

Thermodynamical Approach to Polymer Rheology

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SYNOPSIS

The model of pseudocrosslink is extended to polymer rheology. There exist various sizes b of 4–16 between transition points A and B . Each link is connected with a chain having length n_b and relaxation time τ_b . n_b is equal to b^2 and τ_b is proportional to n_b^2 . A , B , and C (polymer terminal) divide the stress-relaxation spectrum into four zones. In the AB zone, successive dissociation of links occurs from a small size to a large one and rigidity G is decreased with time t as $G \propto t^{-0.5}$ and viscosity η is increased as $G \propto t^{0.5}$. In the BC zone, dissociation of the B link proceeds along a molecule of length n in a mode of squeezing of molecule and η becomes constant, but G still decreases due to increase of unperturbed end-to-end distance of chain and $G \propto t^{-0.5}$. However, dynamic elasticity becomes constant due to a small amplitude. At high shear, links are loosened and G and η are much decreased. Beyond C , molecule flows and η increases as $\eta \propto \dot{\gamma}^{-0.8} n^{3.5}$, but high shear rate $\dot{\gamma}$ diminishes the effect of n due to extension of the molecule. Extensional viscosity η^* is affected by the change of shape as $\eta^* \propto t^{1.5}$ and gives an overshoot. Under load, creep occurs and it is proportional to $t^{1/2-1/3}$. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polymer rheology is concerned with physical properties such as elasticity, viscosity, and viscoelasticity. They are affected by stress, strain, and time as well as temperature. Various theories are proposed based on the hydrodynamical analysis of the rheological data and they are developing with the aid of tensor analysis.¹ At the same time, rheology is much concerned with the thermodynamical transition points such as the glass transition or the flow point.

The author proposed a model of the pseudocrosslink in which the size of links and the length of connected chains and their relaxation times are estimated by thermodynamics and kinetics.^{2–13} In this article, the dynamic and static spectra are derived as a distribution function of relaxation times.

THEORY

Outline of Basic Concept and Result

In the preceding article,¹⁴ a thermodynamical theory for transition points of polymers was established by

the pseudocrosslink model: Polymer chains form links of multi-sizes caused by the entanglement of polymer chains with aid of the cohesion of segments. Links are connected with chains of various length and the distribution of the size b , length n_b , and relaxation time τ_b are determined thermodynamically.

Transitions take place at temperatures T_A and T_B at which b is 4 and 16 or n_b is 4^2 and 16^2 , respectively. In place of the melting point for crystalline polymers, the flow point T_B and the glass transition point T_g are introduced for amorphous polymers. Rheological transitions occur at these points. As to b , n_b , and τ_b , the following constitutive equations are derived thermodynamically as

$$bH_0 = RT \ln n_b^3 \quad (1)$$

$$n_b = b^2 \quad (2)$$

and

$$\tau_b = \tau_0 \exp \{ (bE_0^*) / n_B^{0.5} \} = \tau_0 n_b^2 n_B^{0.5} \quad (3)$$

where H_0 is the cohesion heat and E_0^* is the activation heat of dissociation of a unit link and is taken to be $(\frac{2}{3})H_0$. τ_0 is the time for translation of a unit

segment migrating a distance equal to a segment length l and it is of an order of 10^{-7} at temperature 50°C above T_g .

These equations are extended to establish a new type of rheological theory and the following results are obtained: Equations (1) and (2) give b and n_b as a function of temperature T and eq. (3) gives the relaxation time τ_b . Equations express also the distribution of b , n_b , and τ_b . The size b is distributed between 4 and 16 at the AB zone. Transitions take place at points A , B , and C , C corresponding to the polymer terminal. At the temperature T_g , i.e., 50°C above T_A , the glass transition point G exists, and at B , softening or melting, and at C , viscous flow occur. There are four characteristic zones, e.g., glassy (A or G), highly elastic (AB), rubbery or plastic (BC), and viscous (beyond C) zones.

In the AB zone, links are dissociated successively from a small size to a large one caused by strain or stress. In the BC zone, the B link is dissociated along a molecular chain and it is regenerated at another position and the number of links is kept constant. The process continues to the polymer terminal and it resembles a mode of squeezing a molecule. Beyond C , the molecular chain flows.

The dynamic relaxation spectrum is derived according to the pseudocrosslink model. The spectrum of the AB zone is obtained from a relation that τ_b is proportional to n_b^2 , whereas elasticity E is inversely proportional to n_b according to eq. (3). In the plot of $\log E$ against $\log \tau$, a straight line of a slope of $-\frac{1}{2}$ is obtained. It is followed by the BC zone where the number of the largest link B , ν_B , and the elasticity E_B are kept constant, giving a box-type spectrum.

For the static spectrum elasticity E , elongation α and relaxation time τ are replaced by rigidity G , shear γ , and time-elapsed t , respectively. In the AB zone, G is inversely proportional to $t^{0.5}$, similarly to the dynamic spectrum. However, in the BC zone, the strain in the static spectrum is much larger as compared with the dynamic one and it is influenced by the shear. G_{BC} is not constant but decreases with increasing time. In this zone, the dissociation of the B link advances along a molecular chain. The end-to-end distance of the B chain increases. Since the elongation ratio α is given by a ratio of the end-to-end distance of the chain against its initial unperturbed one, the actual elongation of the chain is different from that of specimen α and is modified as $\alpha(\tau_B/\tau)^{0.5}$. Thus, G for the BC zone is inversely proportional to $t^{0.5}$, similarly to the AB zone.

For viscosity η , it is proportional to ν_b and τ_b . In the AB zone, η is proportional to $t^{0.5}$. In the BC

zone, it becomes a constant, $E_B\tau_{BC}$ or η_{BC} . Here, τ_{BC} or η_{BC} increases with increasing the molecular chain length n and is proportional to $(n/n_B)^{3.5}$. However, in the BC zone, G and η are much decreased by the strain or strain rate as $G \propto \gamma^{-2-3}$ and $\eta \propto \dot{\gamma}^{-0.8}$ and the effect of n disappears. The phenomena are explained quantitatively by the squeezing concept.

Extensional viscosity η^* is a viscosity of the bulk specimen and is affected by the change in the shape of the specimen. In the AB and BC zones the cross-sectional area is decreased whereas the length is increased by the plastic or viscous deformation. It depends on the regeneration rate of links. At high shear or high shear rate, the viscous flow zone invades the AB zone, inducing a steep increase of the extensional viscosity. At a constant load, creep occurs.

Dynamic Relaxation Spectrum

In the zone AB , the relaxation time τ_b is proportional to n_b^2 according to eq. (3), whereas the elasticity E is inversely proportional to n_b and, therefore,

$$E/E_A = (\tau/\tau_A)^{-1/2} \quad (4)$$

This gives a straight line of a slope of $-\frac{1}{2}$ in a log-log plot between E and τ , giving a wedge-type spectrum. Stress relaxation occurs, caused by the successive dissociation of links from the smallest size b of 4 to the largest one of 16 (Fig. 1).

At point B , E attains a constant value of E_B . Beyond point B , the successive dissociation of the B links proceeds along a molecular chain to its terminal, i.e., to point C . The process is of a mode of squeezing a molecular chain: In this case, the number of the B links or the B chains is kept constant as a whole, because the dissociation of links and their regeneration are fast and they attain an equilibrium

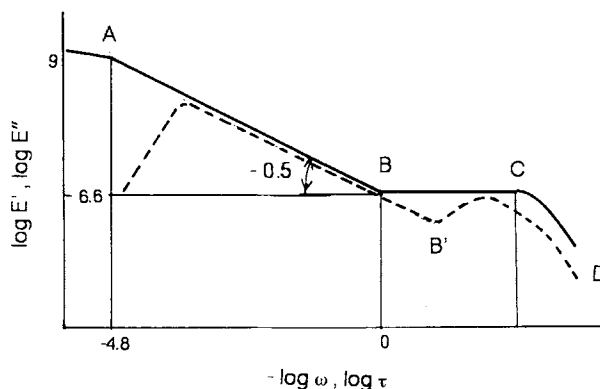


Figure 1 A schematic diagram of a dynamic relaxation spectrum.

and, therefore, the number of links is kept constant. However, E is affected by the elongation and the amplitude when they are large, as explained later.

Shear Rigidity and Viscosity

In the case of shear, the elasticity E is replaced by the rigidity G . In the AB zone, the relaxation time τ is replaced by the time t elapsed during the deformation, because the link of small size b is relaxed during the time t and the links of τ larger than τ_b support the stress. For the rigidity G , eq. (4) holds in the AB zone and is expressed as

$$G_{AB} = G_A(t/\tau_A)^{-1/2} \quad (5)$$

For the BC zone, the number of B links and their relaxation time are constant. In this zone, the dissociation of the B link proceeds along a chain. The dissociation and regeneration of the B link are in an equilibrium as a whole, but in an individual molecular chain, the end-to-end distance of the B link increases in a mode of squeezing a molecular chain. Therefore, actual elongation is to be modified due to the change of the initial end-to-end distance of the B chain and it increases by advancing the position of the link broken. The dissociation of the link takes place successively from points B to C . At an intermediate point X between B and C , the length of chain X increases from n_B to n_X and the initial unperturbed diameter of the coil X increases from $n_B^{1/2}$ to $n_X^{1/2}$. This means that the actual elongation of chain X is smaller than the elongation ratio of the specimen α but is equal to $\alpha(n_B/n_X)^{1/2}$. As a result, the elastic force f or the elasticity E becomes

$$f_X = E_B(\alpha - 1) = E_X(\alpha - 1)(n_B/n_X)^{1/2}$$

or

$$\begin{aligned} E_X/E_B &= \{(n_B/n_X)^{1/2}\alpha - 1\}/(\alpha - 1) \\ &= (n_B/n_X)^{1/2} \quad (6) \end{aligned}$$

Since n_X is proportional to the relaxation time τ_X , it follows that

$$E_X/E_B = (\tau_B/\tau_X)^{1/2}$$

For shear,

$$G_{BC}/G_B = (\tau_B/t)^{0.5} \quad (7)$$

In other words, rigidity decreases with increasing the time and this is realized at a large deformation

unlike the dynamic relaxation spectrum. In this process, the number of the B links decreases but new links are regenerated at other equilibrium positions and the total number of the B links is kept constant (Fig. 2). The mode of squeezing is illustrated in Fig. 3.

For the shear viscosity η , it is changing during time t . Since the AB zone is constructed of a network structure, the shear force $G\gamma$ is balanced at the viscous one $\eta\dot{\gamma}$, γ and $\dot{\gamma}$ being the shear strain and shear rate, respectively; namely, it follows that

$$G\gamma = \eta\dot{\gamma} \quad (8)$$

Taking $\eta/G = \tau$, and $\gamma/\dot{\gamma} = t$, the shear viscosity at zone AB , η_{AB} , becomes

$$\eta_{AB} = G_A(t\tau_A)^{0.5} \quad (9)$$

On the contrary, in the BC zone, eq. (8) does not hold due to restructuring the network by squeezing and

$$\eta_{BC} = G_B\tau_B = \eta_B \quad (10)$$

Thus, the viscosity becomes constant and gives a plateau form in the BC zone whereas the rigidity gives still a wedge form.

Beyond point C of the polymer terminal, the deformation becomes a true viscous flow. It proceeds

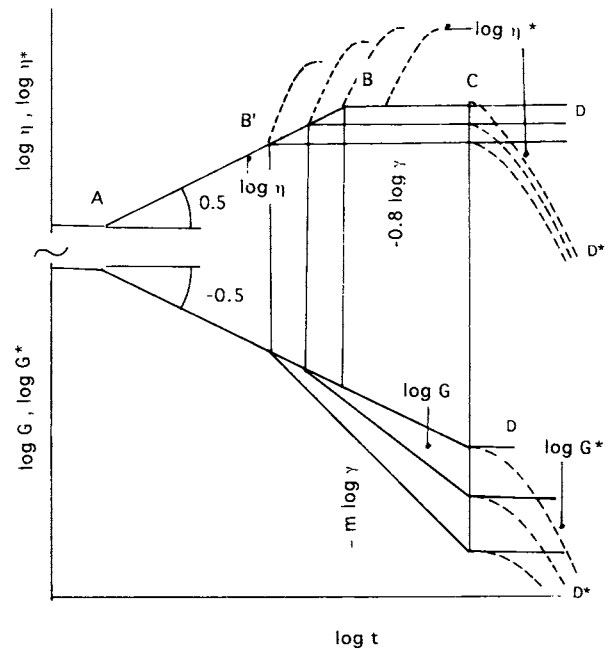


Figure 2 Schematic spectra of rigidity and viscosity: (—) G, η ; (---) G^*, η^* .

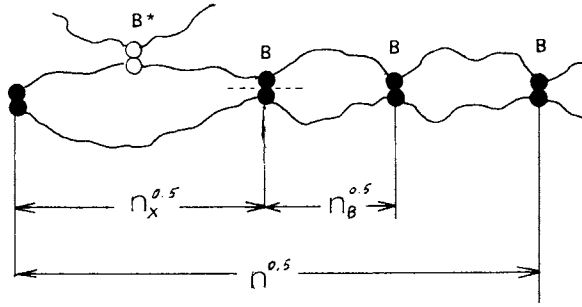


Figure 3 Illustration of squeezing molecular chain showing the *B* link to be dissociated and the *B** link regenerated.

with the disentanglement of the molecular coils. Consequently, the relaxation time is increased by a factor $(n/n_B)^3$ and that due to the increase in the relaxation distance, i.e., $(n/n_B)^{1/2}$ and

$$\eta = \eta_B(n/n_B)^{3.5} \tag{11}$$

This is an equation for the melt viscosity. For oligomers of n less than n_B , eq. (3) holds and η becomes

$$\eta = \eta_0(n/n_0)^{1.5} \tag{12}$$

where the suffix refers to the unit segment.

Effect of High Shear or Shear Rate

In the above equations, the changes of the rigidity and viscosity are caused by the successive dissociation of the links. In the *AB* zone, the dissociation is accompanied by a small strain but it is dissipated during the deformation. In the *BC* zone, however, at high strain or strain rate, it induces the extension of the molecular coil. At the same time, it causes the loosening of the links to decrease the cohesion heat or rigidity and also the activation heat of dissociation or viscosity. Such an effect is estimated by the following procedure:

The elastic force of a chain is given by $kT(\alpha - 1)$ and it acts on a link of the size b to loosen the link by a distance δl , l being the segment length. Here, the factor δ is estimated to be 0.1/3 by taking 0.1 as the free-volume fraction. The molar energy W of the loosening becomes

$$W = bl^2\delta lkT(\alpha - 1)/l^3 = \delta b(\alpha - 1)RT$$

where l^2 and l^3 are the cross-sectional area and volume of a segment, respectively. The elasticity E decreases as

$$E = E_b[\exp(-W/RT) - \exp(W/RT)] = 2G_b \sinh(\delta b\alpha) \tag{13}$$

Here, δb is 0.13–0.53 depending on the value of b of 4–16 and the effect is negligible except for link *B*. The maximum value of α is equal to $n_b^{0.5}$ or b and 16 for the *B* link. Equation (13) is simplified to

$$E = E_X\alpha^{-m}$$

where the exponent m is given by $\log[2 \sinh(0.53 \alpha)]/\log \alpha$ and m is about 1.7–3.5 for α of 4–16. For shear γ , α is replaced by $(\gamma/3) + 1$ and

$$G = (G_B/\alpha^m)(t/t_B)^{-1/2} = \{3G_B(\gamma t)^{-m}\}(t/t_B)^{-1/2} \tag{14}$$

Thus, the rigidity decreases with increasing γ or time t .

Viscosity is also decreased because η is given by $G\tau$, where G is taken to be G_B and τ decreases with increasing γ as

$$\tau = \tau_B/\gamma^m$$

Therefore,

$$\eta = \eta_B/\gamma^m$$

In the *BC* zone, the force is not balanced between $G\gamma$ and $\eta\dot{\gamma}$ as a whole, but in a chain they are balanced and

$$kT\alpha = kT\tau/\dot{\alpha}^m \text{ or } \alpha = (\tau\dot{\alpha})^{m+1}$$

and, therefore,

$$\eta(\dot{\gamma}) = \eta(\dot{\gamma}\tau)^{-m'} \tag{15}$$

Here, m' is $m/(m + 1)$ and is about 0.6–0.8 for m of 1.7–3.5 (Fig. 4). It is noticed that the molecular weight dependence in eq. (11) almost vanishes at a high shear rate, because τ/τ_B is equal to $(n/n_B)^{3.5}$ in the following equation:

$$\eta(\dot{\gamma}) = [G_B(n_B/n)] [\tau_B(n/n_B)^{3.5}]^{1-m'} \dot{\gamma}^{-m'} = G_B\tau_B(\dot{\gamma}\tau_B)^{-0.7} (n/n_B)^{3.5 \cdot 0.3-1} = n_B(\dot{\gamma}\tau_B)^{-0.7}$$

Extensional Viscosity

Extension of the bulk specimen is accompanied by the change of the shape. In elastic deformation, the length of the specimen is increased by α but the

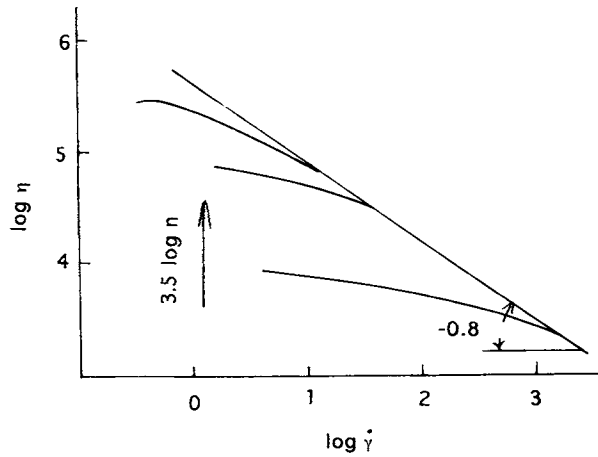


Figure 4 A schematic diagram of melt viscosity as a function of shear rate and molecular length.

cross-sectional area is decreased by a factor of $1/\alpha$, and, therefore, the extensional viscosity η^* is not changed but is equal to the shear viscosity η . On the contrary, in the plastic flow, links or chains migrate to the longitudinal direction and the number of links ν decreases in the cross section whereas it increases in the longitudinal direction by their regeneration. The former is proportional to $e^{-t/\tau}$, whereas the latter increases by $\alpha\{1 - \exp(-t/\tau')\}^{1/3}$, where τ' is a reciprocal rate of regeneration, and

$$1 - e^{-t/\tau'} \cong t/\tau'$$

As a result,

$$G^* = Ge^{-t/\tau} \quad (16)$$

$$\eta^* = \eta e^{-t/\tau} \alpha (1 - e^{-t/\tau'})^{1/3} = \eta e^{-t/\tau} \alpha (t/\tau')^{1/3} \quad (17)$$

At near T_B ,

$$G^* = (G/e) \quad (18)$$

$$\eta^* = (\eta/e) \alpha (t/\tau')^{1/3} \quad (19)$$

On the other hand, below T_B ,

$$G^* = G_A(\tau_A/t)^{0.5} \quad (20)$$

$$\eta^* = \eta_A(\tau_A/t)^{-0.5} \quad (21)$$

At large stress or strain, the elastic deformation occurs rapidly to attain an equilibrium, but the plastic flow is slow. G becomes $G_B(n_B/n)$. τ is affected by the slow regeneration of the B-link and becomes

$$\tau = \tau_B(n/n_B)^{3.5} \alpha (t/\tau')^{1/3}$$

Therefore,

$$G^* = G_B(n_B/n) \quad (22)$$

$$\eta^* = G_B \tau_B (n/n_B)^{2.5} \alpha (t/\tau')^{1/3} \quad (23)$$

Equation (17) gives a maximum or the stress overshoot at a condition that

$$t = 2\tau \quad (24)$$

In addition, it is expected that the maximum in the extensional viscosity is influenced by the molecular length and also by its distribution.

In eq. (17), η^* is larger than η when

$$e^{-t/\tau} \alpha (1 - e^{-t/\tau'})^{1/3} \geq 1$$

Since t is equal to τ in the static spectrum and τ/τ' is equal to an equilibrium constant K for the formation of pseudocrosslinks. When K is larger than unity, it follows that

$$\alpha = e/(1 - e^{-K})^{1/3} \cong e \quad (25)$$

Equation (25) gives the condition for a steep increase in a $\log \eta - \log t$ plot. A steep increase is revealed also in the AB zone because at high shear the BC zone lowered to invade into the AB one.

Compliance and Creep

Compliance J is defined as the reciprocal of the extensional elasticity E^* or $1/E^*$ at a constant load. It is a function of the time t and is empirically¹ expressed as

$$J(t) = 1/E^* = 1/E_A^* + (1/E_A)(t/\tau_A)^{1/2} \quad (26)$$

The first and second terms seem to be effective in the AC and AB zones, respectively.

Creep of raw rubber occurs in storage at room temperature for a long period. It may be induced by a heavy load which lowers the height of the BC zone. In this condition, the extensional viscosity equation may be applied and load f is written by eq. (23) as

$$f = \eta^* \alpha = \eta_B(n/n_B)^{2.5} \alpha (t/\tau')^{1/3} (d\alpha/dt)$$

$$\alpha = [3f\tau^{1/3}/\eta_B(n/n_B)^{2.5}]^{1/2} t^{1/3} \quad (27)$$

Thus, creep is proportional to $\frac{1}{3}$ power of the time.

For eqs. (17), (19), and (21), creep is given, respectively, as

$$\alpha \cong [(2\tau'/\eta)(e^{t'/t})]^{1/2} \quad (17')$$

$$\alpha = [(2\tau'/e\eta)\ln t]^{1/2} \quad (19')$$

and

$$\alpha = (2/\eta_A)(t/t_A)^{1/2} \quad (21')$$

For vulcanized rubber, creep also occurs but is very slow. In this case, the molecular length becomes infinitely large and there exist pseudocrosslinks whose sizes are larger than size B . This means that the hierarchies higher than the BC zone are formed. The translation of the large links or chains proceeds through the hierarchies and their rates become very slow. For the network composed of i stages, the change of the number of the pseudocrosslink ν is given as

$$d\nu/dt = -(k\nu)^i \text{ or } \nu \sim kt^{-1/(i+1)}$$

Here, i is given by a ratio of the length of the lattice formed by the network to the chain length of the B chain. For a cubic specimen of a volume of 1 cm^3 , the former is given by $[(1 \text{ cm}^3)(\nu_1/N)]^{1/3}$ and the latter is n_B^m , where ν_1/N is the degree of vulcanization and l is the segment length of 10^{-7} cm and the exponent m is 1 for the extended chain and 2.5 for the coiled one from eq. (3). Therefore, i is

$$i = (\nu_1/N)^{1/3}/10^{2.4(1-2.5)}10^{-7} = (\nu_1/N)^{1/3}10^{4.6-1}$$

The elasticity E is proportional to $\nu_1 + \nu$ and E is decreasing with increasing time as

$$E = kt^{-m} \quad (28)$$

where m is

$$m = 1/(i + 1) = 10^{-(4.6-1)}/(\nu_1/N)^{1/3}$$

Thus, m is very small and is inversely proportional to $(\nu_1/N)^{1/3}$.

Comparison Between Dynamic and Static Spectra

The vibrational measurement of elasticity or viscosity is a most convenient and popular method. It is easy to obtain data in a wide range of the rate of deformation or the frequency ω , but data on the deformation or amplitude A is little. Ordinarily, A is

small and therefore the effect of deformation is not revealed.

Elasticity for a system of a simple relaxation time is given as

$$E^* = \omega^2\tau^2/(1 + \omega^2\tau^2)E + i\omega\tau/(1 + \omega^2\tau^2)E = E' + iE'' \quad (29)$$

It attains a maximum at $\omega\tau = 1$. For the system of multiple relaxation time, the dynamic relaxation spectrum is given by the spectrum of the maximum points of each system. E' and E'' are proportional to E .

Therefore, the dynamic spectrum is essentially the same as the static one in the AB zone. However, in the BC zone, amplitude A is small and is not enough to advance the dissociation or squeezing, and the effect of the end-to-end distance is not revealed and gives a plateau spectrum in the BC zone unlike in the static deformation. At large amplitude, the squeezing advances to some extent. According to eq. (3), a critical A is

$$A = n_B^2 n_B^{0.5} l (n_X/n_B)^{0.5} \quad (30)$$

where l is the length of segment, or about 1 nm, and n_B is 256 or $10^{2.4}$. Therefore, A is to be larger than n_B , i.e., 1 mm at least. Taking $10^{2.4}$ as n_X/n_B , A becomes 1–10 cm at point C . Thus, the squeezing is insufficient in the ordinary dynamic measurement and it advances only to an intermediate point or E is almost constant.

For the loss modulus E'' , it involves the relaxation time τ and the spectrum of the AB zone is overlapped on that of E' . But E'' in the BC zone is affected by the amplitude. E'' decreases to some extent depending on the amplitude and passes an overshoot. The molecular weight distribution is reflected in the BC zone.

In summary, the dynamic spectrum is simple as compared with the static one. The latter is much influenced by the strain or strain rate and the extensional viscosity is more affected by the change of the shape. Table I lists their differences.

DISCUSSION

Dynamic Relaxation Spectrum

The dynamic relaxation spectrum gives the most fundamental feature of polymers in rheology and it has been studied by many scientists. Various models were proposed such as the spring-bead model by

Table I Comparison Among Dynamic and Static Spectra

Zone	Dynamic	Shear	Extensional	Creep
AB	$E \propto \omega^{0.5}$ (4) $\eta \propto \omega^{-0.5}$ Heavy load	$G \propto t^{-0.5}$ (5) $\eta \propto t^{0.5}$ (9)	$G^* \propto t^{-0.5}$ (20) $\eta^* \propto t^{0.5}$ (21) $G^* \propto t^{-2/3}$ (22) $\eta^* \propto \alpha t^{1/3}$ (23)	$\alpha \propto t^{1/2}$ (21') $\alpha \propto t^{1/3}$ (23')
BC	$E' = E_B$ $E'' = F_B/\tau_B$	$G = G_B t^{-0.5}$ (7) $\eta = \eta_B$ (10)	$G^* = G_B t^{-0.5}$ (16) $\eta^* = \eta_B \alpha t/\tau'$ (19)	$\alpha \propto (\log t)^{1/2}$ (19')
C ~		$G = G_c$ $\eta \propto n^{3.5}$ (11)	$G^* = G_c e^{-t/\tau}$ (16) $\eta^* \propto e^{-t/\tau} \alpha t/\tau'$ (17)	$\alpha \propto e^{t/\tau}/t$ (17')
<u>High shear rate</u>				
BC		$G \propto t^{-0.5} \dot{\gamma}^{-0.5 \sim 3.5}$ (14) $\eta = \eta_B \dot{\gamma}^{-0.8}$ (15)	$G^* = G$ $\eta^* \propto e^{-t/\tau} \alpha t/\tau'$ (17)	$\alpha \propto e^{t/\tau}/t$ (17')
C ~		$G = G_c$ $\eta = \eta_c$	$G^* = G_c e^{-t/\tau}$ $\eta^* = \eta_c e^{-t/\tau} \alpha t/\tau'$	$\alpha \propto e^{t/\tau}/t$

Rouse,¹⁵ the reptation model by deGennes,¹⁶ the tube model by Doi-Edwards,¹⁷ and the free-volume model by Eyring.¹⁸ They are useful but their scopes are limited to one of zones. The transition points are not always clear.

On the other hand, the pseudocrosslink model was proposed by Tobolsky et al.¹⁹ in 1946 and developed by Yamamoto,²⁰ Lodge,²¹ and the author²² in 1955-56. The author presented later the model of multisized links to account for the relaxation spectrum and also transition points.

An actual dynamic spectrum is composed of the elastic zone of a slope of $-\frac{1}{2}$ and the plateau one for the stored elasticity. The Rouse model fits the elastic zone and the tube one fits the plateau one. The model of multisized pseudocrosslink is compatible with the experimental data in the literature and books^{1,23} in the whole zones involving the glassy, elastic, plateau, and viscous zones. Equation (4) fits the spectrum of stored elasticity and that of the loss modulus is given by the reciprocal shear viscosity.

The plateau zone is expected to be influenced by the amplitude as well as by the molecular weight distribution. The latter is described in literature¹ but the former is not known.

The temperature-shift factor was proposed by Williams, Landel, and Ferry¹ and was derived through the Doolittle viscosity equation and the thermal expansion of the free volume. The author derived the same relation in the preceding article directly from the effect of the entrainment of the neighboring segment on the relaxation time.

Shear Viscosity

Shear viscosity was dealt with hydrodynamically by many authors. Since the measurement is carried out with relatively large deformation, the effect of shear or shear rate is large and two types of constitutive equations, a strain-dependent and a rate-dependent one, were proposed by Bernstein et al.²⁴ Leonov,²⁵ Giesekus,²⁶ and Larson.²⁷ Many reviews were presented by Osaki et al.²⁸ and Takahashi and Onogi.²⁹

In these studies, the distribution of strain and stress is taken into consideration. Shear viscosity is expressed as a function of the time difference between the actual time and that memorized in the previous stage.

The plateau zone was explained by Graessley³⁰ and the existence of the critical molecular weight was suggested for the onset of this zone. Doi-Edwards^{17,31} explained the plateau zone by the tube model and pointed out the existence of the transitions corresponding to the entrance and the exit of the tube.

For the melt viscosity, deGennes¹⁵ explained the molecular weight dependence by the reptation model. It suggests that the viscosity is proportional to the 3rd power of the molecular weight but actually to the 3.5th power, and the difference was adjusted by the modification of the tube length.³¹

Osaki et al.^{28,32} investigated the relaxation in concentrated solutions after deformation and that in multisteps and found the enormous dumping of the rigidity caused by the shear. On the other hand, the melt viscosity decreases by high shear rate and Stratton³³ showed that the viscosity is inversely

proportional to the -0.8 -th power of the shear rate and the molecular weight dependence disappears. Doi-Edwards^{17,31} succeeded in the derivation of the rigidity dumping by tensor analysis. They extended the analysis to the shear-rate effect, but the exponent is -1.5 , unlike the actual value of -0.8 .

The above models and theories are useful but their scopes are limited. Therefore, it needs the combination of different models to account for the molecular dynamics in whole zones. The author proposed in the preceding section that the distribution of sizes of links and their relaxation times are the origin of the spectrum. Figure 2 is compatible with the dumping of the shear rigidity in the multistep relaxation³² and Figure 4 fits the result of Stratton.

The dumping of rigidity by shear and the decrease of viscosity by the shear rate arise from the same origin but the exponents in the equations are different. The effect is explained by eq. (15) or by the assumption that the elastic force and viscous one are balanced in a chain.

Extensional Viscosity

Extensional viscosity of high-density polyethylene (HDPE),³⁴ polystyrene,³⁵ the acrylonitrile-butadiene-styrene terpolymer (ABS),³⁶ and rubber³⁷ are available in the literature. The $\log \eta^* - \log t$ plots give straight lines of slopes of 0.5 – 0.6 , as listed in Table II. There are steep increases at time t depending on the rate of extension α , and the $\alpha t + 1$ or α in the above literature is found to be very close to the theoretical value of 2.3 . It may depend on the equilibrium constant K or the temperatures T or T_B . The slope and the overshoot seem to fit eq. (17) and the like.

For rubber, Nakajima and Scobbo,³⁷ claimed that αt is employed instead of t and then the $\log - \log$ plot of η^* against αt becomes a straight line. It corresponds to eq. (19) for the extensional viscosity.

The extensional viscosity shows the stress overshoot. As to the slope theories that were presented,^{38,39} the elucidation of a steep increase oc-

curing in the viscoelastic zone is not always enough. Equation (17) suggested it in the extensional viscosity. On the other hand, various theories suggested that the overshoot occurs also in the shear viscosity. Also, in the shear viscosity, the change of the shape may occur when the diffusion of the polymer chain is not enough to dissipate the shape effect, but more precise experiments are necessary for a conclusion.

As to the dynamic relaxation spectrum, the loss modulus E'' is to be affected by the amplitude, because it was concerned with the measurement in bulk. In ordinary cases, a stress overshoot exists in the plateau zone, but its relation to the amplitude has not been investigated as yet.

Creep

For cellulose acetate solution⁴⁰ and polyisobutyle,¹ eq. (21'), and for synthetic rubbers,⁴¹ eq. (23') seem to be adopted where the exponents are $\frac{1}{2}$ and $\frac{1}{3}$, respectively. The former is the creep in the zone AB whereas the latter may occur under a heavy load and is influenced by the relaxation condition rather than by the thermodynamic one.

For vulcanized rubber, very slow creep occurs and Ono⁴² already derived an exponential equation similar to eq. (20) using the scaling rule. The exponent with respect to time is as small as 0.01 and is inversely proportional to $(n/N)^{1/3}$.

CONCLUSION

The thermodynamical approach is extended to polymer rheology. It is useful for the explanation of the whole spectrum of a dynamic and static one and the correlation to the thermodynamical transition points. Equations derived are almost compatible with experimental data in the literature. It seems to be helpful for understanding the mechanism of rheological phenomena. The correlation between the static spectrum and the dynamic one is clarified.

Table II Summary of Data for Extensional Viscosity

Material	Temp (°C)	Equation for Literature Data	Starting Point	Author
Diene rubber	100	$\log \eta^* = 6.8 - 0.7 \log \omega$	—	Nakajima ³⁷
HDPE	150	$\log \eta^* = 7.0 + 0.65 \log t$	$\alpha = 2.4$	Koyama ³⁴
ABS	150	$\log \eta^* = 6.0 + 0.6 \log t$	$\alpha = 1.8$ 2.5	Aoki-Saito ³⁶
PS	130	$\log \eta^* = 6.0 + 0.5 \log t$	$\alpha = 3.5$	Munstedt ³⁵

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