ORIGINAL CONTRIBUTION

The relaxation of linear flexible polymers which are slightly poly-disperse

Judith K. Jackson
H. Henning Winter

Dedicated to the memory
of Professor Tasos C. Papanastasiou

J.K. Jackson
Prof. H.H. Winter (✉)
University of Massachusetts
Department of Chemical Engineering
and Department of Polymer Science
and Engineering
Amherst, Massachusetts 01003, USA

Abstract The relaxation of slightly poly-disperse linear flexible polymers has been expressed in a simplified blending rule which is presumed to be a weighted linear superposition of the relaxation spectra of mono-disperse components which constitute the blend. Discrete components are characterized by their molecular weight M_i, weight fraction w_i, and relaxation time spectrum $H_i(\lambda)$. In contrast to broadly distributed blends in which the small molecules mobilize the large ones and vice versa, we introduce the term "slightly poly-disperse" for blends with molecular weight distributions narrow enough to have very little change in the longest relaxation times of each molecular weight component. The properties of this blending rule are analyzed and dynamic data is calculated for slightly poly-disperse polystyrene. As an application, the blending rule is used to determine the characteristic mono-disperse parameters (BSW parameters) of two materials, poly (vinyl methyl ether) and polycarbonate, for which we could not determine their BSW parameters directly since they were not available in nearly mono-disperse form. The proposed blending rule can only be applied to systems in which all components are above the entanglement molecular weight, i.e. $M_i \gg M_c$.

Key words Rheology – polymers – poly-dispersity – linear viscoelasticity – relaxation time

Introduction

It has long been of interest to relate the molecular weight distribution of a polymer melt to its linear viscoelastic properties in a general way. The major purpose of such a blending rule is the determination of the molecular weight distribution from linear viscoelastic data of the broadly distributed polymer. The distributed polymer is then expressed as a blend of many mono-disperse fractions (molecular weight M_i, weight fraction w_i), each of them contributing to the overall rheological behavior in a deterministic way. In short, a blending rule attempts to establish a unique relation between the mono-disperse and the poly-disperse spectrum. Such blending rules have typically been successful at describing the linear visco-elastic behavior of some molecular weight distributions and unsuccessful at describing others.

Instead of addressing this problem in its full extent, we focus on the perturbation of the mono-disperse behavior and introduce the notion of a "slightly poly-disperse" (SP) polymer. SP polymers are assumed to be sufficiently poly-disperse so that their rheology is already affected noticeably by the poly-dispersity, however, without showing all the complexity of broadly distributed polymers. In the following, we will postulate that there exists a unique SP blending behavior which, in addition, is expected to be simple at least for linear flexible polymers. Such SP blending rule will be useful to have when working with SP polymers from polycondensation or metallocene catalysis of polyolefines, for instance. We will demonstrate the use

of a simplified blending rule to model the dynamic mechanical data of a SP polymer.

The parameter which defines deviations from mono-dispersity (width of the distribution) is the ratio of weight average to number average molecular weight, M_w/M_n. For linear flexible SP polymers, M_w/M_n is the only parameter needed, but it is not clear up to which of its values a polymer may be viewed as being slightly polydisperse. For rheological properties, we expect that M_w/M_n has to be below 2 or 3. We will attempt to define the limits of SP in this paper.

Our main purpose of formulating a SP blending rule is to determine the mono-disperse behavior of polymers which cannot be synthesized in narrow distributions. In some cases, the narrowest attainable molecular weight distribution gives M_w/M_n of about 2 (e.g., condensation polymers). For these polymers, the distribution is still sufficiently narrow such that the effects of poly-dispersity are small but they are too large to evaluate the mono-disperse behavior directly from experiments. A SP blending rule is needed for the data analysis.

The SP blending rule has to obey several general features of poly-dispersity which need to be mentioned first: The broadening of the MWD does not affect the dynamic glass transition behavior as measured at high frequencies. Strongly affected are the entanglement and flow region, i.e. the behavior at intermediate and low frequencies. This study focuses on these time scales of flow and entanglement behavior. The transition from entanglement to flow behavior broadens with increasing poly-dispersity.

Relaxation of (nearly) mono-disperse linear polymers

Man-made polymers have always been distributed in molecular size (and some of their advantageous properties rely on poly-dispersity). However, it is possible to synthesize polymers of sufficiently narrow distribution so that they seem to practically represent (at least) the rheological properties of perfectly mono-disperse polymers (we will return to this hypothesis at the end of this paper). Linear flexible polymers with such nearly mono-disperse distribution (with $M_w/M_n < 1.10$, about), above their entanglement molecular weight, have been observed to exhibit a universal relaxation pattern (Onogi et al., 1970; Marin et al., 1977; Schausberger et al., 1985; Baumgärtel et al., 1990; Jackson et al., 1994). This relaxation pattern has been shown to be well represented by an empirical relaxation time spectrum, $H(\lambda)$ (BSW spectrum) proposed by Baumgärtel et al. (1990),

$$H(\lambda) = \begin{cases} m G_N^0 \left[\left(\dfrac{\lambda}{\lambda_{max}} \right)^m + \left(\dfrac{\lambda}{\lambda_c} \right)^{-n} \right] & \lambda \leq \lambda_{max}, \\ 0 & \lambda > \lambda_{max} \end{cases} \quad (1)$$

where m is the slope in the entanglement region, G_N^0 is the plateau modulus, n is the glass transition slope, and λ_c is the crossover relaxation time between the entanglement behavior and the glass transition. The BSW spectrum is a linear superposition of the contributions of the dynamic glass transition, $H_g(\lambda) = m G_N^0 (\lambda/\lambda_c)^{-n}$, and that of the entanglement region, $H_e(\lambda) = m G_N^0 (\lambda/\lambda_{max})^m$. The longest relaxation, λ_{max}, scales with the molecular weight, M

$$\lambda_{max} = \lambda_c \left(\frac{M}{M_c} \right)^z. \quad (2)$$

The parameter, M_c, is the crossover molecular weight while z is the scaling exponent of zero shear viscosity with molecular weight, $\eta_0 \sim M^z$, and has values between $3.3 - 3.7$ for most polymers (Berry et al., 1968). Values of the parameters associated with this spectrum (BSW parameters) were evaluated for nearly mono-disperse polystyrene and polybutadiene and the method was described by Jackson et al. (1994). Parameters evaluated from the dynamic moduli of nearly mono-disperse polystyrene are provided in Table 1.

The predictions of the BSW spectrum significantly differ from theoretical predictions of molecular dynamics theories of Doi et al. (1986) but seem to be closely captured by the mode-coupling theory of Schweizer (1989, 1991, 1993).

The empirical BSW spectrum is the most simple known material function for describing G', G'' data of polymers with linear flexible molecules of uniform molecular weight. A more detailed proposal can only be expected from theory. It could not be extracted from the experimental data due to the Morosow (1984) Discrepancy Principle which expresses the fact that a physical model for describing a data set cannot be of higher accuracy than the noise in the data permits. For this reason we decided to stay with the simplest choice of sufficient accuracy, the BSW spectrum.

Unfortunately, many materials cannot be synthesized with M_w/M_n close to 1. As a result the BSW parameters

Table 1 BSW parameters of polystyrene as calculated from mono-disperse data

Parameter	Polystyrene
m	0.23
λ_c [s]	0.0002
M_c [g/mol]	16 600
z	3.43
G_N^0 [Pa]	228 000
n	0.67
T_{ref} [°C]	180
C_1	5.02
C_2 [K]	125.3

cannot be measured directly for such materials but they can be determined from G', G'' data if a blending rule is known. This problem will be pursued later in this study.

Blending rule for bi-disperse polymers

Many researchers proposed blending rules to describe the behavior of bi-disperse blends of linear flexible polymers (Ninomiya, 1959; Bogue et al., 1970; Prest et al., 1973; Kurata et al., 1974; Montfort et al., 1978; Montfort et al., 1979; Watanabe et al., 1984; Watanabe et al., 1985; Schausberger, 1986; Rubinstein et al., 1988; Kornfield et al., 1991; Jackson et al., 1995). Based on the rheological observations on such bi-disperse blends, Prest et al. (1973) and Jackson et al. (1995) suggested that a generalized linear blending rule might be appropriate to describe poly-disperse polymers. This can be expressed in terms of the relaxation time spectrum

$$H(\lambda) = \sum_{i=1}^{N} B_i H_i(\lambda/A_i) , \qquad (3)$$

where H_i is the BSW spectrum of the ith molecular weight, M_i, weighted with the front factor B_i (vertical shift) and shifted on the time scale by A_i. Both shift parameters, B_i and A_i, depend upon the molecular weight distribution. An expression for B_i was proposed (Schausberger, 1986; Jackson et al., 1995),

$$B_i = w_i^2 + w_i' \sum_{j=i+1}^{N} a_{ij} w_j , \qquad (4)$$

where w_i is the weight fraction of the ith molecular weight M_i. The constants a_{ij} depend upon the molecular weight distribution. While the exact dependence is not known, it was shown for highly entangled systems, i.e. $M_i \gg M_c$, that the following simplifications can be made

$$a_{ij} \cong 0 \quad j < i , \qquad (5a)$$

$$a_{ij} \cong 2 \quad j > i . \qquad (5b)$$

This leads to a simplified expression for the weighting factors, B_i,

$$B_i = w_i^2 + 2w_i \sum_{j=i+1}^{N} w_j , \quad M_{i+1} > M_i . \qquad (6)$$

Schausberger (1986) used the above blending rule in conjunction with an expression for the A_i which was not successful in general. Discrepancies also arose when the blending rule was applied to bi-disperse blends where both molecular weights, M_1 and M_2, were not highly entangled as required by the assumptions in Eq. (3).

Jackson et al. determined A_2' values from G', G'' experiments.

Broadly distributed polymers

Broadly distributed polymers are not considered here. Molecular dynamics models based on reptation theory (de Gennes, 1979; Doi et al., 1986) have been proposed to describe the effects of poly-dispersity (Marrucci, 1985; Graessley et al., 1986; Rubinstein et al., 1987, 1988; Watanabe et al., 1989; des Cloizeaux, 1990). Several methods have been proposed specifically for determining the molecular weight distribution from linear viscoelastic data, see for instance the studies of Ninomiya (1959), Bogue et al. (1970), Tuminello (1986, 1991), Tsenoglou (1987), Wasserman and Graessley (1992, 1995). Their ultimate goal has been to redate the relaxation time spectrum of mono-disperse polymers to that of broadly distributed polymers in a unique way, i.e. to decompose the rheological behavior of the broadly distributed polymer into the responses of the components and, hence, identify the distribution of molecular sizes in the polymer.

It is important to note that the broadening of the molecular weight distribution seems to average out the distinct features in the relaxation patterns of the components which constitute the blend. This has the consequence that, for broadly distributed polymers, the description of the component relaxation does not have to be very accurate, as shown by Wasserman (1995) who used the BSW spectrum with an exponent of $m = 0.59$ which is highly unrealistic. For the SP polymers we assume that the general features of each component in the blend remain very similar to that of the corresponding mono-disperse polymer. The knowledge of the spectrum of the mono-disperse polymers is essential for SP blending rules while for broadly distributed polymers it is not.

The main purpose of this work is twofold: 1) to suggest a blending rule which is sufficient to describe *slightly* poly-disperse linear flexible polymers, and 2) to explore two specific applications.

● Prediction of the linear viscoelasticity of *slightly* poly-disperse polymers of known molecular weight distribution and known BSW parameters.
● Extraction of the mono-disperse parameters (BSW parameters) from the data of the *slightly* poly-disperse polymer: This allows comparison of the mono-disperse linear viscoelastic behavior of the numerous polymers which cannot be synthesized with $M_w/M_n < 2.00$.

A blending rule for slightly poly-disperse flexible polymers

It was shown that in the case of *bi-disperse* blends of linear flexible molecules, with components of similar molecular weights, the time shift becomes negligibly small (Jackson et al., 1995):

$$A_i \cong 1 \qquad (7)$$

This is our proposed criterion for calling a blend "slightly poly-disperse" as compared to broadly poly-disperse where time shifts would be important.

The resulting expression for the relaxation time spectrum, $H(\lambda)$, of a slightly poly-disperse polymer which is highly entangled is

$$H(\lambda) = \sum_{i=1}^{N} w_i \left(w_i + 2 \sum_{j>i}^{N} w_j \right) H_i(\lambda) , \quad M_{i+1} > M_i . \qquad (8)$$

Since the limiting conditions under which the assumptions in Eq. (7) (slightly poly-disperse) and Eq. (6) (highly entangled) are valid are not explicitly known, it is necessary to test this blending rule on a material with a known molecular weight distribution and known BSW parameters.

In the following, we test how well this blending rule predicts the linear viscoelastic data of several polymers that have relatively narrow molecular weight distributions. This can be done by introducing a specific distribution function.

Log-normal molecular weight distribution

The choice of distribution function is not so important when staying within the range of SP. We choose the most common type of molecular weight distribution which is best represented by a log-normal function

$$w(M) = \frac{1}{\sqrt{2\pi}} \frac{1}{\sigma M} \exp \left[-\frac{(\ln M - \ln M_m)^2}{2\sigma^2} \right] , \qquad (9)$$

with a mean molecular weight

$$M_m = M_w \exp \left(-\frac{1}{2} \sigma^2 \right) , \qquad (10)$$

and a standard deviation,

$$\sigma^2 = \ln \left(\frac{M_w}{M_n} \right) . \qquad (11)$$

The weight average molecular weight, M_w, and the number average molecular weight, M_n, are commonly determined by fitting the center part of the log-normal function to GPC data. In this way, the high molecular weight tail present in the sample is included even if it is undetectable to the GPC (Schindlauer et al., 1985; Eder et al., 1989).

While the continuous function in Eq. (9) is useful, for many calculations it is desirable to discretize the molecular weight distribution into N discrete weight fractions

$$w_i = w(M_i) \ln \sqrt{M_{i+1}/M_{i-1}} , \qquad (12)$$

of molecular weight, M_i. The N fractions are placed at equidistant molecular weights on the log axis.

When using a log-normal distribution molecular, sizes from zero to infinity are included in the modeling. This is true even for the SP polymers. We therefore have to narrow our definition of "slightly poly-disperse." We have to assume here that the high and low molecular weight tails are so thin that they do not significantly contribute to the experimentally observed stress.

Characteristics of SP blending rule

We expect the PS spectrum to be universal just like the spectrum of linear flexible polymers which are (nearly) mono-disperse. The characteristica of the SP blending rule, which differ from those of broadly distributed polymers, can be summed up as follows:

a) The SP spectrum (relaxation time spectrum of a SP polymer) will depend on the relaxation time spectrum of the corresponding mono-disperse polymer.
b) The average molecular weight, M_w, determines the location of the spectrum on the time axis, but it does not affect the shape of the spectrum (entanglement and flow region).
c) Blending has no noticeable effect on relaxation times, $A_i \cong 1$.
d) High and low molecular weight tails have no noticeable effect.

Experimental

The dynamic moduli of a slightly poly-disperse polystyrene were measured on a Rheometrics Dynamic Spectrometer 7700. Parallel plates with a radius of 12.5 mm were used. The dynamic moduli were measured at several temperatures and a master curve was created at a reference temperature of 180 °C. The weight average molecular weight of the sample (352 000 g/mol) and the poly-dispersity ($M_w/M_n = 2.00$) were previously reported (Baumgärtel, 1991) and are tabulated in Table 2. The dynamic

Table 2 Molecular weight information on polystyrene, polycarbonate, and poly (vinyl methyl ether) samples

Material	M_w [g/mol]	M_w/M_n
PS	3.52E5	2.00
PC	1.50E5	2.40
PVME	8.49E4	1.38

Table 3 BSW parameters of polystyrene, polycarbonate and poly (vinyl methyl ether) as calculated from slightly poly-disperse data

Parameter	PS	PC	PVME
m	0.23	0.23	0.23
l_c [s]	0.0002	0.0025	7.08E-6
M_c [g/mol]	16600	5010	6310
z	3.43	3.45	3.45
G_N^0 [Pa]	282000	4070000	724000
n	0.67	0.80	0.78
T_{ref} [°C]	180	170	70
C_1	5.02	7.62	5.51
C_2 [K]	125.3	69.3	160

moduli are plotted in Fig. 4. The WLF coefficients were calculated and are listed in Table 3.

The dynamic moduli of a highly entangled (= 150000 g/mol) slightly poly-disperse (M_w/M_n = 2.40) polycarbonate (Baumgärtel, 1990) are shown in Fig. 5. The reference temperature of the master curve is 170 °C and the WLF coefficients can be found in Table 3. A summary of the molecular weight information is in Table 2.

The dynamic moduli of a highly entangled (M_w = 84800 g/mol) slightly poly-disperse (M_w/M_n = 1.38) poly (vinyl methyl ether) taken from the literature (Polios, 1996) are shown in Fig. 6 at a reference temperature of 70 °C. Details of the experiments are given in the original publication. The molecular weight information is listed in Table 2 and the WLF coefficients are listed in Table 3.

Modeling procedure

As a starting condition, we assume that the molecular weight distribution is known (from GPC for instance). This allows calculation of $H(\lambda)$ using Eq. (8). Then, it is a simple matter to evaluate the dynamic moduli, $G'(\omega)$ and $G''(\omega)$,

$$G'(\omega) = \int_0^\infty \frac{d\lambda}{\lambda} H(\lambda) \frac{\omega^2 \lambda^2}{1 + \omega^2 \lambda^2} , \tag{13}$$

$$G''(\omega) = \int_0^\infty \frac{d\lambda}{\lambda} H(\lambda) \frac{\omega \lambda}{1 + \omega^2 \lambda^2} . \tag{14}$$

The modeled values of $G'(\omega)$ and $G''(\omega)$ can then be compared with measured data to assess the effectiveness of the blending rule for the material in question.

Modeling when BSW parameters are known

When the BSW parameters are known from the analysis of *nearly* mono-disperse data, as is the case for polystyrene, they can be used in conjunction with the blending rule in Eq. (8) to model the dynamic moduli. This involves the following sequence of steps.

1. Molecular weight distribution calculated: The GPC data for M_w and M_w/M_n is used to determine the parameters of Eqs. (9–11) to describe the molecular weight distribution. The distribution is discretized as given by Eq. (12).

2. Weighting factors B_i calculated using Eq. (6). The weighting factors B_i are calculated for the molecular weight distribution of step 1 above.

3. Evaluation of the relaxation time spectrum: The known parameters of the mono-disperse spectrum, $H_i(\lambda)$, are inserted into Eq. (8) along with the values of B_i calculated in step 2 to evaluate the relaxation time spectrum, $H(\lambda)$, of the *slightly* poly-disperse polymer.

4. Calculation of the dynamic moduli: The relaxation time spectrum, $H(\lambda)$, inserted into Eqs. (13) and (14) allows us to evaluate the dynamic moduli, $G'(\omega)$ and $G''(\omega)$. The model is compared graphically to the measured values.

The above method is limited by the fact that there are many types of polymers for which the BSW parameters have not been evaluated because the polymers are not available in a *nearly* mono-disperse form. For these materials, we suggest a method for evaluating the BSW parameters from the data of the *slightly* poly-disperse polymer.

Evaluating BSW parameters from data of slightly poly-disperse polymers

In cases where the molecular weight distribution of a slightly poly-disperse polymer is available as well as the measured $G'(\omega)$ and $G''(\omega)$ values, the BSW parameters can be determined for that particular polymer chemistry. A best fit of $G'(\omega)$, $G''(\omega)$ data results in a set of BSW parameters which are believed to describe the mono-disperse counterpart of the polymer sample. It is important to note that only the entanglement component, $H_e(\lambda) = m G_N^0 (\lambda/\lambda_{max})^m$, is affected by the blending. The issue then becomes to properly initialize and iterate upon the BSW parameters.

1) Parameter initialization: There are six parameters of the mono-disperse spectrum which must be initialized, the entanglement exponent, m, the plateau modulus, G_N^0, the crossover molecular weight, M_c, the crossover relaxation time, λ_c, the scaling exponent, z, and the glass transition exponent, n.

If materials with different weight average molecular weights, M_w, are available, the scaling exponent, z, is obtained by plotting zero-shear viscosity, η_0, versus M_w on

a log-log scale and fitting a line to the data. The slope of the line is the scaling exponent, z. If different molecular weight samples are not available, z can be estimated as 3.45 since most polymers have z values between 3.40 and 3.50 (Berry et al., 1968).

The entanglement exponent, m, can be estimated as 0.23 for all linear flexible polymers as suggested by previous work with polystyrene and polybutadiene (Jackson et al., 1994). The value of m cannot be determined accurately with our current method so the fixed value of 0.23 was used.

The plateau modulus, G_N^0, can be initialized as the plateau value of the storage modulus, $G'(\omega)$, in the entanglement regime. The glass transition exponent, n, can be set initially to a value equal to the slope of the loss modulus, $G''(\omega)$, in the glass transition regime (log-log scale). The crossover relaxation time, λ_c, should be chosen such that the glass transition regime in G' and G'' agrees with the data. The crossover molecular weight, M_c, should be chosen such that the terminal zone and entanglement of $G'(\omega)$ and $G''(\omega)$ agrees with the data.

2) Iteration: The entanglement exponent, m, and the scaling exponent, z, were chosen fixed, i.e., they were not further adjusted in the iteration phase of the procedure. The other parameters must be changed incrementally until a graphical superposition of the model predictions and the data is achieved. One begins by adjusting G_N^0 to obtain the proper height (not shape) of $G'(\omega)$ in the entanglement plateau region. Once this is achieved, λ_c and n should be adjusted to obtain agreement of the model and the data in the glass transition region. Finally, M_c can be adjusted to achieve agreement between the model and the data in the terminal zone and entanglement regime. When the iteration procedure has been completed and the best graphical superposition of data and model has been achieved, the final parameter values are saved.
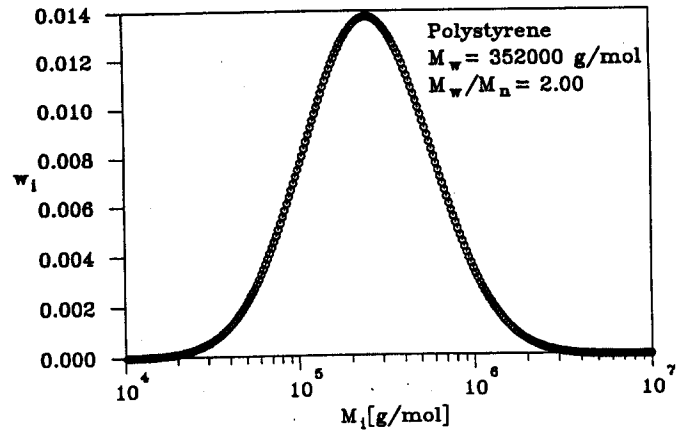

Fig. 1 The molecular weight distribution of polystyrene. GPC data were used to calculate a log-normal molecular weight distribution from Eqs. (9–12)
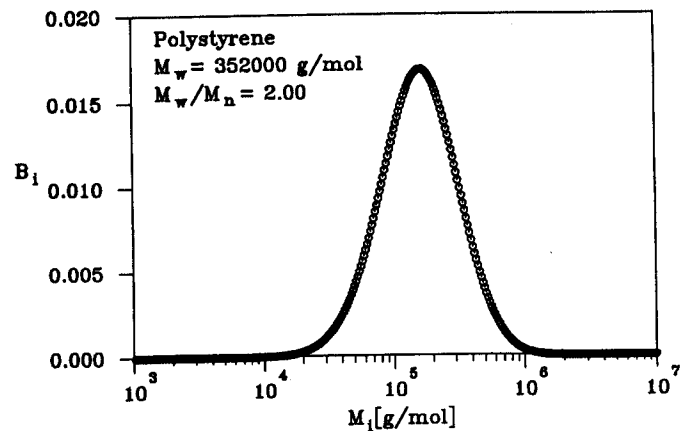

Fig. 2 Vertical shift factors, B_i, as calculated from Eq. (6). The molecular weight distribution displayed in Fig. 1 was used for the calculation

Modeling results

Modeling with known BSW parameters

The blending rule proposed above was tested using the dynamic data of a slightly poly-disperse polystyrene. First, the GPC data of the polystyrene of Table 2 was fitted with Eqs. (9–12) to calculate a discrete molecular weight distribution. The result is plotted in Fig. 1. This molecular weight distribution was entered into Eq. (6) to obtain the weighting factors B_i which are displayed in Fig. 2. The BSW parameters of previous experiments (see Table 1) were chosen for initial calculations. The complete relaxation time spectrum was calculated by summing the contributions of each molecular weight fraction according to Eq. (8). Finally, the dynamic moduli were calculated using the relations in Eqs. (13–14). However, the
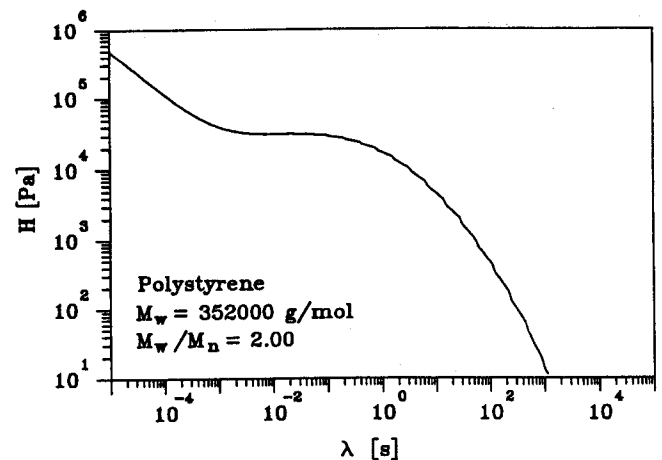

Fig. 3 The relaxation spectrum of polystyrene as calculated from Eq. (8). The BSW parameters in Table 3 and the shift factors in Fig. 2 were used
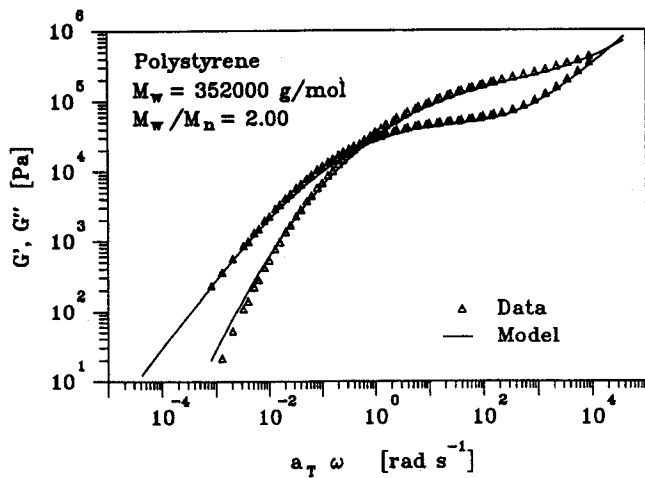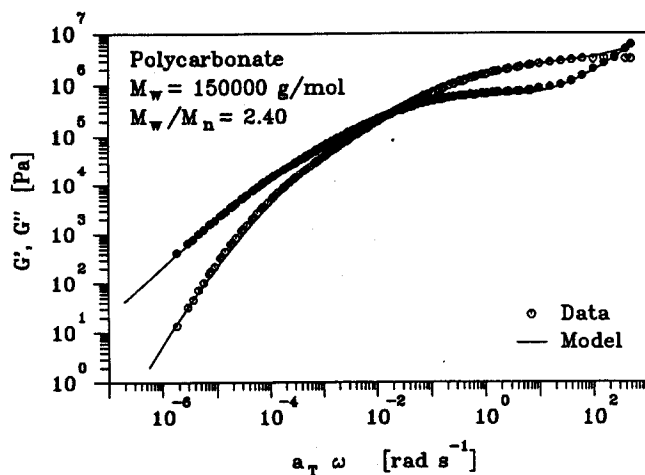
Fig. 4 A comparison of the modeled dynamic moduli of polystyrene (lines) and the measured values (symbols). The molecular weight information is given in Table 2. The modeled moduli were calculated from Eqs. (13–14) using the spectrum displayed in Fig. 3

Fig. 6 A comparison of the modeled dynamic moduli of poly (vinyl methyl ether) (lines) with the measured values (symbols) (data from Polios, 1996). The molecular weight data is listed in Table 2. The moduli are calculated from Eqs. (13–14). The BSW parameters were chosen to give the best fit of the model and the data

comparison with the data was unsatisfactory. The BSW parameters needed to be changed (see new values in Table 3 as compared to initial values in Table 1). The resulting spectrum of the PS blend is shown in Fig. 3 and a comparison of the modeled moduli (lines) and the data (symbols) is presented in Fig. 4. The plateau modulus value is 20% higher than the one determined for nearly mono-disperse polystyrene (Table 1). This may be due to experimental discrepancies.

Determination of BSW parameters

Having tested the blending rule with polystyrene (with known BSW parameters), we applied it to the task of evaluating the BSW parameters of polycarbonate, a typical example of a polymer which cannot be obtained in a nearly mono-disperse form. Using the modeling procedure outlined above, we iterated on the BSW parameters until the best agreement was obtained with the data of the

Fig. 5 A comparison of the modeled dynamic moduli of polycarbonate (lines) with measured values (symbols) (Baumgärtel, 1990). The molecular weight information is given in Table 2. The moduli are calculated from Eqs. (13–14) with the spectrum given by Eq. (8). The BSW parameters were chosen to give the best fit of the model and the data
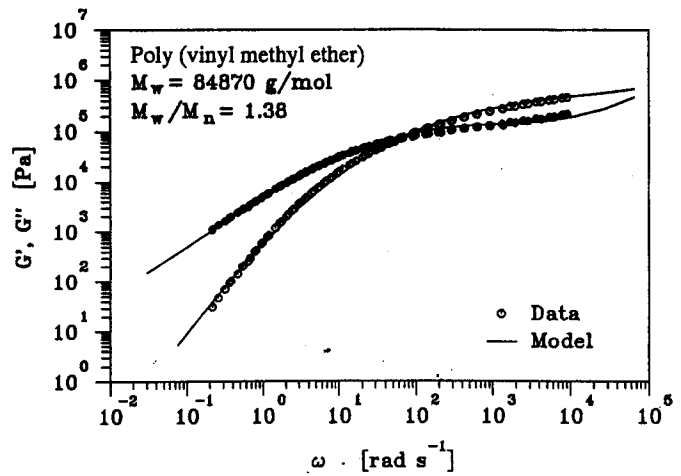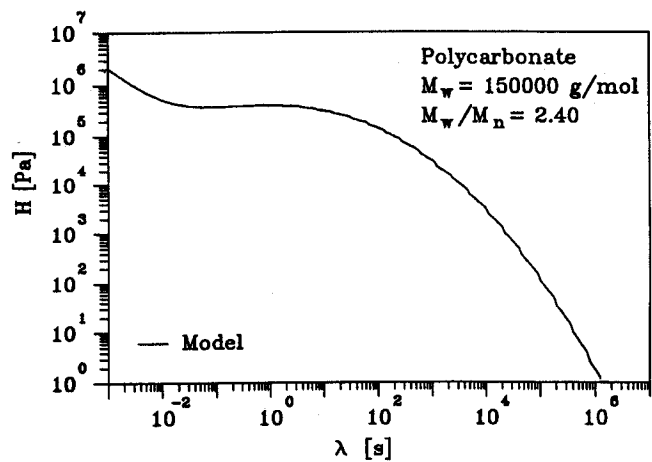

Fig. 7 The relaxation time spectrum for the polycarbonate in Fig. 5 as calculated from Eq. (8). The BSW parameters were chosen such that the best fit of the model and the G' and G'' data was achieved and listed in Table 3

dynamic moduli. The result for polycarbonate is shown in
Fig. 5 where the lines represent the model and the symbols
represent the data. The BSW parameters obtained using
this method are listed in Table 3. The relaxation time spec-
trum calculated for this polycarbonate is displayed in
Fig. 7.

The BSW parameters of poly (vinyl methyl ether) were
obtained from the dynamic moduli plotted in Fig. 6 using
the same procedure as for polycarbonate. The best fit of
the model (lines) to the data (symbols) is shown in Fig. 6.
The BSW parameters obtained are listed in Table 3. The
relaxation time spectrum calculated to achieve the fit with
the data is displayed in Fig. 8.

*Application of the blending rule
to nearly mono-disperse polymers*

One issue of concern is the difference between *nearly*
mono-disperse polymers and *slightly* poly-disperse poly-
mers. Having tested a blending rule which appears to
work well for slightly poly-disperse polymers, it is now
possible to model polystyrene with a range of poly-disper-
sities from $M_w/M_n = 1.00$ to $M_w/M_n = 2.00$ and view
the effect upon the relaxation time spectra and the
dynamic moduli. Six log-normal molecular weight
distributions were generated from Eqs. (9–12) with
$M_w = 352000$ g/mol (to stay with the PS sample above).
The poly-dispersities were set at $M_w/M_n = 1.01$, 1.05,
1.10, 1.25, 1.50, and 2.00 respectively. The resulting
distributions are shown in Fig. 9.

The relaxation spectra calculated using the molecular
weight distributions in Fig. 9, the BSW parameters for
polystyrene in Table 3, and Eq. (8) are displayed in
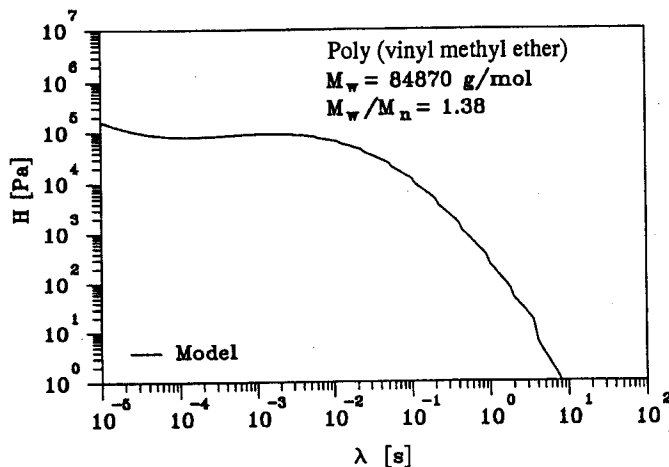Fig. 10. Notice that the spectrum marked with

Fig. 9 Several log-normal molecular weight distributions calculat-
ed from Eqs. (9–12) with $M_w = 350000$ g/mol and $M_w/M_n =$
1.01, 1.05, 1.10, 1.25, 1.50, and 2.00
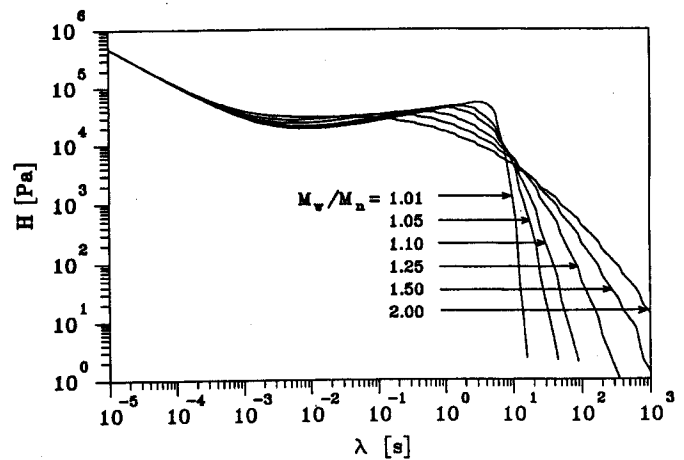
Fig. 10 Relaxation time spectra calculated from Eq. (8) using the
molecular weight distributions in Fig. 9 and the BSW parameters of
polystyrene

$M_w/M_n = 1.01$ is very nearly equal to the idealized BSW
spectrum of Eq. (1). On the other hand, the spectrum
marked with $M_w/M_n = 2.00$ has much longer relaxation
times and a flatter shape than the nearly mono-disperse
spectrum.

The dynamic moduli were calculated using Eqs. (13)
and (14) are shown in Figs. 11 and 12. It is evident that
the moduli with $M_w/M_n < 1.10$ are nearly indistinguish-
able from the mono-disperse limit and can be considered
nearly mono-disperse. When broadening the distribution,
the moduli with $M_w/M_n \geq 1.50$ have noticeably flattened
and must be considered *slightly* poly-disperse. The
distinct slope of the entanglement region cannot be
recognized any more.

Fig. 8 The relaxation time spectrum for the poly (vinyl methyl
ether) in Fig. 7 as calculated from Eq. (8). The BSW parameters
were chosen such that the best fit of the model and G' and G'' data
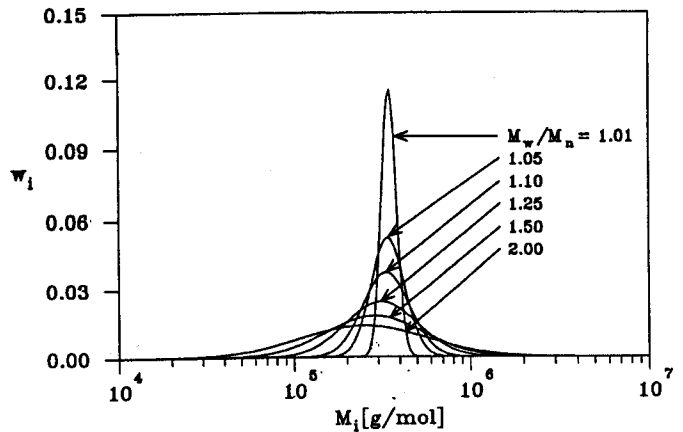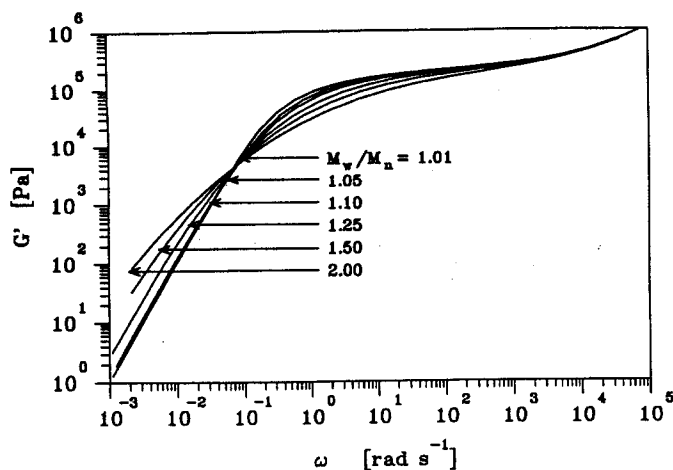was achieved and are listed in Table 3

Fig. 11 Storage moduli, $G'(\omega)$, calculated from Eq. (13) using the spectra displayed in Fig. 10. The broadening of the molecular size distribution expresses itself in the broadening of the transition from the flow to the entanglement zone
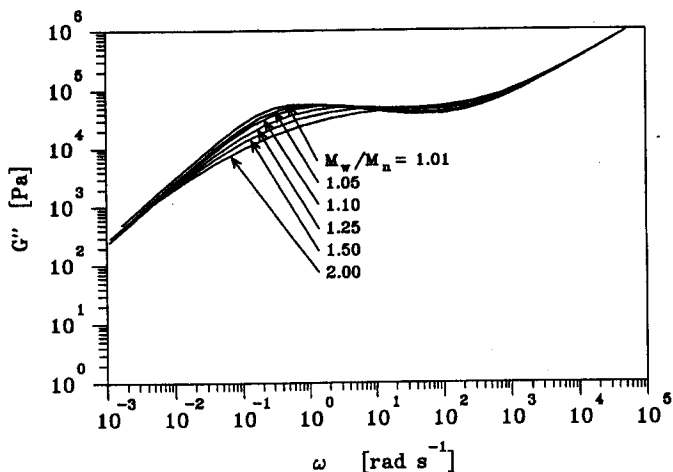

Fig. 12 Loss moduli, $G''(\omega)$, calculated from Eq. (14) using the spectra displayed in Fig. 10

Discussion

Comparison of BSW parameters

The BSW parameters obtained from nearly mono-disperse polystyrene data (Table 1) and the BSW parameters obtained from the slightly poly-disperse polystyrene (Table 2) are in agreement with the exception of the plateau modulus, G_N^0, which showed a variation of 20%. Since the nearly mono-disperse data was obtained from a different instrument than the slightly poly-disperse data,

it is possible that the change is due to equipment differences. In addition, any error in setting the gap between the plates would translate to an apparent change in the G_N^0.

It should be emphasized that the BSW parameters are a linear viscoelastic fingerprint of the material, and as such they should reflect differences in the chemical structure of the polymer. The technique presented here, which allows evaluation of these parameters from slightly poly-disperse data, greatly extends our ability to compare the behavior of materials with different chain chemistry and provides the opportunity to understand the relationship between chemistry and viscoelasticity.

One parameter of interest, M_c, reflects the length of chain required to observe entanglement effects and is an indication of the stiffness of the polymer chain. Clearly, of the three materials considered here, polycarbonate is the most flexible with $M_c = 5010$ g/mol and polystyrene is least flexible with $M_c = 16600$ g/mol. It should be pointed out that M_c is not necessarily equal to the entanglement molecular weight, M_e, which normally is defined by the plateau modulus,

$$M_e = \frac{\rho R T}{G_N^0} , \qquad (15)$$

where ρ is the density, R is the ideal gas constant, and T is the absolute temperature. Several theories have been suggested to relate M_c and M_e, and empiricists have traditionally assumed $M_c = 2M_e$, but the relationship cannot yet be predicted for any material (Ferry, 1980).

A second parameter of interest is the crossover relaxation time, λ_c, which is the longest relaxation time of a chain just long enough to entangle. It is difficult to compare λ_c for different polymers because relaxation times depend upon the reference temperature. Each of the materials discussed here has a different reference temperature and the temperature windows of the master curves and their associated WLF coefficients do not allow shifting of all of the crossover relaxation times, λ_c, to the same reference temperature. It can be suggested, however, that λ_c is a characteristic time which marks the onset of the dynamic glass transition. It is expected that λ_c depends on the distance from the glass transition temperature of the material, T_g.

The other three BSW parameters, the scaling exponent z, the entanglement exponent, m, and the glass transition exponent, n, appear to be insensitive to changes in chain chemistry. In fact, molecular dynamics theories suggest that m and z should be the same for any linear flexible highly entangled polymer (de Gennes, 1979; Doi et al., 1986; Schweizer, 1989, 1991, 1993). For the materials considered here, experimental values of n vary from 0.67 to 0.80 while z varies from 3.43 to 3.45. The entanglement exponent, m, is kept the same for all three materials.

Nearly mono-disperse polymers

The consequences of small deviations from mono-dispersity can be predicted (see Figs. 9−12). The deviations are indeed small for polymers with $1.00 < M_w/M_n < 1.10$. We therefore propose that the earlier method for obtaining BSW parameters from nearly mono-disperse materials (Baumgärtel et al., 1990; Jackson et al., 1994) may be safely applied to polymer standards. The method presented in this paper can be applied to any polymer with $M_w/M_n < 2.00$ and perhaps even to materials with M_w/M_n somewhat greater than 2.00. More experimental data are needed to show the limits of the SP blending rule.

Conclusions

The complexity of blend behavior increases gradually as the distribution of molecular sizes is broadened. The rheology of slightly poly-disperse polymers is still quite simple and closely related to their mono-disperse behavior. The broadening of the molecular size distribution expresses itself in the broadening of the transition from the flow to the entanglement zone. Experiments indicate that this broadening follows a universal pattern, at least up to $M_w/M_n < 2$.

The SP blending rule allows us to address the problems of finding the BSW parameters for polymers which are not available in a mono-disperse form. The measured $G'(\omega)$ and $G''(\omega)$ data can be decomposed into the contributions of mono-disperse components which can then be expressed in terms of its BSW parameters. This technique was applied to slightly poly-disperse polycarbonate and poly (vinyl methyl ether) and characteristic parameters were evaluated. It is suggested that this technique will allow a more thorough investigation of the relationship between chain chemistry and linear viscoelastic behavior, because many materials which can only be synthesized in a slightly poly-disperse form can now be compared to the reference state of the completely mono-disperse polymer. The earlier method of evaluating the parameters associated with the mono-disperse polymer was demonstrated to work only for $M_w/M_n < 1.10$ whereas the currently proposed blending rule applies at least up to M_w/M_n of 2 and perhaps higher, provided that the components all have molecular weights well above M_c.

References

Baumgärtel M, Schausberger A, Winter HH (1990) The relaxation of mono-disperse linear flexible polymers. Rheol Acta 29:400

Baumgärtel M, Winter HH (1990) Unpublished results

Baumgärtel M (1991) The relaxation of linear flexible polymers: correlation between molar mass distribution and rheological data of polymer melts. Ph. D. Dissertation, University of Massachusetts at Amherst

Berry G, Fox T (1968) The viscosity of polymers and their concentrated solutions. Adv Polym Sci 5:261

Bogue D, Masuda T, Einaga Y, Onogi S (1970) A constitutive model for molecular weight and concentration effects in polymer blends. Polym J 5:563

de Gennes P (1979) Scaling concepts in polymer physics. Cornell University Press, Ithaca

des Cloizeaux J (1990) Relaxation and viscosity anomaly of melts made of long entangled polymers. Time dependent reptation. Macromolecules 23 (21):4678

Doi M, Edwards S (1986) The theory of polymer dynamics. Clarendon Press, Oxford

Eder G, Janeschitz-Kriegl H, Liedauer S, Schausberger A, Stadlbauer W (1989) The influence of molar mass distribution on the complex moduli of polymer melts. J Rheol 33(6):805

Ferry J (1980) Viscoelastic properties of polymers. Wiley, New York

Graessley W, Struglinski M (1986) Effects of poly-dispersity on the linear viscoelastic properties of entangled polymers. 2. Comparison of viscosity and recoverable compliance with tube model predictions. Macromolecules 19:1754

Jackson J, De Rosa M, Winter H (1994) Molecular weight dependence of relaxation time spectra for the entanglement and flow behavior of mono-disperse linear flexible polymers. Macromolecules 27 (9):2426

Kornfield J, Fuller G, Pearson D (1991) Third normal stress difference and component relaxation spectra for bi-disperse melts under oscillatory shear. Macromolecules 24 (19):5429

Kurata M, Osaki K, Einaga Y, Sugie T (1974) Effect of molecular weight distribution on viscoelastic properties of polymers. J Polym Sci 12:849

Marin G, Graessley W (1977) Viscoelastic properties of high molecular weight polymers in the molten state. I. Study of narrow molecular weight distribution samples. Rheol Acta 16:527

Marrucci G (1985) Relaxation by reptation and tube enlargement: A model for poly-disperse polymers. J Polym Sci 23:159

Montfort J, Marin G, Arman J, Monge P (1978) Blending law for binary blends of fractions of linear polystyrene. Polymer 19:277

Montfort J, Marin G, Arman J, Monge P (1979) Viscoelastic properties of high molecular weight polymers in the molten state. II. Influence of the molecular weight distribution on linear viscoelastic properties. Rheol Acta 18:623

Morozov V (1984) Methods for solving incorrectly posed problems. Springer, Berlin

Ninomiya K (1959) Effects of blending on the stress-relaxation behavior of poly-vinyl acetate in the rubbery region. J Colloid Sci 14:49

Onogi S, Masuda T, Kitigawa K (1970) Rheological properties of anionic polystyrenes. I. Dynamic viscoelasticity of narrow-distribution polystyrenes. Macromolecules 3:109

Polios I (1994) Private communication

Polios IS, Soliman M, Lee C, Gido SP, Schmidt-Rohr K, Winter HH (1996) Late stages of phase separation in a binary polymer blend studied by rheology, optical and electron microscopy, and solid state NMR to be submitted to Macromolecules

Prest W (1973) Blending laws for high-molecular weight polymer melts. Polym J 4:163

Prest W, Porter R (1973) The effects of high-molecular-weight components on the viscoelastic properties of polystyrene. Polym J 4:154

Rubinstein M, Helfand E, Pearson D (1987) Theory of poly-dispersity effects on polymer rheology. Binary distribution of molecular weights. Macromolecules 20:822

Rubinstein M, Colby R (1988) Self-consistent theory of poly-disperse entangled polymers: Linear viscoelasticity of binary blends. J Chem Phys 89(8):5291

Schausberger A, Schindlauer G, Janeschitz-Kriegl H (1985) Linear elastico-viscous properties of molten standard polystyrenes. I. Presentation of complex moduli; role of short range structural parameters. Rheol Acta 24:220

Schausberger A (1986) A simple method of evaluating the complex moduli of polystyrene blends. Rheol Acta 25:596

Schindlauer G, Schausberger A, Janeschitz-Kriegl H (1985) Linear elastico-viscous properties of molten standard polystyrenes. I. Improvement of conventional characterization on molar mass distribution. Rheol Acta 24:228

Schweizer KS (1989) Microscopic theory of the dynamics of polymeric liquids: General formulation of a mode-mode-coupling approach. J Chem Phys 91:5802–5821

Schweizer KS (1989) Mode-coupling theory of the dynamics of polymer liquids: Qualitative predictions for flexible chain and ring melts. J Chem Phys 91:5822–5839

Schweizer KS (1991) Mode-mode-coupling theory of the dynamics of polymeric liquids. J Non-Cryst Solids 131–133:643–649

Schweizer KS (1993) Mode-coupling theory of macromolecular liquids. Physica Scripta T49:99

Tsenoglou C (1987) Viscoelasticity of binary homopolymer blends. ACS Polymer Preprints 28:185–186

Tuminello WH (1986) Molecular weight and molecular weight distribution from dynamic measurements of polymer melts. Polym Eng Sci 26:1339–1347

Tuminello WH, Cudre-Mauroux N (1991) Determining molecular weight distributions from viscosity versus shear rate flow curves. Polym Eng Sci 31:1496–1507

Wasserman S, Graessley W (1992) Effects of poly-dispersity on linear viscoelasticity in entangled polymer melts. J Rheol 36(4):543

Wasserman S (1995) Calculating the molecular weight distribution from linear viscoelastic response of polymer melts. J Rheol 39:601

Watanabe H, Kotaka T (1985) Viscoelastic properties and relaxation mechanisms of binary blends of narrow molecular weight distribution polystyrenes. Macromolecules 17:2316

Watanabe H, Sakamoto T, Kotaka T (1985) Entanglements in linear polystyrenes. Macromolecules 18:1436

Watanabe H, Tirrell M (1989) Reptation with configuration-dependent constraint release in the dynamics of flexible polymers. Macromolecules 22(2):927