The measured Huggins coefficients show minima due to coil compression by intermolecular interactions that correlate with the excluded volume parameter z. Unexpectedly high values of the Huggins coefficient near the θ-state of K-PSS are attributed to short-range attractive forces that affect both inter- and intramolecular behavior. Even larger values of the Huggins coefficient at low ionic strengths arise from intermolecular interactions as for charged polymer latices. Existing theory, however, fails to predict the magnitudes accurately.

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On the Universality of Viscoelastic Properties of Entangled Polymeric Systems

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ABSTRACT: Viscoelastic properties were examined for solutions with various molecular weights, M, and concentrations, c, of poly(α-methylstyrene) and polystyrene in chlorinated biphenyl. The number of entanglements per molecule, N, was evaluated from the plateau modulus, G_N. The longest relaxation time, τ_1, was evaluated from the relaxation modulus, $G(t)$; the relaxation time of an entanglement strand, τ_s, was evaluated from the complex modulus in the glass-to-rubber transition region; and another time constant, τ_k, was defined as the time at which the quantity $G(t,\gamma)/G(t)$ levels off, where $G(t,\gamma)$ is the relaxation modulus at a finite magnitude of shear, γ. Reduced storage and loss moduli, $G'(\omega)/G_N$ and $G''(\omega)/G_N$, regarded as functions of reduced angular frequency, $\omega\tau_s$, were determined if the number N was given, irrespective of the combinations of M and c or of the polymer species. The same held true for a nonlinear function, $G(t,\gamma)/G(t)$, regarded as a function of γ and reduced time, t/τ_s. The ratios τ_1/τ_s and τ_k/τ_s were unique functions of N for all the solutions studied and were proportional to $N^{3.5}$ and $N^{2.0}$, respectively. The magnitudes of these ratios were in accord with the interpretation that τ_1 corresponds to the reptation time and τ_k to the time for complete equilibration of the fluctuation of chain contour length in the tube model theory.

Introduction

According to the current concept of polymer entanglement,[1,2] two polymeric systems having an identical number of entanglements per molecule, N, should exhibit a common viscoelastic behavior in the sense that the shape of the curve corresponding to log (viscoelastic function) plotted against log t or log ω is the same. Here t is the time and ω is the angular frequency. The quantity N is written as

$$N = M/M_e \tag{1}$$

where M is the molecular weight and M_e is the entanglement molecular weight. The latter is determined from the rubbery plateau modulus, G_N, through

$$G_N = cRT/M_e \tag{2}$$

where c is the mass concentration, R is the gas constant, and T is the absolute temperature. Thus for a system with a given M and c, the shape of a viscoelastic function in

appropriate scales will be determined by a scale unit, G_N, for the viscoelastic modulus functions such as the relaxation modulus and the complex modulus. Two systems with different combinations of M and c will show the same viscoelastic behavior in appropriately reduced scales provided that the value of N evaluated from M and G_N is the same. This statement was revealed to be true for the linear as well as nonlinear viscoelasticity of a series of polystyrene (PS) solutions. The purpose of the present study is to examine if it is also true over different polymer species.

The observations for PS solutions[3-5] may be summarized as follows. In the glass-to-rubber transition region, the storage modulus, $G'(\omega)$, and the loss modulus, $G''(\omega)$, for samples with various M and c could be described with universal functions, g_A' and g_A'', and two parameters, G_N and τ_s, as

$$G'(\omega) = G_N g_A'(\omega\tau_s) \tag{3a}$$

$$G''(\omega) = G_N g_A''(\omega\tau_s) \tag{3b}$$

The quantity τ_s was a function of T and c. At relatively long times, ranging from the terminal flow region to the long-time end of the rubbery plateau region, the complex modulus could be described with universal functions, g_C' and g_C'', and two parameters, G_N and τ_1, as

$$G'(\omega) = G_N g_C'(\omega\tau_1) \qquad (4a)$$

$$G''(\omega) = G_N g_C''(\omega\tau_1) \qquad (4b)$$

where τ_1 is the longest relaxation time.[6] This was evaluated by fitting an approximation formula

$$G(t) = G_1 \exp(-t/\tau_1) \qquad (5)$$

to the data at very long times. It may be noted that the same factor G_N can be used in eq 3 and 4. The ratio τ_1/τ_s was determined solely by N and

$$\tau_1/\tau_s \propto N^{3.5} \qquad (6)$$

For studying the nonlinear viscoelasticity, we defined a function

$$h(t,\gamma) = G(t,\gamma)/G(t) \qquad (7)$$

from the relaxation modulus, $G(t,\gamma)$, obtained for a finite value of magnitude of shear, γ. The function $h(t,\gamma)$ for various PS solutions could be described by a universal function, f, and a parameter, τ_k, as

$$h(t,\gamma) = f(t/\tau_k,\gamma) \qquad (8)$$

where τ_k was defined as the time where $h(t,\gamma)$ levels off. We observed that

$$\tau_1/\tau_k \propto N^{1.5} \qquad (9)$$

Combined with eq 6, this implies

$$\tau_k/\tau_s \propto N^2 \qquad (10)$$

It has been conjectured[3-5,7-9] that τ_1 corresponds to the reptation time and τ_k to the equilibration time of the fluctuation of chain contour length in the tube model theory.[2,10,11]

In the present study, we measure the viscoelastic quantities $G'(\omega)$, $G''(\omega)$, $G(t)$, and $G(t,\gamma)$ for solutions of poly(α-methylstyrene) (PMS) with sharp molecular weight distributions. We examine if the above-mentioned properties for PS solutions are also observed for PMS solutions; if the "universal" functions of eq 3, 4, and 8 are common to the PS and PMS solutions; and if the proportionality coefficients of relations 6, 9, and 10 are independent of polymer species.

Materials and Method

Materials. Two poly(α-methylstyrene) samples, BB15 and BB13, with molecular weights 6.85×10^6 and 2.71×10^6, respectively, were used.[12] These samples had very sharp molecular weight distributions; the ratio of weight-average molecular weight, M_w, to number-average molecular weight, M_n, was less than 1.01. The details of the synthesis, column fractionation, and characterization were published elsewhere.[12]

Polystyrene samples F288 and F850 were supplied by Toyo Soda Manufacturing Co. According to the supplier's data, M_w = 2.89×10^6 and 8.42×10^6, respectively, and M_w/M_n = 1.09 and 1.17, respectively.

The solvent, Aroclor 1248, supplied by Monsanto Chemical Co, is a mixture of chlorinated biphenyl of various degrees of chlorination. The viscosity and density of the solvent and the procedure of solution preparation were described elsewhere.[5] The concentrations studied are shown in Table III.

Measurements. The strain-dependent relaxation modulus $G(t,\gamma)$ was measured with a cone-and-plate type rheometer[13] over the ranges of magnitude of shear, γ, from 0.3 to 7 and of time, t, from 1 to 10^4 s. The relaxation modulus was independent of γ when γ was less than 0.7. The value of $G(t,\gamma)$ in this range was
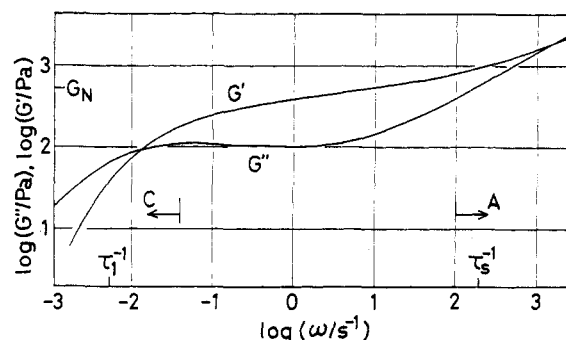

Figure 1. Storage modulus, G', and loss modulus, G'', for a PMS solution; $M = 6.85 \times 10^6$ and $c = 0.071$ g cm^{-3}. Arrows A and C represent the frequency ranges where eq 3 and 4, respectively, are applicable for the series of solutions studied.
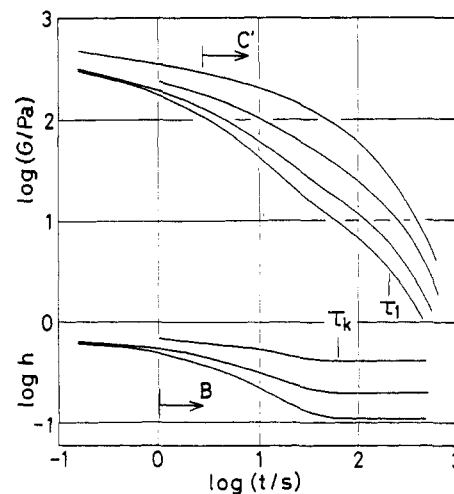

Figure 2. Relaxation modulus, $G(t,\gamma)$, and nonlinear function, $h(t,\gamma)$, for a PMS solution; $M = 6.85 \times 10^6$ and $c = 0.071$ g cm^{-3}. Magnitudes of shear, γ, are 0, 3, 5, and 7 for $G(t,\gamma)$ (upper four curves) and 3, 5, and 7 for $h(t,\gamma)$ (lower three curves). Arrow B indicates the range of time where eq 8 is valid and arrow C' represents the range where $G(t)/G_N$ is a universal function of t/τ_1 for all the solutions studied.

regarded as the linear relaxation modulus, $G(t)$. Measurements were usually performed at 30 °C. In some cases, measurements at other temperatures in the range from 5 to 50 °C were also performed and the data were reduced to the reference temperature 30 °C with the method of reduced variables.[14]

The storage modulus, $G'(\omega)$, and the loss modulus, $G''(\omega)$, were measured with a Rheopexy Analyzer (Iwamoto Seisakusho Co., Ltd., Kyoto). This was used in the cone-and-plate mode. The range of angular frequency, ω, was from 0.0628 to 6.28 s^{-1}. Measurements were carried out at several temperatures ranging from 3 to 65 °C. All the data were reduced to the reference temperature, 30 °C, with the method of reduced variables.

In order to check the consistency of data obtained with two apparatuses, the linear relaxation modulus, $G(t)$, was estimated from complex modulus data with an approximation formula.[15] The estimated values agreed with the directly measured values to within ±5%.

Results and Discussion

Viscoelastic Functions. As an example, the set of results for viscoelastic functions is shown in Figures 1 and 2 for the 0.071 g cm^{-3} solution of PMS BB15 with $M = 6.85 \times 10^6$. The storage modulus, $G'(\omega)$, and the loss modulus, $G''(\omega)$, are shown in Figure 1; the strain-dependent relaxation modulus, $G(t,\gamma)$, and the function $h(t,\gamma)$ are shown in Figure 2. Evidently, the dynamic data of Figure 1 cover part of the terminal flow region, the rubbery plateau region, and part of the glass-to-rubber transition region. The data for the terminal flow region are supplemented by the

Table I
Complex Modulus for a PMS Solution in Aroclor at 30 °C ($M = 6.85 \times 10^6$ and $c = 0.071$ g cm^{-3})

log (ω/s^{-1})	log (G'/Pa)	log (G''/Pa)	log (ω/s^{-1})	log (G'/Pa)	log (G''/Pa)
-2.8	0.68	1.45	0.4	2.64	2.02
-2.6	1.13	1.61	0.6	2.69	2.05
-2.4	1.44	1.76	0.8	2.70	2.13
-2.2	1.77	1.86	1.0	2.73	2.17
-2.0	1.86	1.93	1.2	2.76	2.23
-1.8	2.03	1.98	1.4	2.80	2.32
-1.6	2.13	2.01	1.6	2.83	2.41
-1.4	2.23	2.04	1.8	2.86	2.50
-1.2	2.33	2.05	2.0	2.90	2.61
-1.0	2.38	2.04	2.2	2.96	2.73
-0.8	2.44	2.03	2.4	3.02	2.85
-0.6	2.48	2.02	2.6	3.07	2.96
-0.4	2.53	2.01	2.8	3.14	3.07
-0.2	2.57	2.01	3.0	3.22	3.18
0	2.59	2.00	3.2	3.28	3.30
0.2	2.62	2.01	3.4	3.38	3.41

Table II
Linear Relaxation Modulus, $G(t)$, and Nonlinear Function, $h(t,\gamma)$, for a PMS Solution in Aroclor at 30 °C ($M = 6.85 \times 10^6$ and $c = 0.071$ g cm^{-3})

log (t/s)	log (G/Pa)	$h(t,3)$	$h(t,5)$	$h(t,7)$
-0.8	2.67		0.64	0.62
-0.6	2.64		0.62	0.60
-0.4	2.62		0.59	0.58
-0.2	2.58		0.57	0.54
0	2.54	0.70	0.54	0.50
0.2	2.50	0.66	0.51	0.44
0.4	2.45	0.62	0.46	0.38
0.6	2.41	0.59	0.40	0.32
0.8	2.35	0.53	0.36	0.27
1.0	2.30	0.49	0.31	0.22
1.2	2.23	0.45	0.27	0.17
1.4	2.14	0.42	0.23	0.135
1.6	2.07	0.41	0.22	0.118
1.8	1.92	0.41	0.20	0.110
2.0	1.78	0.41	0.20	0.110
2.2	1.60	0.41	0.20	0.110
2.4	1.37	0.41	0.20	0.110
2.6	0.99			
2.8	0.51			

Figure 3. Storage modulus, G', and loss modulus, G'', for a PS solution (solid lines); $M = 2.89 \times 10^6$ and $c = 0.076$ g cm^{-3}. Dashed lines were derived from Figure 1 as described in text.

Figure 4. Nonlinear function $h(t,\gamma)$ for a PS solution (circles); $M = 2.89 \times 10^6$ and $c = 0.076$ g cm^{-3}; $\gamma = 3$, 5, and 7 from top to bottom. Solid lines were derived from Figure 2 as described in the text.

linear relaxation modulus data represented by the uppermost curve of Figure 2.

The quantity $h(t,\gamma)$ is a decreasing function of t and γ. It levels off at a time, denoted τ_k, for any value of γ. The limiting values of $h(t,\gamma)$ at long times are in excellent agreement with the prediction of the tube model theory.[11]

Comparison of the results for various combinations of M and c and for PS and PMS solutions is described below. In order to facilitate comparison with the data from other laboratories, the numerical data for Figures 1 and 2 are given in Tables I and II, respectively.

Evaluation of Parameters The complex modulus for a PS solution, $M = 2.89 \times 10^6$ and $c = 0.076$ g cm^{-3}, is represented by continuous lines in Figure 3. We note that the shape of the curves is very similar to that of Figure 1 except that the width of the plateau region is about one decade smaller than in Figure 1. The dashed lines are reproduced from Figure 1: $0.83G'$ and $0.83G''$ are plotted against appropriately reduced frequencies so that the curves overlap those for the PS solutions at low frequencies (region C) and high frequencies (region A). The superposition of data for two samples is excellent in either of the regions A and C. Similar comparison with the data of Figure 1 can be done for other solutions. The separation between regions A and C varies from sample to sample. The linear relaxation moduli for various samples can also be compared with each other in an obvious manner. For example, the shape of the curve of the relaxation modulus
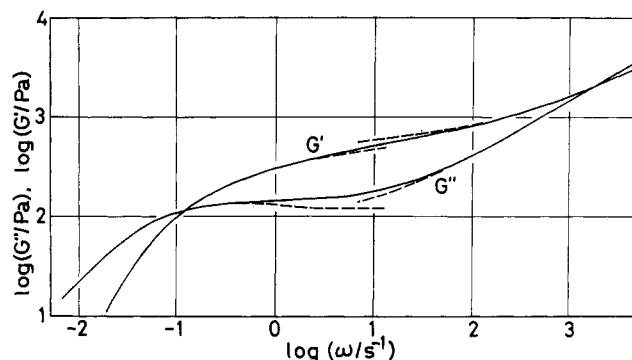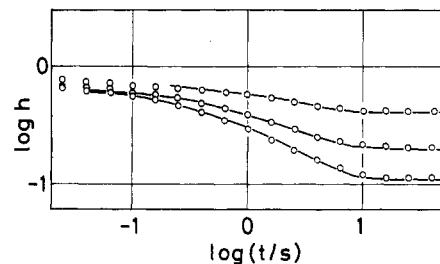
for the sample of Figure 3 agrees with that of Figure 2 at $t > 0.8$ s. Thus the range of t where the relaxation modulus has a common shape is wider than the range of ω^{-1} where the complex modulus has the same shape at low frequencies.

On the basis of these observations, it would be reasonable to conclude that eq 3 and 4 can be applied to the PS and PMS solutions. If we take one system as the reference sample, we can easily determine the relative values of G_N, τ_1, and τ_s for any other system. The relative values will be sufficient for the discussions in the following section. However, we determine definite values to maintain consistency with previous studies.[3-5,7-9] The longest relaxation time was determined by fitting eq 5 to the relaxation modulus at long times. The procedure of determining G_N and τ_s was given previously.[5] The results are listed in Table III.

The function $h(t,\gamma)$ for the same sample as of Figure 3 is represented by circles in Figure 4. The solid lines are obtained by shifting the $h(t,\gamma)$ curves of Figure 2 along the

<div align="center">

Table III
Viscoelastic Parameters

</div>

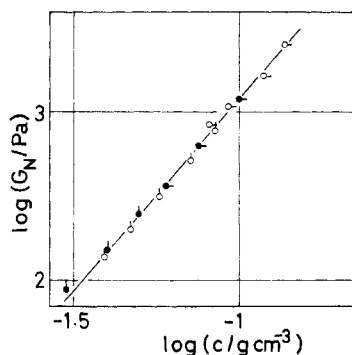| $M/10^6$	$c/(10^{-2}$ g cm$^{-3})$	$G_N/(10^2$ Pa$)$	N	$\tau_s/(10^{-3}$ s$)$	$\tau_k/$s	$\tau_1/$s
		Poly(α-methylstyrene)				
6.85	8.5	7.7	24.6	5.6	74	423
	7.1	5.2	19.9	5.4	61	205
	5.7	3.2	15.2	6.6	39	95
	4.7	2.02	11.7	7.8	32	41
	3.9	1.38	9.6	8.4	21.3	24.7
2.71	13.9	25.4	19.8	6.0	58	262
	11.9	16.6	15.0	5.5	43	124
	9.4	10.9	12.5	5.6	23.8	43
	8.2	8.4	11.1	4.9	15.1	19.3
		Polystyrene				
8.42	5.0	2.50	16.7	8.0	65	212
	3.8	1.50	12.5	7.9	31	85
	3.0	0.88	9.8	9.0	27.3	39
2.89	10.0	11.9	13.7	3.1	15.6	45
	7.6	6.3	9.4	4.4	13.0	19.3
	6.0	3.7	7.1	5.1	8.9	9.1

Figure 5. Plateau modulus, G_N, for solutions of PS (filled circles; pip up, $M = 8.42 \times 10^6$, and pip right, $M = 2.89 \times 10^6$) and PMS (unfilled circles; pip up, $M = 6.85 \times 10^6$, and pip right, $M = 2.71 \times 10^6$).

abscissa. It may be obvious that the universal relation, eq 8, can be applied to the two samples. We define the parameter τ_k as the time at which the function $h(t,\gamma)$ levels off. This statement may be a little ambiguous as a definition. However, the relative values can be well determined if we compare $h(t,\gamma)$ functions of various systems. The results for τ_k are included in Table III.

Due to the somewhat arbitrary nature of the definitions, the values of the parameters given in Table III may not be directly compared with the parameters included in molecular theories. When parameters are needed for subtle problems, one is asked to use the data of Table I to extract his own parameters.

Plateau Modulus. The plateau moduli, G_N, for PS (filled circles) and PMS (unfilled circles) are shown in Figure 5 as a function of concentration, c. Evidently, the data for PS and PMS can be approximated by a line corresponding to

$$G_N = 2.4 \times 10^5 c^{2.3} \text{ Pa} \qquad (11)$$

Incidentally, the plateau modulus of undiluted PMS samples with sufficiently high molecular weights is reported to be approximately equal to that of PS.[16]

Ratios of Characteristic Times. The ratio τ_1/τ_s is plotted against N in Figure 6 for PS (filled circles) and PMS (unfilled circles) solutions. The number of entanglements per molecule, N, was evaluated from the molecular weight and the plateau modulus. The line is drawn with a slope 3.5. One may say that the ratio τ_1/τ_s is uniquely determined by N and is approximately proportional to $N^{3.5}$. Compared at the same value of N, the ratio τ_1/τ_s for PMS solutions is always slightly smaller than that
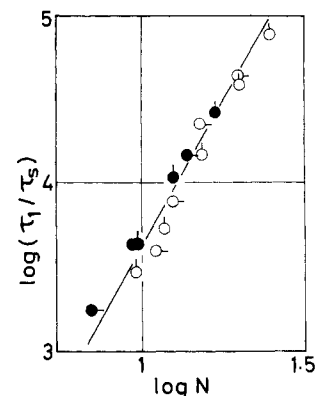

Figure 6. Ratio τ_1/τ_s for solutions of PS (filled circles) and PMS (unfilled circles). For pips, see caption of Figure 5. The line is drawn with a slope 3.5.
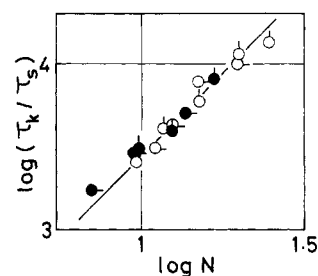

Figure 7. Ratio τ_k/τ_s for solutions of PS (filled circles) and PMS (unfilled circles). For pips, see caption of Figure 5. The line is drawn with a slope 2.

for PS solutions. Still the difference, corresponding to about 5% difference in the N values, may be regarded to be in the error range.

The ratio τ_k/τ_s is plotted against N in Figure 7. The line is drawn with a slope 2. One may say that the ratio τ_k/τ_s for PMS and PS solutions is determined by N and is approximately proportional to N^2.

From the results presented in Figures 3, 4, 6, and 7, we may conclude that the universality of the viscoelastic properties as described in the Introduction holds good over two polymer species, PM and PMS.

Other Polymers. The test of universality is rather difficult for the following reasons: The polymer must have a very sharp molecular weight distribution; the measurement must cover the time (frequency) range corresponding to the flow region and the glass-to-rubber transition region; and the large stepwise shear deformation for measurement of the strain-dependent relaxation modulus is often dif-

ficult to achieve with ordinary rheometers.

A few published results for linear viscoelasticity could be compared with the present results. For poly(methyl methacrylate) and its solutions, Masuda et al. carried out an exhaustive study.[17-19] Their results may be summarized, in the present terminology, as

$$\tau_1/\tau_s \propto N^a \tag{12}$$

where a is about 4 and varies for polymers of different methods of synthesis. Thus, it is unlikely that the common relation applicable to PS and PMS solutions is applicable to PMMA.

Graessley et al. reported linear viscoelasticity data for polybutadiene (PB) and hydrogenated PB (HPB).[20,21] They observed that at fixed concentration, the longest relaxation time is proportional to $M^{3.5}$. Moreover, the reduced quantities $G'(\omega)/G_N$ and $G''(\omega)/G_N$ regarded as functions of $\omega\tau_1$ were universal functions for PS, PB, HPB, and their solutions. However, their "universal" functions do not agree with the present ones represented by Figure 1. The maximum and the minimum of the G'' curve are more marked than in Figure 1. Evidently, detailed comparison of data from various laboratories would be necessary. The universality of the proportionality coefficient of eq 6 cannot be examined with their data due to the lack of high-frequency data.

Comparison with Tube Model Theory. The quantities τ_s, τ_k, and τ_1 may be compared with the characteristic times τ_A, τ_B, and τ_C,[6] which appear in the tube model theory.[2,10,11] Here τ_A is the relaxation time of an entanglement strand, τ_B is the equilibration time of the fluctuation of the chain contour length, and τ_C is the reptation time.

The line in Figure 6 can be written as

$$\tau_1/\tau_s = 1.3N^{3.5} \tag{13}$$

Let us assume that $\tau_1 = \tau_C$ and $\tau_s = \tau_A$ and rewrite the right-hand side in a form comparable with the modified tube model theory which takes account of the contour length fluctuation.[22] Then we obtain

$$\tau_C/\tau_A \simeq 14N^3(1 - 1.47N^{-1/2})^2 \tag{14}$$

The numerical factor, 1.47, in the parentheses was given by Doi with a variational calculation. The numerical coefficient 14 is to be compared with the theoretical value, 6.

The line in Figure 7 can be written as

$$\tau_k/\tau_s = 28N^2 \tag{15}$$

In an earlier study, the quantity τ_k was estimated to be 4.5 times as large as τ_B.[4] It was assumed there that τ_B would be equal to $2\tau_C$ for $N = 2$. If we apply the same reasoning to the present data, we obtain

$$\tau_k/\tau_B = 3.8 \tag{16}$$

in good agreement with the earlier estimate, 4.5.

On the other hand, if we assume $\tau_B = 2\tau_A$ when $N = 1$,[2] and $\tau_A = \tau_s$, then we obtain

$$\tau_k/\tau_B = 14 \tag{17}$$

The discrepancy between eq 16 and 17 is due to the difference between the τ_B values estimated from τ_1 and τ_s, respectively, and therefore is related to the fact that the coefficient of eq 14 is a little larger than the theoretical value. The too large coefficient may possibly imply that the segmental friction coefficient associated with the chain motion along the tube is larger than that for the short-range motion. Lin has recently proposed a similar idea but to the opposite direction.[23] If one evaluates M_e from the equation $G_N = (4/5)(cRT/M_e)$ instead of eq 2, one obtains different values for the numerical coefficients. However, it may not be worth discussing the coefficients further here. The prefactor in the expression for G_N depends on the type of approximation.[2,11,24] Also, the definition of the present quantities may not be so definite to allow further discussion. Studies of the numerical coefficients of eq 13 and 15 for other polymer species may lead to a better understanding of the molecular motion in entangled systems.

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