The Viscoelastic Properties of Undiluted Linear Polymers of Narrow Molecular Weight Distribution in the Terminal Zone[*]

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The viscoelastic properties of undiluted narrow molecular weight distribution (MWD) samples of linear poly(α-methylstyrene) (P-α-MS), polystyrene (PS), and poly(*cis*-isoprene) (PI) have been studied and values of the viscosity η, the steady-state compliance J_e, and the maximum relaxation time τ_m have evaluated from the creep curves. The relationship between these viscoelastic parameters and the molecular weight M for the three systems are presented together with that for other polymers of narrow MWD, and are compared with predictions of various theories.

The η-M relationship for narrow MWD polymers at higher molecular weights does not differ from that for linear polymers of broad MWD, and is approximated by the well-known 3.4 power law. For PI and PS rather rapid change in the molecular weight dependence of J_e has been exhibited at the critical molecular weight M_b. In the region $M < M_b$, J_e has varied approximately as the first power of M in agreement with the Rouse prediction. On the other hand at higher molecular weights, $M > M_b$, J_e is nearly independent of M. The latter relationship is consistent with that predicted by the theories of Hayashi and Graessley. The values of M_b are 50,000 and 100,000 for PI and PS, respectively. These values are considerably higher than those of M_c defined as the intercept of the extrapolated first and 3.7th power regions in the log η versus log M plot, 10,000 and about 35,000 for the respective systems. The τ_m—M relationship of PS for $M > \sim 80,000$ is well represented by the 3.3 power dependence on M. For PI τ_m varies as the 3.7 power of M in the region $6,000 < M < 1,120,000$. The τ_m—M relation is described again by the theories of Hayashi and Graessley. The relationship among the entanglement spacing M_e, M_c and M_b has been also discussed.

INTRODUCTION

The relation between the viscoelastic properties of polymers and the molecular weight has been under intensive investigation, both theoretically and experimentally, for a number of years. Various theories describing viscoelastic behavior of polymer on molecular concepts have been developed, and among these the Rouse-Bueche theory[1,2] and its modification by Ferry, Landel, and Williams[3] have much advanced our understanding in the field. The general validity of these theories can be examined by a comparison of the results obtained for a number of polymers of very narrow molecular weight distribution (MWD) with the theoretical predictions, since the original form of these predictions are applicable only to a polymer where all molecules are of the same length, *i.e.* to a *monodisperse* polymer. Until the late in 1950's, however, experimental studies, intending to make severe test of the theoretical predictions for the undiluted linear polymer systems, have been hampered by the limited quantity of well characterized narrow MWD

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polymer available, because the careful fractionation required to obtain sufficient amount of narrow MWD polymer was quite tremendous.

The advent of the "living polymer" technique by Szwarc *et al.*,[4] being followed by recent advances in anionic polymerization techniques after 1955, has overcome the objectional feature of the experimental study by making it possible to produce reasonably large quantities of a linear polymer of narrow MWD and desired molecular weight.   Furthermore, the fractionation method by using a large scale elution column, together with the existence of a rapid and at the same time accurate method of measuring MWD using the ultracentrifuge, has provided the stimulus for the experimental study to investigate the viscoelastic response of undiluted polymers of various types by creep or stress relaxation measurements.

The experimental study of viscoelastic properties of undiluted linear polymers of differing molecular weight and of narrow MWD started in 1965 in our laboratory, and very narrow MWD samples of poly(α-methylstyrene) and poly(*cis*-isoprene) over a wide range of molecular weight were prepared by the anionic polymerization followed by the elution column fractionation procedure.   Anionically polymerized polystyrenes of differing molecular weight were generously provided by Professor S. Onogi and Dr. T. Masuda of this University, and a fractionation using a large scale Desreux column was again employed to prepare samples of very narrow MWD.   Tensile and shear creep studies were made on samples of poly(α-methylstyrene) and polystyrene, and those of poly(*cis*-isoprene), respectively.

To the knowledge of the present authors, Tobolsky, Aklonis, and Akovali[5] have first demonstrated very different dependence on molecular weight of quantities, which characterize the viscoelastic response of undiluted linear polymers in the terminal zone, from that predicted by the various theories.   They have critically examined by stress relaxation measurements the predictions of the Rouse-Bueche theory and of the Ferry–Landel-Williams modification using five samples of narrow MWD polystyrene ranging in molecular weight between 80,000 and 270,000.   Such an experimental study is also of considerable significance in gaining insight into the nature of the entanglement couplings between molecular chains which determine the viscoelastic behavior of the undiluted and the concentrated polymer systems.   In recent years many experimental investigations of viscoelastic properites of undiluted polymer systems have been made by several groups of researchers, including our research group, with various types of linear polymer of narrow MWD.[6~23]

In the present paper the observed dependence on molecular weight of the characteristic parameters in the terminal zone— the viscosity, the steady-state compliance, and the maximum relaxation time—for our very narrow MWD samples of poly(α–methylstyrene), polystyrene, and poly(*cis*-isoprene) is reported together with that obtained by other research groups.   These observations will be compared with the predictions of various theories and discussed in relation to the entanglement problem in the undiluted polymer systems.

THEORETICAL PREDICTIONS

The theory of Rouse[1] and Bueche[2] has been proposed to describe the viscoelastic properties of dilute polymer solutions.   The polymer molecule is assumed to consist of

sub-molecules each behaving like a mass attached to a spring, the whole being treated as if suspended in a Newtonian liquid. The segmental friction factor ζ_0 is considered independent of molecular weight.

The Ferry-Landel-Williams modification[3] of the Rouse-Bueche theory for undiluted polymers of sufficiently high molecular weight has been made by assuming that ζ_0 is replaced by a new friction factor ζ for all relaxation times larger than some critical value, *i.e.*

$$\zeta/\zeta_0=(M/2M_e)^{2.4} \tag{1}$$

where M is the molecular weight of a monodisperse polymer and M_e the average molecular weight between entanglement points. The new friction factor ζ, unlike ζ_0, is not molecular weight independent, but varies as the 2.4 power of M.

The theory of Chompff and Duiser[24] is also based on the model of Rouse for a single molecule, and a modification has been made by the same idea as that of Ferry, Landel, and Williams,[3] *i.e.*, by assuming that entanglements affect only the friction properties of polymer chains. The Chompff-Duiser theory yields the results similar to the Ferry-Landel-Williams modification. Thus the theory may be regarded as the rigorous verification of the Ferry-Landel-Williams modification derived in rather intuitive manner.

In the Hayashi theory[25] the Rouse model is again used, but in contrast with the theories mentioned above the intermolecular interaction between a given molecule and medium is assumed to contain both the viscous and the elastic effects. The idea has been formulated by putting that

$$\begin{aligned} \zeta_p&=\zeta_0, & k_p&=k & &\text{for } p>M/M_e \\ \zeta_p&=\zeta_0(M/pM_e)^{2.5}, & k_p&=k(M/pM_e) & &\text{for } p<M/M_e \end{aligned} \tag{2}$$

where ζ_p and k_p are respectively the effective friction and the effective force constants for the p-th mode, and k is the force constant in the Rouse-Bueche theory.[1,2]

Very recently a new theory has been proposed by Graessley to describe the viscoelastic properties of the entangled polymer system.[26] The highly uncorrelated nature of entanglement drag interactions has been pointed out, and the basic Rouse model has been changed to a new one so that uncorrelated interactions can be imposed. In the treatment entanglement coupling points are assumed to be spaced at equal intervals along the polymer chain, and a polymer molecule is represented by a set of spring-bead elements, each fixed at one end to the center of gravity of the chain. When the chain is in unperturbed state beads are distributed about the center of gravity of the chain in the same way as the segment density distribution. To any mechanical excitation each bead is supposed to respond as if they are connected to the center of gravity of the chain by a linear spring with force constant chosen to produce the correct segment density distribution in the undisturbed system. In the highly entangled state of monodisperse polymer systems the Graessley theory yields the same dependence on molecular weight of viscoelastic parameters as that predicted by the Hayashi theory.[25] Also, the predicted molecular weight dependence of viscosity for the large entanglement density is in agreement with that predicted by another theory which has been developed formerly by Graessley.[27] The former theory predicts that the viscosity varies as the first power of molecular weight at the limit of low entanglement density.

In Table 1 are shown the predictions of various theories described briefly in the forego-

Table 1. Theoretical Predictions of Power Dependence on Molecular Weight of Viscoelastic Parameters

Theory	η	J_e	τ_m	Reference
Rouse-Bueche	1	1	2	1, 2
Ferry-Landel-Williams	3.4	1	4.4	3
Chompff-Duiser	3.4	1	4.4	24
Hayashi [a]	3.5	0	3.5	25
Graessley [b]	3.5	0	3.5	26, 27

a. For $M > M_e$.
b. At high entanglement densities.[27] For $M < M_e$, η varies as the first power of M.[26]

ing lines, insofar as the dependence on molecular weight of the viscosity η, the steady-state compliance J_e, and the maximum relaxation time τ_m are concerned. As will be shown later, the prediction by the Rouse-Bueche theory is quantitatively incorrect in many respects. The basic Rouse model has nevertheless served as a starting point for the discussion of the viscoelastic properties of undiluted and concentrated polymer systems.

EXPERIMENTAL

The anionic polymerization and the fractionation procedures used have been reported elsewhere.[7,14,16,21,23] In Table 2-4 are given molecular weights of the narrow MWD samples of poly(α-methylstyrene) (P-α-MS), polystyrene (PS), and poly(cis-isoprene) (PI) which were used in the present study. The values of the ratio M_w/M_n were not exceeded by 1.2 for all the samples studied.

The term "narrow MWD" has been used by various researchers in somewhat less strict sense. We here arbitrarily refer to the narrow MWD polymer as a polymer of the heterogeneity ratio M_w/M_n less than 1.2. In what follows we will use the term "narrow MWD" according to this criterion.

Table 2. Narrow MWD Poly(α-Methylstyrene): Molecular Weight and Viscoelastic Parameters at 200°C.

Sample	M_w [a]	M_n [b]	M_w/M_n [c]	Log η [d] (poise)	Log J_e [e] (cm^2/dyne)
MS-1	1,740,000	—	1.00	11.80	−6.27
2	189,000	187,000	1.01	9.37	−5.90
3	229,000	227,000	1.01	9.68	−6.10
4	105,000	102,000	1.02	8.81	−5.59
5	123,000	151,000	1.02	9.12	−5.66
6	386,000	403,000	1.01	10.14	−6.17
7	69,000	57,400	—	7.83	−4.93

a. Evaluated from intrinsic viscosity measurements in toluene at 25°C.
b. Osmometry in toluene at 37°C.
c. Sedimentation in cyclohexane at 39°C(theta point).
d. Obtained from tensile viscosities by dividing by 3.
e. Obtained from steady-state tensile compliances by multiplying by 3.

Table 3.   Narrow MWD Polystyrene: Molecular Weight
and Viscoelastic Parameters at 160°C.

Sample	M_n [b]	M_v [c]	M_w [d]	Log η [e] (poise)	Log J_e [f] (cm²/dyne)	Log τ_m (sec)
L-1[a]	—	2,900,000	2,600,000	10.32	−5.74	5.00
2[a]	—	1,040,000	1,060,000	8.95	−5.72	3.71
49	630,000	650,000	—	8.23	−5.76	2.78
41	252,000	275,000	—	6.98	−5.68	1.96
39	165,000	190,000	—	6.48	−5.74	1.25
38	122,000	122,000	—	5.88	−5.70	0.68
36	78,000	75,000	—	5.11	−5.68	0.03

a.   Estimated M_w/M_n <1.05 from the sedimentation velocity boundary curves.
b.   Osmometry in toluene at 37°C.
c.   Viscometry in cyclohexane at 35°C.
d.   Sedimentation equilibrium in cyclohexane at 39°C.
e.   Obtained from tensile viscosities by dividing by 3.
f.   Obtained from steady-state tensile compliance by multiplying by 3.

Table 4.   Narrow MWD Poly(cis-Isoprene): Molecular Weight
and Viscoelastic Parameters at −30°C.

Sample	M_w	M_n	Log η [d] (poise)	Log J_e [e] (cm²/dyne)	Log $\tau_{m\zeta}$ [f] (sec)
I-29[a]	3,100	—	4.37	−7.63	−2.13
28[a]	5,700	—	4.62	−6.73	−1.34
27[a]	6,800	—	4.67	−6.72	−1.24
20[b]	17,500	—	5.85	−6.11	0.22
17[b]	25,200	—	6.17	−5.99	0.73
14[b]	43,200	—	6.97	−5.70	1.77
21	57,600	60,600	7.78	−5.86	2.63
23	103,000	114,000	8.83	−5.86	3.58
25	159,000	176,000	9.25	−5.84	4.05
31	395,000	370,000	10.70	−5.85	5.33
32	620,000	620,000	11.43	−5.82	6.17
34[c]	1,120,000	—	12.25	−5.92	7.06

a.   Estimated M_w/M_n <1.2 from the sedimentation velocity boundary curves.
b.   Estimated M_w/M_n <1.1 from the sedimentation velocity boundary curves.
c.   Determined M_w/M_n as 1.01 from the sedimentation velocity boundary cruves.
d.   At constant friction factor at −30°C; the friction factor of I-34 was taken as the standard.
     For the six samples of lower molecular weight, log η_ζ was calculated from η at −55°C
     using eq. (3) in ref. 23.
e.   For the six samples of lower molecular weight, J_e at −55°C was reduced to that at
     −30°C by multiplying by a factor of 218/243.
f.   At constant friction factor at −30°C.

For P-α-MS and PS tensile creep measurements were made with a creep balance type
apparatus described previously.[7,14] Shear creep measurements with a torsion pendulum[21,23]
were performed to determine viscoelastic properties of PI samples.

RESULTS AND DISCUSSION

Since our present interest is in the values of η, J_e, and τ_m, and their dependence on molecular weight, the observed creep curves and also the master curves, which were obtained by shifting the experimental creep curves according to the time-temperature superposition principle, are not reproduced here. For all the three systems studied the superposition of the primary creep curves was successful within experimental error.

The values of η and J_e were estimated by using the extrapolation method of Ninomiya.[28] For PS and PI systems τ_m was calculated by using the procedure X,[29] after the creep compliance was converted to the relaxation modulus.[30] The values of these viscoelastic parameters are listed in Table 2-4.

The Relationship between the Viscosity and the Molecular Weight.

Figure 1 shows the double logarithmic plot of η at 200°C versus M_w for P-α-MS. For the sake of comparison, the viscosity data obtained by Fujimoto et al.[9] are also shown in the figure by circles with bar. Since the viscosity data at 186°C were tabulated in their paper, the data were reduced to 200°C with the aid of the shift factor a_T for the time-temperature reduction, given in their report. It is seen that the η-M relation can be represented by a straight line drawn in the figure with the slope of 3.3, except for a plot of our highest molecular weight sample. The value of 3.3 for the slope is very close to
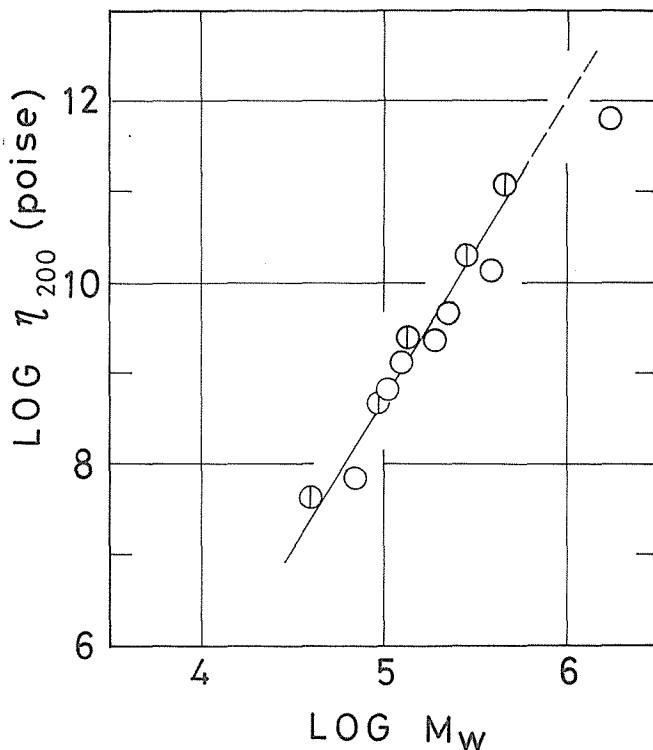

Fig. 1. The logarithmic plot of η at 200°C against M_w for poly (α-methylstyrene).

○, our data; ⊕, Fujimoto et al.[9] The straight line has the slope of 3.3.

the well-known value[31] of 3.4 for a number of polymers at higher molecular weights.

In Table 5 are summarized the observed power dependence of η on M for narrow MWD PS in the region of high molecular weight, or in the entangled state. The viscosity data of narrow MWD samples, which come up to our standard for the narrow MWD polymer mentioned above, are collected in the table from existing literature. Except for rather large values of the exponent reported earlier by Tobolsky et al.[5] and othres,[8,34,37] again it is seen that the well-known 3.4 power law is approximately followed by higher molecular weight PS of narrow MWD. The high value of the exponent of 4.0, however, has been revised subsequently to that of 3.4 by Tobolsky et al.[12,22] A summary of the η -M relation for PS in the higher molecular weight region has been reported recently by Casale et al.[38] not only for narrow MWD samples but also for broad MWD ones.

The values of the critical molecular weight M_c, which is determined from the intercept of two straight lines in the logarithmic plot of η against M, are reported as to be round 35,000 for undiluted PS samples of broad MWD.[31]

Very few reliable data can be found from recent publications for the η -M relation of undiluted PS of narrow MWD in the region $M < M_c$. The values of about unity for the exponent in power dependence of η on M have been reported in this molecular weight region.[13,18,19]

The data of the viscosity η_ζ at constant friction factor for our PI samples are plotted logarithmically against M_w in Fig. 2 together with those of Holden.[39] The details in estimating the values of η_ζ plotted in Fig. 2 have been described elsewhere.[21,23] It can be seen that the plot is well represented by two straight lines with the slopes of 1.0 and 3.7 at molecular weights below and above $M_c = 10,000$, respectively.

The viscosity data for other class of narrow MWD polymers, including polar polymers such as poly(vinyl acetate), are collected from the recent publications and given in Table

Table 5. Power Dependence of Viscosity on Molecular Weight
in the Entangled State for Narrow MWD Polystyrene

Molecular Weight Range	Number of Samples	Exponent	Investigator (s)	Reference
78,100— 249,000	7	3.14	McCormick et al.	32
72,500— 568,000	22	3.14	Rudd	33
127,000— 310,000	4	4.0	Tobolsky-Murakami	34
43,000— 460,000	6	3.4	Ballman-Simon	35
80,000— 267,000	5	4.0	Tobolsky et al.	5
48,500— 242,000	5	3.34	Stratton	36
74,600— 583,000	3	4.0	Ueno-Murakami	37
82,000—1,320,000	9	3.75	Akovali	8
82,500—1,800,000	7	3.4	Tobolsky et al.	12
46,900— 581,000	9	3.7	Onogi et al. [a]	13
75,000—2,900,000	7	3.3	Nemoto	16
47,000— 600,000	5	3.4	Plazek-O'Rourke [a]	18
51,000— 500,000	4	3.7	Mills-Nevin [a]	19
157,000— 610,000	5	3.4	Zosel	20
82,500— 450,000	7	3.4	Tobolsky et al.	22

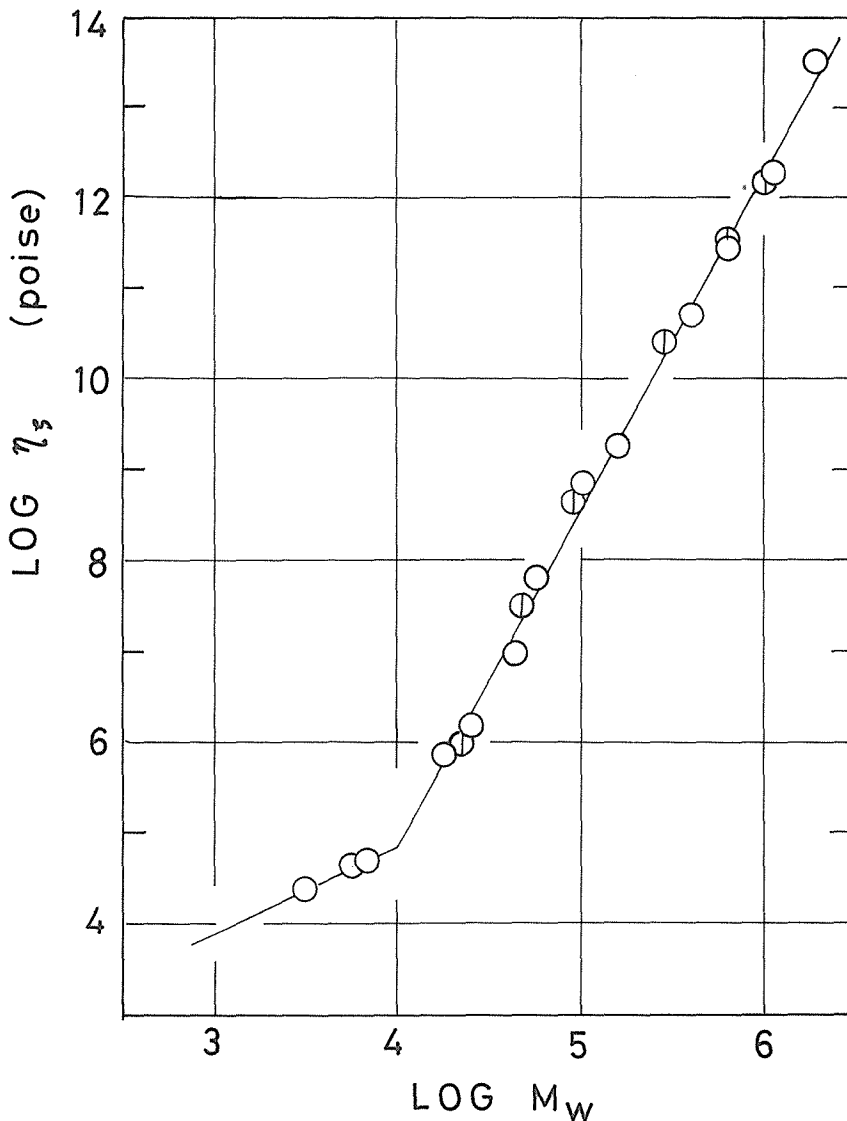a. Reported also viscosity data for samples of lower molecular weight ($M < M_c$).

Fig. 2. The logarithmic plot of η_ζ at constant friction factor against M_w for poly (*cis*-isoprene).

○, our data; ◐, Holden,[39] The two straight lines have the slopes of 1.0 and 3.7.

6. Again it is apparent in the table that η varies as the first power of M in the range $M < M_c$, and that the observed values of the exponent at $M > M_c$ do not appreciably deviate from the well-known value of 3.4.

As has been pointed out above the η-M relation observed for a number of undiluted polymers of narrow MWD can be expressed approximately by the 3.4 power law in the higher molecular weight region, $M > M_c$. η at $M < M_c$, on the other hand, varies roughly as the first power of M. The transition in the dependence of η on M in the vicinity of M_c appears to be rather abrupt for a number of undiluted polymers of narrow MWD except for poly(dimethylsiloxane),[11] which exhibits rather gradual change in the slope

Table 6. Power Dependence of Viscosity on Molecular Weight
for Narrow MWD Polymers

Polymer	Molecular Weight Range	Number of Samples	Exponent	Reference
Poly (butadiene) [a]	61,000—524,000	8	3.4	40
Poly (butadiene) [b]	67,500—240,000	4	3.6	17
Poly (isobutylene)	370,000—895,000	5	3.2	41
Poly (dimethylsiloxane) [c]	3,000— 13,000	3	1.15	11
	74,800—252,000	4	3.7	
Poly (dimethylsiloxane)	3,200— 30,000	3	1	42
	30,000— 51,000	5	3.6	
Poly (vinyl acetate)	5,500— 10,500	2	1	6
	112,000—262,000 [d]	2	3.4	
Poly (methyl methacrylate)	45,200—158,000	4	3.8	15

a. Prepared by *n*-buthyllithium-initiatiated polymerization.
b. The contents of *cis-*, *trans-*, and vinyl structures are ~45, ~43, and ~10%, respectively.
c. In log η vs. log M_w plots the slope of the graph changes gradually in the range $13,000 < M_w < 70,000$.
d. Viscosity data for three samples of higher molecular weight are omitted here, because for these samples a possibility associated with some branching has been noticed by them.[6]

of the η-M relation. Consulting the theoretical predictions given in Table 1, it may be concluded that all theories listed in Table 1, except for that of unmodified Rouse–Bueche,[1,2] predict a correct dependence of η on M in the higher molecular weight region, or in the entangled state.

The Relationship between the Steady-State Compliance and the Molecular Weight.

Figure 3 shows the J_e-M relation for narrow MWD P-α-MS at 200°C. The data at 186°C obtained by Fujimoto *et al.*[9] were also plotted in the figure. Their data were reduced to 473°K (200°C) by multiplying by a factor of 459/473. The dotted line represents the dependence of J_e on M predicted by the Rouse model for undiluted polymer system,[3] *i.e.*

$$J_{eR} = (2/5) (M/\rho\ RT) \tag{3},$$

where ρ is the density of polymer, and the product RT has its usual meaning.

In the region $M > \sim 100,000$ J_e appears to be nearly independent of M, while at lower molecular weights our data of J_e exhibit a quite different dependence on M from that predicted by the Rouse model. For our P-α-MS samples the values of J_e at lower molecular weights increase rather rapidly with decreasing molecular weight inconsistent with the observed dependence by Fujimoto *et al.*[9] in this region of molecular weight. The reason for the difference has not been known to us yet. Still it seems to be certain that J_e is nearly independent of M in the region of higher molecular weights, in contrast to the prediction of the Rouse-Bueche theory[1,2] and its modified version.[3]

In recent years, a number of data of the J_e-M relationship for narrow MWD samples of PS have been reported by various researchers, including our research group. Reliable data are collected after a close inspection of each description concerning MWD of samples used in their study according to our criterion of the narrow MWD polymer, and are plotted logarithmically in Fig. 4 after having been reduced to 160°C. The prediction
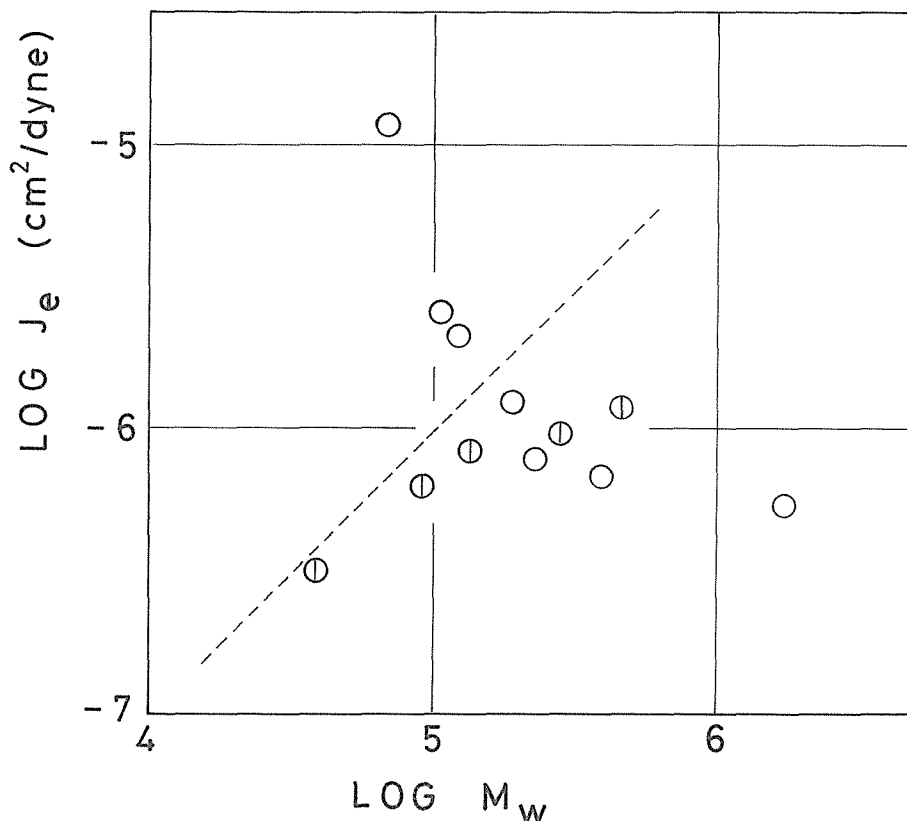
Fig. 3. The logarithmic plot of J_e at 200°C against M_w for poly(α-methylstyrene).

○, our data; ⊕, Fujimoto *et al*.[9] The dotted line represents the Rouse prediction.

of the Rouse theory is indicated also by the dotted line in the figure. It is seen that the observed values of J_e are roughly in agreement with the prediction of the Rouse theory in the region $M < \sim 100{,}000$. At higher molecular weights, on the other hand, J_e is nearly independent of M as has been already pointed out for narrow MWD P-α-MS. This behavior is in good agreement with the predictions of the Hayashi[25] and the Graessley[26] theories, which stand for describing the viscosity of polymers in the highly entangled state. It should be noted here that J_e changes its dependence on M rather abruptly at a certain molecular weight, $M_b \simeq 100{,}000$. This value of M_b is considerably higher than that of M_c, about 35,000. Recently Graessley and Segal[45] have reported on concentrated solutions of narrow MWD samples of PS that J_e depends on polymer concentration c and molecular weight according to the relation

$$J_e = [a_1/(1+a_2 cM)] J_{eR} \qquad (4)$$

where a_1 and a_2 are constants, independent of c and M. In eq. (4) the density of polymer ρ, appearing in eq. (3) for J_{eR} is replaced by c. Prest *et al*.[43b] have calculated the J_e-M relationship of undiluted PS by eq. (4) with the aid of values of the constants evaluated by Graessley and Segal.[45] In Fig. 4, plot of the Graessley-Segal equation is reproduced
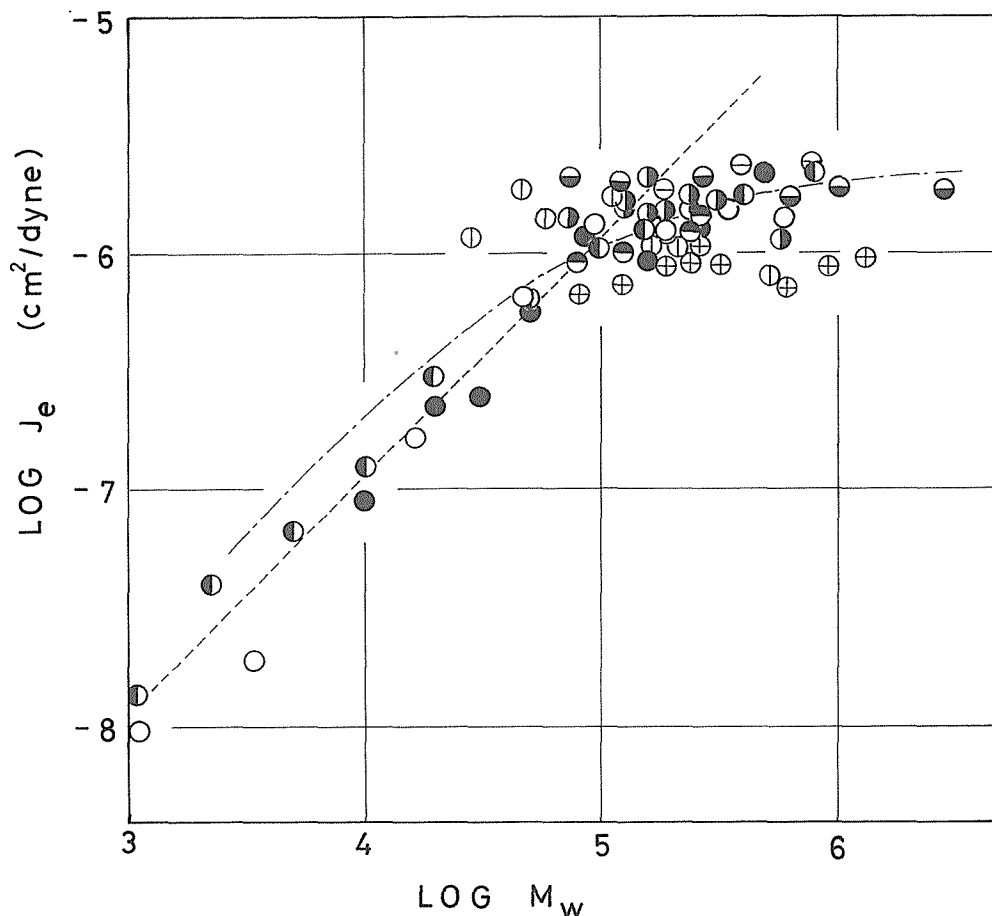
Fig. 4. The logarithmic plot of J_e at 160°C against M_w for polystyrene.

◯, Plazek-O'Rourke;[18]	⬤, Mills-Nevin;[19]
◐, O'Reilly-Prest;[43]	◑, Murakami et al.;[37,44]
◓, Tobolsky et al.;[5]	◒, Nemoto;[16]
⊕, Akovali;[8]	⦶, Onogi et al.;[13]

⊖, Mieras-Rijn.[10] The dotted and the chain lines represents the Rouse prediction and the Graessley-Segal equation, respectively.

from Fig. 6 of the paper of Prest et al.[46b], and represented by a chain line. The log J_e versus log M relationship described by eq. (4) shows rather gradual transition from the low-molecular-weight property to the high-molecular-weight one, while this is not the case for the observed J_e-M relation as noted in the foregoing lines.

Another attempt to describe the measured dependence of J_e on M over wide range of molecular weight, encompassing the region of M_b, has been made recently by Mills and Nevin.[19] Their idea is based upon the Flory's treatment[46] to account for the ineffective contributions from free chain ends for the elastic response of the network structure. The relation derived from this idea has displayed a change in the slope of log J_e versus log M plot in the vicinity of M_b for the narrow MWD PS system.

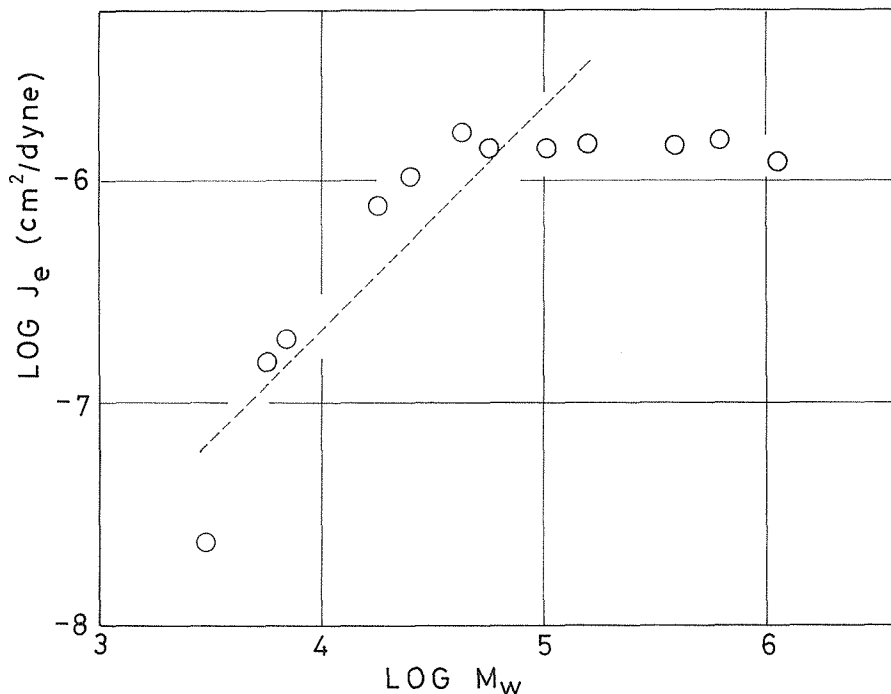Figure 5 gives the log J_e versus log M_w plot for PI at −30°C. The feature of the

Fig. 5.　The logarithmic plot of J_e at $-30°C$ against M_w for poly(*cis*-isoprene).
The dotted line represents the Rouse prediction.

plot is quite resemble to that for narrow MWD PS. Close inspection, however, reveals that J_e of the lowest molecular weight sample is slightly lower than the theoretically predicted value, indicated by the dotted line in the figure, while those of the remaining five samples of the lower molecular weight are slightly higher. The value of M_b is estimated from the figure about 50,000, and is higher than that of M_c, 10,000.

For the narrow MWD samples of P-α-MS, PS, and PI the characteristic features of the observed dependence of J_e on M are summarized as follows:

　(a)　The molecular weight independent nature of J_e at $M > M_b$, in agreement with the theoretical predictions by Hayashi and Graessley;

　(b)　Approximately the first dependence of J_e on M at $M < M_b$, consistent with the prediction of the basic Rouse model;

　(c)　Rather abrupt change in the slope of log J_e versus log M plot at M_b;

　(d)　The relation $M_b > M_c$; $M_b \simeq 3M_c$ for PS and $M_b \simeq 5M_c$ for PI.

These features may be considered at present as the experimentally established ones for at least nonpolar polymers of narrow MWD.

Now it is of great interst to see whether the features can be indicated or not by narrow MWD polymers belonged to other class. Unfortunately, we can hardly find compliance data of undiluted polar polymers of narrow MWD from existing literature. Among them reliable data of J_e for poly(vinyl acetate) (PVAc)[6] and poly(methyl methacrylate) (PMMA)[15] have been selected and plotted logarithmically against M_w in Fig. 6. Though available data, according to our criterion of the narrow MWD polymer, are very few for the both systems, it seems to be not so prejudiced to expect that M_b for PMMA would
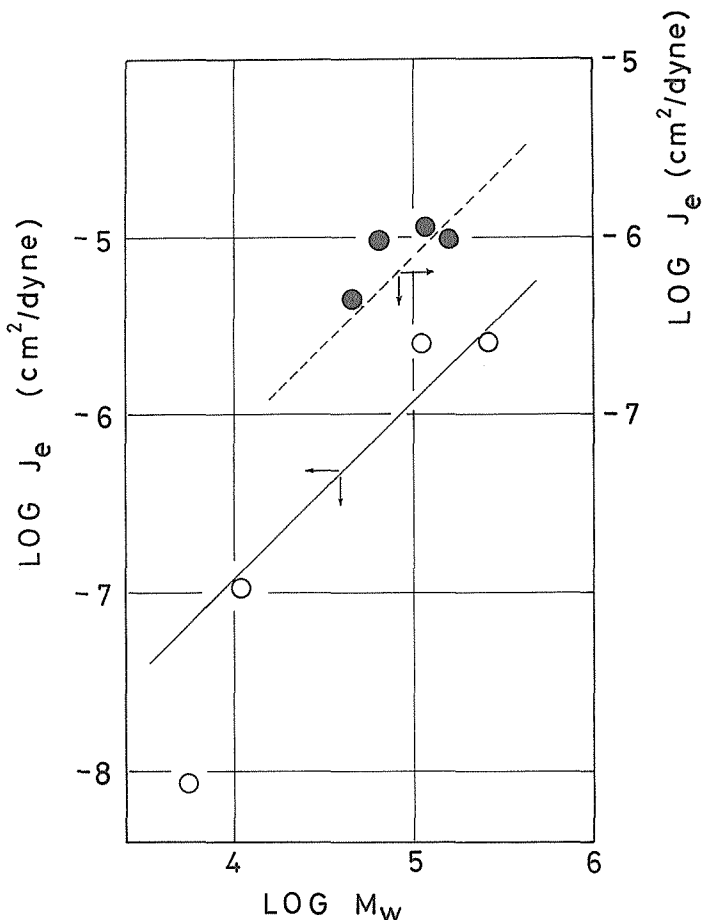
Fig. 6. The logarithmic plot of J_e against M_w.

○, poly(vinyl acetate) at 75°C;[6]
●, poly(methyl methacrylate) at 220°C.[15]
The Rouse prediction is represented by the solid line for poly(vinyl acetate), and by the dotted line for poly(methyl methacrylate).

be located near 100,000 and that above and below M_b the values of J_e are independent and dependent linearly of M, respectively. The value of M_b, 100,000, thus estimated is considerably higher than that of $M_c\sim$32,000.[31] For PVAc the expectation mentioned above is rather skeptic, nevertheless in the region of low molecular weight the J_e-M relation appears to be well compared with the prediction of the Rouse model. The feature (a) described above has been observed in the J_e-M relation of narrow MWD poly (dimethylsiloxane).[11]

The Relationship between the Maximum Relaxation Time and the Molecular Weight

The values of τ_m at 130°C for PS are plotted logarithmically against M_w in Fig. 7. Again, data obtained at different temperatures by various researchers have been reduced to 130°C by using their own values of a_T determined from mechanical measurements.
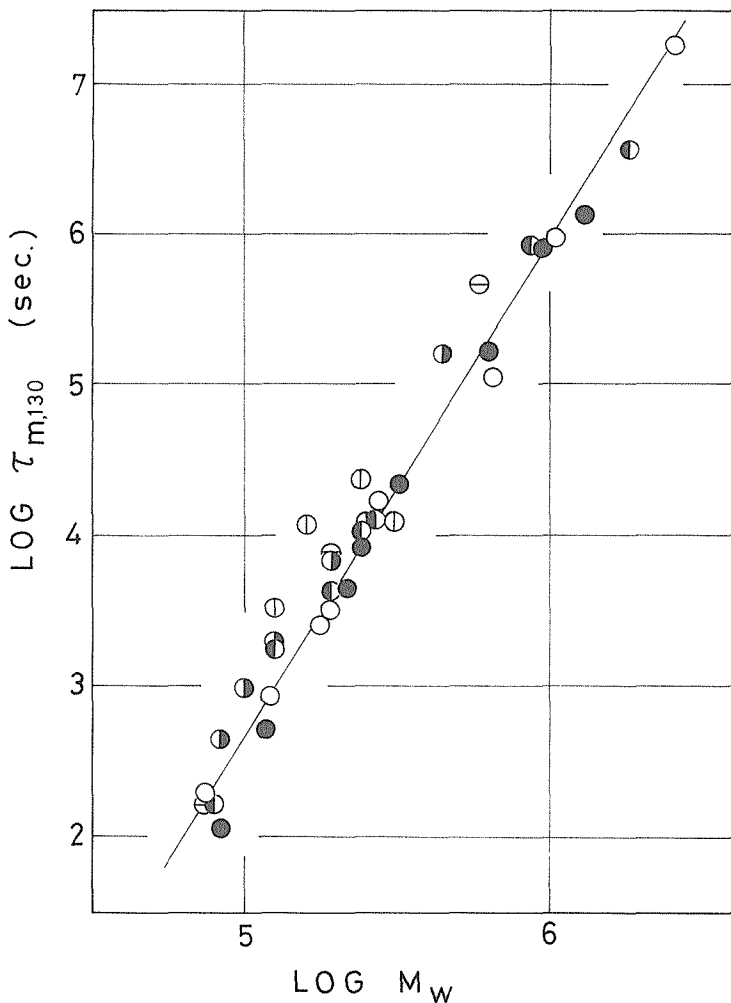
Fig. 7. The logarithmic plot of τ_m at 130°C against M_w for polystyrene.

○, Nemoto;[16]   ●, Akovali;[8]
◑, Tobolsky *et al.*;[12]   ◐, Tobolsky *et al.*;[22]
⦶, Tobolsky-Murakami;[34]   ⦶, Ueno-Murakami.[37]
The straight line has the slope of 3.3.

The straight line in the figure has the slope of 3.3. Though there exists some scattering around the line, it seems that the molecular weight dependence of τ_m for this system may be well represented by the straight line in the region of M greater than 80,000, which is very close to M_b.

For PI system the values of $\tau_{m\zeta}$ at constant friction factor have been calculated and plotted logarithmically against M_w in the Fig. 8. It is rather surprising that the log $\tau_{m\zeta}$ versus log M_w plot exhibit no distinct break at M_b and supports a straight line with the slope of 3.7 over almost the whole region of M studied, $3,100 < M < 1,120,000$, as indicated by the solid line. It is, however, uncertain whether or not there exists a break at M_c, because the experimental error involved in $\tau_{m\zeta}$ seems too large and, furthermore,
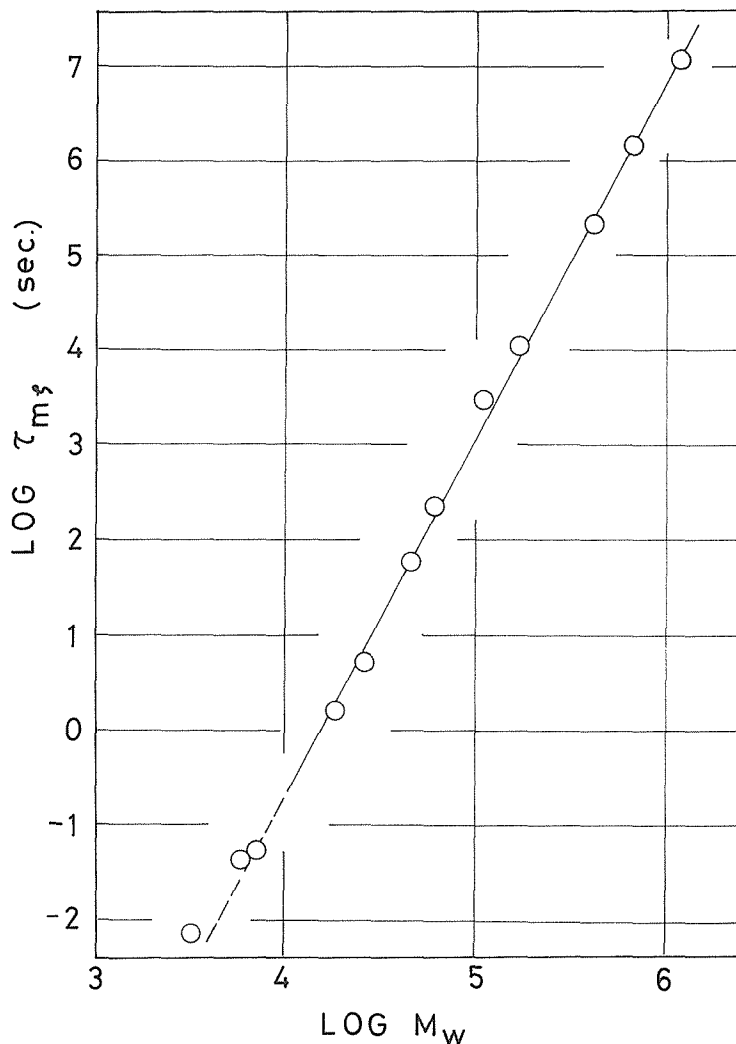
Fig. 8. The logarithmic plot of $\tau_{m\zeta}$ at constant friction factor against M_w for poly(cis-isoprene). The straight line has the slope of 3.7.

the lack of sufficient number of data in the region of M concerned. At any rate, it may be concluded that the observed dependence of $\tau_{m\zeta}$ on M described above is represented satisfactorily by the theoretical prediction by Hayashi[25] and Graessley.[26]

Entanglement Compliance and Entanglement Spacing.

The compliance J_e , which is associated with the conceptional scheme of network for uncrosslinked polymer system, can be evaluated from the retardation spectrum.[47] The approximate values of J_{eN} can also be obtained as the value of the compliance J_{inf} at the inflection point of the creep curve. The value of J_{eN} for the present three systems have been evaluated by these methods and compared with those of J_e at higher molecular weights.

For the systems PS and PI values of J_{eN} obtained by the two methods were in agreement with each other, and were nearly independent of M. For P-α-MS J_{inf} has been

evaluated, and J_{inf}'s in the region $M > \sim 120,000$ were found to be approximately independent of M. But the values of J_{inf} of P-α-MS in the region $M < \sim 120,000$ depended strongly on M, and increased appreciably with decreasing molecular weight. The observed dependence of J_{inf} on M at lower molecular weights has been still remained as an unsolved problem.

At higher molecular weights values of J_e of the systems P-α-MS and PS are higher than those of J_{eN} by a factor two. For the PI system, however, the ratio J_e/J_{eN} is about $8 \sim 10$ for the samples with $M > M_b$.

The average molecular weight M_e between entanglement coupling points can be simply related with J_{eN} by

$$J_{eN} = M_e/\rho \; RT \tag{5}.$$

The values of M_e evaluated by this relation were 16,000, 23,000, and 3,000 for P-α-MS, PS, and PI, respectively. For P-α-MS and PS, if 28,000[9] and 35,000,[31] respectively, are taken as values of M_c, the relation between M_e and M_c is roughly approximated by $M_c \simeq 2M_e$. The relation is $M_c \simeq 3M_e$ for the PI system, in contrast to the large value of J_e/J_{eN}.

Actually, J_e at higher molecular weights may be determined by the slowest relaxation process in the fully entangled system, and the situation would be well explained by the idea in the theoretical treatments of Graessley[26] and others[25] described in the foregoing lines. J_{eN} also reflects the entanglement network of the system. It is associated with the contribution from the relaxation modes separated from the terminal mode which is responsible for J_e. The quantitative relationship between J_e and J_{eN} in the entangled system, as well as that between M_e and M_c, seems to be still an open question at present, and further studies, both experimental and theoretical, are needed.

The characteristic role of the value of M_b has been emphasized in interpretting the J_e-M relationship. In order to describe viscoelastic properties of undiluted polymers of narrow MWD in the terminal zone, J_e at higher molecular weights, or alternatively the critical molecular weight M_b which is greater than M_c by a factor of about $3 \sim 5$ for the present systems, would be one of the most important parameters as well as M_e and M_c.

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