Blending law for binary blends of fractions of linear polystyrene

J. P. Montfort, G. Marin, J. Arman and Ph. Monge
Laboratoire de Thermodynamique, Université de Pau et des Pays de l'Adour, 64000 Pau, France
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The dynamic behaviour of binary blends of linear polystyrene fractions in the terminal zone of the relaxation spectrum presents interesting peculiarities which have been discussed in a previous paper by Montfort. The viscoelastic properties are characterized by a representation in the complex plane of viscosities. In this paper, we propose an empirical blending law which represents such behaviour over a large range of frequencies. The conclusions of this law on the limiting values of η_0 and J_e^0 are compared with those deduced from the blending laws of Graessley and BMEO.

INTRODUCTION

The study of binary blends of polystyrene fractions exhibits a phenomenon of double relaxation in the terminal zone of the relaxation spectrum. Each field can be attributed to the prevailing action of one of the two components of the blend. This study, undertaken by one of our team, has been the object of a recent paper[1]. In the first section, we will sum up the main results of the study.

We will then describe the observed behaviour by stating a blending law expressing the properties of the blend as a function of the properties of each component and of the composition of the blend. The expression for the complex viscosity of blends, $\eta_b^*(\omega)$, that is proposed accounts for viscoelastic properties in the plateau zone and the terminal zone, and particularly for the variations of the limiting values η_{0b} and J_{eb}^0.

Other authors have proposed blending laws[2-5] that express the relaxation times distribution function of the blend, $H_b(\tau)$, as a function of that of each component. We will especially refer to the quadratic laws of Graessley[2] and BMEO[3]. An interesting critical study of these two laws has already been undertaken[6]. We will limit ourselves to examining the conclusions of both laws on limiting values η_{0b} and J_{eb}^0 and in particular, their agreement with the experimental results.

EXPERIMENTAL

The dynamic measurements were made with a Contraves—Kepes balance rheometer. The sample, located between two concentric rotating spheres, experiences a sinusoidal shearing[1].

Complex viscosity was measured in the temperature range $150°-190°C$, at frequencies varying from 10^{-4} to 20 Hz.

Materials

The fractions, manufactured by the Waters Associates Corporation, have a polydispersity lower than 1.1. We have used four fractions with an average molecular weight higher than the critical molecular weight for viscosities, M_c[17] (*Table 1*).

From these fractions, we have made up three series of blends. Each blend is designated as follows. The letter M is followed by six figures: the first two relate to the component with the lowest weight (component 1); the next two to the component with the highest weight (component 2); the last two represent the weight fraction Φ of component 2 in the blend. We will call r the weight ratio of both components: $r = M_{w1}/M_{w2}$.

Considering the fractions as strictly monodisperse products, the average weight M_w of the blend can be calculated from the weight fractions by the expression:

$$M_w = (1 - \Phi)M_{w1} + \Phi M_{w2} \qquad (1)$$

This value is entered in *Table 2*, which contains data relating to all the blends.

Table 1 Narrow molecular weight distribution polystyrene samples

Sample	M_w
PS 04	35 000
PS 11	110 000
PS 20	200 000
PS 40	400 000

Table 2 Features of the binary blends

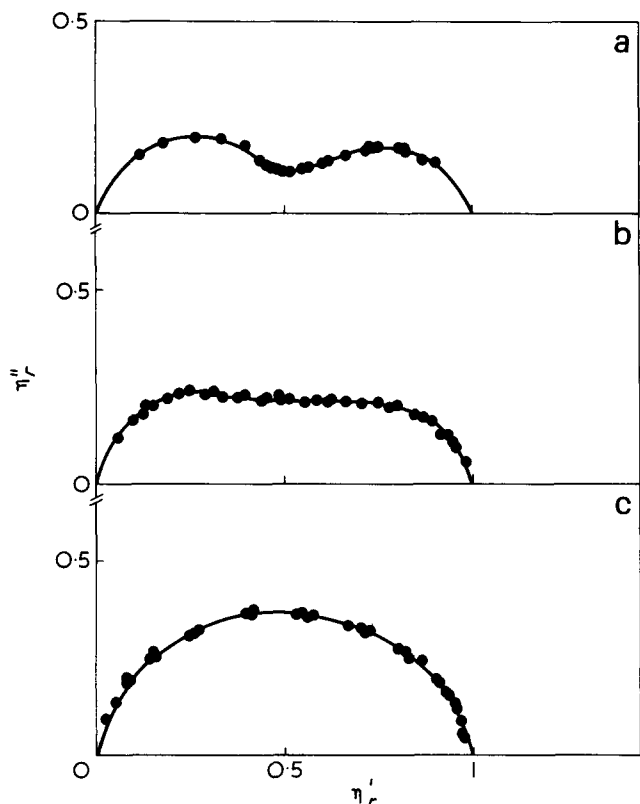| Series	Components	r	Blends	ϕ	M_w
M 0440	PS 04 +	11.5	M 044005	0.05	53 350
	PS 40		M 044015	0.15	90 500
M 1140	PS 11 +	3.64	M 114005	0.05	124 500
	PS 40		M 114010	0.10	139 000
			M 114015	0.15	153 500
			M 114025	0.25	182 500
			M 114050	0.50	255 000
M 1120	PS 11 +	1.82	M 112015	0.15	123 500
	PS 20		M 112030	0.30	137 000
			M 112070	0.70	173 000

Figure 1 Master curves of reduced complex viscosity for binary blends M 044005 (a), M 114015 (b) and M 112015 (c)

Measurements and results

We have shown[1] that:

(1) the use of complex viscosity $\eta^*(\omega)$ is interesting in order to represent the viscoelastic behaviour of high polymers in the terminal zone of the relaxation spectrum. It allows us to define: the zero shear viscosity

$$\eta_0 = \lim_{\omega \to 0} \eta'$$

the steady-state compliance

$$J_e^0 = \frac{1}{\eta_0^2} \lim_{\omega \to 0} \frac{\eta''}{\omega}$$

and for the fractions, an average relaxation time

$$\tau_0 = \frac{1}{\omega_m}$$

where ω_m is the frequency corresponding to the maximum of η'';

(2) in the complex plane, we can superpose the curves relating to one sample (fraction or binary blend) by representing the reduced complex viscosity:

$$\eta_r^* = \frac{\eta^*}{\eta_0} = \frac{\eta'}{\eta_0} - j\frac{\eta''}{\eta_0} = \eta_r' - j\eta_r''$$

(3) the curves η_r' and η_r'' can be represented as a function of frequency by master curves, using a shift factor, a_T, which has the same value for all the fractions and their binary blends.

The thermal variations of η_0 and τ_0 for the fractions show that, in the experimental temperature range (156° to 186°C):

$$a_T = \frac{\tau_0 T}{\tau_0 T_0} = \frac{\eta_0 T}{\eta_0 T_0}$$

which implies that J_e^0 (which is proportional to the ratio τ_0/η_0, as indicated by Rouse's theory[7] applied to an undiluted polymer[8]) is independent of temperature, within the limited temperature range;

(4) the curves relating to binary blends show a double relaxation phenomenon. The relative importance of each field varies in the same way as the proportion of the corresponding component in the blend. Their coupling is all the greater as the ratio r is nearer to unity (*Figure 1*).

(5) the variations observed for the limiting values η_{0b} and J_{eb}^0 of binary blends are in agreement with those given in the literature: the variations of η_{0b} as a function of the molecular weight can be expressed by $\eta_0 = kM_w^{3.4}$, as for the fractions[9–11] (*Figure 2*).

J_{eb}^0 passes through a maximum for a certain composition of the blend[10,12,13] (*Figure 3*).

Equations (1) and (2) indicate that η_{0b} can be expressed as a function of η_{01} and η_{02} in the form:

$$\eta_{0b}^{1/3.4} = (1 - \phi)\eta_{01}^{1/3.4} + \phi\eta_{02}^{1/3.4} \qquad (3)$$
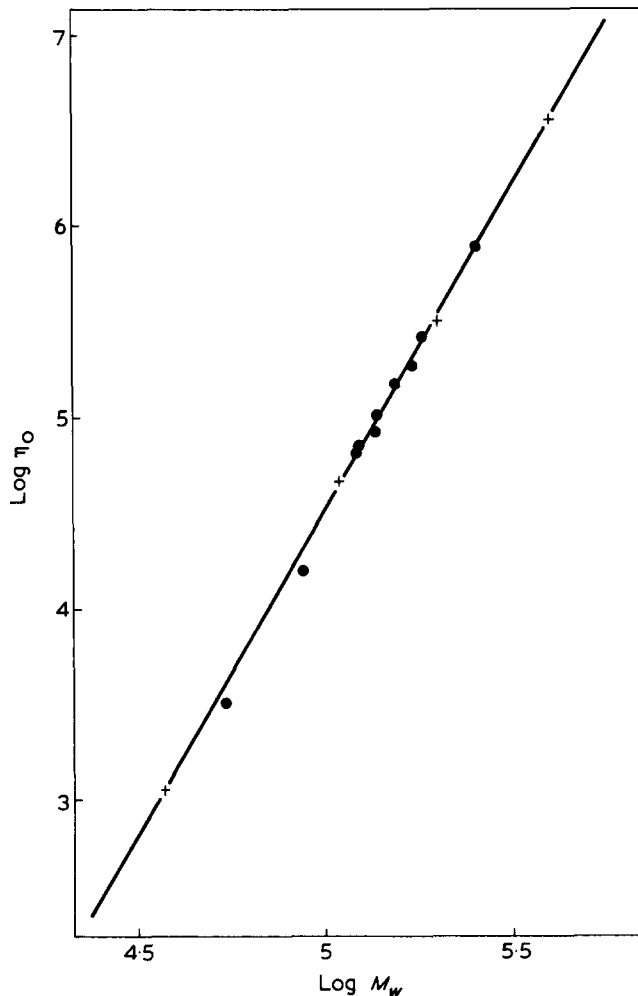

Figure 2 Zero shear viscosity plotted logarithmically against the molecular weight M_w for the fractions and their binary blends at 186°C
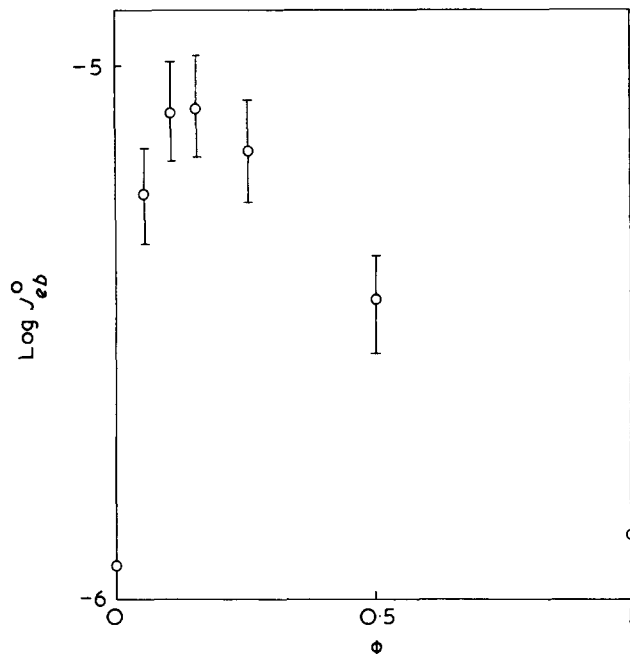
Figure 3 Steady state compliance for binary blends of the series M 1140

BLENDING LAW

We will use an analytical model in order to describe the rheological behaviour of these binary blends. After stating the law, we will compare it with the experiments and draw a parallel with the blending laws of Graessley and BMEO.

Stating the blending law

Let us try to state a simple relationship relating the complex viscosity of binary blends to the various parameters of the system. That is:

$$\eta_b^* = F(\omega, \phi, r, \eta_{01}, \eta_{02}, \tau_{01}, \tau_{02}, T)$$

The number of independent parameters can be reduced: the variable T (temperature) governs the variations of η_{0i} and τ_{0i} ($i = 1,2$) and can then be considered as an implicit variable; the expression for the complex viscosities η_i^* for the components can be expressed by

$$\eta_i^* = \eta_{0i}\eta_{ri}^*(\omega\tau_{0i}) \tag{4}$$

Hence, we can write:

$$\eta_b^* = F(\phi, r, \eta_1^*, \eta_2^*)$$

An extension of the blending law for limiting viscosities can then be written under the form:

$$\eta_b^*(\omega)^{1/P} = (1 - \alpha)\eta_1^*(\omega)^{1/P} + \alpha\eta_2^*(\omega)^{1/P} \tag{5}$$

with $\alpha = f(\phi,r)$, which meets the time/temperature superimposition principle.

When $\omega \to 0$, this expression leads to the relation:

$$\eta_{0b}(\omega)^{1/P} = (1 - \alpha)\eta_{01}^{1/P} + \alpha\eta_{02}^{1/P}$$

which must agree with equation (3). Hence we infer:

$$\alpha = \frac{(1 - \phi + r\phi)^{3.4/P} - 1}{r^{3.4/P} - 1} \tag{6}$$

using

$$r = \frac{M_{w2}}{M_{w1}} = \left(\frac{\eta_{02}}{\eta_{01}}\right)^{1/3.4}$$

This equation indicates that the proposed law [equation (5)] only depends on one adjustable parameter, p. In particular, if $p = 3.4$, $\alpha = \phi$.

We can also write equation (5) in the form:

$$\eta_{0b}^{1/P}\eta_{rb}^*(\omega)^{1/P} = (1 - \alpha)\eta_{01}^{1/P}\eta_{r1}^*(\omega)^{1/P} + \alpha\eta_{02}^{1/P}\eta_{r2}^*(\omega)^{1/P}$$

or

$$\eta_{rb}^*(\omega)^{1/P} = (1 - \theta)\eta_{r1}^*(\omega)^{1/P} + \theta\eta_{r2}^*(\omega)^{1/P} \tag{7}$$

with

$$\theta = \alpha\left(\frac{\eta_{02}}{\eta_{0b}}\right)^{1/P} = \frac{r^{3.4/P}}{r^{3.4/P} - 1}\frac{(1 - \phi + r\phi)^{3.4/P} - 1}{(1 + \phi + r\phi)^{3.4/P}}$$

Comparison with the experimental data

We will define the variations of parameter p as a function of ϕ and r from our experimental results and those of Masuda[10].

Test on η^* or G^*. For each blend, we are looking for the best value of p by adjusting the experimental values of η_b and the values drawn from equation (5), taking into account both the experimental values of η_1^* and η_2^* at the same frequency and the value of parameters ϕ and r.

For this, we need pairs of experimental values of (η_1^*, η_2^*) corresponding to the same frequency range. The experimental device does not enable us to obtain a sufficient overlapping. Sometimes even the frequency ranges are separated, as is shown by the curves relating to the PS 11 and the PS 40 in *Figure 6*.

Hence, we must search for an analytical expression accounting for our results on fractions in the experimental field and to assume analytical extensions in the frequency range that is beyond our reach. We have used an expression proposed by Le Traon[16] in the form:

$$\eta^* = \eta_0 \frac{1 + ja}{1 + j(\omega\tau + a)} \tag{8}$$

where a is a parameter with the same value for all fractions studied ($a = 0.22 \pm 0.01$) and τ is linked with τ_0 by the relation:

$$\tau_0 = \frac{\tau}{(1 + a^2)^{1/2}}$$

Figure 4 shows the agreement between the experimental points and the curves inferred from Le Traon's expression.

Using this analytical expression, and taking into account the accuracy of the measurements (with a relative uncertainty of 5%), the best agreement is obtained for series M 1120 (*Figure 5*) and M 1140 (*Figure 6*) with $P = 10 \pm 1$.
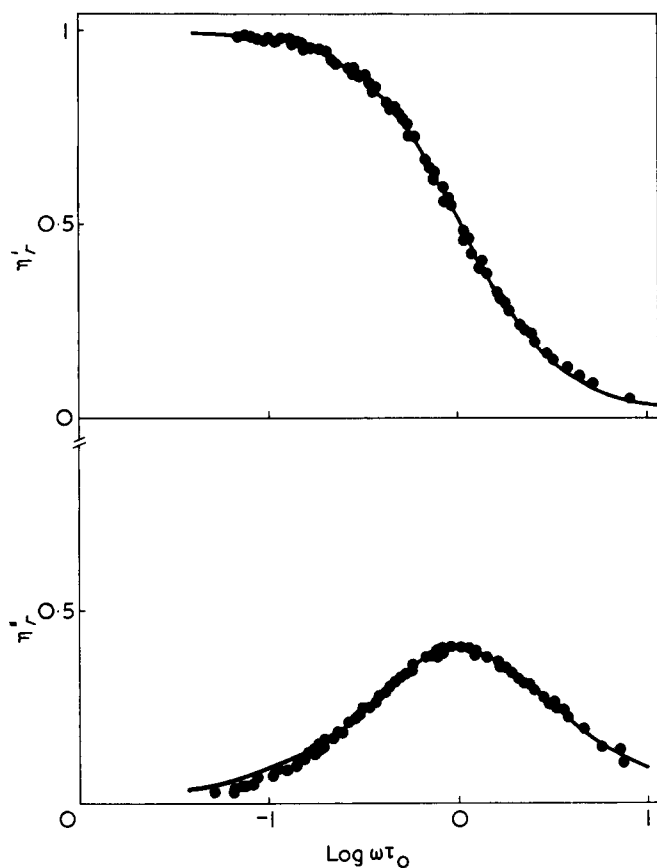
Figure 4 Frequency dependences of the componenents of the reduced complex viscosity for the fractions studied; the curves are deduced from equation (8)

Conversely, for series M 0440, the use of equation (7) does not lead to a satisfactory agreement. We have represented on *Figure 7* the curves corresponding to $p = 10$. The origin of the discrepancy certainly lies in the use of Le Traon's expression for representing the behaviour of the PS 04. In particular, in the higher frequency range, this analytical form leads to values for $\eta''(\omega)$ which are too low.

In order to confirm the validity of the proposed law, it should then be possible to discard an analytical expression representing the complex viscosity of fractions and to dispose of data in the same frequency range.

Then we have used the results of Masuda *et al.*[10] for the variations of the complex modulus G_b^* of binary blends of polystyrene fractions (*Table 3*).

Knowing that $G^* = j\omega\eta^*$, the blending law can be written

$$G_b^*(\omega)^{1/P} = (1 - \alpha)G_1^*(\omega)^{1/P} + \alpha G_2^*(\omega)^{1/P} \tag{9}$$

We have noticed on the corresponding curves the values of G_1^* and G_2^* for one particular frequency and entered these values into equation (9). The values of α are obtained from equation (6).

The curve obtained for the M 065850 (*Figure 8*) with $p = 10$ is in good agreement with the experimental points. This blend, which corresponds to a value of r just near 10 — then comparable with our series M 0440 — shows that the discrepancy noticed on this series was actually due to the use of Le Traon's expression.

Equation (9) correctly represents the other results of Masuda. *Figure 9* shows the agreement for the series BB3 (the blend M 051780 is not represented) with again $p \simeq 10$.

Test on the limiting values η_{0b} *and* J_{eb}^0. Equation (5) should also account for the experimental variations of the limiting values η_{0b} and J_{eb}^0.

The experimental blending law on limiting viscosities [equation (3)] is verified by the relation that we propose, as α has been defined from this blending law.

The expression for J_{eb}^0 can be inferred from equation (7), knowing that:

$$J_{eb}^0 = \frac{1}{\eta_{0b}^2} \lim_{\omega \to 0} \frac{\eta_b''}{\omega} = \frac{1}{\eta_{0b}} \lim_{\omega \to 0} \frac{\eta_{rb}''}{\omega}$$

and hence,

$$J_{eb}^0 = \frac{1}{\eta_0} \lim_{\omega \to 0} \left\{ \frac{1}{\omega} \mathrm{Im}\ [(1 - \theta)\eta_{r1}^*(\omega)^{1/P} + \theta\eta_{r2}^*(\omega)^{1/P}]^P \right\}$$

It may be noted[17] that for viscoelastic liquids at very low frequencies, the storage and loss moduli reduce to:

$$G' = \omega^2 \eta_0^2 J_e^0$$

$$G'' = \omega \eta_0$$

hence

$$\eta^* = \eta_0(1 - j\omega\eta_0 J_e^0)$$
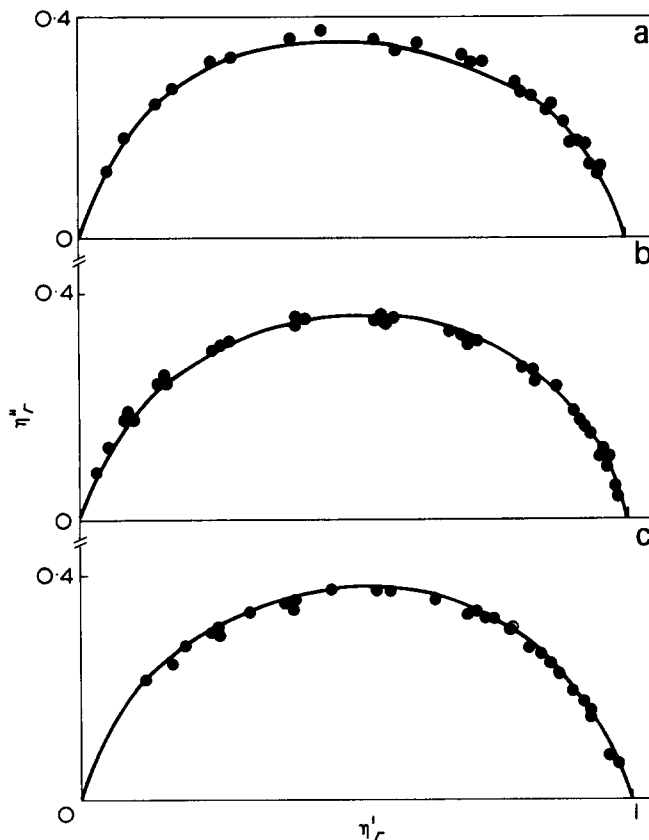
and

$$\eta_r^* = 1 - j\omega\eta_0 J_e^0$$

Figure 5 Curves of the reduced complex viscosity deduced from the blending law [relations (7) and (8)] for the series M 1120 a: M 112015; b: M 112030; c: M 112070
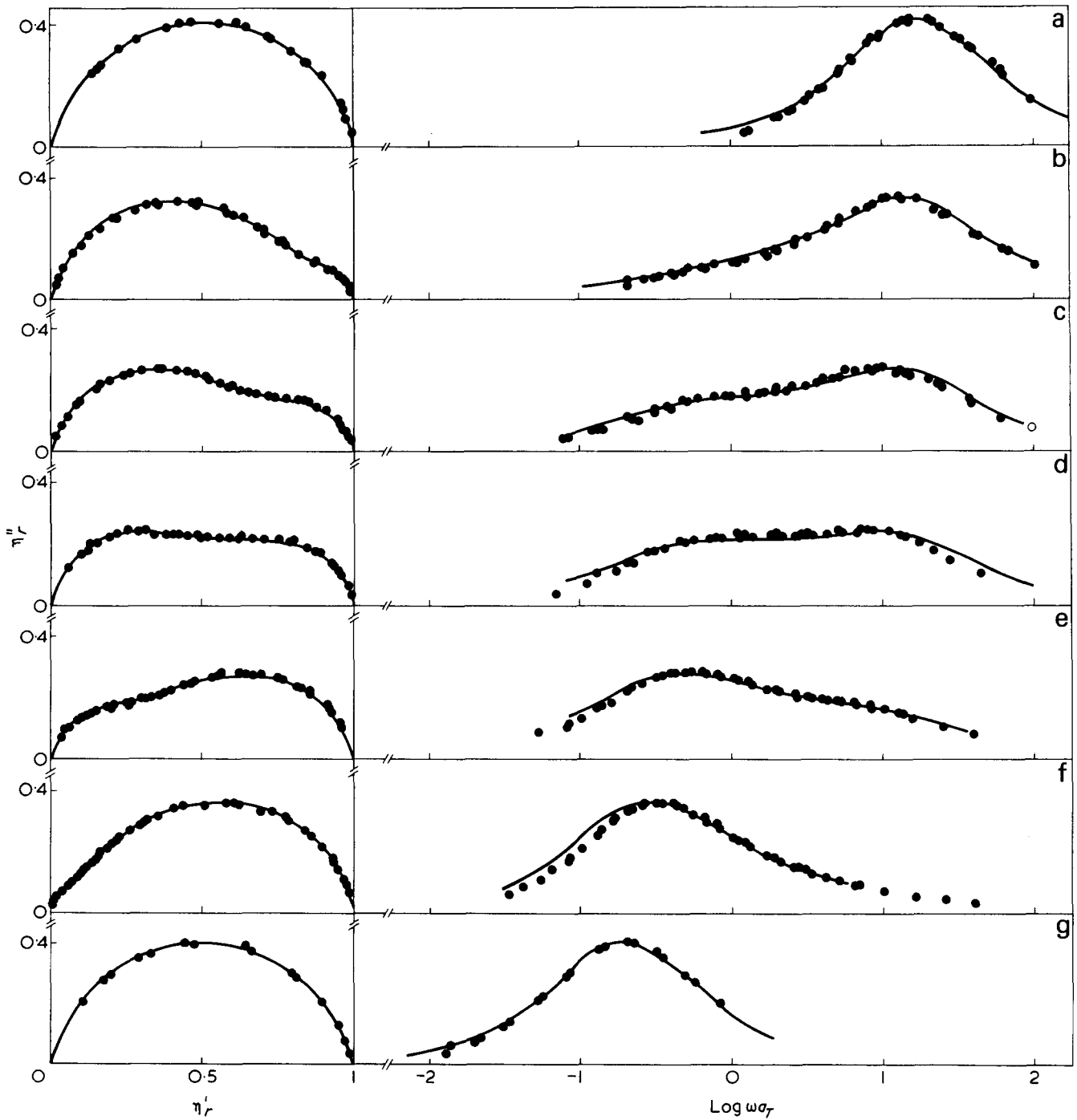
Figure 6 Curves of the reduced complex viscosity deduced from the blending law for the series M 1140: (a) PS 11; (b) M 114005; (c) M 114010; (d) M 114025; (e) M 114025; (f) M 114050; (g) PS 40; at T = 186°C

The latter expression implies for η_{r1}^{*} and η_{r2}^{*}:

$$\eta_{rb}^{''} = \omega\left[(1 - \theta)\eta_{01}J_{e1}^{0} + \theta\eta_{02}J_{e2}^{0}\right]$$

and hence

$$J_{eb}^{0} = \frac{(1 - \theta)\eta_{01}J_{e1}^{0} + \theta\eta_{02}J_{e2}^{0}}{\eta_{0b}}$$

We have seen that $\eta_{0}J_{e}^{0}$ is proportional to an average relaxation time of the terminal zone (for instance, to τ_{0}). Hence, we can deduce from equation (3):

$$J_{eb}^{0} = J_{e1}^{0}\frac{1 - \theta + T\theta}{(1 - \phi + r\phi)^{3.4}} \tag{10}$$

with

$$T = \frac{\eta_{01}J_{e1}^{0}}{\eta_{02}J_{e2}^{0}} = \frac{\tau_{01}}{\tau_{02}}$$

Curve A in *Figure 10* shows that there is satisfactory agreement between the experimental points (series M 1140) and the curve inferred from equation (10). This expression also accounts for the results obtained by other authors on
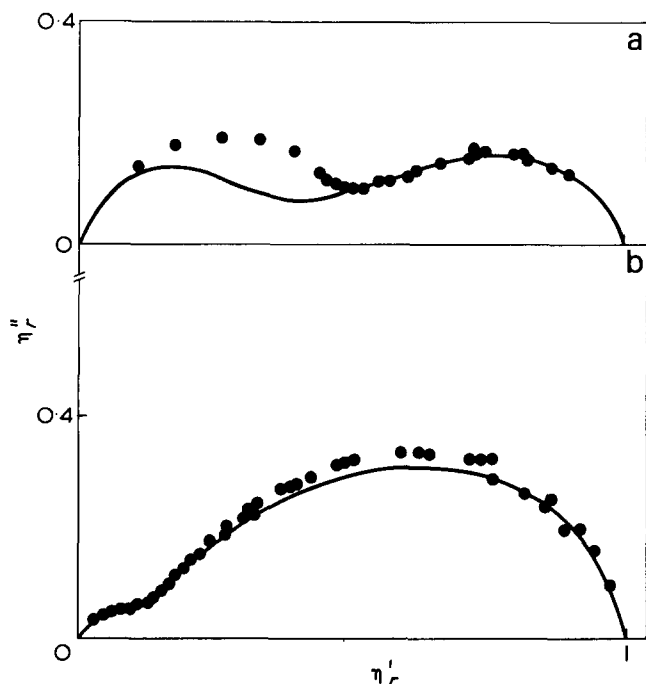
Figure 7 Curves of the reduced complex viscosity deduced to the blending law for the series M 0440: (a) M 044005; (b) M 044015

Table 3 Binary blends studied by Masuda et al.[10]

Series	Components	r	Blends	ϕ	M_W
BB 1	PS 06 + PS 58	9.9	M 065850	0.50	320 000
BB 2	PS 21 + PS 35	1.63	M 213550	0.50	288 000
BB3	PS 05 + PS 17	3.56	M 051720 M 051740 M 051760 M 051780	0.20 0.40 0.60 0.80	70 900 95 000 119 000 143 000

binary blends of polystyrene fractions, as is shown by *Figure 11*.

Quadratic laws of Graessley and BMEO. Other authors have dealt with the binary blends of polystyrene fractions and attempted to account for their rheological behaviour, in particular from an analysis of the function of distribution of relaxation times $H_b(\tau)$. So they have stated blending laws expressing $H_b(\tau)$ as a function of the relaxation spectrum of each component $H_1(\tau), H_2(\tau)$ and of the composition of the blend.

In the quadratic laws of Graessley and BMEO, η_{0b} and J_{eb}^0 can be expressed as functions of the composition of the blend.

(1) The Graessley blending law is written:

$$H_b(\tau) = (1 - \phi)^2 H_1(\tau) + \phi(1 - \phi)[H_{12}(\tau) + H_{21}(\tau)] + \phi^2 H_2(\tau)$$

in which $H_{12}(\tau)$ and $H_{21}(\tau)$ are terms of coupling.

It leads to the following expressions:

$$\eta_{0b} = \eta_{01}[(1 - \phi)^2 + d_1\phi(1 - \phi) + R\phi^2]$$

$$J_{eb}^0 = J_{e1}^0 \frac{(1 - \phi)^2 + d_2\phi(1 - \phi) + R^2\phi^2}{[(1 - \phi)^2 + d_1\phi(1 - \phi) + R\phi^2]^2} \tag{11}$$

in which $R = (M_{w2}/M_{w1})^{3.5}$ and d_1 and d_2 are functions depending on various parameters of the system and whose values have been tabulated.

The expression for η_{0b} gives values of the limiting viscosity blends which are too high, whereas that of J_{eb}^0 satisfactorily accounts for the experiment, as is shown by the curve B in *Figure 10*.

(2) The BMEO blending law is written:

$$H_b(\tau) = (1 - \phi)^2 H_1 \left(\frac{\tau}{\lambda_{11}}\right) + 2\phi(1 - \phi) H_{12} \left(\frac{\tau}{\lambda_{12}}\right) + \phi^2 H_2 \left(\frac{\tau}{\lambda_{22}}\right)$$

$\lambda_{11}, \lambda_{12}$ and λ_{22} are shift factors which permit us to express η_{0b} and J_{eb}^0 as:

$$\eta_{0b} = kM_w^{3.5}$$

$$J_{eb}^0 = J_{e1}^0 \left(\frac{M_z}{M_w}\right)^2 = J_{e1}^0 \frac{(1 - \phi + r^2\phi)^2}{(1 - \phi + r\phi)^4} \tag{12}$$

The expression for η_{0b} is in agreement with the experimental law [equation (3)], but that of J_{eb}^0 is not suitable. The curve C of *Figure 10* shows indeed that the values of
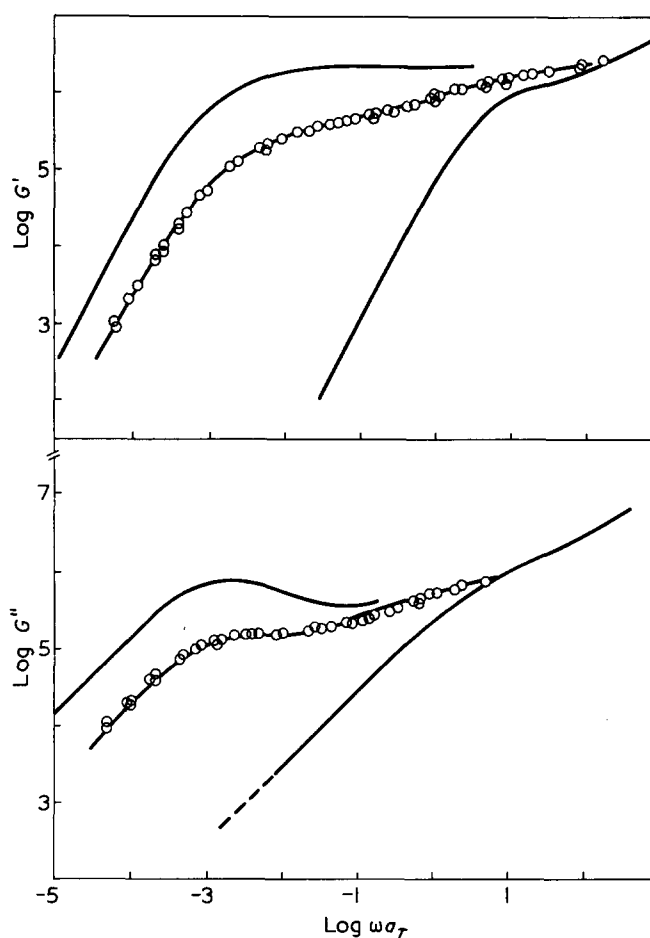

Figure 8 Frequency dependences of the components of the dynamic modulus for the blend M 065850 (results of Masuda[10]): the curve is deduced from the blending law [equation (9)]. The extreme curves represent the experimental variations of the dynamic modulus of the components of the blend
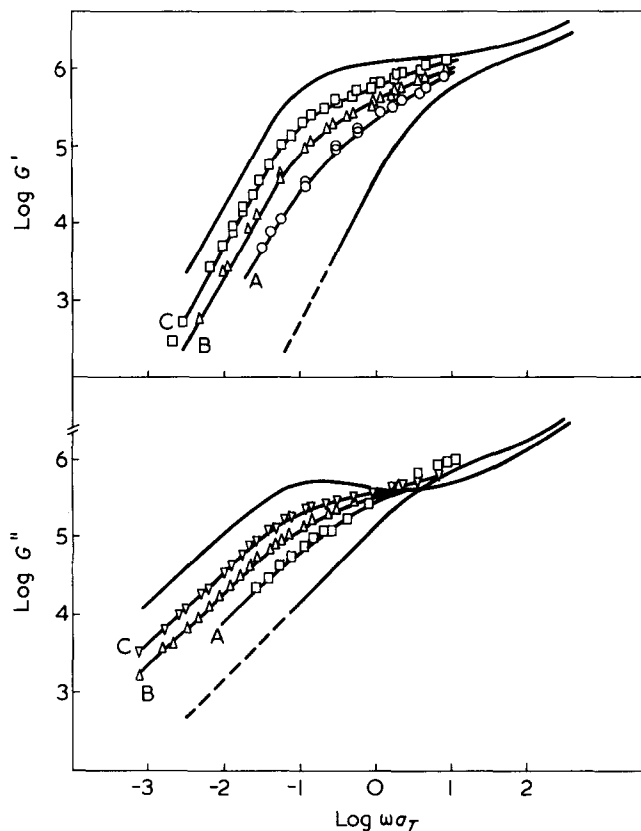
Figure 9 Curves of the dynamic modulus deduced to the blending law for the series BB3 (results of Masuda): A, M 051720; B, M 051740; C, M 051760
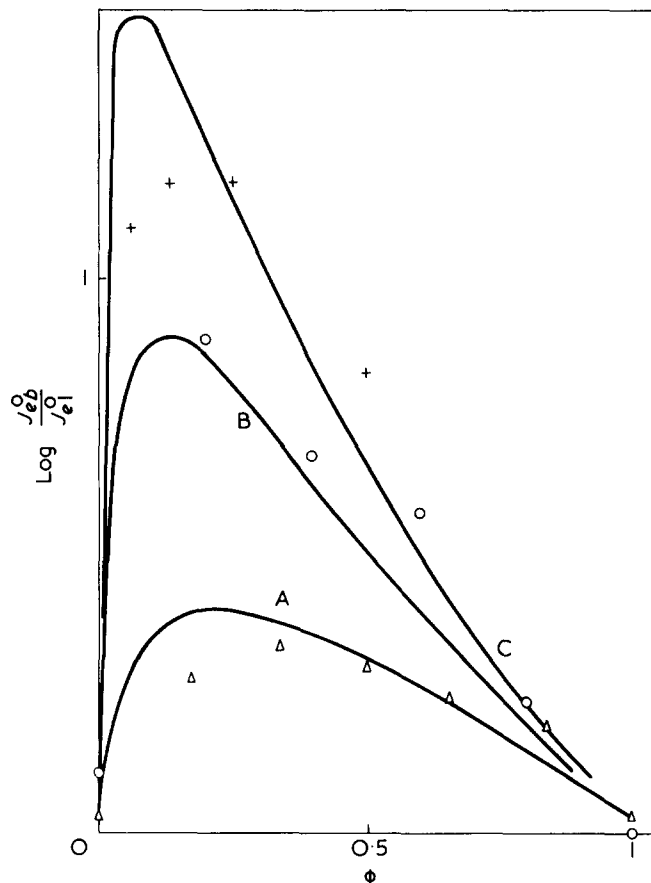

Figure 11 Steady state compliance for results of other authors: A, reference 12; B, reference 10; C, reference 13. Curves relative to equation (10) deduced from our blending law
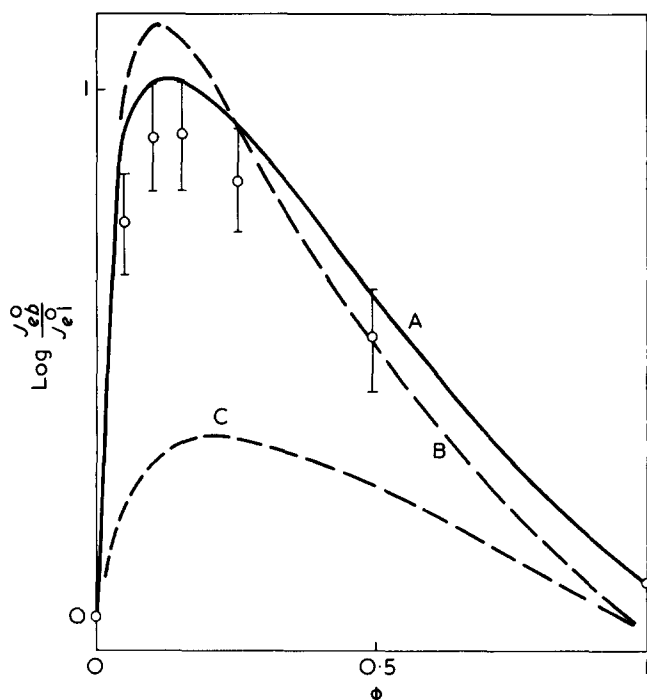

Figure 10 Steady state compliance for the series M 1140: A, is relative to our blending law (relation 10); B, to the law of Graessley (equation 11); C, to the law of BMEO (equation 12)

J_{eb}^0 calculated from BMEO blending law are too low.

Thus, the quadratic laws mentioned above are in agreement with the experiment for only one limit viscoelastic value $-J_{eb}^0$ for the Graessley law and η_{0b} for the BMEO law.

CONCLUSION

The blending law that we propose accounts for the viscoelastic properties of binary blends of polystyrene fractions with a molecular weight higher than the critical weight M_c. It involves only one adjustable parameter p that might be independent of the composition of the blend. It allows one to predict the behaviour of blends over a large frequency range, if one chooses a satisfactory analytical expression for representing the complex viscosity η^* (or the complex modulus G^* or the complex compliance J^*) of a monodisperse polymer.

It should be possible to apply this law to binary blends of narrow distribution samples of other polymers.

Finally, the extension of this law to those polymers which have a large continuous distribution of molecular weights will permit one to investigate precisely the effects of this distribution on the rheological properties of such systems.

ACKNOWLEDGEMENT

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