

Onset of Entanglement

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ABSTRACT: The onset of entanglement was determined from studying the viscoelastic spectra of the blends consisting of two nearly monodisperse polystyrene polymers: component one having a molecular weight slightly less than the entanglement molecular weight $M_e (=4\rho RT/5G_N)$, whereas that of component two being greater than M_e (such a blend is referred to as the blend solution). It is shown that because of the absence of the hydrodynamic interaction the viscoelastic spectrum of the blend solution can be described by applying the Rouse theory to both components in the entanglement-free region. As entanglements among the chains of component two occur, when its weight fraction, W_2 , increases above a critical point, the viscoelastic response of component one remains described by the Rouse theory. With the Rouse viscoelastic response of component one as the internal reference, the onset of chain entanglement among the chains of component two can be determined by monitoring the deviation of the viscoelastic response of component two from being described by the Rouse theory as a function of increasing W_2 . According to the study, entanglement starts to occur in the close neighborhood of M_e' (the entanglement molecular weight of the blend solution and $M_e' = M_e W_2^{-1}$) for the polymer blend solution or equivalently M_e for the monodisperse polymer melt well below M_e' or M_c ($M_c' = M_c W_2^{-1}$, where M_c is the critical molecular weight of the zero shear viscosity of the polymer melt).

Introduction

Polymer viscoelastic properties are strongly influenced by chain entanglement.^{1,2} Chain entanglement in a polymeric liquid occurs naturally when both the concentration and molecular weight are high enough. A strong indication of chain entanglement is the modulus plateau that can be observed for nearly monodisperse high molecular weight samples. The entanglement molecular weight M_e can be calculated from the measured plateau modulus G_N according to^{3,4}

$$M_e = 4\rho RT/5G_N \quad (1)$$

Another strong indication of chain entanglement is the steep increase of the zero shear viscosity with increasing molecular weight (the $\eta_0 \propto M^{\beta}$ relation) above the critical molecular weight, M_c .^{1,2,5} For many different kinds of linear flexible polymers, the ratio of M_c/M_e is about 2.4, which indicates the close relation between M_c and M_e . In the molecular weight region, $<M_c$, the glass transition temperature decreases appreciably with decreasing molecular weight.^{6–8} Thus, in this low molecular weight region the molecular weight change affects the viscosity value through the frictional factor as well as the structural factor. By correcting for the difference in the glass transition temperature, so that the viscosity data at different molecular weights are compared on the basis of presumably the same friction constant, it has been found that the zero shear viscosity increases linearly with molecular weight in the molecular weight region below M_c ,^{1,5} in apparent agreement with the prediction of the Rouse theory.^{2,9,10} Mainly based on this, it has been accepted generally that the Rouse theory is applicable below M_c .^{1,5,11} Such an acceptance is equivalent to saying that a polymer melt of molecular weight between M_c and M_e is free of entanglement. Such a viewpoint was recently questioned^{12–14} based on analyzing the viscoelastic and diffusion data in terms of the extended reptation theory¹⁵ developed by including three intramolecular

chain motions on the basis of the Doi–Edwards theory.¹⁶ Detailed discussion on this was presented in ref 14. Here we confirm this conclusion from an approach totally independent of the slip-link picture of the Doi–Edwards theory.

Systems prepared from blending two nearly monodisperse polystyrene samples, component one, with a molecular weight M_{w1} slightly smaller than the entanglement molecular weight, M_e , and component two, with a molecular weight M_{w2} much larger than M_e , have been studied for their viscoelastic spectra. As far as the reduction of entanglement among the component-two chains by dilution is concerned, component one can be regarded as a solvent. Thus the blend systems are referred to as the blend solutions.

In this article, we first show that the whole viscoelastic spectrum in the entanglement-free region is described by applying the Rouse theory to both components with the same size and friction constant for the Rouse segment. With the Rouse viscoelastic response of component one as the internal reference, the onset of entanglement among the chains of component-two can be determined by monitoring the deviation of the viscoelastic response of component two from the Rouse theory as a function of increasing weight fraction of component two W_2 . The result indicates that entanglement begins to occur at M_e' ($=M_e W_2^{-1}$) within experimental error for the blend solution or equivalently at M_e for the polymer melt in agreement with the conclusion of the previous studies.

Concentration Dependence of Entanglement

The entanglement molecular weight in the blend solution increases with dilution, i.e., with the increase of W_1 . The preparation of a blend solution can be imagined in the following way. If we start with the pure component-two polymer (i.e., $W_2 = 1$), which forms entanglements extensively because $M_{w2} \gg M_e$, and cut half of the chains in the sample system to sections shorter than the entanglement length (M_e) to serve as

solvent molecules, while keeping the other half of the chains intact, each point along a long uncut chain now has one-half chance to encounter an equivalent point belonging to a short chain (solvent chain) and one-half chance to encounter that belonging to a long chain. It takes a chain section of M_e along a long chain in the original pure melt state to form one entanglement with another chain; then now, based on probability, it will take a section of $2M_e$ along the long chain in the blend solution to form one entanglement with another long chain. Thus, the entanglement molecular weight in a blend solution denoted as M_e' should change with weight fraction W_2 as

$$M_e' = M_e W_2^{-1} \quad (2)$$

Equation 2 was well supported by experimental results of the blend solution systems. Two independent studies of polystyrene blend solution systems^{17,18} showed that the plateau modulus changes with W_2 as $G_N' \propto W_2^2$ in agreement with eq 2, for

$$G_N' = 4W_2\rho RT/5M_e' \quad (3)$$

and that the line shape of the viscoelastic spectrum in the entanglement region is a universal function of the normalized molecular weight M_{w2}/M_e' with M_e' given by eq 2 (of course, including the case of $M_e' = M_e$ for $W_2 = 1$). In particular, the universality with respect to the normalized molecular weight was observed extensively through the quantitative line shape analyses of the viscoelastic spectra in terms of the extended reptation theory. The study may be considered to be quite complete for the polystyrene polymer. All together, 10 nearly monodisperse melts^{12,13,15} and six blend solutions¹⁷ at different normalized molecular weights (ranging from 1.24 to 31.3) were studied, whose results indicate the said universality. If a simple solvent of small molecules is used to prepare the polymer solution, eq 3 is expected to change somewhat because of the difference in density and chemical structure as well as the thermodynamic interaction between polymer and solvent.¹⁹ For simple polymer solutions, results of $G_N' \propto C^a$ with $a = 2-2.3$ have been observed,^{1,20,21} where C is the concentration in grams per milliliter.

For a polymer sample of molecular weight, M_{w2} , we can choose a weight fraction W_2 according to eq 2 so that $M_{w2} < M_e'$ in preparing a blend solution, which should be free of entanglement. Using eq 2, we can define a critical concentration W_c as

$$W_c = M_e/M_{w2} \quad (4)$$

With respect to W_c , one aims to carry out experiments to find answers to two questions: First, at $W_2 < W_c$, can both the viscoelastic responses of component one and component two be described by the Rouse theory? Second, because entanglement will eventually occur with increasing W_2 , how close to W_c can the deviation of the viscoelastic response of component two from the Rouse theory first be observed as an indication for the onset of entanglement.

Rouse Viscoelastic Spectrum

It can be easily shown that the sub-Rouse-segmental processes (the processes that lead to the internal viscosity^{1,10}), as observed in the very short time region of the stress relaxation, contribute to the total storage modu-

lus spectrum only in the very high frequency region corresponding to their rates; however, they affect the loss modulus spectrum greatly across a wide range of lower frequencies. Here, we consider motional modes associated with chain sections with sizes down to the Rouse segment in comparing theory and experiment. Thus, the line shape of the loss modulus spectrum is not suitable for analysis, and we need be concerned only with the equation for the storage modulus spectrum.

The Rouse theory gives the storage modulus spectrum for a monodisperse polymer of molecular weight M or equivalently N Rouse beads as^{9,10}

$$g'(\omega, M) = \sum_{p=1}^{N-1} (\rho RT/M) \omega^2 \tau_p^2 / (1 + \omega^2 \tau_p^2) \quad (5)$$

with τ_p given as

$$\tau_p = \zeta \langle b^2 \rangle / [24 kT \sin^2(\pi p/2N)] \\ = \{ K \pi^2 / [24 \sin^2(\pi p/2N) N^2] \} M^2 \quad (6)$$

for $p = 1, 2, 3, \dots, (N-1)$, where ζ is the frictional constant experienced by each bead, $\langle b^2 \rangle$ is the mean square length of each Rouse segment, and $K = (\zeta \langle b^2 \rangle N^2 / kT \pi^2 M^2)$ is referred to as the frictional factor, which is independent of molecular weight and whose strong temperature dependence (basically equivalent to that of ζ) is often described by the Fulcher and Tammann-Hesse equation or equivalently by the Williams-Landel-Ferry equation.¹ Then the viscoelastic spectrum of the blend solution can be expressed as

$$G'(\omega) = W_1 \int A_1(M) g'(\omega, M) dM + \\ W_2 \int A_2(M) g'(\omega, M) dM \quad (7)$$

where $A_1(M)$ and $A_2(M)$ represent the normalized nearly monodisperse molecular weight distributions of components one and two, respectively. The nearly monodisperse distribution $A_1(M)$ or $A_2(M)$ of the polystyrene samples used in preparing the blend solutions can be described by the Schulz distribution^{12,22,23}:

$$A(M) = [Z^{Z+1}/\Gamma(Z+1)] (M/M_n)^Z (1/M_n) \exp(-ZM/M_n) \quad (8)$$

where Γ is the gamma function and Z determines the polydispersity as given by

$$M_w/M_n = (Z+1)/Z \quad (9)$$

Experiment

A series of blend-solution samples at different concentrations were prepared from two nearly monodisperse polystyrene polymers: F10 having $M_w = 1.03 \times 10^5$; $M_w/M_n = 1.01$ and F1 having $M_w = 9.1 \times 10^3$; $M_w/M_n = 1.02$, which are standard samples from TSK.²⁴ For the F1 polymer, the molecular weight values obtained from the light scattering measurement (9.1×10^3) and the intrinsic viscosity measurement (9.0×10^3) by TSK are in good agreement. For the F10 sample, $M_w = 9.6 \times 10^4$ from light scattering and $M_v = 1.03 \times 10^5$ from intrinsic viscosity were given by the TSK characterization. The difference between these two values is somewhat greater than we expected. Thus, we took the measurement of the diffusion constant D_0 of the polymer at infinite dilution in the cyclohexane solution at the θ temperature (35 °C) with the photon-correlation spectroscopy. Using the relations between D_0 and M_w obtained by King et al.,²⁵ Han and McCrackin,²⁶ and Huber

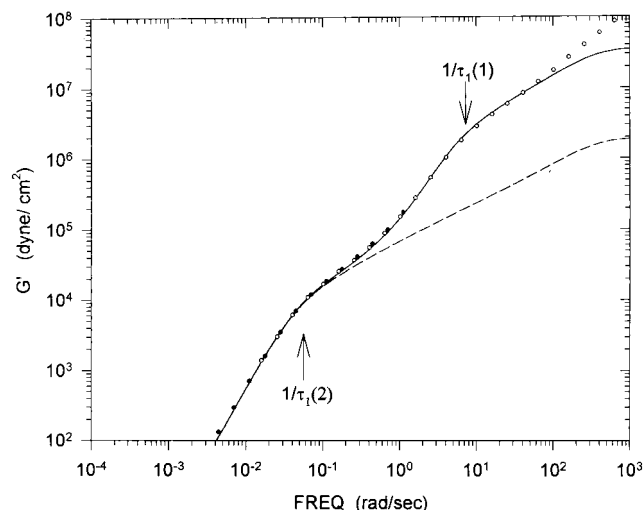


Figure 1. Comparison of the measured storage modulus spectrum (○ and ●) and that calculated from the Rouse theory (—) for sample A. (---) indicates the separation of the contributions from the F1 and F10 components. The arrow at $1/\tau_1(1)$ indicates the frequency that is the reciprocal of the relaxation time of the first Rouse mode of the F1 component, whereas the arrow at $1/\tau_1(2)$ indicates the same of the F10 component.

et al.,²⁷ the obtained average M_w value is $1.07 \times 10^5 \pm 2.5\%$. Thus, the M_w value given by TSK for F10 may be too low. In addition, the viscoelastic spectra of the present F10 sample and an old F10 sample of $M_w = 1.02 \times 10^5$ (from both light scattering and IV measurements), are virtually the same from the transition region to the terminal region. Thus, we judge that the M_w value of F10 is accurate enough to be used as its M_w as given above.

The samples denoted as A, B, C, and D prepared from blending F1 as component one and F10 as component two have the weight fraction ratio $W_1/W_2 = 0.95/0.05, 0.8/0.2, 0.7/0.3$, and $0.6/0.4$, respectively. For achieving homogeneous blending, the two components were first dissolved in toluene and then precipitated by the addition of methanol. The obtained precipitate was dried in the vacuum oven with the addition of 0.1% of antioxidant. Samples for the measurements of the viscoelastic spectra were first molded into disks of 25-mm diameter with a specially designed mold that can be placed in a vacuum oven. The molded disk samples were kept in the vacuum for at least 3 days before measurement.

The linear viscoelastic spectra of the blend solution samples were measured with a Rheometrics Dynamic Spectrometer (manufactured by Rheometrics, Inc.). The spectra of the studied samples as shown in Figures 1 and 2 comprise the results measured at two different temperatures by applying the frequency-temperature superposition principle. Even though we need be concerned only with the storage modulus spectra in the line shape analyses as explained above, the loss modulus spectra were included in the superposition process for composing the storage modulus master spectra shown in Figures 1 and 2.

Comparison of Theory and Experiment

According to eq 4, only sample A has both components free of entanglement. The viscoelastic spectrum of sample A thus can be calculated from the Rouse theory (eqs 5–7) with the molecular weight distributions $0.95 \times A_1(M)$ and $0.05 \times A_2(M)$ for the two components. The Z value for $A_1(M)$ is 50 (corresponding to $M_w/M_n = 1.02$ for F1), whereas that of $A_2(M)$ is 90 (corresponding to $M_w/M_n = 1.01$ for F10). Because of the nature of the distribution of the Rouse relaxation times, we observed that the calculated spectrum is virtually independent of the polydispersity used in the calculation, if the

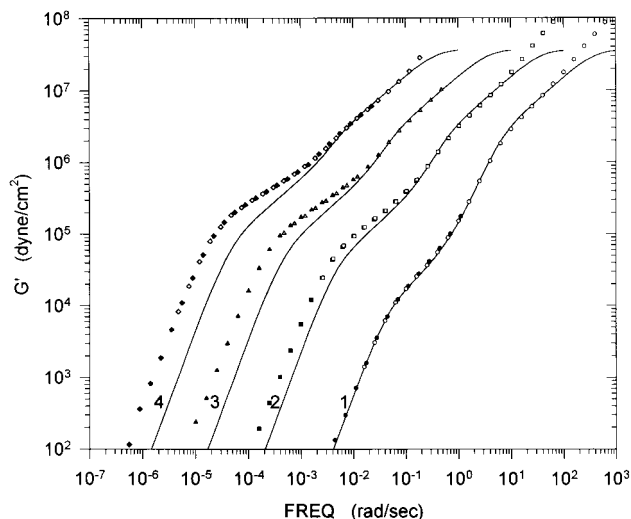


Figure 2. The comparison of the measured storage modulus spectra of samples A (○ and ●), B (□ and ■), C (△ and ▲), and D (◇ and ◆) with those calculated using the Rouse theory for both the F1 and F10 components. In calculating the spectra, the frictional factor K is set to be 10^{-8} for sample A (line 1); 10^{-9} for sample B (line 2); 10^{-10} for sample C (line 3); and 10^{-11} for sample D (line 4) to avoid overlapping of the lines and the data points. The comparison is made for each sample with the measured spectrum shifted along the frequency coordinate to match the calculation in the high-frequency region corresponding to the response of the F1 component.

molecular weight distribution is sufficiently narrow or Z is sufficiently large (≥ 50). Both the F1 and F10 polymer samples basically satisfy this condition; a small change of polydispersity has little effect on the spectrum line shape shown in Figure 1. The molecular weight for the Rouse segment m was shown to be approximately 850 for polystyrene by several studies of different methods.^{28–31} Thus, the number of Rouse beads N per chain in eq 6 is set to be the integer of $M/850$ in calculating the spectrum. Because M is a variable in the distributions $A_1(M)$ and $A_2(M)$, N changes accordingly. In fact, as long as N is sufficiently large or m is sufficiently small, the calculated spectrum shape in the frequency range of our interest is not affected by the precise value chosen for m . The spectrum also was calculated with the density value (1.007 g/cm^3) and temperature ($\sim 400 \text{ K}$) corresponding to the conditions of the measurement. The measured spectrum is shifted along the frequency coordinate to be superposed on the spectrum calculated with the frictional factor K set at 10^{-8} . No shift along the modulus coordinate is involved in obtaining the very good superposition of the measured and the calculated as shown in Figure 1. This indicates that the viscoelastic responses of both the F1 and F10 components in sample A are well described by the Rouse theory and that the force constant on the Rouse segment, which gives rise to the modulus, is of entropic origin as the Rouse segment is defined statistically.^{2,10} In Figure 1, the dashed line (calculated by setting $W_1 = 0$) indicates the separation of the contributions from the F1 and F10 components. It is clear that the two “bumps” on the storage modulus spectrum correspond to the viscoelastic responses of the two components in the blend solution: the high-frequency one for the F1 component and the low-frequency one for the F10 component. The good prediction by the theory of the relative position of the two bumps as well as their shapes as shown in Figure 1 clearly illustrates that the molecular weight dependence (i.e., $\tau_1 \propto M^2$) as

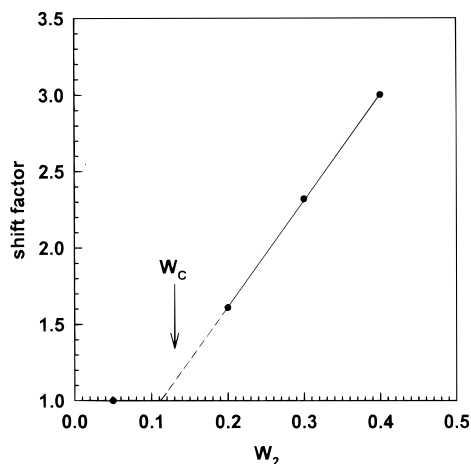


Figure 3. The shifting factors along the frequency coordinate obtained from superposing the measured on the calculated in the low-frequency region of the spectra shown in Figure 2. The arrow indicates W_c calculated from eq 4.

well as the p dependence (i.e., $\tau_p \propto 1/\sin^2(p\pi/2N)$) of the viscoelastic relaxation time are well described by the Rouse theory (eq 6). The locations of $1/\tau_1$ for both components are indicated by an arrow in Figure 1.

Entanglement among the polymer chains belonging to the F10 component can occur as W_2 increases above a certain point, which will render the spectrum in the low-frequency region corresponding to the viscoelastic response of the F10 component no longer described by the Rouse theory. For samples B, C, and D, we can assume that entanglement does not occur to the F10 component and use the Rouse theory to calculate the whole spectrum for both components. Because the F1 chains remain free of entanglement regardless of the weight fraction W_2 , the region around the high-frequency bump in the viscoelastic spectrum remains well described by the Rouse theory. Thus, we can use the Rouse viscoelastic response of the F1 component as the internal reference by matching the measured and calculated spectra in the high-frequency bump region. In doing the matching only a shift along the frequency coordinate is allowed as in the superposition of the measured and calculated spectra of sample A. Then with the internal reference done this way, the deviation of the measured spectra of samples B, C, and D from the calculated spectra in the low-frequency region will reflect the influence of entanglement on the viscoelastic behavior of the F10 component. As expected the deviation increases with increasing concentration W_2 . As shown in Figure 2, in the low-frequency region both the measured and calculated storage modulus spectra parallel each other [both lines of $\log(G')$ vs $\log(\omega)$ are straight and have the expected slope of 2] with the former more removed toward the lower frequency from the latter as W_2 increases. The shifting factor along the frequency coordinate obtained from superposing the two parallel lines can be used to characterize the degree of the deviation. Because of the use of the F1 polymer's viscoelastic response as the internal reference, the shifting factor determined this way is free of any change of the frictional factor caused by any outside influences, such as changes in concentration and temperature; in other words, it reflects entirely the change of the structural factor of the relaxation time of mainly the slowest mode of component two due to the occurrence of entanglement. In Figure 3, we show the shifting factors obtained for the samples studied as a function

of concentration W_2 . From extrapolating the shifting factors toward the smaller W_2 region, the point where the extrapolation line crosses the no-shift line can be determined. This point, denoted as W_c^0 , can be considered as the last point, at which no change in the structural factor caused by entanglement has yet occurred, or as the onset point of entanglement. W_c^0 occurred in the close neighborhood of W_c calculated according to eq 4. In other words, based on the present line-shape study, entanglement starts to occur at M_e' within experimental error for the blend solution, if M_{w2} is the variable rather than W_2 . The involved uncertainty that may arise from the spectrum analysis and the extrapolation procedure should be no more than 20%. The possible uncertainty is far less than the difference between M_e' and M_c' . In addition, the obtained W_c^0 value being on the lower side of W_c favors that the onset of entanglement should be closer to the entanglement molecular weight calculated from eq 1 than to the value calculated without the 4/5 factor in eq 1.

Discussion

In this study the use of the blend solution system and the Rouse viscoelastic response of the F1 component as the internal reference for the viscoelastic spectrum line-shape analysis has several advantages. First, the absence of the hydrodynamic interaction greatly simplifies the study of the viscoelastic spectrum line shape as a function of concentration. The hydrodynamic interaction, which occurs in a simple polymer solution, will be screened gradually as the polymer concentration increases.^{2,32,33} Both the hydrodynamic interaction screening and entanglement effects tend to widen the spectrum breadth. Thus, if the studied system involves the hydrodynamic interaction, one needs to separate the contributions to the spectrum broadening caused by the two different mechanisms. Second, in the blend solution system, both components share the same free volume distribution and have the same frictional constant for their Rouse segments.^{1,2,10} This eliminates any uncertainties that may arise from correcting for the molecular weight dependence of the friction constant if a one-component system is used for studying the molecular weight dependence of the relaxation times of the Rouse normal modes.¹ Because of the narrow molecular weight range, in which the Rouse theory can be expected to be applicable, the study of using one-component systems is particularly limited. Third, the viscoelastic spectrum of the blend solution covers a sufficiently wide frequency range, which allows the line-shape analysis to be a sensitive means for studying factors that affect the polymer viscoelastic behavior, such as entanglement in the present case.

The zero shear viscosity, which is equivalent to the integration of the whole stress relaxation curve over time, evens out a great deal of details in the viscoelastic spectrum. Thus, in general, the line-shape analysis of the viscoelastic spectrum reveals a great deal more than the single value of the zero shear viscosity. The line-shape analysis of the viscoelastic spectrum is particularly valuable, when a valid molecular theory is applicable. In this study, by comparing with the spectra calculated from the Rouse theory, the onset of entanglement can be clearly determined to occur at M_e' within experimental error. The traditional idea of regarding the Rouse theory as being applicable below M_c' or M_e is thus incorrect.

In this study the onset point of entanglement was obtained in a way that is fundamentally different from the way M_e or M_e' is determined. For differentiating them, we denote the presently determined onset point as M_e^0 . According to eq 1 or 3, the value of M_e or M_e' is obtained from the plateau modulus extracted from the viscoelastic spectrum in the molecular weight region well above the entanglement point ($M_w \gg M_e$ for monodisperse polymer melt; or $M_{w2} \gg M_e'$ for the polymer blend solution).^{3,4,12,13,17} According to studies of the viscoelastic spectra^{12,13,17} and comparisons of viscoelastic and diffusion data,¹⁴ the uses of M_e and M_e' as defined by eqs 1 and 2 lead to quantitative and consistent agreement between experiment and the extended reptation theory.¹⁵ On the other hand, the present determination of M_e^0 for the blend solution is independent of the slip-link idea in the Doi–Edwards theory and is approached from the low molecular weight side (i.e., from the entanglement-free region). It is based entirely on comparing the measured spectra with the Rouse theory as W_2 increases from below to above the entanglement point. The present approach of using the Rouse theory as a reference for detecting the onset of entanglement in the blend solution is equivalent to that taken in a previous study of analyzing the line shapes of the nearly monodisperse polystyrene melts of molecular weights at $0.76M_e$ and $1.24M_e$ in terms of the Rouse theory.¹³ In contrast to the monotonic spectra of the nearly monodisperse melts in the previous study, the blend solution systems used in the present study have two characteristic bumps in their storage modulus spectra, which allow for a far more illustrative comparison with the Rouse theory. Nevertheless, the results of the previous study clearly indicated that the onset point of entanglement M_e^0 occurs between $0.76M_e$ and $1.24M_e$ for the nearly monodisperse melt. Thus, based on the present and previous results, we can conclude that the onset point of entanglement M_e^0 is equivalent to the entanglement molecular weight M_e for the monodisperse system or M_e' for the blend solution system within a small range of uncertainty or experimental error. This conclusion is quite significant, particularly in understanding the physical nature of entanglement.

Conclusion

The absence of hydrodynamic interaction in the blend solution system allows us to describe the viscoelastic spectrum in terms of the Rouse theory, when the system is free of entanglement. By making use of this unique property of the blend solution, a scheme of study has been conceived for determining the onset of entanglement M_e^0 . The result of the study is consistent with the onset of entanglement in the monodisperse melt, which had been determined previously. The close agreement of M_e^0 with M_e or M_e' is significant, when we recognize that the determination of M_e or M_e' is ultimately based on the slip-link idea in the Doi–Edwards theory, whereas the determination of M_e^0 is totally independent

of the Doi–Edwards theory. The onset point M_e^0 is well below the critical molecular weight M_c' or M_c of the zero shear viscosity. The result directly supports the conclusion that entanglement already exists between M_e and M_c , which was pointed out earlier in the study of analyzing the viscoelastic spectra of a series of nearly monodisperse polystyrene melts and in the demonstration of the quantitative agreement between the viscoelastic data and diffusion data in terms of the extended reptation theory.

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References and Notes

- (1) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
- (2) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: New York, 1986.
- (3) Lin, Y.-H. *Macromolecules* **1987**, *20*, 3080.
- (4) Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. *Macromolecules* **1994**, *27*, 4639.
- (5) Berry, G. C.; Fox, T. G. *Adv. Polym. Sci.* **1968**, *5*, 261.
- (6) Fox, T. G.; Loshaek, S. *J. Polym. Sci.* **1955**, *15*, 371.
- (7) Fox, T. G.; Flory, P. J. *J. Polym. Sci.* **1954**, *14*, 315.
- (8) Lin, Y.-H. *Macromolecules* **1990**, *23*, 5292.
- (9) Rouse, P. E. Jr. *J. Chem. Phys.* **1953**, *21*, 1271.
- (10) Bird, R. B.; Curtiss, C. F.; Armstrong, R. C.; Hassager, O. *Dynamics of Polymeric Liquids*, 2nd ed.; Wiley: New York, 1987; Vol. 2.
- (11) Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 27.
- (12) Lin, Y.-H. *Macromolecules* **1986**, *19*, 159.
- (13) Lin, Y.-H. *Macromolecules* **1986**, *19*, 168.
- (14) Lin, Y.-H. *Macromolecules* **1991**, *24*, 5346.
- (15) Lin, Y.-H. *Macromolecules* **1984**, *17*, 2846.
- (16) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789; **1978**, *74*, 1802.
- (17) Lin, Y.-H. *Macromolecules* **1987**, *20*, 885.
- (18) Watanabe, H.; Sakamoto, T.; Kotaka, T. *Macromolecules* **1985**, *18*, 1436.
- (19) De Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
- (20) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 1.
- (21) Isono, Y.; Fujimoto, T.; Takeno, N.; Kajiura, H.; Nagasawa, M. *Macromolecules* **1978**, *11*, 888.
- (22) Schulz, G. V. *Z. Phys. Chem. Abt. B.* **1939**, *43*, 25.
- (23) Tung, L. H. In *Polymer Fractionation*; Cantow, M., Ed.; Academic Press: New York, 1967.
- (24) Synthesized and characterized by Tosoh Corporation, Tokyo, Japan.
- (25) King, T. A.; Knox, A.; Lee, W. I.; McAdam, J. D. G. *Polymer* **1973**, *14*, 151.
- (26) Han, C. C.; McCrackin, F. L. *Polymer* **1979**, *20*, 427.
- (27) Huber, K.; Bantle, S.; Lutz, P.; Burchard, W. *Macromolecules* **1985**, *18*, 1461.
- (28) Norisuye, T.; Fujita, H. *Polym. J.* **1982**, *14*, 143.
- (29) Benoit, H.; Doty, P. *J. Phys. Chem.* **1953**, *57*, 958.
- (30) Inoue, T.; Okamoto, H.; Osaki, K. *Macromolecules* **1991**, *24*, 5670.
- (31) Lin, Y.-H.; Lai, C. S. *Macromolecules* **1996**, *29*, 5200.
- (32) Muthukumar, M.; Freed, K. F. *Macromolecules* **1977**, *10*, 899; **1978**, *11*, 843.
- (33) Martel, C. J. T.; Lodge, T. P.; Dibbs, M. G.; Stokich, T. M.; Sammler, R. L.; Carriere, C. J.; Schrag, J. L. *Faraday Symp. Chem. Soc.* **1983**, *18*, 173.

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