, narrowly distributed polybutadienes with $M_2/M_1 = 4.35 \times 10^6 / 4.07 \times 10^4$ at 25°C. Data (circles) by struglinski. (b) Steady-state shear compliance $(J_e^0)_B$ vs. w_2 , solid lines by the present theory, see the text for captions for the other lines.

of Kurata's law;¹² dash-dot lines by Watanabe and Kotaka¹³ for $M_2/M_1 \geq 8$ and at $w \geq 0.4$; and dotted lines by Watanabe et al¹⁴ for $M_2/M_1 \leq 2$ or by Doi and Edwards' law² irrespective of the blend ratio. The figures show that our theory is in good accord with experimental results, while other laws do not agree with each other and reveal some discrepancies with data. Although not included here further, our laws also describes well other data for blends with intermediate blend ratio between 10.7 and 2.

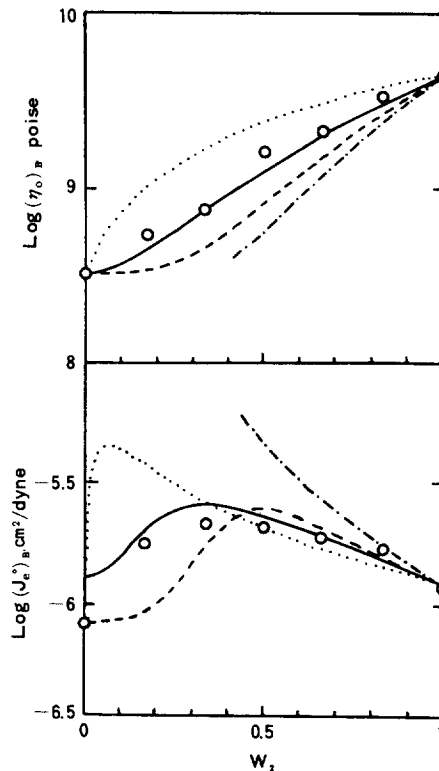


Fig.3. : (a) $(\eta_0)_B$ vs. w_2 for binary blends of polystyrenes with $M_2/M_1 = 2.67 \times 10^5 / 1.25 \times 10^5$ at 129°C. Data by Akovali.¹⁶ (b) $(J_e^0)_B$ vs. w_2 . Others are the same as the captions to Fig.2.

CONCLUSIONS

We proposed a modified tube model which provides us a background to predict viscoelastic properties of binary blends of linear homopolymers with different MW's. Based on our proposed equivalent primitive chain model, we derived a blending law for the stress equation which incorporates intramolecular chain dynamics as well as intermolecular interactions. It is expected that the blending law can yield both linear and nonlinear rheological properties because the deformation-dependent function $Q(E)$ of eqs. (3) and (28) is given for any type of deformation or flow and the algorithm in the Doi-Edwards theory for

extending the stress equation to a general constitutive equation is still valid in the current case.

The good agreement of our theory with the experimental observations of $(\eta_0)_B$ and $(J_e^0)_B$, which are very sensitive to molecular structure and relaxation time, leads us to extend the current theory to polydisperse polymers with known, arbitrary MWD.

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