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/cm²	J_{eN}^0, cm²/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.

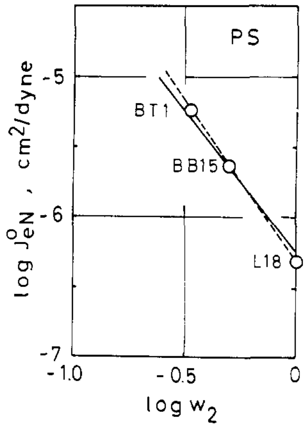

Figure 17. Entanglement compliance J_{eN}^0 of BB15, BT1 and L18 plotted logarithmically against the weight fraction of the high molecular weight component, w_2. The solid line has the slope of -2, and the broken line of -2.3.

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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(1) G. A. Miller and C. S. Lee, *J. Phys. Chem.*, **72**, 4644 (1968).

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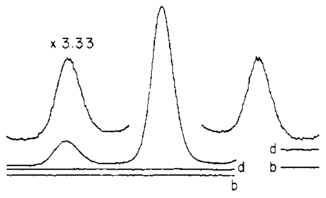

Figure 1. Spectrum of light scattered by polystyrene 705 in benzene at 25° with dark current base line (*b*) and horizontal component of the depolarized spectrum (*d*); $c = 3.41 \times 10^{-4}$ g/ml. The side peaks are separated 0.17 cm^{-1} from the central peak.

that the "high" value is correct.[3] Nevertheless, we felt it would be interesting to apply the Brillouin scattering method to the determination of the molecular weight of a generally available standard polymer sample to provide additional, indirect evidence of the reliability of the "high" value of the scattering power of benzene.

In the Brillouin scattering method, the side peaks serve as references, and a measurement of the ratio of the intensity of the central peak to the sum of intensities of the side peaks, J, is related to the weight-average molecular weight, M, in a manner analogous to the Rayleigh ratio for total, isotropic light scattering. For a dilute, ideal solution, the relation is

$$J = J_0 + BKMc \qquad (1)$$

where J_0 is the value of J of the pure solvent, c is the concentration of polymer, and B and K are constants. Using the conventional concentration units of grams of polymer per milliliter of solution, we have

$$K = \frac{C_p}{RT^2}\left[\frac{\partial n/\partial c}{\partial n/\partial T}\right]^2$$

where n is the refractive index, T is the absolute temperature, C_p is the heat capacity at constant pressure of 1 ml of solvent, and R is the gas constant. The constant B depends only on the solvent, and for a "nonrelaxing" solvent,[1] is given by $B = J_0$. For a relaxing solvent, we have

$$B = \frac{(J_0 + 1)(\gamma - 1)}{\gamma(1 + f)}$$

where

$$f = \frac{2x}{1 - x} + \frac{\gamma x^2}{(1 - x)^2}$$

and

$$x = 1 + \frac{\beta_T(\partial n/\partial T)}{\alpha(\partial n/\partial P)}$$

Here, γ is the ratio of heat capacities, C_p/C_v, α is the thermal expansivity, β_T is the isothermal compressibility, and P is the pressure. The quantity x is generally positive and no greater than a few hundredths.

For real polymer solutions it is common to express the chemical potential of the solvent, μ_1, in the form of a virial equation

$$\mu_1 - \mu_1^0 = -RTV_1c(1/M + A_2c + A_3c^2 + \cdots)$$

where V_1 is the partial molar volume of the solvent, and A_2 and A_3 are the second and third virial coefficients. Equation 1 then takes on the form

$$\frac{BKc}{J - J_0} = (1/M + 2A_2c + 3A_3c^2 + \cdots) \qquad (2)$$

Using the above approach, we have measured the molecular weight of standard sample 705 polystyrene (supplied by the National Bureau of Standards) in benzene, a strongly relaxing solvent, and in toluene, a weakly relaxing solvent. These two liquids are thermodynamically good solvents for polystyrene. PS 705 is a polymer of narrow molecular weight distribution. Its molecular weight is low enough so that there is negligible dissymmetry in the angular dependence of the scattered intensity. Our results, to be discussed below, agree with a previous determination by the relative method with the "high" value of the Rayleigh ratio of benzene as a standard.

Experimental Section

The apparatus for recording Brillouin spectra, which included a He-Ne laser source at 6328 Å and a piezoelectrically scanned Fabry-Perot interferometer, has been described elsewhere.[1] The only change made was to place a rotatable nicol prism between the pin hole and the photomultiplier to analyze the components of the scattered light. The scattering angle was approximately 90°. A typical recorder trace of a spectrum is given in Figure 1. Since relatively large intensity ratios were involved, it was necessary to establish the correct base line before measuring the areas under the peaks. First, the photomultiplier output was measured with the laser off to give the dark current base line. Then the spectrum of the anisotropically scattered light was scanned through the nicol prism set to pass horizontally polarized light. Since the Brillouin spectrum was scanned with the prism set for vertically polarized light, the correct base line was four-thirds the intensity of the horizontal component of the scattered light.[4] The depolarized spectrum was too broad to be resolved by the interferometer for the solvents used here and gave a constant intensity over the entire free spectral range of the interferometer. At higher concentrations, as in Figure 1, it was necessary to expand the photometer scale to read accurately the area under the Brillouin peaks. Overlap of adjacent peaks was not severe and the previous procedure[1] could be followed for dividing the areas under the peaks.

The solvents, benzene and toluene, were Fisher Certified reagents. The most concentrated solution was made by dissolving the required amount of polymer in the solvent with prolonged shaking. Less concentrated solutions were made by subsequent dilution with more solvent. Solutions were forced through a very fine, sintered glass filter to remove dust. The scattering cell had been previously washed in the condensing vapors of the solvent. After the spectrum of a solution had been recorded, the concentration was accurately determined by evaporating a 50-ml aliquot to dryness and weighing.

Results

The experimental intensity ratios, given in Tables I and II, were assumed to obey eq 2 with the third and higher virial coefficients equal to zero. A least squares fit gave, for PS 705 in benzene

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(4) D. A. Pinnow, S. J. Candau, and T. A. Litovitz, *J. Chem. Phys.*, **49**, 347 (1968).

TABLE I
EXPERIMENTAL INTENSITY RATIOS, *J*, OF PS 705 IN BENZENE AT 25°

10^4c, g/ml	J
0	0.86
1.05	1.34
2.31	1.91
3.41	2.39
7.17	3.84
9.75	4.87
14.98	6.13

TABLE II
EXPERIMENTAL INTENSITY RATIOS, *J*, OF PS 705 IN TOLUENE AT 25°

10^4c, g/ml	J
0	0.43
1.56	1.12
2.38	1.53
4.76	2.40
7.63	3.33
10.57	4.23
14.70	5.22

TABLE III
LIGHT SCATTERING PARAMETERS AT 25°

	Benzene	Toluene
C_p	0.3616[a]	0.3580[a]
$\partial n/\partial T$	-6.27×10^{-4} [a]	-5.51×10^{-4} [a]
$\partial n/\partial c$	0.102[b]	0.1065[c]
K	0.0542	0.0757
x	0.046[a]	0.015[a]
γ	1.431	1.350
J_0	0.86	0.43
B	0.509	0.360

[a] Reference 1; C_p is in cal/ml deg. [b] Extrapolated to 6328 Å and 25° from data in ref 4. [c] Extrapolated from data in the "Polymer Handbook," J. Brandrup and E. H. Immergut, Ed., Interscience Publishers, New York, N. Y., 1966, Chapter IV.7.

TABLE IV
WEIGHT-AVERAGE MOLECULAR WEIGHT OF PS 705

Source	Solvent	Method	10^{-5} M
NBS[a]	Cyclohexane	Light scattering	1.793
NBS[a]	Cyclohexane	Sedimentation	1.898
Ref 6	Benzene	Light scattering	1.76
Present	Benzene	Brillouin spectrum	1.733
Present	Toluene	Brillouin spectrum	1.733

[a] Data provided with sample.

$$c/(J - J_0) = 2.092 \times 10^{-4} + 0.0453c$$

and in toluene

$$c/(J - J_0) = 2.117 \times 10^{-4} + 0.0648c$$

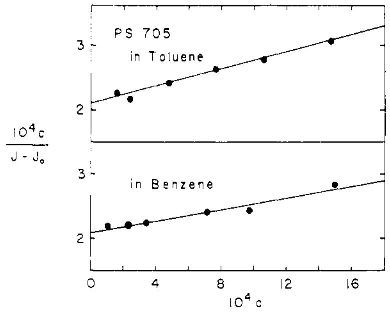

Figure 2. Intensity ratios plotted in accordance with eq 2.

Using the parameters in Table III, we obtain a molecular weight of 1.73×10^5 g/mol and a second virial coefficient, A_2, of 6.2×10^{-4} mol ml/g^2 in benzene, and 8.8×10^{-4} in toluene. We have revised slightly our values of γ from the values used previously,[1] after an extensive review of the literature. Also our J_0 value for benzene is lower because of our more careful attention to the base-line problem. The result is to shift our B values down by a few per cent. The value of A_2 in toluene appears to be too large[5] and may reflect a systematic error in determining J at higher concentrations, caused perhaps by greater overlap of the central peak with the side peaks. Table IV lists values of M from different sources.

Our value of M for PS 705 supports the "high" value for the Rayleigh ratio of benzene by the following reasoning. The molecular weight of PS 705 has been determined by Smith[6,7] using benzene as a scattering standard. The measurements were done at 30° and three wavelengths, 5460, 4358, and 3650 Å. The Rayleigh ratios of benzene which were chosen at these wavelengths were 17.2×10^{-6}, 48.7×10^{-6}, and 112.0×10^{-6} cm^{-1}, respectively, all at a scattering angle of 90°. These are typical "high" values and were based on the measurements of Tomimatsu and Palmer.[8] Smith's results would agree exactly with ours if these Rayleigh ratios were lowered, on the average, by only 2%. The "low" values of the Rayleigh ratio of benzene are about 40% lower, hence clearly incompatible with our results linked with those of Smith.

From the scatter in our data (Figure 2) we find the standard deviation of the mean in the ordinate to reflect a precision of ±1% in M. In addition, there is an uncertainty of perhaps 4% in the product, BK, which gives an overall uncertainty of 5% in M.

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