An experimental appraisal of the Cox–Merz rule and Laun’s rule based on bidisperse entangled polystyrene solutions

Yu H. Wen, Hui C. Lin, Chang H. Li, Chi C. Hua

Department of Chemical Engineering, National Chung Cheng University, Chia-Yi 621, Taiwan, ROC

Received 25 May 2004; received in revised form 11 September 2004; accepted 7 October 2004
Available online 22 October 2004

Abstract

The empirical relationship provided by the Cox–Merz rule or Laun’s rule has frequently been employed for linking rheological data collected in steady-state shear experiment to those in dynamic oscillatory experiment for entangled polymer liquids. Good applicability of these empirical rules has generally been found, especially for nearly monodisperse systems; for polydisperse systems, however, discrepancies have occasionally been reported without explanations. To throw some light on the impact of blending on the applicability of these empirical rules for entangled polymer liquids, we scrutinize simultaneously the steady state and dynamic oscillatory data on a series of bidisperse entangled polystyrene solutions. The primary finding is that deviations from the predictions of these empirical rules are generally observable as the long chain becomes markedly dilute, especially for the case of Laun’s rule. The phenomenological effects of blending are tentatively interpreted in view of the contribution of chain stretching.

q 2004 Elsevier Ltd. All rights reserved.

Keywords: The Cox–Merz rule; Laun’s rule; Entangled polymer

1. Introduction

In rheological applications, the Cox–Merz rule [1] or Laun’s rule [2] (see corresponding formulas in Section 3; see also Ref. [3]) has frequently been employed for transforming rheological data or for checking consistency of the data collected in different experiments. For instance, because the linear viscoelastic data can, in general, be obtained more easily, these empirical rules can thus be utilized to predict corresponding viscometric properties in steady shear flows. In general, these empirical rules have found good applicability for entangled polymer liquids, especially for nearly monodisperse systems. For polydisperse systems, however, discrepancies have occasionally been reported without plausible explanations. For example, Yasuda and co-workers [4] have observed pronounced discrepancies with the prediction of the Cox–Merz rule at high shear rates for an entangled polystyrene solution with a broad weight distribution, whereas excellent agreement was generally found for other, nearly monodisperse solutions. Although there have been some conjectures concerning the effect of polydispersity in these experiments [5,6], no definitive conclusions have hitherto been reached in view of existing experimental data. On the other hand, we note that abuse of these empirical rules, frequently out of the range of entangled polymer liquids for which they were originally established, appears to be common. In this respect, Osaki and co-workers have pointed out [7] and shown experimentally [8] the general inapplicability of the Cox–Merz rule for nonentangled polymer solutions. Hence, experimental or theoretical investigations that may throw light on how well these empirical rules generally perform and, in particular, on the solution properties that might restrict their applicability are imperatively demanded.

To explore the impact of blending on the applicability of the aforementioned empirical rules for entangled polymer liquids, we scrutinize simultaneously the steady state and dynamic oscillatory data on a series of bidisperse entangled polystyrene solutions. On the basis of current experimental findings, we report specific blending conditions under which violations with these empirical rules appear to become
common, as well as the degree of deviation for each individual case. Then, the phenomenological effects of blending are tentatively interpreted in view of the contribution of chain stretching, leaving open other potential factors to future evaluations. This paper is organized as follows: Section 2 describes the experimental methods; Section 3 presents experimental results and corresponding analyses; finally, Section 4 summarizes the central findings of this study.

2. Experimental

Narrow weight distribution polystyrenes (PS), diethyl phthalate (DEP), and tricresyl phosphate (TCP) used in this study were purchased from Sigma–Aldrich Co. Nearly monodisperse as well as a series of bidisperse entangled polystyrene solutions (7 or 20 wt%) were prepared by first dissolving polystyrene with different molecular weights in DEP or TCP and then adding a large amount of cosolvent, methylene chloride, to ensure complete dissolution and homogeneity. After two weeks of mild and steady shaking at the ambient temperature, high volatility methylene chloride was removed first in a draft hood for one week and then in a vacuum oven for another two weeks. Subsequent rheological measurements were conducted after complete removal of cosolvent had been identified. Bidisperse entangled polystyrene solutions with a broad range of blending ratios of short to long chains were prepared; corresponding material properties were estimated on the basis of experimental observables and are tabulated in Table 1 along with those of monodisperse sample solutions. The nomenclature of bidisperse solutions is exemplified as follows: S2L4.3-10/17 denotes that the short-chain polymer \( (M_w = 2.0 \times 10^6 \text{ g/mol}) \) is mixed with the long-chain polymer \( (M_w = 4.3 \times 10^6 \text{ g/mol}) \) with a ratio 10/17 by weight.

To ensure consistency, rheological measurements have been conducted on two different rheometers (RDA II, Rheometric Scientific; MCR 500, Paar Physica) equipped with 25 mm diameter cone-and-plate (cone angle 2°, for taking steady-state data) or parallel-plates fixture (for taking dynamic oscillatory data) at 25, 40, and 90 °C, respectively. Prior to each measurement, bubbles produced during sample loading were removed via thermal convection at 90 °C for 1–5 h. Figs. 1 and 2 show, respectively, typical results of small-amplitude oscillatory measurement and startup of steady shear measurement on a nearly monodisperse sample solution, PS2M2a. The strain magnitudes used in dynamic oscillatory experiments were carefully selected by performing amplitude sweep that determined the limit of the linear viscoelastic range for the individual solutions. On the other hand, the maximum shear rate achieved (ca. 300 s\(^{-1}\)) in steady shear experiment was noted to be apart from the onset of flow instabilities. The average number of entanglements per chain for each sample solution was estimated using the relation \( Z_{\text{eq}} = M_w/(M_c)_{\text{sol}} \), where the molecular weight between adjacent entanglements in solution \((M_c)_{\text{sol}}\) was estimated as follows: For solutions in the concentrated regime (i.e. concentration above ca. 9 wt%) \((M_c)_{\text{sol}} = 13,300 \phi^{-1}\) was employed [9,10], whereas for solutions in the semidilute regime \((M_c)_{\text{sol}} = 10,200 \phi^{-1.3}\) was employed [11], where \( \phi \) is the polymer volume fraction. Other material properties tabulated in Table 1 were estimated using typical relations:

\[
\eta_0 = \eta' (\omega) \big|_{\omega \to 0},
\]

\[
\eta_0^* = \eta_0^2 [G'/\omega^2]_{\omega \to 0},
\]

and \( \tau_{\text{rep}} = \eta_0 \phi^0 \), where \( \eta_0, \eta_0^*, G', \) and \( \tau_{\text{rep}} \) denote the zero-shear-rate viscosity, the steady-state compliance, the storage modulus, and the reptation time, respectively. One can see from this table that the material properties obtained are typical of entangled polymer liquids. For instance, the zero-shear viscosity, \( \eta_0 \), for monodisperse sample solutions with the same polymer concentration scales closely with the power of 3.5 of polymer molecular weight, whereas the steady-state compliance, \( \eta_0^* \), is roughly independent of the molecular weight [12]. In order not to introduce systematical errors in the evaluation of the Cox–Merz rule or Laun’s rule, only raw experimental data were utilized in the subsequent analysis, namely, no attempts were made to transform rheological data collected at different temperatures by using time-temperature superposition. In addition, Table 2 lists the estimated Rouse time constants for some of the sample solutions, provided for a later discussion on the role played by chain stretching in this experiment.

3. Results and discussion

3.1. The Cox–Merz rule

The Cox–Merz rule states that the shear-rate dependence of the steady-state viscosity, \( \eta(\dot{\gamma}) \), is equivalent to the frequency dependence of the complex viscosity, \( \eta' (\omega) \):

\[
\eta(\dot{\gamma}) = |\eta'(\omega)|_{\omega=\dot{\gamma}} = \sqrt{[(G'/\omega)^2 + (G''/\omega^2)]_{\omega=\dot{\gamma}}} \quad (1)
\]

where \( G' \) and \( G'' \) are the storage and loss moduli, respectively. For monodisperse entangled polystyrene solutions, excellent agreement with this empirical rule has been found for all the cases investigated, as exemplified in Fig. 3. Thus, the current experimental results are in accord with earlier experimental findings.

To proceed with the case of bidisperse solutions, it appears relevant to mention first the extensional-flow experiments conducted by Münstedt [13], who has impressively demonstrated that a polystyrene melt with a high-molecular-weight tail in the weight distribution was able to exhibit distinctively pronounced strain-hardening in the transient elongational viscosity that, however, was absent for other polydisperse melt samples. Additionally, the composition of the melt sample that demonstrated the most prominent strain-hardening phenomenon may be closely mimicked by a bimodal distribution in polymer
weight. On the other hand, by noting an essential difference in the high shear rate/frequency responses for entangled polymer liquids [5], it has been suggested that chain stretching will ultimately result in violations of the empirical rules under investigation. In correlating the aforementioned observation and prediction, it appears that the present experiment based on bidisperse polystyrene solutions may thus provide an ideal test of the conjectured effect of chain stretching. Consequently, a series of bidisperse entangled polystyrene solutions have been prepared, with a ratio of chain length around two and polymer weight from 10:17 (long-chain rich) to 15:1 (short-chain rich) (see Table 1). Particular attention will be paid to the cases in which the long-chain component remains dilute.

The general observation for bidisperse sample solutions is the following: As the weight fraction of the long chain remains comparable to that of the short chain, the validity of the Cox–Merz rule is found to be largely unaffected by blending, as shown in Fig. 4 for the case S2L4.3-4/1. As the long chain becomes increasingly dilute, however, certain systematical deviations at high shear rates become observable, as shown in Figs. 5 and 6. Namely, the steady-state

### Table 1

Material properties for polystyrene solutions investigated in this study

<table>
<thead>
<tr>
<th>Monodisperse solutions</th>
<th>Sample code</th>
<th>$M_w$ ($10^{-6}$ g/mol)</th>
<th>PL</th>
<th>Solvent</th>
<th>Wt%</th>
<th>$Z_{eq}$</th>
<th>$\eta_0$ (Pa s)</th>
<th>$J_0^s$ (Pa^{-1})</th>
<th>$\tau_{rep}$ (s)</th>
<th>$T$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS1M</td>
<td>1.04</td>
<td>1.07</td>
<td>DEP</td>
<td>7</td>
<td>3.4</td>
<td>6.63 x 10^{2}</td>
<td>5.85 x 10^{-4}</td>
<td>0.39</td>
<td>298</td>
<td></td>
</tr>
<tr>
<td>PS2Ma</td>
<td>2.0</td>
<td>1.09</td>
<td>DEP</td>
<td>7</td>
<td>6.5</td>
<td>1.73 x 10^{4}</td>
<td>3.66 x 10^{-4}</td>
<td>6.33</td>
<td>298</td>
<td></td>
</tr>
<tr>
<td>PS4.3M</td>
<td>4.3</td>
<td>1.16</td>
<td>DEP</td>
<td>7</td>
<td>14.0</td>
<td>9.43 x 10^{4}</td>
<td>6.98 x 10^{-4}</td>
<td>65.8</td>
<td>298</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bidisperse solutionsa</th>
<th>Sample code</th>
<th>Polymer weight fraction (S:L)</th>
<th>PL (S/L)</th>
<th>Wt%</th>
<th>$Z_{eq1}$</th>
<th>$Z_{eq2}$</th>
<th>$\eta_0$ (Pa s)</th>
<th>$T$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2L4.3-10/17</td>
<td>10:17</td>
<td>1.14</td>
<td>7</td>
<td>6.9</td>
<td>14.8</td>
<td>6.99 x 10^{2}</td>
<td>313</td>
<td></td>
</tr>
<tr>
<td>S2L4.3-10/14</td>
<td>10:14</td>
<td>1.15</td>
<td>7</td>
<td>6.9</td>
<td>14.8</td>
<td>5.85 x 10^{2}</td>
<td>313</td>
<td></td>
</tr>
<tr>
<td>S2L4.3-1/1</td>
<td>1:1</td>
<td>1.15</td>
<td>7</td>
<td>6.9</td>
<td>14.8</td>
<td>5.75 x 10^{2}</td>
<td>313</td>
<td></td>
</tr>
<tr>
<td>S2L4.3-4/1</td>
<td>4:1</td>
<td>1.1</td>
<td>7</td>
<td>6.9</td>
<td>14.8</td>
<td>2.87 x 10^{2}</td>
<td>313</td>
<td></td>
</tr>
<tr>
<td>S2L4.3-7/1</td>
<td>7:1</td>
<td>1.07</td>
<td>7</td>
<td>6.9</td>
<td>14.8</td>
<td>2.6 x 10^{2}</td>
<td>313</td>
<td></td>
</tr>
<tr>
<td>S2L4.3-8/1</td>
<td>8:1</td>
<td>1.06</td>
<td>7</td>
<td>6.9</td>
<td>14.8</td>
<td>1.99 x 10^{2}</td>
<td>313</td>
<td></td>
</tr>
<tr>
<td>S2L4.3-10/1</td>
<td>10:1</td>
<td>1.05</td>
<td>7</td>
<td>6.9</td>
<td>14.8</td>
<td>1.59 x 10^{2}</td>
<td>313</td>
<td></td>
</tr>
<tr>
<td>S2L4.3-12/1</td>
<td>12:1</td>
<td>1.04</td>
<td>7</td>
<td>6.9</td>
<td>14.8</td>
<td>1.52 x 10^{2}</td>
<td>313</td>
<td></td>
</tr>
<tr>
<td>S2L4.3-15/1</td>
<td>15:1</td>
<td>1.04</td>
<td>7</td>
<td>6.9</td>
<td>14.8</td>
<td>1.46 x 10^{2}</td>
<td>313</td>
<td></td>
</tr>
<tr>
<td>S0.7L2-5/1</td>
<td>5:1</td>
<td>1.17</td>
<td>20</td>
<td>11.2</td>
<td>32.2</td>
<td>7.7 x 10^{3}</td>
<td>313</td>
<td></td>
</tr>
<tr>
<td>S0.7L2-10/1</td>
<td>10:1</td>
<td>1.1</td>
<td>20</td>
<td>11.2</td>
<td>32.2</td>
<td>3.59 x 10^{3}</td>
<td>313</td>
<td></td>
</tr>
<tr>
<td>S0.7L2-10/1</td>
<td>10:1</td>
<td>1.1</td>
<td>20</td>
<td>11.2</td>
<td>32.2</td>
<td>2.39 x 10^{2}</td>
<td>363</td>
<td></td>
</tr>
<tr>
<td>S0.7L2-12/1</td>
<td>12:1</td>
<td>1.09</td>
<td>20</td>
<td>11.2</td>
<td>32.2</td>
<td>1.3 x 10^{3}</td>
<td>313</td>
<td></td>
</tr>
</tbody>
</table>

a All binary blends were prepared using TCP as a solvent.

Fig. 1. Dynamic moduli measured in small-amplitude oscillatory experiments for a monodisperse solution, PS2Ma; measurements were conducted at 25 °C.
viscosity data at high shear rates exhibit a slight yet systematical upturn with respect to the complex viscosity data. Moreover, we note that the sample compositions for these cases are indeed very close to that employed in Münstedt’s experiment where prominent chain stretching had been identified. Further dilution of the long chain ultimately brings the solution back to near monodispersity, and the comparison was found (but not shown here) to be no different from those observed earlier for monodisperse sample solutions. It should be mentioned that excellent reproducibility of the dynamic oscillatory data was generally fulfilled, and the error bars of steady-state viscometric data, including the first normal stress difference coefficient, evaluated on the basis of three independent experimental runs were generally found to be less than the size of the symbols utilized in the plot. Therefore, the previously observed deviations at high shear rates cannot be attributed to the effect of experimental uncertainties. Specifically, the maximum deviation observed in Fig. 5 or 6 based on the complex viscosity data is ca. 18%.

3.2. Laun’s rule

Laun’s rule relates the first normal stress difference coefficient \(\Psi_1(\dot{\gamma})\) measured in steady shear experiments to the dynamic moduli as

\[
\Psi_1(\dot{\gamma}) = 2(G'/\omega^2)[1 + (G''/G_0^0)^2]\bigg|_{\omega = \dot{\gamma}}
\]

where the power-law index \(a\) was originally given as 0.7. In contrast with the case of the Cox–Merz rule, the validity of Laun’s rule has not been so extensively tested against experimental data on various polymer liquids. In fact, even the exponent \(a\) in Eq. (2) is itself a debating issue (see, for example, discussion in Ref. [5] and references cited therein). Hence, three common choices: \(a = 0, 0.5, \text{and} 0.7\) are simultaneously investigated in this study.

Fig. 7 shows a typical transient behavior of the first normal stress difference coefficient for a monodisperse entangled polystyrene solutions, respectively. Finally, in view of the conjectured role of chain stretching, subsequent investigations on Laun’s rule should serve as a better probe because the normal stress measurements are more susceptible to the effect of chain stretching.

Table 2

<table>
<thead>
<tr>
<th>Sample code</th>
<th>(\tau_{R_0} (s))</th>
<th>(\tau_{K} (s))</th>
<th>(\tau_{R} (s))</th>
<th>(T (K))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS2Mbr</td>
<td>0.62</td>
<td>0.73</td>
<td>0.38</td>
<td>313</td>
</tr>
<tr>
<td>PS2Mb</td>
<td>0.014</td>
<td>0.09</td>
<td>0.025</td>
<td>363</td>
</tr>
</tbody>
</table>

\(a\) \(\tau_{R_0} = (6M_e/\pi c RT)(1.5M_e/M)^{2.4}\) [14], where \(c\) is the polymer weight per unit volume, and \(M_e\) is the entanglement molecular weight in solution.

\(b\) \(\tau_{K} = \tau_{rep}/3Z_{eq}\) where \(\tau_{rep}\) is estimated in a way as described in the text.

\(c\) \(\tau_{R} = \tau_{cross}/3Z_{eq}\) where \(\tau_{cross}\) is the inverse frequency of the crossover of \(G'\) and \(G''\).
sample solution. The transient overshoots observed here are typical of entangled polymer solutions subject to fast shearing, and are known to be indicative of chain stretching. Due to the effect of transducer compliance, however, the transient normal stress data at short times could be unreliable, particularly at low shear rates; nevertheless, the steady-state values that were actually utilized in this experiment should be unaffected. An examination of Laun’s rule for a monodisperse sample solution is given in Fig. 8, where the dynamic oscillatory data have been utilized together with Eq. (2) to obtain the predictions for the first normal stress difference coefficient. This comparison reveals that the choice $a = 0.5$, instead of $a = 0.7$ as originally chosen, leads in general to the best agreement; and the prediction becomes the worst with the choice $a = 0$, especially at high shear rates (note that $a = 0$ corresponds to the case in which $\Psi_1$ of a polymer liquid is solely determined by the corresponding storage modulus, $G'$, both quantities being regarded as well representing the response of polymer elasticity.) Similar results were found for other monodisperse sample solutions. It is important to realize that the original Laun’s rule with $a = 0.7$ had primarily been constructed on the basis of experimental data on commercial, polydisperse melt samples, such as low- or high-density polyethylene. As we show momentarily, the previous choice (i.e. $a = 0.7$) is indeed a better one for most bidisperse sample solutions.

In fact, the essential observations for monodisperse sample solutions carry into bidisperse solutions, until the long chain becomes markedly dilute. Figs. 9 and 10 show the results for two bidisperse sample solutions with a composition similar to that considered in Fig. 5 or 6, where

---

**Fig. 3.** Comparison between steady-shear and complex viscosities for a monodisperse solution, PS2Ma; measurements were conducted at 25 °C.

**Fig. 4.** Comparison between steady-shear and complex viscosities for a bidisperse solution, S2L4.3-4/1; measurements were conducted at 40 °C.
there first appeared discernible deviations from the prediction of the Cox–Merz rule. Notably, one sees a pronounced systematical upturn of the first normal stress data at high shear rates with respect to the predictions based on Laun’s rule using dynamic oscillatory data. This type of ‘positive’ deviation is indeed very similar to that observed earlier in Fig. 5 or 6 for the Cox–Merz rule; it is also in accord with the conjectured effect of chain stretching in these experiments [5]. Specifically, the maximum deviations from the predictions of Eq. (2) are as high as $350\pm 30\%$ with $a=0.5$ and ca. $200\pm 20\%$ with $a=0.7$, respectively. By contrast, one sees in Fig. 11 no such deviations at a higher temperature, which is again consistent with the notion that chain retraction is accelerated at a higher temperature so that the impact of chain stretching is less prominent. It is also noteworthy that the comparisons shown in Ref. [3] (p. 152) have revealed a similar deviation as observed here for Laun’s rule.

At this point, an interesting question is whether the observed deviations from the Cox–Merz rule or Lanu’s rule do indeed correlate with the effect of chain stretching? To help clarify this issue, the associated Rouse time constants have been estimated and tabulated in Table 2. The current estimates of the Rouse time constant for the long-chain component make use of both an empirical relation [14] as well as the standard relation $\tau_R = \tau_{rep}/3Z_{eq}$, based on data for monodisperse sample solutions with the same polymer concentration as for the bidisperse solutions of interest. From Table 2, one sees that the estimated Rouse times are of the same order of magnitude in each case, and are indeed quite close for the case $T=40^\circ C$. According to the estimated Rouse times, chain stretching of the long chain...
is predicted to be active in most of the shear rate/frequency regime for the comparisons made in Figs. 8–10 (where $\tau_R^{-1} \approx 2 \text{s}^{-1}$), in contrast with the case in Fig. 11 (where $\tau_R^{-1} \approx 50 \text{s}^{-1}$). Thus, it is curious to know whether the effect of flow-induced entanglement loss, predicted to be pronounced even in steady-state shear flows [6], may have greatly suppressed the capability of chain stretching under monodisperse or usual blending conditions. Since Münstedt’s experiment has essentially implied that dilute long chain being dissolved in a short-chain matrix is exceptionally favorable for significant chain stretching to develop, it might well be that under a similar blending condition the net entanglement loss on the long-chain component is effectively suppressed [6] and an apparent violation of the Cox–Merz rule or Laun’s rule can thus be appreciated.

Another essential observation that also coincides with Münstedt’s observations in extensional-flow experiments for the effect of polydispersity is that the apparent effect of blending on the applicability of the Cox–Merz rule or Laun’s rule does not seem to correlate with the polydispersity index (PI), as also provided in Table 1, for the sample solutions that exhibited the most pronounced deviations generally bear only a small PI value. Moreover, we mention that the conjectured effect of chain stretching can also explain the central observation that no similar relationships have been established for extensional flows of entangled polymers, in particular, or for nonentangled polymer solutions, in general, where the constituting chain can stretch significantly with flow. Of course, experimental evidence is so far insufficient for one to conclude whether ‘chain stretching’ is among the primary factors governing the applicability of the investigated empirical rules.

![Fig. 7. Transient behavior of the first normal stress difference coefficient for a monodisperse solution, PS2Mb, following startup of steady shearing at various shear rates; measurements were conducted at 40 °C.](image1)

![Fig. 8. Comparison between experimentally measured first normal stress difference coefficient (points) and predictions (lines) based on Laun’s rule using dynamic modulus data with various values of power-law index $a$ in Eq. (2) for a monodisperse solution, PS2Mb; measurements were conducted at 40 °C.](image2)
Therefore, it is wished that the current experiment will stimulate more extensive experimental or theoretical investigations focusing on the molecular origins of these empirical rules.

4. Conclusions

The effect of blending on the applicability of the Cox–Merz rule or Laun’s rule has been systematically investigated on the basis of a series of nearly monodisperse as well as bidisperse entangled polystyrene solutions. For the case of nearly monodisperse solutions, both rules were found to hold excellently, although a slightly different exponent, \( a = 0.5 \), in Laun’s rule was found to be better applicable to the current data (it is surmised by the authors that the exponent \( a = 0.7 \) was originally chosen by Laun because data on polydisperse melt samples had primarily been utilized to construct the empiricism). This observation is in good agreement with earlier experimental findings. For the case of bidisperse solutions, however, experimentally measured steady-state viscometric properties at high shear rates exhibited systematical, positive deviations from the predictions of either rule based on dynamic oscillatory data as the long chain becomes markedly dilute. Specifically, the Cox–Merz rule finds good applicability in general (i.e. the deviation generally falls below 18\%\%), whereas the validity of Laun’s rule appears to be more susceptible to the effect of blending (i.e. the deviation can be as high as 35\%\%). This type of deviation is indeed very similar to what had earlier been observed for some commercial, polydisperse entangled polymer solutions or melts [3]. However, the effect of blending currently revealed does not seem to correlate with the polydispersity index, for the sample solutions that exhibited the most pronounced deviations generally bear only a small PI value. This

Fig. 9. Comparison between experimentally measured first normal stress difference coefficient (points) and predictions (lines) based on Laun’s rule using dynamic modulus data with various values of \( a \) for a bidisperse solution, S0.7L2-10/1; measurements were conducted at 40 °C.

Fig. 10. Comparison between experimentally measured first normal stress difference coefficient (points) and predictions (lines) based on Laun’s rule using dynamic modulus data with various values of \( a \) for a bidisperse solution, S0.7L2-12/1; measurements were conducted at 40 °C.
observation may explain the fact that conflict with either rule had only occasionally been reported for some polydisperse entangled polymer liquids. On the other hand, the current experimental trends are tentatively interpreted in view of the contribution of chain stretching; the inferred correlation, nevertheless, is inconclusive and further experimental or theoretical appraisals are imperatively demanded.

Acknowledgements

The authors thank the reviewer for instructive comments and information. The financial supports from the National Science Council as well as from the Excellency Project sponsored by the Education Ministry of the ROC through grant numbers: 92-2116-E-194-001 and 91-E-FA04-2-4A, respectively, are gratefully acknowledged.

References