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An Aspect of Universality in Polymer Viscoelasticity

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In melts and concentrated solutions of high molecular weight (MW) polymers, because of the constraint effect due to chain entanglements, each chain can be viewed as confined inside a tube. To move its whole length around, the chain has to slide back and forth along its own contour. This snakelike motion (reptation) was first proposed for a chain moving in a fixed network and conjectured as might be applicable in polymer melts by de Gennes.[1] Modeling the chain motion as reptation and relating the macroscopic stress anisotropy to a deformed tube associated with a "labeled" chain (averaged over the ensemble), Doi and Edwards[2-5] developed a very successful rheological constitutive equation. In their development, it is assumed that the deformed tube associated with a labeled chain is randomized by the reptation motion of the labeled chain alone. Such a process can be referred to as the *pure* reptation. The tube represents a mean field of constraint formed by entanglements of the labeled chain with other chains. Thus, this can also be referred to as a mean-field assumption. This assumption is against the intuitive inclination of most people that disentanglement due to the moving away of the neighboring chains should also have randomization effects on the tube associated with the labeled chain.[6-12] However, extensive and consistent quantitative analyses of the linear viscoelastic spectra[13-22] in terms of the theories[13,20,21] developed upon the Doi–Edwards theory consistently indicate that the mean-field assumption is correct in a monodisperse system. The interrelations of the developed monodisperse melt theory,[13-15] monodisperse concentrated solution theory[20] and binary theory[21,22] predict that universality in linear viscoelastic spectra exists between the monodisperse melt and the monodisperse concentrated solution. This universality is confirmed by experimental results independently obtained by Watanabe et al.[23] and us.

The theoretical $G(t)$ functions of monodisperse melts, monodisperse concentrated solutions, and binary blends and their interrelations are given in the previous papers.[20-22] Here, to illustrate the universality in viscoelastic spectra existing between the monodisperse melts and the monodisperse concentrated solutions, we show the calculated spectra in Figures 1 and 2. Experimentally, we have to deal, at best, with nearly monodisperse samples obtained by anionic polymerization. As long as the molecular weight distribution (MWD) of the sample is very narrow, it has been shown from extensive detailed shape analyses of the viscoelastic spectra that the linear additivity rule of the contributions from individual MW components to $G(t)$ is valid.[13-16,20-22] For our present illustration purpose, we can calculate the theoretical spectra by convoluting the $G(t)$ functions with the Schulz function.[14-15,20,22]

Shown in Figure 1 are the storage modulus spectra $G'(\omega)$ for nearly monodisperse polymer melts calculated with the Z parameter of the Schulz function equal to 25 (equivalent to $M_w/M_n = 1.04$) as a function of MW. It shows the characteristic changes of the spectra with MW, such as the disappearance of the modulus plateau and the shift of the terminal zone to the higher frequency with decreasing MW, which have been exhibited in the comparison of the measured spectra of different MW samples by Onogi et al.[24] and Lin (in the $G(t)$ form).[14]

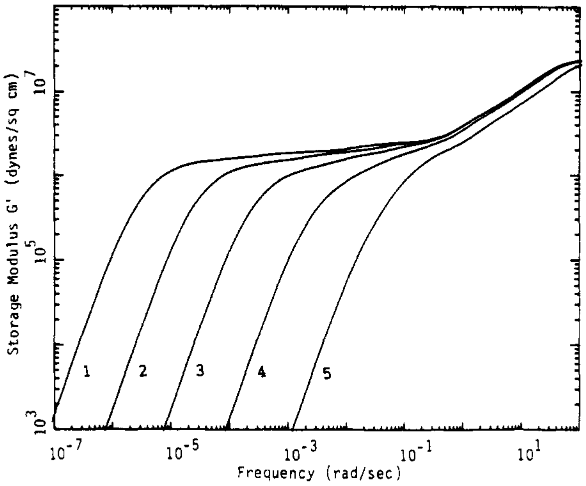

Figure 1. Storage modulus spectra $G'(\omega)$ calculated by convoluting the monodisperse melt theory with the Schulz MWD using $Z = 25$. Lines 1–5 are calculated for $M_w = 56M_e$, $28M_e$, $14M_e$, $7M_e$ and $3.5M_e$, respectively. The spectra are calculated with the friction factor $K = 10^{-8}$ and the plateau modulus $G_N = 2 \times 10^6$ (see refs 13 and 14). The glass–rubber transition region of a spectrum at MW below $10M_e$ is affected by the MW dependence of the friction factor K' in the $\mu_A(t)$ process region. $K'/K = 3.3$, 3.3, 3.3, 2.85, and 1.6 for lines 1–5, respectively (see Figure 17 of ref 14 or eq 5 of ref 17). Slight waviness is visible in lines 1 and 2 between the glass–rubber transition region and the plateau region; this is due to the fact that the theoretical relaxation form of the $\mu_X(t)$ process is not known and is assumed to be single-exponential decay (see refs 13 and 14 for details).

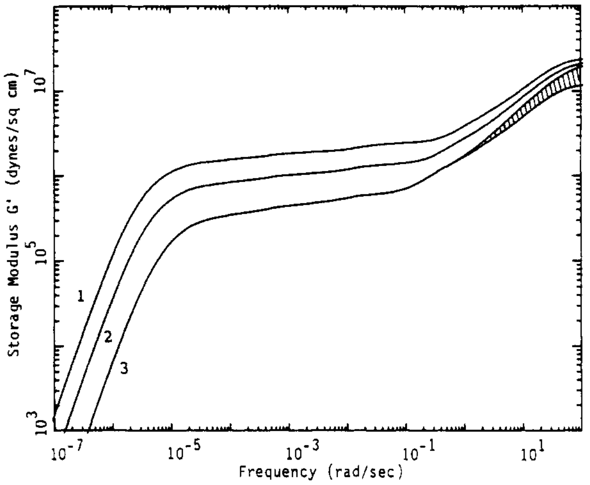

Figure 2. Storage modulus spectra $G'(\omega)$ calculated by convoluting the monodisperse concentrated solution theory with the Schulz MWD: $Z = 25$ for the high-MW component ($M_w = 56M_e$); $Z = 120$ for the low-MW component ($M_w = 0.76M_e$). Lines 1–3 are for $W_H = 1$, 0.75, and 0.5, respectively. The shaded area of spectrum (line) 3 is the contribution of the free Rouse chain motion associated with the low-MW component. Line 3, excluding the shaded area, is superposable onto line 2 of Figure 1 following the shifting scheme described in the text.

In Figure 2, we show the calculated storage modulus spectra of nearly monodisperse concentrated solutions with $M_H = 56M_e$ ($Z = 25$) and $M_L = 0.76M_e$ ($Z = 120$, equivalently $M_w/M_n = 1.008$; the low-MW component serves as the solvent) at different W_H (the weight fraction of the high-MW component) values. The spectra are calculated with the M_e' value given by

$$M_e' = M_e W_H^{-1} \tag{1}$$

(See the appendix of ref 20 for the theoretical prediction

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of eq 1.) The increase of M_e' with dilution leads to several consequences:

(1) The plateau modulus decreases with dilution according to

$$G_N' = G_N W_H^2 \qquad (2)$$

(2) The relaxation time τ_C (see equ 11 of ref 20)[13,14,20] is shortened by dilution, while the friction factor is kept the same. This leads to moving the terminal region to a higher frequency.

(3) Because of the $M_e'^{\,2}$ dependence of $\tau_A{}^1$ (see eq 5 of ref 20),[13,14,20] the lowest mode of the $\mu_A(t)$ process is moved to a lower frequency.

As a result of points (2) and (3), the relaxation time ratio $\tau_C/\tau_A{}^1$ becomes smaller. This is demonstrated by the shortening of the distance between the terminal zone and the glass–rubber transition zone. All three effects have been observed experimentally, and the magnitudes of the changes are in agreement with the theory quantitatively as demonstrated in the detailed spectrum shape analyses.[20]

Spectrum 2 of Figure 1 and spectrum 3 of Figure 2 having the same normalized MW are superposable on each other except in the very high frequency region, where the free Rouse chain dynamics associated with the low-MW component (as the solvent) contributes to the latter (the shaded area of spectrum 3 of Figure 2).

Let the MW of spectrum 2 of Figure 1 be M and the MW of spectrum 3 of Figure 2 be M'. We know that $M' = 2M = MW_H{}^{-1}$, $M_e' = M_eW_H{}^{-1}$, and thus $M/M_e = M'/M_e'$. (See the figure captions of Figures 1 and 2.) From the structural factors of $\tau_A{}^1$ (the relaxation time of the lowest mode of the $\mu_A(t)$ process) and τ_C (see eqs 5 and 11 of ref 20), one can obtain $\tau_A{}^1 = K'M_e{}^2W_H{}^{-2}/6$ and $\tau_C = K(M^3W_H{}^{-2}/M_e)(1 - (M_e/M)^{0.5})^2$ for spectrum 3 of Figure 2, while $\tau_A{}^1 = K'M_e{}^2/6$ and $\tau_C = K(M^3/M_e)(1 - (M_e/M)^{0.5})^2$ for spectrum 2 of Figure 1. The same $W_H{}^{-2}$ dependence occurs to τ_X and τ_B. The dependence of the relaxation times on W_H results in spectrum 3 of Figure 2 occurring at a lower frequency than spectrum 2 of Figure 1 by a factor of $W_H{}^2$. Second, the plateau modulus of spectrum 3 of Figure 2 is lower than that of spectrum 2 of Figure 1 by a factor of $W_H{}^2$ according to eq 2. Thus, spectrum 2 of Figure 1 can be superposed on spectrum 3 of Figure 2 by shifting the former along the modulus coordinate down by a factor of $W_H{}^2$ and along the frequency coordinate down by a factor of $W_H{}^2$.

Watanabe et al.,[23] on the basis of observing experimental results, proposed a shifting scheme identical to what is described above (see Figure 8 of ref 23). For two nearly monodisperse polystyrene samples having the same normalized MW, one being a pure melt of M_H = 172 000 (M_w/M_e = 12.74) and M_w/M_n = 1.07 and another being a concentrated solution consisting of a high-MW component (M_w = 427 000, M_w/M_n = 1.05) and a low-MW component (M_w = 10 500, M_w/M_n = 1.08) at W_H = 0.4 (equivalently, the solution having M_w/M_e' = 12.65), they have found that the two spectra, following the shifting scheme, are virtually totally superposable on each other (see Figure 7 of ref 23). This is in agreement with the universality between the monodisperse melt theory and the monodisperse concentrated solution theory.

The superposability is also observed among a polystyrene melt (M_w = 102 000, M_w/M_e = 7.55), a polyisoprene melt (M_w = 31 100, M_w/M_e = 7.46), and a polyisoprene (M_w = 63 100)/polyisoprene (M_w = 3100 < M_e) 50/50 blend (equivalent to a concentrated solution of M_w/M_e' = 7.56) as shown in Figure 3. These samples have virtually the same normalized MW. The polyisoprene spectra were measured at about 233 K and give M_e = 4170. The spectra of the polyisoprene samples are shifted to superpose onto that of the polystyrene sample, which is the F10 sample studied in ref 14. The solid line is the theoretical curve calculated for F10. Between the two polyisoprene samples, the W_H dependence of the plateau modulus follows that given by eq 2 virtually exactly (see the note in ref 25).

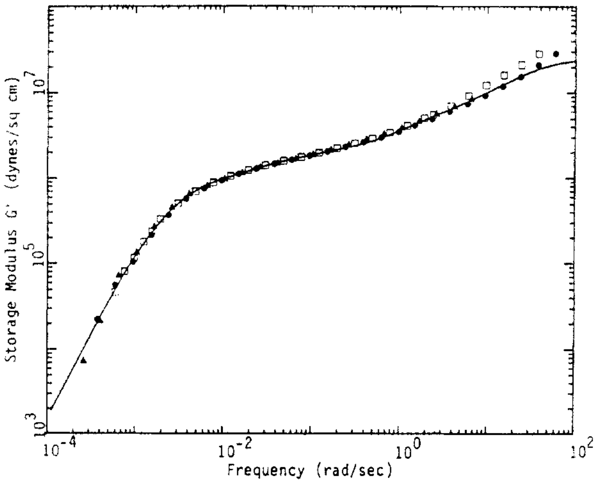

Figure 3. Comparison of the calculated storage modulus spectrum (the solid line) and the measured ones: (●) for polystyrene (M_w = 102 000, M_w/M_e = 7.55); (▲) for polyisoprene (M_w = 31 100, M_w/M_e = 7.46); (□) for a concentrated polyisoprene solution (a blend of polyisoprene (M_w = 63 100)/polyisoprene (M_w = 3100 < M_e) 50/50; equivalent to M_w/M_e' = 7.56). The theoretical curve and the data of the polystyrene sample are the same as those shown in Figure 18a of ref 14. The measured spectra of polyisoprene samples have been shifted to superpose onto the theoretical curve.

To obtain the identical normalized MW for a melt and a concentrated solution, different polymer samples with different MWs have to be used. Good superposability among the spectra of the same normalized MW demonstrated in the above two examples indicates that the MWDs of the samples used in the comparison should resemble each other very well. Nevertheless, this kind of comparison is still under the uncertainty of the MWD difference, though very small, between the samples.

In a previous study,[20] viscoelastic spectra of a series of nearly monodisperse concentrated solutions, with the high-MW component having different MWs, have been analyzed in detail in terms of the monodisperse concentrated solution theory. The MWDs which give the very good fitting between the calculated and measured spectra are identical to those that respectively have been obtained in the detailed shape analyses of the viscoelastic spectra of the pure high-MW component melt samples in terms of the monodisperse melt theory.[14] This proves, beyond any small difference of MWD that can occur between two samples, the existence of universality in viscoelastic spectra between melt and concentrated solutions as predicted by the theory.

The interrelations among the monodisperse melt theory, monodisperse concentrated solution theory, and binary theory predict the universality in linear viscoelastic spectra existing between the monodisperse melt and the monodisperse concentrated solution. This prediction is confirmed by several experimental results. This agreement between theory and experiment proves that the basic assumption upon which the Doi–Edwards theory and thus the monodisperse theory were developed, namely, that the bulk polymer viscoelastic behavior can be reduced to the dynamics of a single chain in a mean field imposed by the other chains, is correct in a monodisperse system.

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(25) Note: In ref 20, it was stated that for polyisoprene a slightly stronger concentration dependence of the plateau modulus ($G_N \propto W_H^x$, $x = 2.1-2.3$) has been observed. This was based on a very early preliminary testing. Recalling what was involved in the preliminary test, a mistake might have been made, which caused making of the above statement. A more recent result of polyisoprene as shown in Figure 3 of this paper indicates that $G_N' = G_N W_H^2$ (eq 2) is virtually exactly obeyed.