

## Shear Properties of Polystyrenes in the Transition Region

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### Synopsis

Shear properties of commercially available polystyrenes with narrow molecular weight distribution have been measured in the transition region from 100°C to 150°C and over a frequency range from 50 Hz to 1000 Hz. The effect of molecular weight or shear properties is established with four polymers ranging in molecular weight from 20,000 to 860,000. A broad, bimodal distribution is also studied. The properties of these polymers, with two different diluents added, illustrate the rather marked qualitative difference in effects caused by diluents.

### INTRODUCTION

As the field of polymer physics has developed over the past twenty years, many theories have been proposed and much experimental work published in such areas as solution properties, melt properties, and mechanical properties of the plastic or elastomer. Frequently it has been difficult to make a good correlation between different experiments because the materials used were either not well characterized or were significantly different. Thus, a good comparison between theory and experiment is difficult because the results of different experimental techniques sometimes may be more affected by the material than by the method of measurement.

Recently, well-characterized polystyrenes with narrow molecular weight distribution have become available and are now sold commercially. Thus, it seems advantageous to use these materials for evaluation of experimental methods, both old and new, in order that a good correlation can be achieved between results of different investigators.

This paper presents data obtained by a relatively new method described by Miles and co-workers.<sup>1,2</sup> The instrument measures both components of the complex shear modulus over a wide range of temperature and sample stiffness. This method has been applied to well-characterized polystyrenes to determine the shear modulus over the temperature range from 100°C to 150°C and frequencies from 50 Hz to 1000 Hz. The materials used were commercially available polystyrenes with narrow molecular weight distribution. Molecular weights varied from 20,000 to 860,000. Effects of mixed molecular weights and added diluents were investigated briefly.

## EXPERIMENTAL

### Materials

All polystyrene samples were commercial products obtained from ArRo Laboratories, Joliet, Illinois. The properties of these polymers, as given by ArRo Laboratories, are listed in Table I. They were used as received without further purification. Aroclor 1254 is a product of Monsanto Company and the 1-bromonaphthalene was a laboratory grade from J. T. Baker Chemical Company. Both were used as received.

TABLE I

Catalog no.	Molecular weight	MW/MN ratio
300-3	19,800	less than 1.06:1
300-7	51,000	less than 1.06:1
300-1	160,000	less than 1.06:1
300-5	860,000	less than 1.15:1

### Apparatus

All measurements were made using a Melabs shear generator Model CSG-1. Auxiliary apparatus included an Optimization AC-50 power oscillator, an Applied Cybernetics Model LA240FM amplifier and an Ad-Yu Model 248A vector voltmeter, used with the shear generator as recommended by the manufacturer. The temperature of the shear generator was controlled with an autotransformer and monitored with a Minco Model 100A thermal indicator. The sensor was placed in a small well in the monitor transducer so it was assumed to represent the sample temperature fairly well. In several cases measurements at a given temperature were made on both a heating and cooling cycle. The agreement between such readings indicated that temperature equilibrium was established in the sample for all readings.

Samples were prepared by placing about 300 mg of polymer in a small pellet-type press, heating to about 175°C, and then pressing the sample to a thickness of 1.5 mm. In the case of the lowest molecular weight sample, the pellet shattered when removed from the press, so it was necessary to prepare the sample by melting polymer in place in the shear generator.

When diluent was added to the polymer, the mixture was made up in a small aluminum foil dish. The aluminum foil was carefully folded to tightly enclose the mixture and then heated to 170°C for 1/2 hr. After cooling, the aluminum foil was opened and the glassy polymer removed, broken into small pieces, and placed in the pellet press used for pure polymer. The material was then pressed into a flat sample as described above. This procedure appeared to yield a homogeneous mixture of polymer and diluent.

In all cases the mixture contained 0.200 g polymer and 0.070 g diluent, so the diluent concentration was 26% by weight for all samples.

For higher molecular weights, where a small flat sample was obtained from the press, the sample was placed in the instrument between the driver and monitor shear plates and the clamping screw was tightened lightly by hand. The chamber was closed and heated to about 160°C. It was then opened and the clamping screw was tightened with the wrench provided. Any excess polymer was trimmed off with a sharp knife and the chamber was closed. After the temperature had stabilized again, the autotransformer was adjusted so that the chamber cooled at a rate of about 10°C per hour. Readings of the output signal, in phase and in quadrature with the driving signal, were taken at approximately 5°C intervals as the sample cooled.

The frequency range covered was from 50 Hz to 1000 Hz. The upper frequency was determined by limitations of the shear generator and the lower frequency was determined by limitations of the vector voltmeter used.

## RESULTS

Since all of the data presented here covers a wide temperature range but rather limited frequency range, it seems most appropriate to make comparisons on the basis of temperature dependence at one frequency. In this way, the results as they are obtained can be compared without resort to time-temperature superposition which would be necessary to get useful information about the frequency dependence.

The observed amplitudes are directly related to  $G'$  and  $G''$ , the shear moduli, through geometric factors and the calibration constant for the instrument. However, the data is presented as  $G'$  and  $\tan \delta = G'/G''$ , since these two quantities seem to give the best graphic picture of the material's behavior.

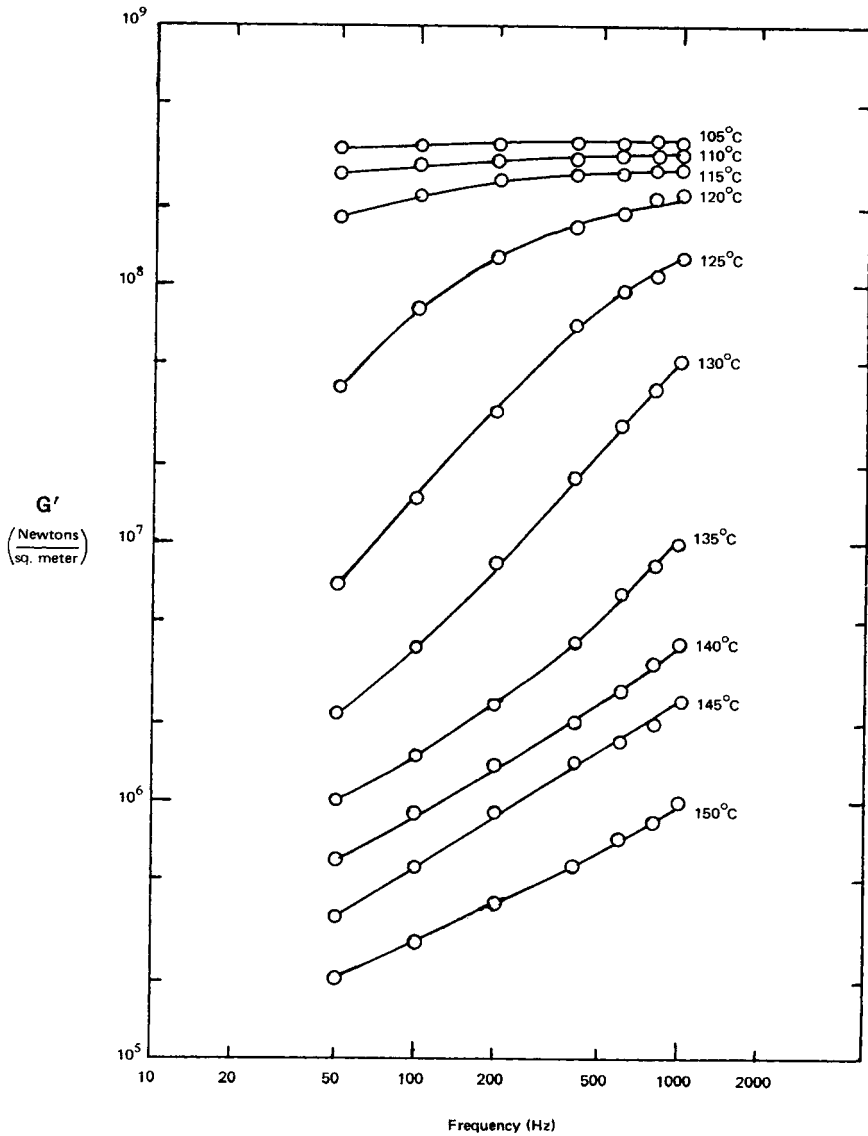
Therefore, all data are presented as graphs of  $G'$  or  $\tan \delta$  versus temperature at a frequency of 1000 Hz, except for Figure 1 where the frequency dependence is shown for one typical polymer at several temperatures.

### Molecular Weight Effects

The complex modulus was determined individually for all four polystyrenes over the temperature range from 100°C to 150°C. This covered the transition region for these polymers. The results are given in Figure 2. Figure 2a presents the rigidity modulus and Figure 2b gives the loss factor.

It can be seen that there is very little molecular weight effect above 100,000. The loss factors are identical within experimental error for the three highest molecular weights but differ significantly at 20,000. The rigidity modulus does not vary for the two highest molecular weights. The sample of molecular weight 51,000 shows a behavior intermediate between the 20,000 and 160,000 materials, except that at low temperature, approaching the glassy region, it has a modulus equal to that for the 20,000 sample.

Therefore, we see that molecular weight effects exist below molecular weight 100,000, where the modulus in the glassy region is significantly



(a)

Fig 1. (continued)

lower than for higher molecular weight. In addition, the modulus remains lower through the transition region and the loss maximum appears at lower temperatures for molecular weights below 50,000.

### Molecular Weight Distribution

To examine the effect of molecular weight distribution, a sample was prepared by mixing equal weights of polymers having molecular weights

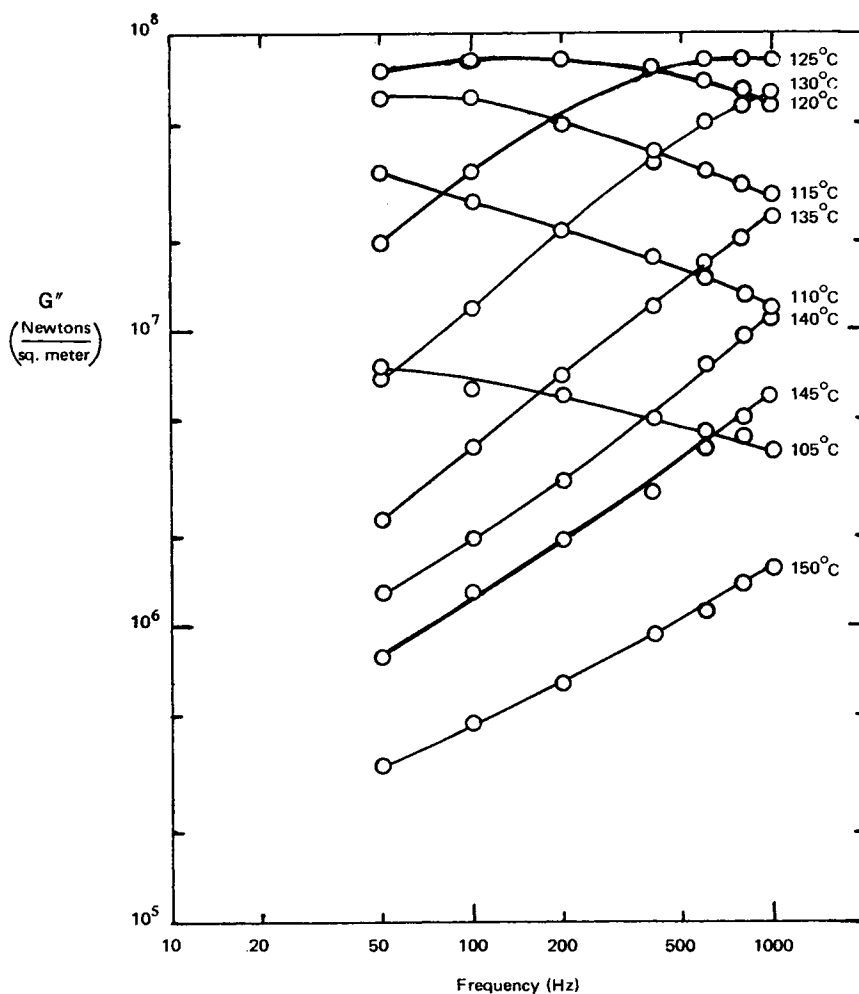


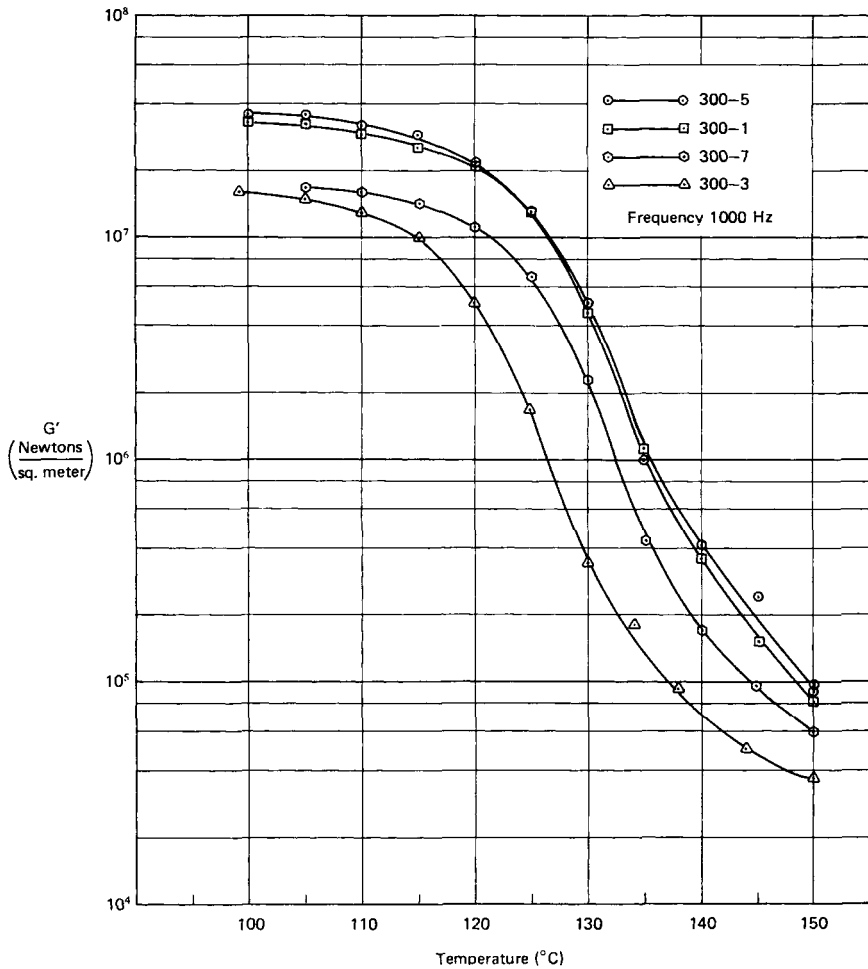
Fig. 1. Shear moduli  $G'(a)$  and  $G''(b)$  for polymer 300-5 at several temperatures from 100 to 150°C.

860,000 and 19,800. The calculated average molecular weights for this mixture are:

Number-average molecular weight = 39,000

Weight-average molecular weight = 440,000

The rigidity modulus for this mixture is shown in Figure 3a together with the corresponding curve for the narrow distribution material of molecular weight 51,000. Since the molecular weight dependence has been shown to be slight, it appears that the number-average molecular weight is the best measure of behavior in the transition region; but, as the glassy state is ap-



(a)

Fig. 2. (continued)

proached, the modulus approaches that of a material of equivalent weight-average molecular weight.

Figure 3b shows the loss factor for the mixed sample, together with similar curves for narrow distribution polymers of both high and low molecular weights. In general, the mixed material loss factor is intermediate between the other two; but as the glassy region is approached, it becomes significantly lower than that for either of the pure materials.

It is risky to draw general conclusions from so little data, but these observations indicate that the flow behavior of such a polymer is determined primarily by the low molecular weight material whereas the mechanical properties of the glassy polymer are governed by the high molecular weight

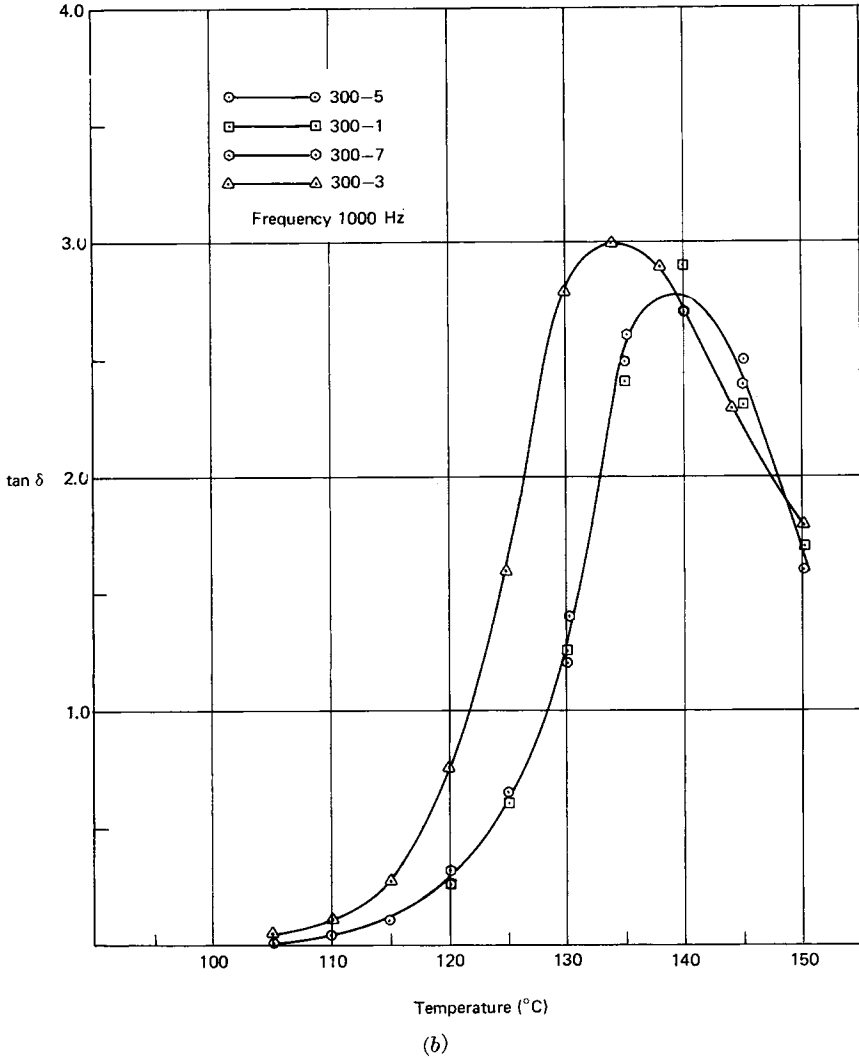
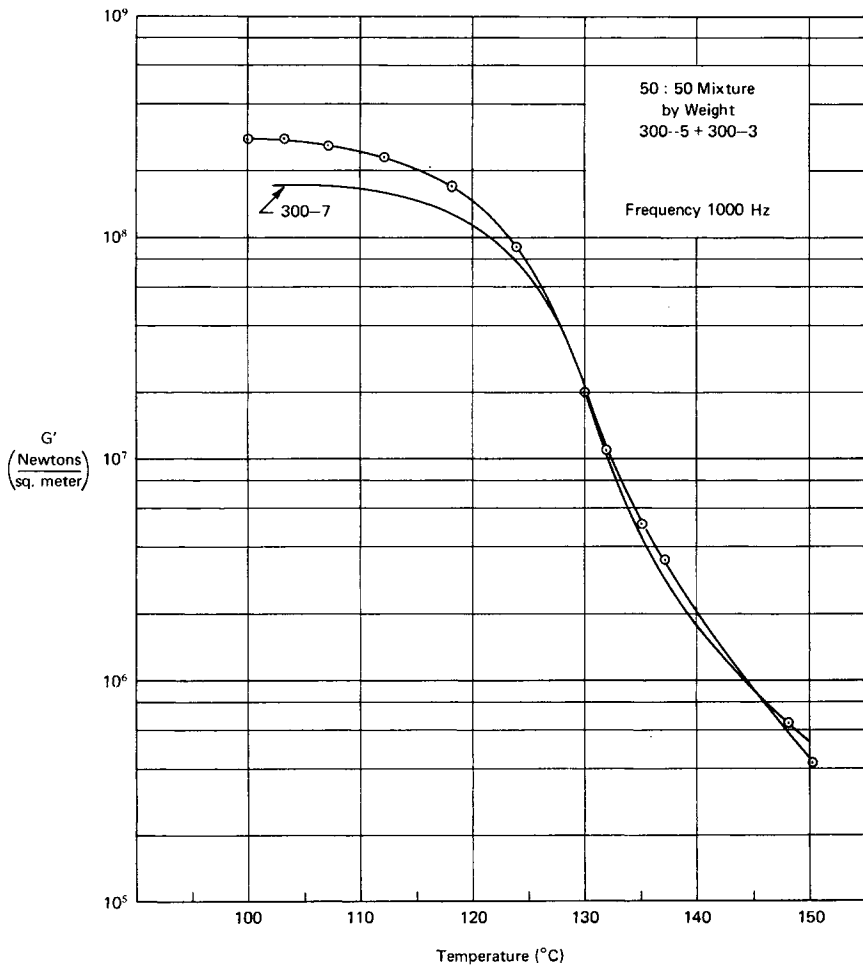


Fig. 2. Shear modulus (a) and loss tangent (b) for several polymers from 100 to 150°C.

portion. Thus we see why a material of appropriate molecular weight distribution will have a better combination of properties for molding than any narrow distribution polymer.

#### Effect of Added Diluent

For this study, it was of interest to investigate the effect of added diluent, or plasticizer, on the mechanical properties at each molecular weight. It was anticipated that addition of diluent would shift the frequency dependence so that molecular weight effects would become more pronounced. Two diluents were chosen for this study, 1-bromonaphthalene and Aroclor



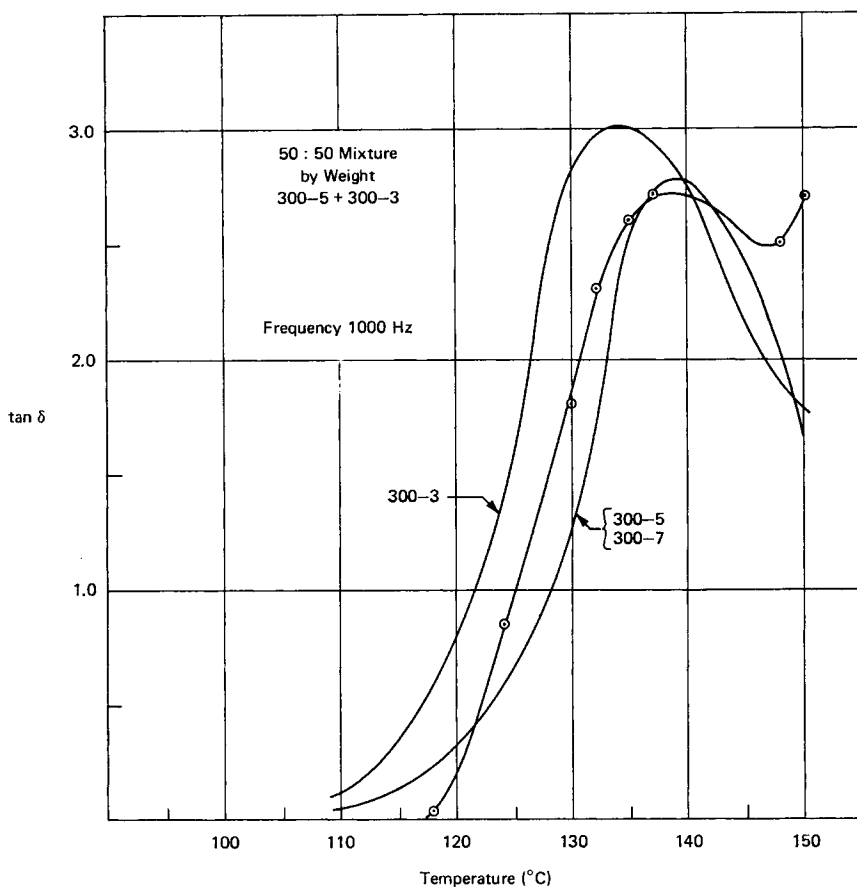
(a)

Fig. 3. (continued)

1254. They were selected on the basis of low vapor pressure and ready availability in the laboratory. The results are shown in Figure 4.

Comparison of the modulus curves in Figure 4a with those for the pure materials in Figure 2a shows two interesting features. As expected, the molecular weight dependence changes. In the presence of diluent significant difference in behavior can be seen between molecular weights 860,000 and 160,000, whereas for pure materials these two curves were almost superimposed. If one compares the temperatures at which the material has a modulus of  $10^7$  Newtons/m<sup>2</sup>, it is found to be lowered from 135 $^{\circ}\text{C}$  to 103 $^{\circ}\text{C}$  for molecular weight 860,000, from 135 $^{\circ}\text{C}$  to 100 $^{\circ}\text{C}$  for molecular weight 160,000, and from 132 $^{\circ}\text{C}$  to 78 $^{\circ}\text{C}$  for 51,000. Thus curves which were originally displaced by 3 $^{\circ}\text{C}$  have been separated until they are displaced by 25 $^{\circ}\text{C}$ .





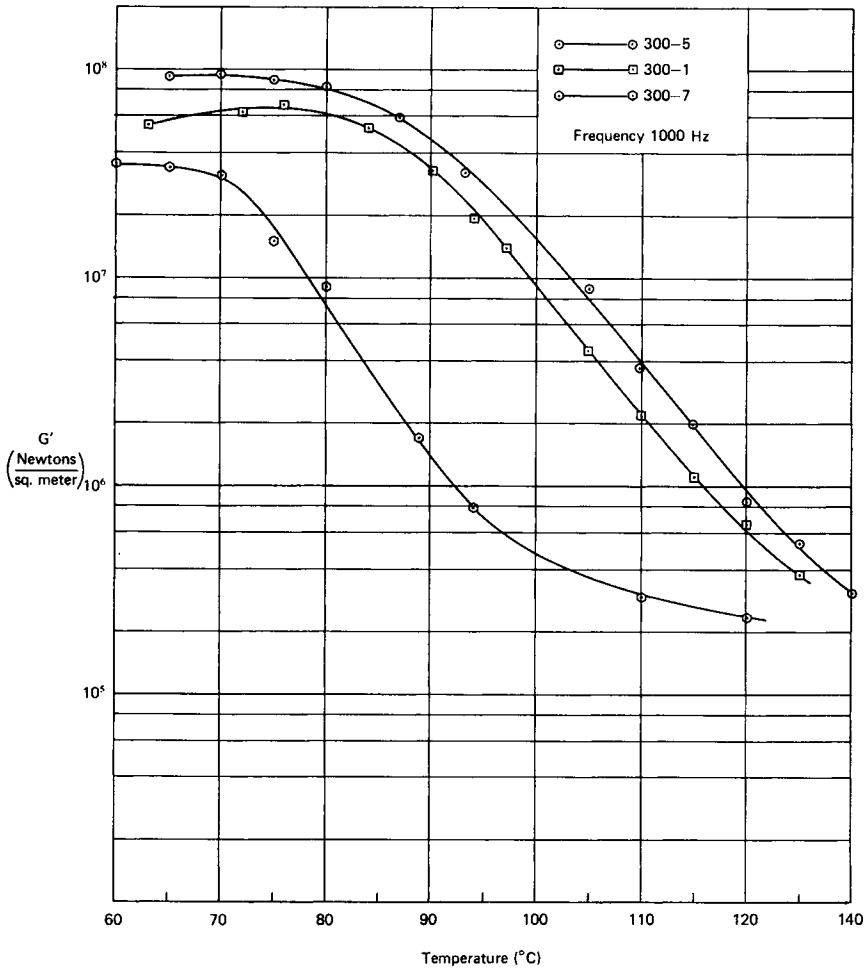
(b)

Fig. 3. Shear modulus (a) and loss tangent (b) for a mixed polymer of two different molecular weights.

The second difference in the curves is that as the material becomes glassy, as indicated by a flattening of the modulus curve, the magnitude of the modulus is lower by a factor of about 5 for the dilute or plasticized material than it is for the pure polymers.

Figure 2b gives the loss factor for the various materials and clearly shows a new effect which was not so obvious in the modulus curves. In place of the sharp, well-defined loss curve obtained with pure materials, the peak is now broad and diffuse with clear indications of several underlying maxima. Thus, when 1-bromonaphthalene is used as plasticizer, several relaxation mechanisms are possible which are not possible in the pure polymer, even at molecular weight 20,000.

In contrast to the results with 1-bromonaphthalene, when Aroclor 1254 is used as diluent, the loss factor is much the same as for the pure material, except that the maximum is shifted to about 120°C instead of 140°C for the



(a)

Fig. 4. (continued)

pure polymer. The modulus reaches an upper value about equal to that of the 1-bromonaphthalene plasticized sample, but the transition region occurs at about  $10^\circ$  higher temperature.

Looking at the temperature at which the sample has a modulus of  $10^7$  N/m<sup>2</sup>, we find, for a molecular weight of 860,000, that this temperature is  $135^\circ\text{C}$  for the pure material,  $115^\circ\text{C}$  when plasticized with Aroclor 1254, and  $104^\circ\text{C}$  when plasticized with 1-bromonaphthalene. These results are shown in Figure 5.

## DISCUSSION

This work has presented the shear modulus and loss factor for a series of polystyrenes in the transition region where the modulus varies from  $10^5$

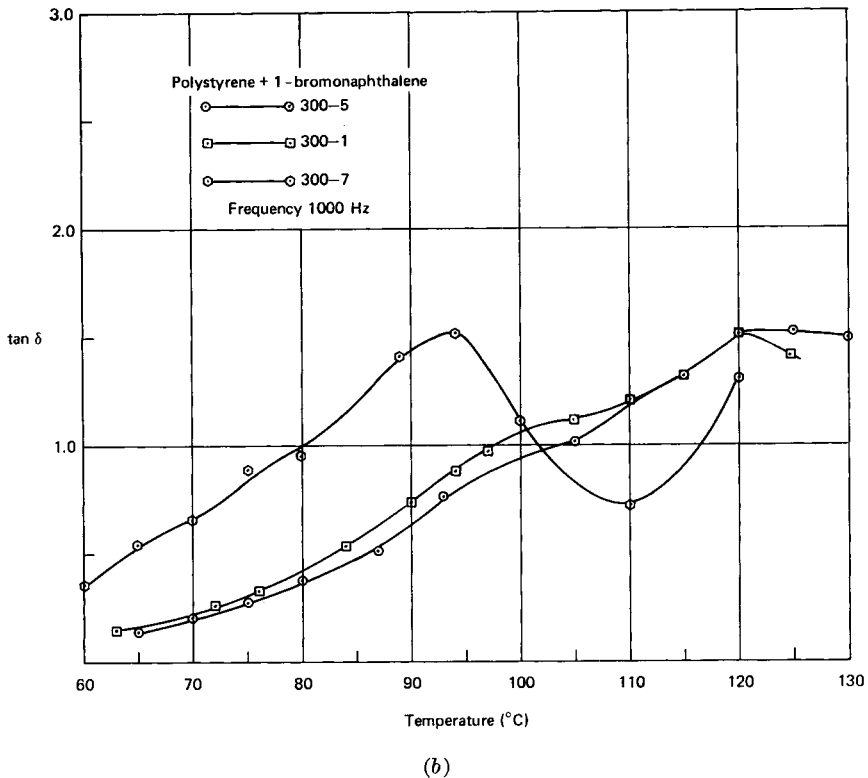
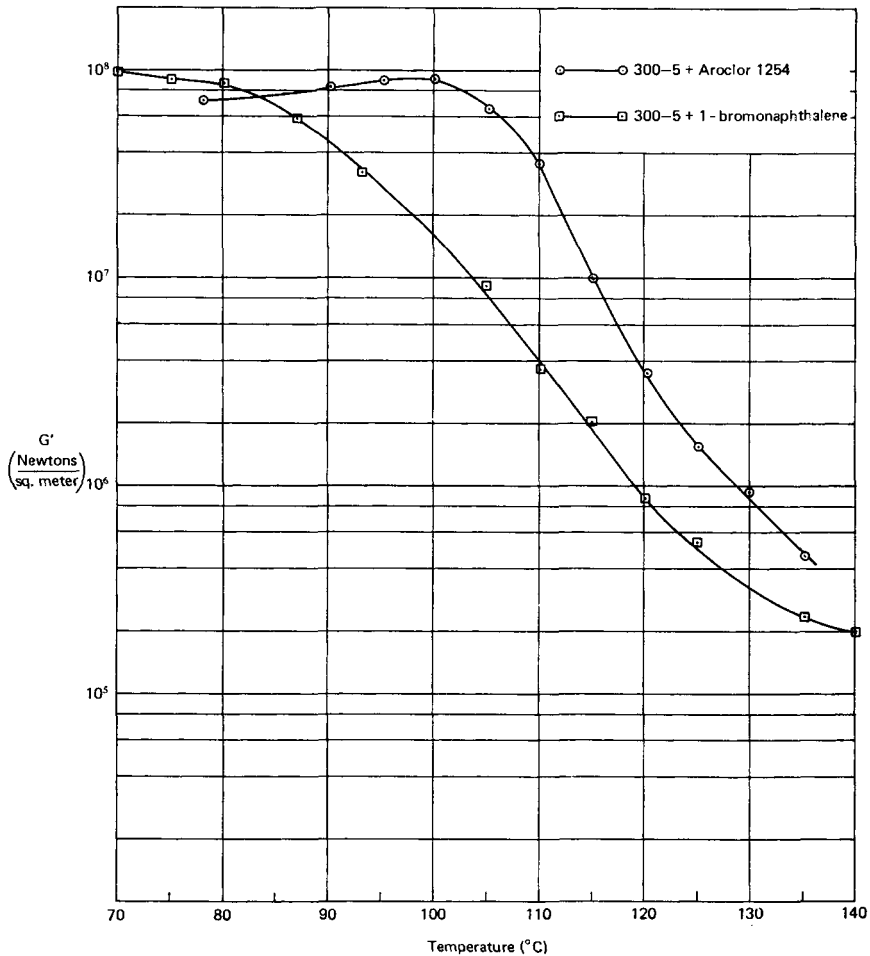


Fig. 4. Shear modulus (a) and loss tangent (b) for three polymers mixed with 1-bromonaphthalene.

to  $5 \times 10^8 \text{ N/m}^2$ . When the polymers have narrow molecular weight distribution, the modulus and loss factor curves are nearly identical above molecular weight 100,000. Below this value there is some molecular weight dependence.

The same qualitative results are observed at 100 Hz and 1000 Hz although quantitatively a temperature shift of  $9^\circ\text{C}$  is necessary to make the curves superimpose.

These results are in contrast to those of Onogi et al.<sup>3</sup> who studied polystyrene melts where the modulus varied from  $10$  to  $10^5 \text{ N/m}^2$ . In this region, they found some molecular weight dependence at 1000 Hz and a more pronounced dependence at 100 Hz up to molecular weights of 200,000. At this point it is difficult to say whether this difference is attributable to differences in behavior in the melt region versus that in the rubbery and transition region, to differences in the polymers used in the two studies, or to the fact that their measurements were made at much lower frequencies and extended by time-temperature superposition. This question can only be resolved by making measurements on identical materials using techniques where some overlap is possible in both temperature and frequency.



(a)

Fig. 5. (continued)

When a bimodal distribution is generated by mixing equal weights of the highest and lowest molecular weight polymers, a material is obtained which has properties approaching these of the low molecular weight fraction at high temperatures and those of the high molecular weight fraction when it becomes glassy at low temperatures. Thus one would expect this material to flow relatively easily and yet maintain a high modulus in its glassy form.

It is not easy to compare these results with those of Onogi et al., but, in the limited region where the results overlap, there is at least qualitative agreement. They found very anomalous behavior for prepared samples having bimodal distribution, but it only showed up at lower frequencies and lower modulus than those studied here. Nevertheless, the difference be-

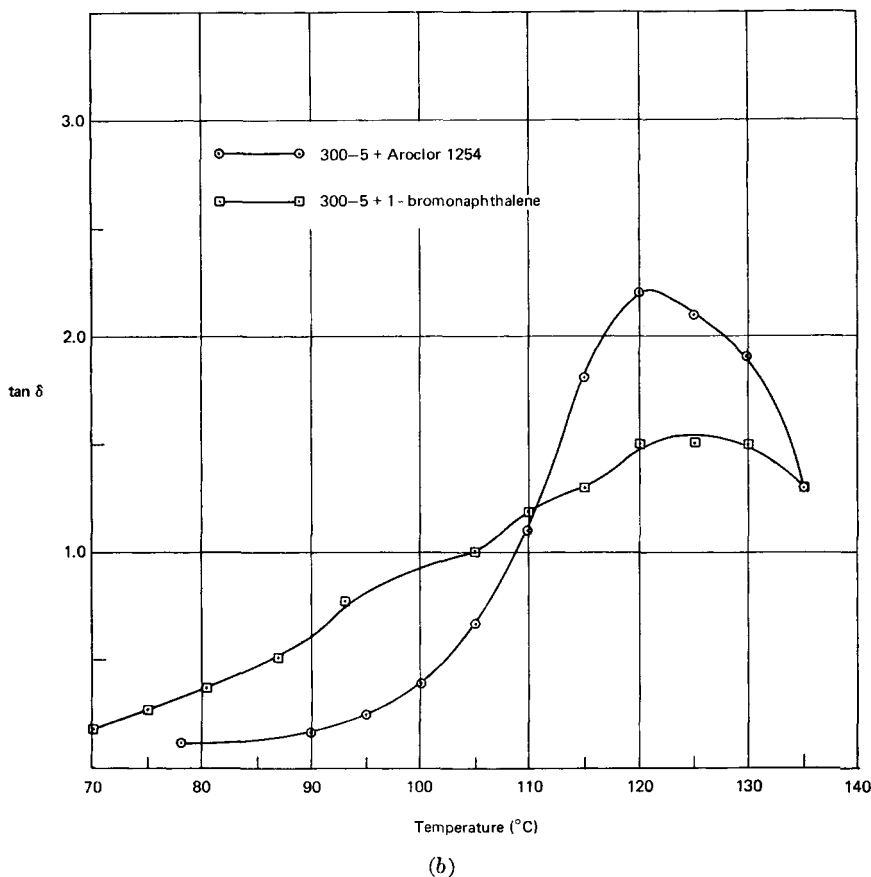


Fig. 5. Shear modulus (a) and loss tangent (b) for one polymer mixed with 1-bromonaphthalene and with Aroclor 1254.

tween broad, bimodal and broad, monomodal distributions should be examined in the transition region to provide a comparison with their work.

Having found some interesting behavior with a mixture of two polymers of widely different molecular weight, it was of interest to examine the effect of low molecular weight additives.

The results obtained with 1-bromonaphthalene clearly indicate that several distinct relaxation mechanisms are effective when polystyrene is diluted with this substance. This is true for all molecular weights above 50,000. No data were obtained at lower molecular weight. On the other hand, when Aroclor 1254 is used as diluent, the behavior suggests a single relaxation mechanism as in the pure polymer.

For both diluents the modulus achieved at low temperatures is about the same and lower by 5 than that of pure material. It seems, therefore, that molecular motion in the glassy region is easier in the presence of diluent but that the nature of the dilution material is not important. Ease of seg-

mental motion of the polymer is determined by the volume fraction of low molecular weight material which can easily adjust to stress changes.

Molecular motion in the transition region is much more complex and presumably depends on thermodynamic interactions between diluent and polymer. Thus a strong interaction may lead to diluent molecules gathering around part of a polymer molecule and effectively "dissolving" it. Then motion of that part will be easier and very different than motion of the remainder of the molecule which is strongly entangled with other large molecules.

Detailed study of this point requires more experimental data than is given here. Specifically, more diluent concentrations must be used, thermodynamic interaction parameters for each polymer-diluent correlation would be helpful, and comparison with other overlapping experimental techniques using the same polymers and diluents might be informative.

Part of this work was done while the author was with Melabs, Palo Alto, Calif.

### References

1. D. O. Miles, *J. Appl. Phys.*, **33**, 1422 (1962).
2. D. O. Miles, G. C. Knollman, and A. S. Hamamoto, *Rev. Sci. Inst.*, **36**, 158 (1965).
3. S. Onogi, H. Kato, S. Ueki, and T. Ibaragi, *J. Polym. Sci. C 15*, 481 (1966).

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