Table V
Entanglement Modulus and Entanglement Spacings from the Marvin–Oser Theory

Sample	Mol wt	$G_{eN}{}^0$, dyn/cm^2	M_e	Z_e
L18	581,000	3.86×10^6	9,300	179
L19	513,000	4.35×10^6	8,300	159
L22	275,000	3.48×10^6	10,300	199
L15	215,000	3.48×10^6	10,300	199
	Av	3.79×10^6	9,600	184

values of G'' and J'' are related to $G_{eN}{}^0$ and $J_{eN}{}^0$ by

$$G''_{max} = 0.207 G_{eN}{}^0 \tag{17}$$

and

$$J''_{max} = 0.417 J_{eN}{}^0 \tag{18}$$

Therefore, from G''_{max} we can determine $G_{eN}{}^0$ using eq 17, and hence M_e and Z_e using eq 14. The values thus determined for some of the narrow-distribution polystyrenes shown in Figure 2 are listed in Table V. The values in this table differ from those in Table IV by a factor of 1.9. Recently, it has been reported[33] that M_e calculated by the use of the Hayashi theory[30] for several polymer systems is two or three times larger than that obtained by the Marvin–Oser theory.[28]

Acknowledgments. This study was supported by a grant for scientific research (Kagaku Kenkyūhi) from the Ministry of Education. The authors wish to thank Professor John D. Ferry, University of Wisconsin, for his helpful discussions during his stay at our department in 1968. The gpc measurements by Mrs. K. Koga are also gratefully acknowledged.

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(33) K. Osaki, Ph.D. Thesis, Kyoto University, 1968.

Rheological Properties of Anionic Polystyrenes. II. Dynamic Viscoelasticity of Blends of Narrow-Distribution Polystyrenes

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ABSTRACT: The dynamic viscoelastic properties of broad-distribution polystyrene and blends of narrow-distribution polystyrenes have been measured in the molten state. A comparison of the frequency dependences of the storage shear modulus G', loss modulus G'', and relaxation spectrum $H(\tau)$ of the blends and the broad-distribution polymer with those of the narrow-distribution polymers reveals that the effect of molecular weight distribution is very marked in the terminal and rubbery zones. The log G' *vs.* log ω curve for a binary blend composed of two components having very different molecular weights manifests the "two-step" rubbery plateau, suggesting that the blend has two sets of relaxation times associated with different kinds of entanglement couplings. The zero-shear viscosity η_0 of the blends is almost equal to that of a narrow-distribution polymer having the same weight-average molecular weight M_w, but the elasticity coefficient A_G for the blends is proportional to $M_w{}^{4.3}$, as against $M^{7.5}$ for the narrow-distribution polystyrene. The steady-state compliance $J_e{}^0$ of the blends is proportional to $w_2{}^{-2}$ when w_2, the weight fraction of the high molecular weight component, is close to unity. The entanglement compliance $J_{eN}{}^0$ is also approximately proportional to $w_2{}^{-2}$, and $J_{eN}{}^0$ is lower than $J_e{}^0$ by a factor of about 3. The existence of three kinds of entanglement couplings has been pointed out, in which molecular chains of high–high, high–low, and low–low molecular weight components are involved.

Many investigations of the effect of molecular weight distribution on the rheological properties of amorphous polymers have revealed that the rheological properties in the terminal and rubbery zones are strongly affected by the molecular weight distribution. In the preceding paper of this series,[1] the viscoelastic properties of anionic polystyrenes having narrow distributions were reported, and it was found that the change from the rubbery to the flow region is very sharp, and that the distribution of relaxation times corresponding to entanglement slippage is very narrow.

In general,[2] the effect of molecular weight distribution on the rheological properties of polymers can be studied either employing polymer samples having a well-defined continuous distribution of molecular weights or using binary blends composed of the same species of polymers having different molecular weights. With broad-distribution polymer, however, no concrete result can be expected, because parameters to describe the shape or breadth of the distribution can hardly be found at present. In studies with blend samples, on the other hand, some parameters such as the molecular weights of the components and the blending ratio are known. However, most studies[2–7] of the rheological

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(1) S. Onogi, T. Masuda, and K. Kitagawa, *Macromolecules*, **3**, 109 (1970).

(2) J. D. Ferry, "Viscoelastic Properties of Polymers," John Wiley & Sons, Inc., New York, N. Y., 1961; also 2nd ed, Chapter 13, in press.

(3) K. Ninomiya, J. D. Ferry, and Y. Oyanagi, *J. Phys. Chem.*, **67**, 2297 (1963).

(4) M. Horio, T. Fujii, and S. Onogi, *ibid.*, **68**, 778 (1964).

(5) S. Onogi, *Nippon Kagaku Zasshi*, **87**, 1245 (1966).

(6) S. Onogi, H. Kato, S. Ueki, and T. Ibaragi, *J. Polym. Sci., Part C*, **15**, 481 (1966).

(7) S. Onogi, T. Masuda, and T. Ibaragi, *Kolloid-Z. Z. Polym.*, **222**, 110 (1968).

TABLE I

THE MOLECULAR WEIGHTS AND DISTRIBUTIONS OF THE NARROW-DISTRIBUTION COMPONENTS OF THE BINARY AND TERNARY BLENDS AS WELL AS THE BROAD-DISTRIBUTION PS7

		Mol wt			Mol wt (gpc)		
Series no.	Components	M_w	M_n	M_w/M_n	M_w	M_n	M_w/M_n
BB1 & BT1	L18	581,000	550,000	1.06	616,000	563,000	1.09
	L16	58,700	62,200	0.94	59,000	52,300	1.13
	L 9	8,900	8,800	1.01	11,900	9,100	1.31
BB2	L 5	351,000	330,000	1.06	409,000	363,000	1.12
	L15	215,000	215,000	1.00	229,000	203,000	1.13
BB3	L27	167,000	199,000	0.84	185,000	164,000	1.13
	L34	46,900	49,500	0.95	43,100	38,400	1.12
	PS7	303,000	193,000	1.57	313,000	170,000	1.84

properties of binary blends hitherto carried out did not afford sufficient information to serve for quantitative treatment of the effect of blending or molecular weight distribution, mainly because of the considerably broad distribution of the component polymers employed, even though some of them were fractionated. Accordingly, in order to study successfully the effect of molecular weight distribution on the viscoelastic properties of blends, the components should have so narrow distribution that the effect of the distribution is within experimental errors.

In this paper, viscoelastic properties have been measured for blends of narrow-distribution polystyrenes having different molecular weights, and the results have been compared with those obtained with the individual components to find a quantitative relationship between the rheological properties and the molecular weight distribution. A second aim of this paper is to contribute to the development of the concept of entanglement couplings of macromolecular chains by clarifying the effect of blending of narrow-distribution polymers having different molecular weights on rheological behavior in the rubbery and terminal zones.

Experimental Section

Materials. The narrow-distribution polystyrenes obtained by anionic polymerization and employed in the preceding paper[1] as well as broad-distribution polystyrene PS7 prepared by bulk polymerization with azobisisobutyronitrile as the initiator were used in this study. The molecular weights of all the samples are tabulated in Table I. In this table, BB and BT denote binary and ternary blends, respectively. The methods of characterization of the narrow-distribution polystyrenes were the same as in the preceding paper,[1] but for PS7, the following equation[8] was used to determine the weight-average molecular weight M_w

$$[\eta] = 1.2 \times 10^{-4} M_w^{0.71} \qquad (1)$$

in toluene at 30°.

The blending of the component polymers was carried out by dissolving suitable mixtures of narrow-distribution components, in benzene with shaking at about 30% concentration. The solvent was then removed by freeze-drying. The blends thus obtained were then thoroughly dried in a vacuum oven at 60°.

The gel permeation chromatograms of the blends are shown in Figures 1–3. The blends BB15 and BB25 are composed of equal amounts of two components which have molecular weights above the critical molecular weight M_C, and BT1 of equal amounts of three components, one of which has a molecular weight below M_C. The weight fraction of the high molecular weight component in the BB3 series varies from 0.8 to 0.2. The last figure of the sample code for the binary blends represents ten times the weight fraction of the high molecular weight component. The

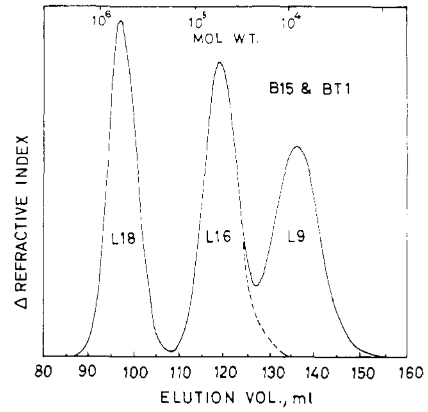

Figure 1. Gel permeation chromatograms for the blends BB15, BT1, and the components. The scale of the refractive index is arbitrary.

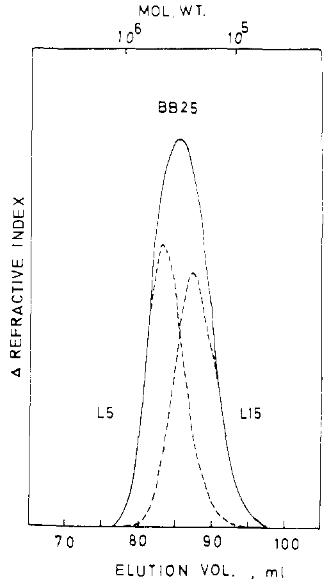

Figure 2. Gel permeation chromatograms for the blends BB25 and the components. The scale of the refractive index is arbitrary.

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(8) T. Oyama, K. Kawahara, and M. Ueda, *Nippon Kagaku Zasshi*, **79**, 727 (1958).

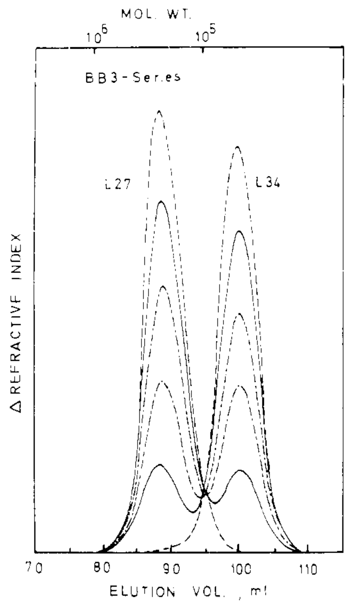

Figure 3. Gel permeation chromatograms for the BB3 series and the components. The scale of the refractive index is arbitrary.

ratios of the molecular weights of the higher molecular weight components to those of the lower molecular weight ones are, respectively, 9.9, 1.6, and 3.6 for BB1, BB2, and BB3. As seen in Figures 1-3, the molecular weight distributions of the components are completely separated from each other for BB15, BT1, and the BB3 series, but not for BB25.

Measurements. The measurements of viscoelastic properties were carried out by means of the same concentric cylinder type rheometer as in the previous papers.[1,4-7] The details of the rheometer and measuring techniques, therefore, are not described here.

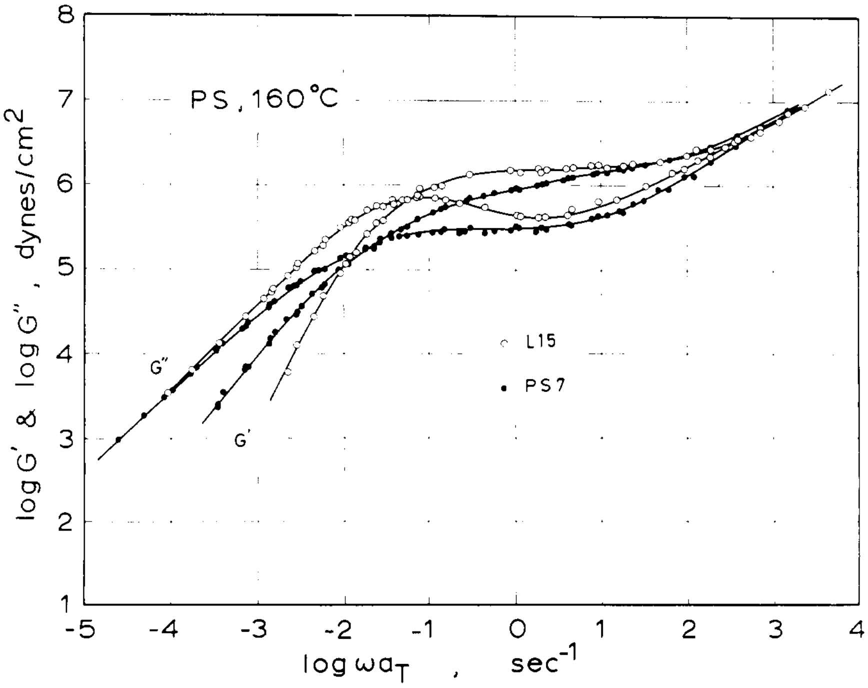

Figure 4. Frequency dependences of G' and G'' for the narrow-distribution polystyrene L15 and the broad-distribution PS7 reduced to 160°.

The shift factors determined in the course of the time-temperature superposition of the viscoelasticity data for the blends were the same as those for the components, so far as the components had molecular weights above M_C. In the case of the ternary blend BT1 containing L9 having lower molecular weight ($M = 8900$), the shift factor was rather smaller because of the excess free volume.[1,9]

Results and Discussion

Frequency Dependences of Viscoelastic Functions. In Figure 4, master curves of the storage shear modulus G' and loss modulus G'' of the narrow-distribution polystyrene L15 are compared with those of the broad-distribution PS7. This figure reveals that the viscoelastic functions depend strongly on the molecular weight distribution, especially in the terminal and rubbery plateau zones. The log G'' *vs.* log ω curve for a narrow-distribution polystyrene has a peak at the end of the rubbery zone, while that for the broad-distribution polymer does not. Another remarkable difference between two polymers is that the curve for the narrow-distribution polymer shows a sharp break at the transition from the rubbery to the terminal zone, in marked contrast to that for PS7. The G' curve for PS7 extends to lower frequencies owing to high molecular weight fraction included in it. All the curves unite in the transition zone, indicating that the viscoelastic properties are not affected by the molecular weight distribution at high frequencies or short time scales.

The master curves of G' for the blends BB15 and BT1 are shown in Figure 5, together with those for the components, L18, L16, and L9. The G' curve for L18 has a longer and flatter plateau as compared with that for L16. The curve for L9, having a molecular weight lower than M_C, shows no plateau and diverges from the others in the transition zone owing to the excess free volume. One of the binary blends, BB15,

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(9) G. C. Berry and T. G Fox, *Advan. Polym. Sci.*, **5**, 261 (1968).

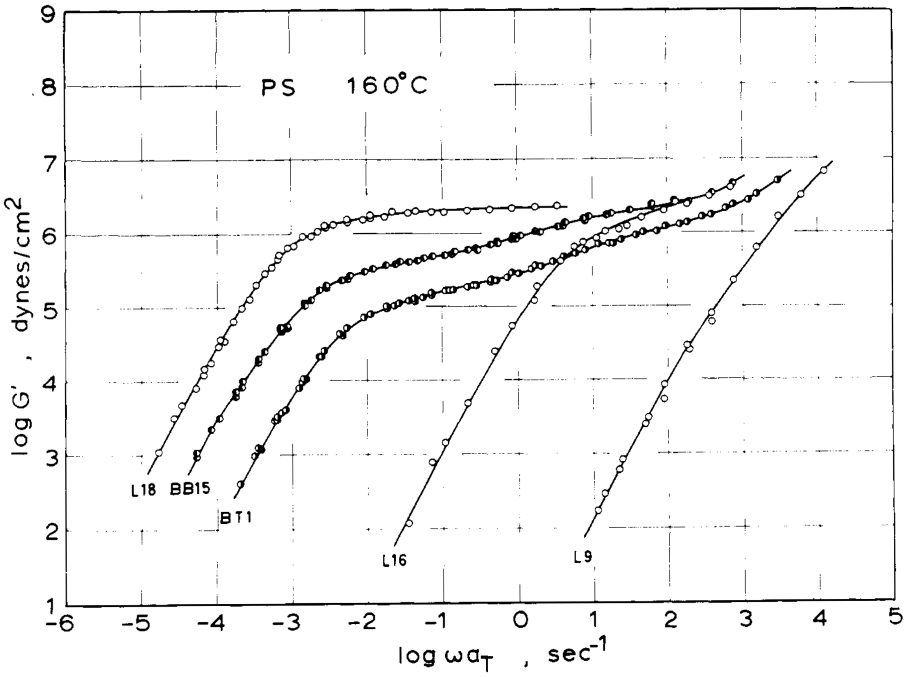

Figure 5. Frequency dependences of G' for BB15, BT1, and their components, reduced to 160°.

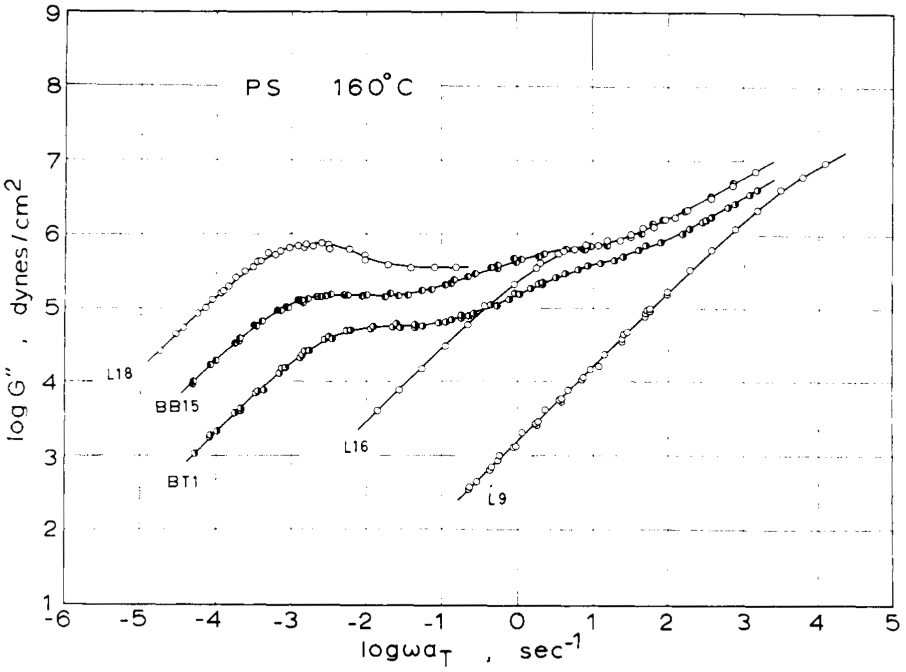

Figure 6. Frequency dependences of G'' for BB15, BT1, and their components, reduced to 160°.

which contains equal amounts of L18 and L16, manifests a "two-step" plateau in the rubbery zone. The lower step on the low-frequency side is clearly lower than the higher step, which is as high as the plateau of the components. The G' curve for BT1, composed of three components, also shows a two-step plateau; both steps are lower than that of BB15 because the contents of L18 and L16 are lower and the other component, L9, does not contribute to the development of the plateau but only to the shift of the transition zone.

As seen in Figure 6, the master curves of G'' for the blends also show two peaks, though they sometimes appear rather as shoulders, while those for each component show only one peak. The two peaks for the blends seem to correspond to those of the components. Figures 5 and 6 suggest the existence of two groups of relaxation times associated with entanglement slippage in the binary blends of narrow-distribution polystyrenes having molecular weights higher than M_C.

Figures 7 and 8 show, respectively, the frequency dependences of G' and G'' for the binary blend BB25 and its components. The molecular weights of the components of this blend are not very different from each other but are higher than M_C, as seen from Table I. Therefore, no significant change due to the blending is observed in the frequency dependences. In our recent papers,[4–7] it has been found for many polymers that the viscoelastic functions such as dynamic

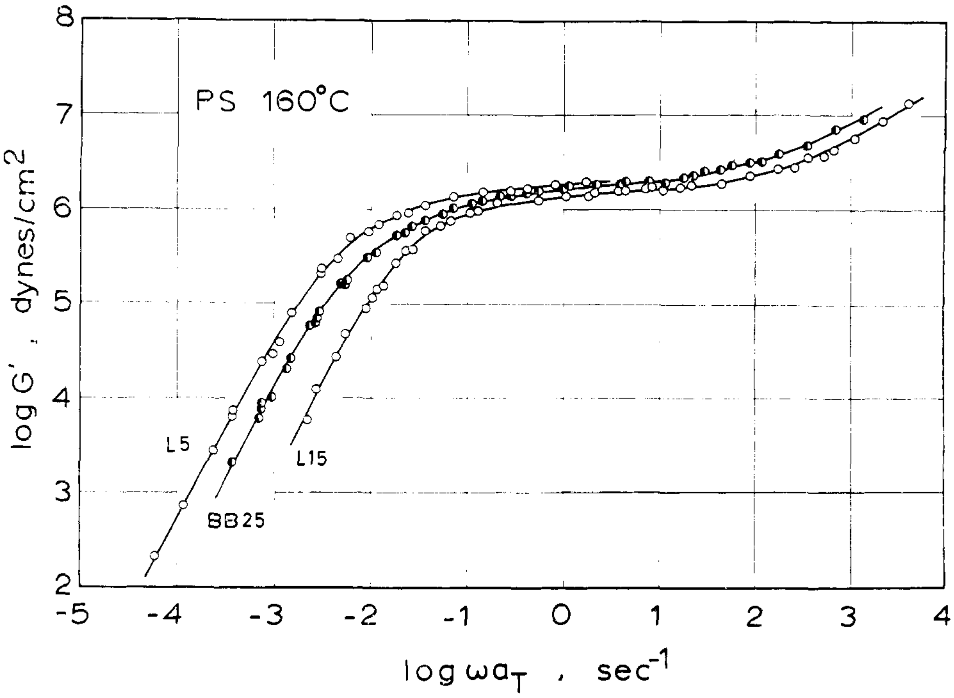

Figure 7. Frequency dependences of G' for BB25 and its components, reduced to 160°.

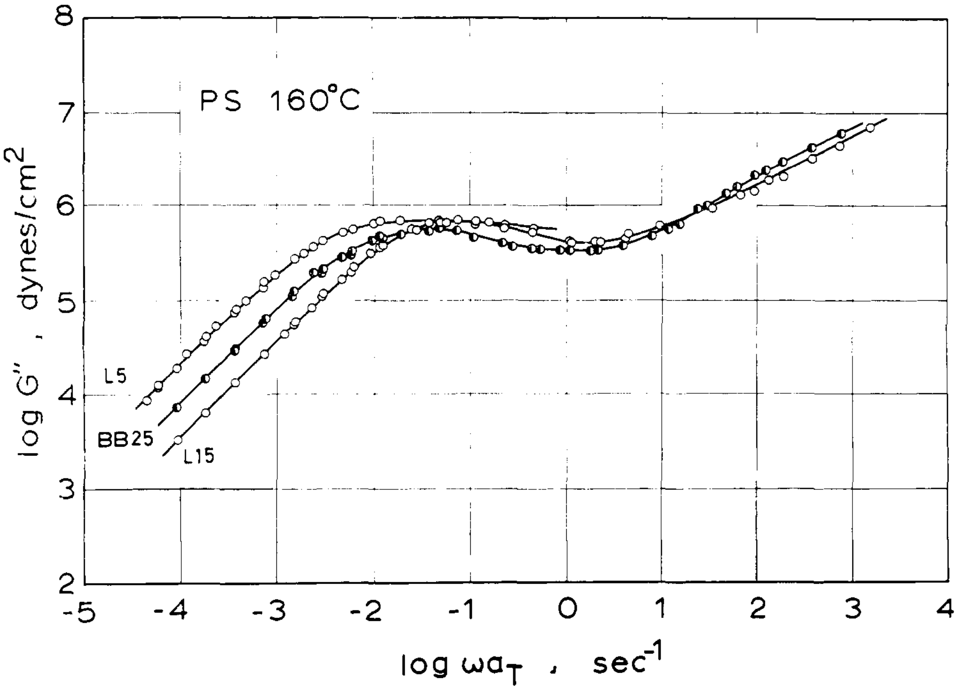

Figure 8. Frequency dependences of G'' for BB25 and its components, reduced to 160°.

viscosity $\eta' = G''/\omega$ and G' of binary blends can be superposed with respect to the blending ratio so long as the molecular weight distribution is not changed very much by the blending. The above result for BB25 is a case where the molecular weight distributions of the components overlap, and little change in viscoelastic functions is brought about by the blending.

In Figures 9 and 10 are shown similar curves for the binary blend series BB3, which include components having molecular weights above M_C and show bimodal distribution of molecular weight as seen in Figure 3. The behavior of these blends is intermediate between those of BB15 and BB25. Two-step plateaus are found for this series, especially for the blends, such as BB32 and BB34, containing small amounts of the high molecular weight component L27.

Relaxation Spectrum. In the preceding paper,[1] it was found for high molecular weight and narrow-distribution polystyrenes that the distribution of relaxation times characteristic of entanglement couplings appears as a peak in the G'' curve and is separated from that of the glass transition. In the previous section of this paper, the frequency dependence curves of G' and G'' for blends composed of two components

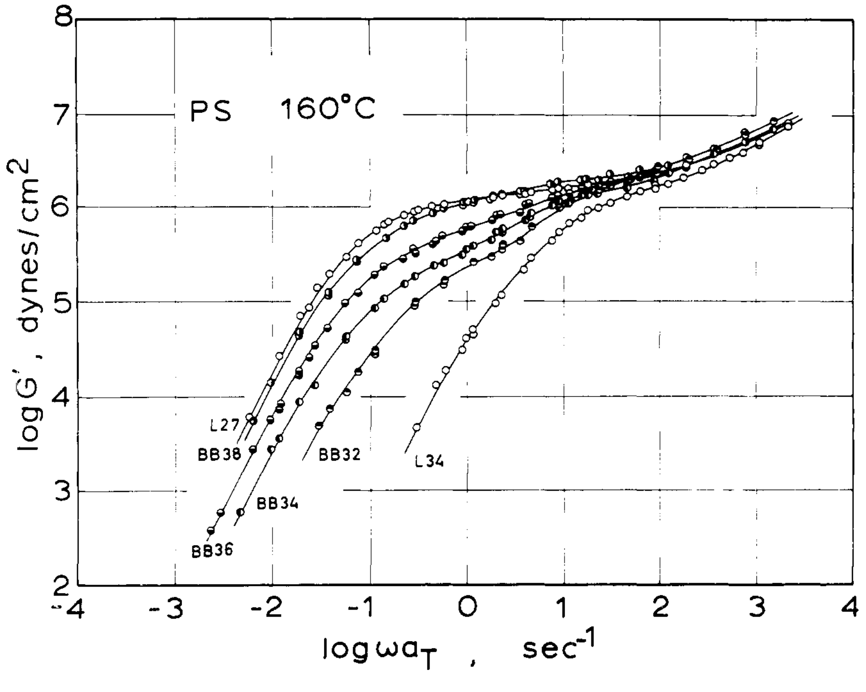

Figure 9. Frequency dependences of G' for the BB3 series and the components, reduced to 160°.

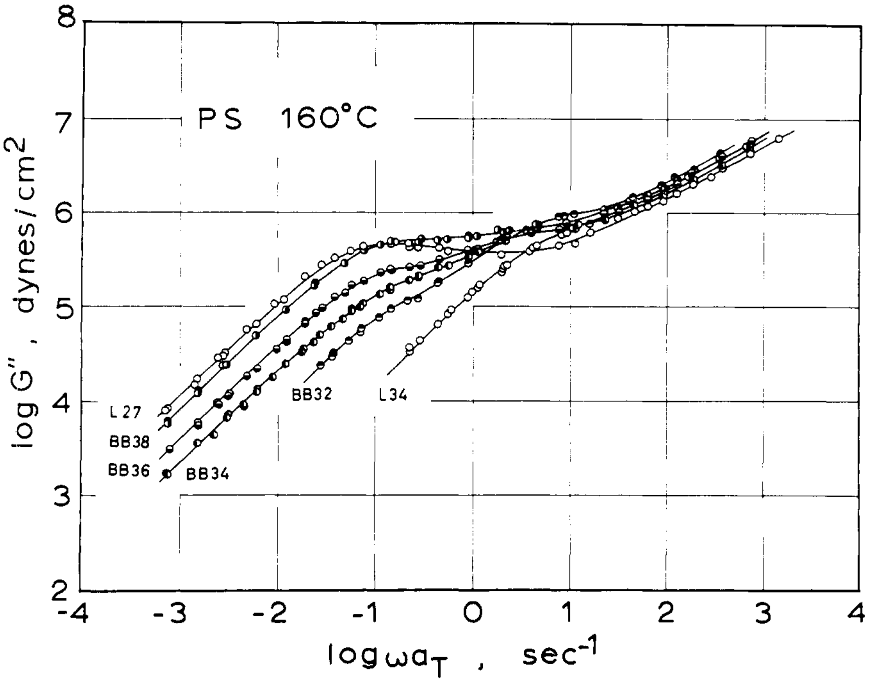

Figure 10. Frequency dependences of G'' for BB3 series and the components, reduced to 160°.

having very different molecular weights suggested the existence of two groups of relaxation times associated with entanglement slippage. Therefore, it is very interesting to compare the relaxation spectrum of a narrow-distribution polymer with those of broad-distribution polymers or blends.

To obtain the relaxation spectrum from the dynamic viscoelasticity data, the Tschoegl equations[10] were used; they may be written as

$$H(\tau) = \begin{cases} \left. \dfrac{dG'}{d\ln\omega} + \dfrac{1}{2}\dfrac{d^2G'}{d(\ln\omega)^2} \right|_{1/\omega=\sqrt{2}\tau} \\ \text{(when the slope of } H(\tau) \text{ is positive)} \\ \left. \dfrac{dG'}{d\ln\omega} - \dfrac{1}{2}\dfrac{d^2G'}{d(\ln\omega)^2} \right| \dfrac{1}{\omega}_{1/\omega=\tau/\sqrt{2}\tau} \\ \text{(when the slope of } H(\tau) \text{ is negative)} \end{cases} \qquad (2)$$

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(10) J. D. Ferry, private communication.

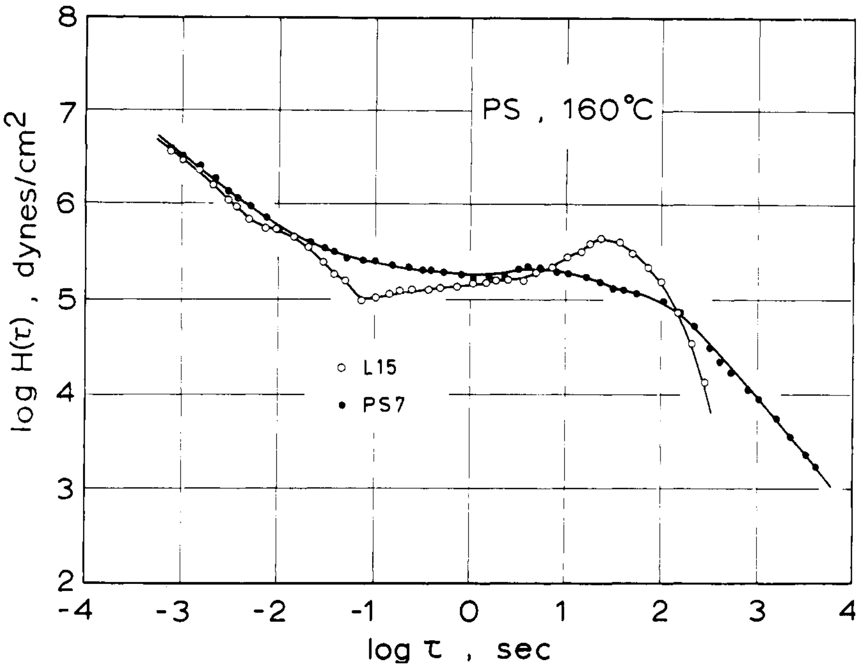

Figure 11. Relaxation spectra for the narrow-distribution L15 and broad-distribution PS7 at 160°.

$$H(\tau) = \begin{cases} \dfrac{2}{\pi}\left[G'' + \dfrac{4}{3}\dfrac{\mathrm{d}\,G''}{\mathrm{d}\ln\omega} + \dfrac{1}{3}\dfrac{\mathrm{d}^2G''}{\mathrm{d}\,(\ln\omega)^2}\right]_{1/\omega=\sqrt{5}\,\tau} \\ \text{(when the slope of } H(\tau) \text{ is positive)} \\ \dfrac{2}{\pi}\left[G'' - \dfrac{4}{3}\dfrac{\mathrm{d}\,G''}{\mathrm{d}\ln\omega} + \dfrac{1}{3}\dfrac{\mathrm{d}^2G''}{\mathrm{d}\,(\ln\omega)^2}\right]_{1/\omega=\tau/\sqrt{5}} \\ \text{(when the slope of } H(\tau) \text{ is negative)} \end{cases} \qquad (3)$$

The relaxation spectrum obtained by the use of these equations is very similar to that obtained by the third-order approximation method of Schwarzl and Staverman[1,11] or the first-order approximation method of Fujita.[12] The relaxation spectra for the narrow- and broad-distribution polystyrenes, L15 and PS7, determined from the master curve of G' using eq 2, are shown in Figure 11. These spectra agree very well with those determined from G'' using eq 3. As seen from Figure 11, the spectrum for L15 has a peak in the long time region, and then falls off rapidly with increasing relaxation time. The spectrum for PS7, on the other hand, shows no peak and extends gradually to a very long time. It can be concluded from these results that, for the narrow-distribution polystyrenes, the distribution of relaxation times associated with the entanglement couplings is not box-type as predicted by the Hayashi theory[13] but shows a peak as predicted by the other theories, such as the modified Rouse theory[1,14] and the Chompff–Duiser theory,[15] and that the broadness of the molecular weight distribution is directly reflected on the spread of the distribution of relaxation times. The coincidence of the spectra for the narrow- and broad-distribution polymers in the short time region suggests that the viscoelastic properties in the transition zone are never affected by the molecular weight distribution.

The relaxation spectra for the blend BB15 and its components, L18 and L16, are shown in Figure 12. For each component, a maximum can be observed in the relaxation spectrum. This maximum corresponds to a single plateau in the G' curve shown in Figure 5 and a single maximum in the G'' curve in Figure 6. On the contrary, the spectrum for the blends BB15 has two maxima corresponding to the two-step plateau observed in the G' curve in Figure 5 and the G'' curve in Figure 6. The peak on the long time side is lower than that of L18 and seems to be shifted slightly to the short time side. The other peak, on the short time side, is slightly lower and broader than that of L16 and is shifted to the long time side. Such shifts of the peaks are considered to correspond to the phenomenological interaction parameters λ_1 and λ_2 in the Ninomiya theory[16] for the viscoelasticity of binary blends. It is also considered that a relaxation mechanism having long relaxation time ($\cong 10^{2-3}$ sec) is involved in the entanglement couplings between molecules of the high molecular weight component alone, while another mechanism having short relaxation times ($\cong 10^{-1}$ sec) is associated with the couplings between molecules of the low molecular weight component alone. The

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(11) F. Schwarzl and A. J. Staverman, *Appl. Sci. Res.*, **A4**, 127 (1953).

(12) H. Fujita, *J. Appl. Phys.*, **29**, 943 (1958).

(13) S. Hayashi, *J. Phys. Soc. Jap.*, **18**, 131, 249 (1963); **19**, 101, 2306 (1964).

(14) J. D. Ferry, R. F. Landel, and M. L. Williams, *J. Appl. Phys.*, **26**, 359 (1955).

(15) (a) A. J. Chompff and J. A. Duiser, *J. Chem. Phys.*, **45**, 1505 (1966); (b) A. J. Chompff and W. Prins, *ibid.*, **48**, 235 (1968).

(16) (a) K. Ninomiya, *J. Colloid Sci.*, **14**, 49 (1959); (b) K. Ninomiya and J. D. Ferry, *ibid.*, **18**, 421 (1963).

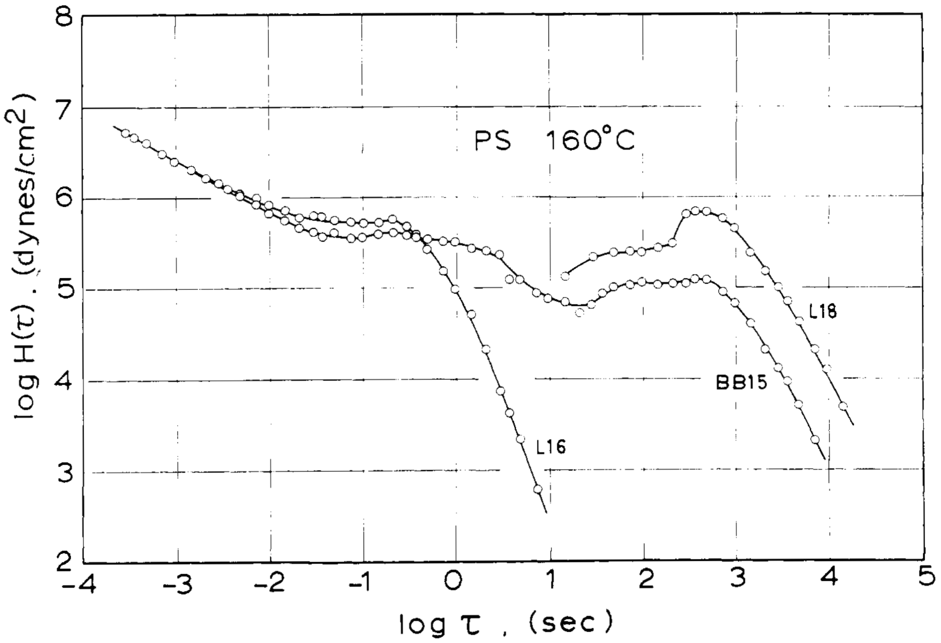

Figure 12. Relaxation spectra for BB15 and its components at 160°.

lowering of both the peaks from those of the components may be ascribed to the decrease in the content of each component.

The spread of the peak on the short time side to the long time side is probably caused by the existence of another kind of entanglement coulping between molecules of the high and low molecular weight components. This type of coupling has relaxation times longer than those of the mechanism involved in the entanglement couplings between molecules of the low molecular weight component alone.

Rheological Behavior in the Terminal Zone. The viscoelastic behavior of polymer liquids in the terminal zone is generally characterized by the zero-shear viscosity η_0, elastic coefficient A_G, and/or steady-state compliance J_e^0. These parameters are defined as

$$\eta_0 = \lim_{\omega \to 0} \frac{G''}{\omega} \tag{4}$$

$$A_G = \lim_{\omega \to 0} \frac{G'}{\omega^2} \tag{5}$$

$$J_e^0 = \lim_{\omega \to 0} J' = A_G/\eta_0^2 \tag{6}$$

In Figure 13, η_0 values for the narrow-distribution polystyrenes and blends used in this study are plotted logarithmically against the calculated weight-average molecular weight. The open circles indicate the narrow-distribution polymers,[1] and the closed circles the blends. The molecular weights of the blends were calculated by the following equation, since each component has very narrow distribution

$$M = \sum_i w_i M_i \tag{7}$$

where w_i and M_i are, respectively, the weight fraction and the molecular weight of each component. In the case of binary blends composed of two components having molecular weights above M_C, the weight fraction is equal to the volume fraction. As seen from Figure 13, the experimental points for the blends mount fairly well on the line drawn for the narrow-distribution polymers,[1] whose slope is 3.7 above M_C.

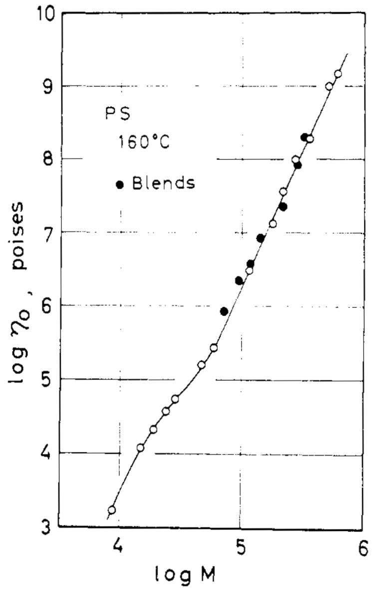

Figure 13. Zero-shear viscosity η_0 of the blends (closed circles) and narrow-distribution polystyrenes (open circles) plotted logarithmically against M_w at 160°.

The molecular weight dependence of the elasticity coefficient A_G defined by eq 5 is shown in Figure 14 for the blends as well as for the narrow-distribution polystyrenes. The molecular weights for the blends were again calculated by eq 7. The slope of the solid straight line[1] in Figure 14 is 7.5. In marked contrast to the case of η_0, A_G values for the blends do not agree with and are clearly higher than those for the narrow-distribution polymers, excepting BB25 for which the difference from the narrow-distribution polymers is rather slight because the molecular weights of its

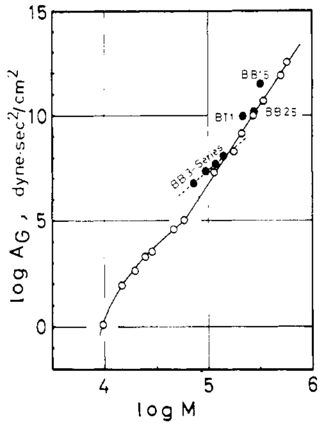

Figure 14. Elasticity coefficient A_G for the blends (closed circles) and narrow-distribution polystyrenes (open circles) plotted logarithmically against M_w at 160°.

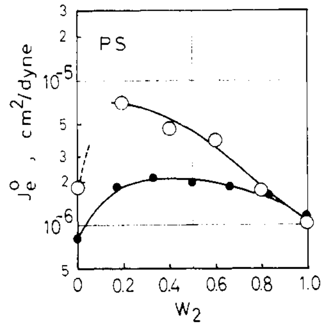

Figure 15. Steady-state compliance J_e^0 of the BB3 series blends plotted against the weight fraction of the high molecular weight component, w_2. The data indicated by the closed circles are those of Akovali.[17]

components are close to each other. For the BB3 series, A_G of the samples containing small amounts of the high molecular weight component deviates from the straight line for the narrow-distribution polymers, and the plot can be approximated by a straight line, shown by the broken line in Figure 14, having a slope of about 4.3. This result indicates that the elastic behavior of polymer liquids in the terminal zone is strongly affected by the molecular weight distribution, and that A_G will successfully be expressed not by M_w but by certain higher-order moments of the molecular weight distribution.

The steady-state compliance J_e^0 of the binary blend BB3 series is plotted against the weight fraction of the high molecular weight component, w_2, in Figure 15. In this figure, the result reported by Akovali[17] for binary blends of narrow-distribution polystyrene is also reproduced with the closed circles. The log–log plot of J_e^0 against w_2 for the same and other samples is given in Figure 16. The values of J_e^0 for binary blends are always higher than those for either component, and display a maximum at an intermediate composition. The maximum value of J_e^0 increases and the corresponding w_2 decreases the ratio of molecular weights of the components increases. In the process of the superposition of frequency dependence curves of G' for blends with respect to the composition, the vertical shift factor C_M can be determined, as was reported in our recent papers.[5–7] This shift factor C_M represents the ratio of J_e^0 of the blend to that of one of the components and depends on differences in the molecular weights and distributions of the component polymers. For the narrow-distribution polystyrenes shown in Figure 16, each curve can be approximated by a straight line having the slope of -2 near $w_2 = 1.0$. This does not agree with the prediction of the Ninomiya theory[16] that J_e^0 should be proportional to w_2^{-1}. The straight line extends farther to the low w_2 side as the ratio of molecular weights of the components increases. It is very interesting to compare this result with that for concentrated polymer solutions. It has been found by a few authors[18] that J_e^0 for concentrated polymer solutions is proportional to c^{-2} in the entanglement region, c being the concentration of polymer. Therefore, it can be concluded that the low molecular weight component in a binary blend does not contribute to J_e^0 in the high concentration region at all, just as with solvents in polymer solutions, even when its molecular weight is higher than M_C.

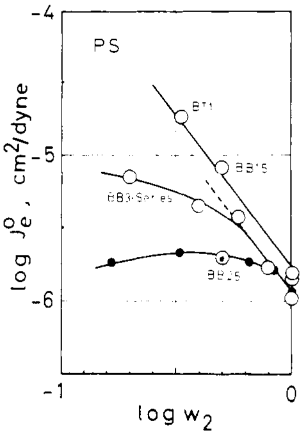

Figure 16. Steady-state compliance J_e^0 for the blends plotted logarithmically against the weight fraction of the high molecular weight component, w_2. The data indicated by the closed circles are those of Akovali.[17]

Rheological Behavior in the Rubbery Zone. As was seen in Figure 5, blends composed of narrow-distribution polystyrenes manifest the two-step plateau in the rubbery zone, and the lower step at low frequency or long time scale lowers with decreasing w_2. For the sake of quantitative considerations, the entanglement modulus G_{eN}^0 and entanglement compliance J_{eN}^0 of BB15 and BT1 were calculated by the method proposed by Ferry, *et al.*[2,19] In general, these parameters can be obtained by the integration of G'' over ln ω encompassing the maximum of G''. In this study, G'' *vs.*

$$G_{eN}^0 = 1/J_{eN}^0 = \frac{2}{\pi}\int_{-\infty}^{a'} G''\,\mathrm{d}\ln\omega \qquad (8)$$

ln ω curves have been numerically integrated from ln $\omega = -\infty$ to the maximum of G'', and the result has

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(19) J. F. Sanders, J. D. Ferry, and R. H. Valentine, *J. Polym. Sci., Part A-2*, 6, 967 (1968).

TABLE II
THE ENTANGLEMENT MODULUS G_{eN}^0 AND ENTANGLEMENT COMPLIANCE J_{eN}^0 OF THE BLENDS BB15 AND BT1 AS WELL AS THE COMPONENT L18

Sample	w_2	G_{eN}^0, dyn/cm^2	J_{eN}^0, cm^2/dyn
L18	1.0	2.05×10^6	4.91×10^{-7}
BB15	0.50	4.26×10^5	2.34×10^{-6}
BT1	0.33	1.70×10^5	5.87×10^{-6}

been doubled. This procedure produces no serious error.[1]

The calculated values of G_{eN}^0 and J_{eN}^0 are tabulated in Table II. The values of G_{eN}^0 agree very well with the height of the plateau of the G' curves shown in Figure 5. Log J_{eN}^0 for the blends BB15 and BT1 is plotted against log w_2 in Figure 17. For the ternary blend BT1, w_2 is regarded as 0.33. The solid line in this figure has the slope of -2, and the broken line, of -2.3, suggesting that the lower step of the two-step plateau of the G' curve in Figure 5 is approximately proportional to w_2^2. Comparing Figure 16 with Figure 17, it can be said that the dependences of J_e^0 and J_{eN}^0 on w_2 are quite similar, and J_e^0 is about three times larger than J_{eN}^0.

These results appear to support our view that the lower step of the two-step rubbery plateau observed for the blends is associated with the entanglement couplings between molecules of the high molecular weight component alone. However, this must be confirmed by a further study employing blends composed of various components as well as polymer solutions as an extreme case.

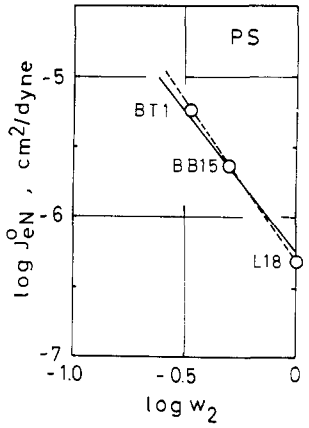

Figure 17. Entanglement compliance J_{eN}^0 of BB15, BT1 and L18 plotted logarithmically against the weight fraction of the high molecular weight component, w_2. The solid line has the slope of -2, and the broken line of -2.3.

Rheological studies with blends composed of narrow-distribution polymers seem to be very promising to clarify not only the effect of molecular weight distribution on rheological properties but also the nature of entanglement couplings between molecular chains.

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Brillouin Spectra of Solutions. I.
Molecular Weight Determination of Standard Polystyrene 705

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ABSTRACT: The molecular weight of standard sample 705 polystyrene (National Bureau of Standards) has been determined from the intensity ratio of the Brillouin spectra of dilute solutions in benzene and toluene. By coupling these results with a previous molecular weight determination by the conventional light scattering method, we are able to offer further support for a "high" value of the Rayleigh ratio of benzene.

The determination of the weight-average molecular weight of polymers in solution by the conventional scattering technique requires the measurement of the ratio of the intensity of the scattered light to that of the incident light beam. Since the scattered light is many orders less intense than the incident beam, this ratio is difficult to measure, and it is common practice to avoid this difficulty by measuring intensities relative to some standard solvent, such as benzene. An alternate method of determining polymer molecular weights in solution by light scattering is to resolve the spectrum of scattered light into its three peaks, the two Brillouin side peaks and the central peak.[1] The method avoids the need to refer to the intensity of the incident beam or, as the case may be, the scattering power of benzene.

The values of the scattering power of benzene, expressed either as the Rayleigh ratio or the turbidity, as determined by different workers, have tended to fall into two groups, the "high" and the "low" values.[2] The two groups differ by some 40%. It is now accepted

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