

## Effect of Dispersity on the $T_{II}$ ( $> T_g$ ) Transition in Polystyrene

C. A. GLANDT, H. K. TOH,\* and J. K. GILLHAM, *Polymer Materials Program, Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08540*, and R. F. BOYER,† *Dow Chemical Company, Midland, Michigan 48640*

### Synopsis

The presence of a high temperature ( $> T_g$ ) relaxation in amorphous polystyrene has been investigated further. In the previous work,<sup>1</sup> the techniques of differential thermal analysis (DTA) and torsional braid analysis (TBA) were employed to study polystyrene as a function of "monodisperse" molecular weight. The occurrence of the  $T_{II}$  transition appeared to be associated with the attainment of a critical viscosity level which also corresponded with a free volume level. An entanglement network developed at a critical value of molecular weight,  $M_c$ , giving a break in the  $T_{II}$ -versus- $M$  plots. The present work deals with the influence of dispersity on the  $T_{II}$  transition, below and above  $M_c$ . A series of binary blends of "monodisperse" anionically polymerized polystyrenes with systematic changes in  $\bar{M}_n$  and heterogeneity index ( $\bar{M}_w/\bar{M}_n$ ) was tested by TBA. The results show that when both components have molecular weights below  $M_c$ , single and average values of  $T_g$  and  $T_{II}$  are observed which are linearly related to  $\bar{M}_n^{-1}$ , as predicted by free volume arguments. Although a single  $T_g$  is observed when one component has a molecular weight above and the other has a molecular weight below  $M_c$ , the components appear to undergo the  $T_{II}$  relaxation independently. The results indicate that both the glass transition and the  $T_{II}$  transition are basically governed by the same type of molecular motion but at different length ranges.

### INTRODUCTION

The high-temperature relaxation in amorphous noncrosslinked polymers has been presented in the literature as an elusive phenomenon and as one which is controversial in nature.<sup>2</sup> A recent systematic study<sup>1</sup> investigated variation of the transition with change in molecular weight for "monodisperse" anionically and thermally polymerized polystyrenes. In that work, supported polymer samples were employed to characterize the liquid region using the techniques of torsional braid analysis (TBA)<sup>3</sup> and differential thermal analysis (DTA).

In particular, a definitive loss peak obtained above  $T_g$  using the dynamic mechanical technique was associated with the liquid-liquid transition.

Preliminary results on blends<sup>1</sup> suggested that further elucidation of the phenomenon would be gained by examining broadened distributions. In this work, bimodal distributions with a wide range of heterogeneity indices ( $\bar{M}_w/$

\* On leave from the Malaysian University of Science, Pinang, Malaysia.

† Present address: Midland Macromolecular Institute, Midland, Michigan 48640

$\bar{M}_n$ ) were tested by TBA. The thermomechanical spectra were obtained between  $T < T_g$  and 200°C in both directions of change in temperature.

## EXPERIMENTAL

### Chemicals

Table I shows the molecular weights and dispersities of the polystyrenes used in the preparation of the binary blends (source: Pressure Chemical Co.,

TABLE I  
Molecular Weights and Heterogeneity Indices of Anionic Polystyrenes<sup>a</sup>

Batch no.	$\bar{M}_n$	$\bar{M}_w^c$	$\bar{M}_v^e$	$\bar{M}_w/\bar{M}_n$
14b	1,990,000 <sup>b</sup>	2,050,000	2,340,000	<1.30
13a	640,000 <sup>b</sup>	670,000	678,000	<1.10
3b	355,000 <sup>b</sup>	392,000	388,000	<1.10
1c	193,000 <sup>b</sup>	200,000	186,000	<1.06
4b	111,000 <sup>b</sup>	111,000	111,000	<1.06
7b	36,000 <sup>b</sup>	33,000	38,000	<1.06
2b	20,200 <sup>b</sup>	20,800	20,400	<1.06
8b	9,600 <sup>d</sup>	—	9,300	<1.10
11b	3,100 <sup>d</sup>	—	3,600	<1.10
12b	2,050 <sup>d</sup>	—	2,120	<1.10

<sup>a</sup> Polymers and characterization: Pressure Chemical Co., Pittsburgh, Pa

<sup>b</sup> Membrane osmometry.

<sup>c</sup> Light scattering

<sup>d</sup> Vapor-pressure osmometry.

<sup>e</sup> Intrinsic viscosity.

TABLE II  
Composition of Bimodal Blends:  $\bar{M}_n = 70,000^a$

$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$(\bar{M}_n)_A < M_c$	$(\bar{M}_n)_B > M_c$	Weight fraction B
70,000	2.3	20,200	193,000	0.794
70,000	8.0	9,600	640,000	0.876
70,000	27.2	3,100	1,990,000	0.957

<sup>a</sup> See Fig. 5.

TABLE III  
Composition of Bimodal Blends:  $\bar{M}_n = 8,000^a$

$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$(\bar{M}_n)_A$	$(\bar{M}_n)_B$	Weight fraction B
8,000	1.1	3,100	9,600	0.905
8,000	1.9	3,100	20,200	0.723
8,000	1.2	2,050	9,600	0.945
8,000	3.1	3,100	36,000	0.67
8,000	8.9	3,100	111,000	0.63
8,000	27.6	3,100	355,000	0.61

<sup>a</sup> See Fig. 6.

TABLE IV  
Effect of  $\bar{M}_n$  of Bimodal Blends on  $T_g$  and  $T_{ll}$ :  $\bar{M}_A$  and  $\bar{M}_B < M_c^a$

Weight percentage		$T_{ll}, ^\circ\text{C}$ [Hz]	$T_g, ^\circ\text{C}$ [Hz]	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$(1/\bar{M}_n) \times 10^4$
$(\bar{M}_n)_A = 2,050$	$(\bar{M}_n)_B = 20,200$					
0	100	141 [0.34]	108 [.21]	20,200	<1.1	0.495
20	80	130 [0.34]	97 [.19]	7,380	2.2	1.35
40	60	121 [0.34]	90 [.18]	4,450	2.9	2.25
60	40	110 [0.35]	81 [.21]	3,230	2.9	3.1
80	20	103 [0.33]	75 [.21]	2,510	2.3	3.91
100	0	95 [0.35]	67 [.20]	2,050	<1.1	4.88

<sup>a</sup> See Figs. 1 and 7.

TABLE V  
Effect of  $\bar{M}_n$  of Bimodal Blends on  $T_g$ :  $\bar{M}_A < M_c, \bar{M}_B > M_c^a$

Weight percentage		$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$(1/\bar{M}_n) \times 10^5$	$T_g, ^\circ\text{C}$
$(\bar{M}_n)_A = 9,600$	$(\bar{M}_n)_B = 111,000$				
100	0	9,600	<1.1	10.4	103
90	10	10,500	1.9	9.5	104
80	20	11,900	2.5	8.4	104.5
75	25	12,400	2.8	8.0	105
70	30	13,200	3.0	7.6	105.7
60	40	15,100	3.3	6.7	106.5
50	50	17,600	3.4	5.6	107.5
40	60	21,200	3.3	4.7	108.4
30	70	26,600	3.0	3.7	109.5
20	80	35,600	2.5	2.8	110.5
10	90	53,900	1.9	1.8	111
5	95	78,600	1.3	1.3	112.5
0	100	111,000	<1.1	0.9	114

<sup>a</sup> See Figs. 3 and 8.

Pittsburgh, Pennsylvania). In blends, A refers to the lower molecular weight component and B to the higher molecular weight component (Tables II-V).

### Specimen Preparation

Four series of blends (i.e., I, II, III, and IV) were prepared. Details of series I and II are shown in Figures 1-4, and details of the compositions of the blends for series III and IV are shown in Tables II and III.

A multifilamented heat-cleaned glass braid acting as support for the polymer was impregnated in the requisite toluene solution. 15% solutions (g polymer/ml toluene) were used for series I and II, whereas 5% solutions were used for series III and IV.

### TBA

The coated braid was mounted as part of a freely oscillating torsional pendulum.<sup>3</sup> A fully automated TBA unit was employed.<sup>4</sup> In this, a repetitive

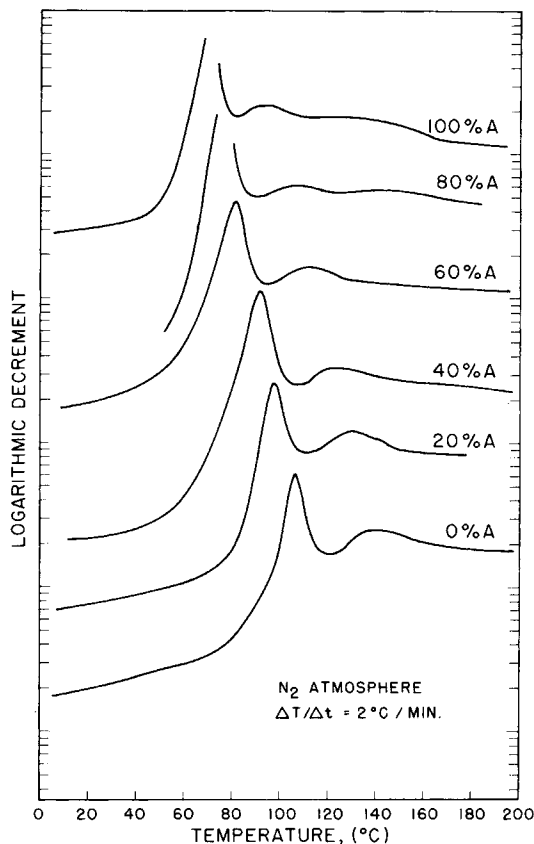


Fig. 1. Effect of blending of anionic polystyrene (A + B) on TBA logarithmic decrement spectra:  $(\bar{M}_n)_A = 2,050$ ;  $(\bar{M}_n)_B = 20,200$ .

sequence of transducer alignment, wave initiation, calculation of the mechanical parameters of the composite specimen and their digital print-out with temperature (mV) on paper tape, and analog plotting of the two mechanical parameters versus temperature on an XYY plotter operated automatically throughout the experiment. The mechanical behavior of the composite specimen is characterized in terms of two parameters: relative rigidity ( $= 1/P^2$ , where  $P$  = period in seconds of the damped oscillations) and logarithmic decrement ( $\Delta = \ln A_i/A_{i+1}$ , where  $A_i$  is the peak amplitude of the  $i$ th oscillation). In a typical experiment, the specimen was dried in a fast-flowing atmosphere of nitrogen while being heated from 25° to 200°C. The thermomechanical behavior was monitored in nitrogen as follows:

*Series I and II* (Figs. 1–4): drying, R.T.  $\rightarrow$  200°C; experiment, 200°  $\rightarrow$  -190°  $\rightarrow$  200°C; data shown,  $T < T_g \rightarrow \sim 200^\circ\text{C}$ .

*Series III and IV* (Figs. 5 and 6): drying, R.T.  $\rightarrow$  200°C; experiment, 200°  $\rightarrow$   $T < T_g \rightarrow$  200°C; data shown,  $T < T_g \rightarrow \sim 200^\circ\text{C}$ .

Since the occurrence of the  $T > T_g$  transition was clearly observed in the logarithmic decrement-versus-temperature curves, transitions were defined as the temperature of the maxima of loss peaks. Examples of the relative rigidity-versus-temperature plots are shown in Figures 2 and 4: the insensitiv-

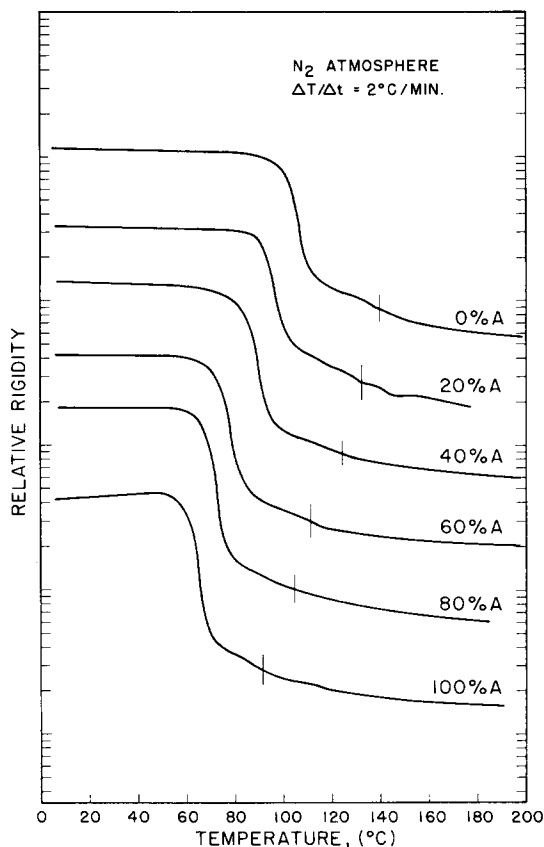


Fig. 2. Effect of blending of anionic polystyrene (A + B) on TBA relative rigidity spectra:  $(\bar{M}_n)_A = 2,050$ ;  $(\bar{M}_n)_B = 20,200$ .

ity of the rigidity function to the transition is apparent. [Vertical tick marks designate the location of the maxima in the logarithmic decrement in Fig. 2 where a unique  $T_{II}$  transition occurred for each polymer blend. The blends used for Fig. 4 did not reveal a single  $T_{II}$  transition (see below).]

## RESULTS AND DISCUSSION

Four sets of experiments were performed:

I. Binary blends of varying molar ratios of two "monodisperse" polymers with molecular weights of both components below the critical molecular weight ( $M_c$ ).

II. Binary blends of varying molar ratios of two "monodisperse" polymers with molecular weight of one component below and the other above the critical value.

III. Binary blends of different molecular weight distributions prepared from various "monodisperse" samples to give  $\bar{M}_n = 70,000$  and  $\bar{M}_w/\bar{M}_n$  varying from 2.3 to 27.2.

IV. Binary blends of different molecular weight distributions prepared

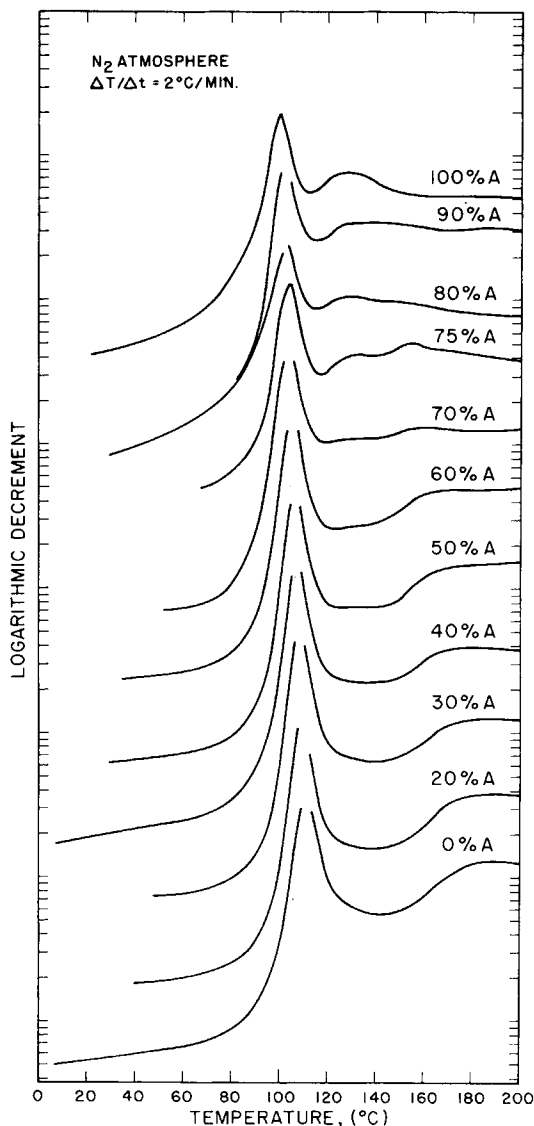


Fig. 3. Effect of blending of anionic polystyrene (A + B) on TBA logarithmic decrement spectra:  $(\bar{M}_n)_A = 9,600$ ;  $(\bar{M}_n)_B = 111,000$ .

from various "monodisperse" samples to give  $\bar{M}_n = 8000$  and  $\bar{M}_w/\bar{M}_n$  varying from 1.1 to 27.6.

The thermomechanical spectra (logarithmic decrement) for the four series of experiments are shown in Figures 1, 3, 5, and 6. The curves presented are for the increasing temperature programming mode ( $T < T_g \rightarrow \sim 200^\circ\text{C}$ ) and have been displaced vertically by arbitrary amounts for the purpose of clarity.

A brief discussion of the data follows:

1. From Figure 1, the single glass transitions and the single high-temperature transitions ( $T_H$ ) are observed. The values of the transition temper-

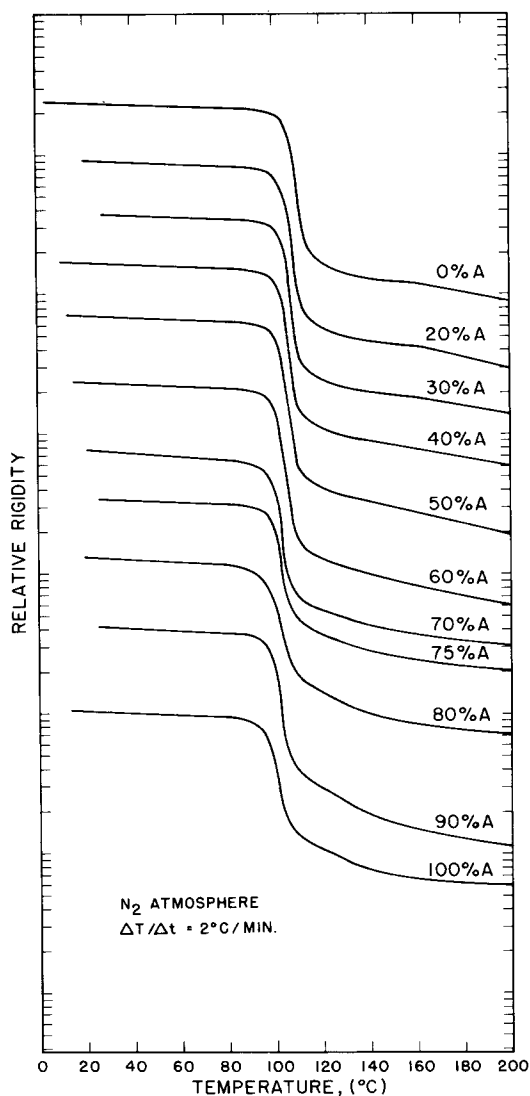


Fig. 4. Effect of blending of anionic polystyrene (A + B) on TBA relative rigidity spectra:  $(\bar{M}_n)_A = 9,600$ ;  $(\bar{M}_n)_B = 111,000$ .

atures are tabulated in Table IV and are plotted versus  $1/\bar{M}_n$  in Figure 5. A linear relationship was obtained for both  $T_g$  and  $T_{ll}$ . This clearly indicates that when the molecular weights of both components are below  $M_c$ , both  $T_g$  and  $T_{ll}$  depend on the total number of chain ends regardless of the degree of dispersity. This is further emphasized by the significant departure from linearity of the plot  $T_{ll}$  versus  $\bar{M}_w^{-1}$  which is also shown in Figure 5. The range of heterogeneity indices was from 1.1 to 2.9 in these experiments.

The nature of the glass transition is controversial and has been considered in terms of being an iso-free-volume,<sup>5-7</sup> an iso-entropic,<sup>8</sup> and an iso-viscous phenomenon.<sup>9</sup> In the previous investigation,<sup>1</sup> "monodisperse" samples ( $\bar{M}_w/\bar{M}_n \sim 1.1$ ) were employed and led to  $T_{ll}$  values which could be associ-

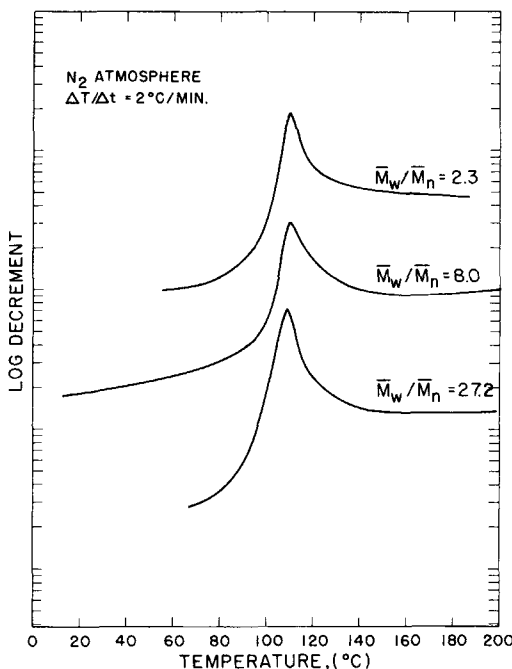


Fig. 5. Effect of  $\bar{M}_w$  on  $T_g$  and  $T_u$  for blends of anionic polystyrene with  $\bar{M}_n = 70,000$ .

ated with both an iso-free-volume and an iso-viscous basis for the  $T_u$  process.

The implication of the present results is that both the glass transition and the  $T_u$  transition are basically governed by the same type of molecular motion.<sup>1,2</sup> Since the  $T_u$  transition occurs at a higher temperature than the glass transition, the molecular motion associated with the  $T_u$  transition is longer range than the  $T_g$  transition and may involve shifting of the whole molecule by cooperative segmental motion. More supportive evidence for this statement will be seen in section 2 below.

2. The data for this series of blends, where  $\bar{M}_n = 9,600$  and  $111,000$  for the two components, are shown in Figures 3 and 4. Single glass transition temperatures are observed in the data. However, the  $T_u$  transitions show complexities which are discussed later.

Table V summarizes details of the compositions examined, together with determined values of the glass transition temperatures. The  $T_g$  values are plotted versus  $1/\bar{M}_n$  in Figure 8. Two linear regions are observed which intersect at  $\bar{M}_n \approx 50,000$ . This behavior agrees fairly well with that reported for "monodisperse" polystyrene samples<sup>1</sup> where the intersection occurred at  $\bar{M}_n \approx 66,000$ . Each of the regions can be expressed<sup>10</sup> by

$$T_g = T_g^\infty - K_g \bar{M}_n^{-1}.$$

The critical molecular weight has been associated with chain entanglements.<sup>1</sup>

For  $T_u$  of monodisperse polymers, it was also concluded<sup>1</sup> that

$$T_u = T_u^\infty - K_u \bar{M}_n^{-1}$$



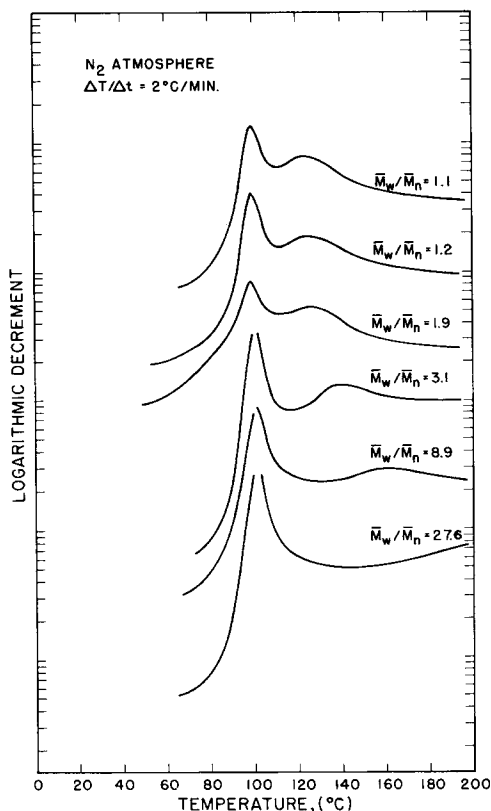


Fig. 6. Effect of  $\bar{M}_w$  on  $T_g$  and  $T_{ll}$  for blends of anionic polystyrene with  $\bar{M}_n = 8,000$ .

and two sets of constants were found above and below a critical molecular weight. The onset of entanglements associated with the  $T_{ll}$  transition, which for "monodisperse" anionic polystyrene is around 40,000,<sup>1</sup> does not cause any change in the  $T_g$  versus  $1/\bar{M}_n$  relation until a later stage where more entanglements are present. It is observed for "monodisperse" samples<sup>1</sup> that  $M_c(T_g) > M_c(T_{ll})$  or that a certain "concentration of entanglements" must be present to severely restrict the segmental motions which are associated with  $T_g$ .

As seen from Figure 3, in blends of polystyrenes with molecular weight of one of the components below and of the other above  $M_c$ , the  $T_{ll}$  transition region shows a complex pattern which appears to indicate a summation of two individual loss peaks rather than an averaged one. This effect is especially evident in blends of 80/20 and 75/25 wt/wt combinations of the  $\bar{M}_n = 9,600$  and 111,000 molecular weight species, respectively. As the content of the low molecular weight component is lowered, its  $T_{ll}$  loss peak is obscured by the loss level of the high molecular weight component. However, a weighted superposition of the loss levels for the two components appears to account for the shape of all curves. These results are similar to those reported with bimodal blends of polybutadiene<sup>11</sup> where the concentrations of the low molecular weight component determined only the intensities of the maxima of the loss tangents but not the temperatures of their occurrences. Due to the low

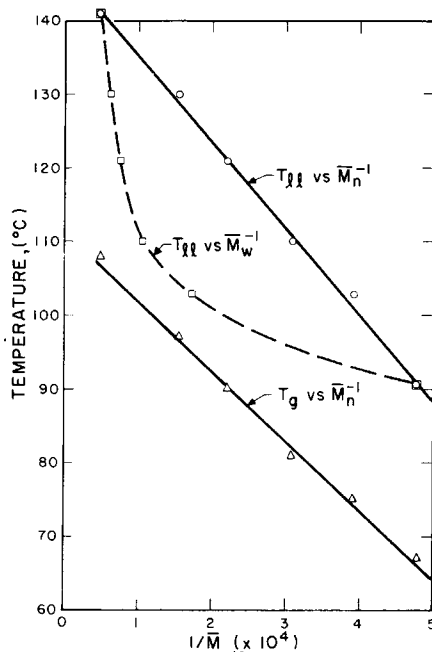


Fig. 7. Effect of  $\bar{M}_n$  and  $\bar{M}_w$  on  $T_g$  and  $T_{ll}$  for anionic polystyrene blends:  $(\bar{M}_n)_A = 2,050$ ;  $(\bar{M}_n)_B = 20,200$ .

value for  $M_c$  for polybutadiene,<sup>12</sup> the molecular weights of both components were above  $M_c$  for all of the blends. This situation has been studied also for polystyrene by the present authors using a bimodal blend with components  $A\bar{M}_n = 111,000$  and  $B\bar{M}_n = 2,000,000$  in a weight ratio of 4:1, respectively. The occurrence of a loss peak (data not shown) which corresponded to the  $T_{ll}$  transition of the low molecular weight component was in agreement with the results of blending of polybutadiene.<sup>11</sup>

The low molecular weight species ( $M < M_c$ ) appear to undergo a liquid-liquid relaxation independently of the high molecular weight species ( $M > M_c$ ).

If the assumption that the  $T_{ll}$  transition involves a shifting of the whole molecule by cooperative segmental motion is acceptable, then it follows that the presence of entanglements would severely restrict this process (much more than it would restrict mere segmental motion) and a higher temperature will be required for the same transition to occur for the high molecular weight component. From the type of behavior that is observed, it is concluded that the low molecular weight component is not affected, with regard to the  $T_{ll}$  transition, by the high molecular weight network.

3. In this series, blends were prepared from various "monodisperse" anionic polystyrenes to give  $\bar{M}_n = 70,000$  and  $\bar{M}_w/\bar{M}_n$  from 2.25 to 27.2 (Table II). Figure 5 shows that only one glass transition is observed for each blend and that the common value (384°K) corresponds to the prediction of Figure 8 ( $T_g$ -versus- $1/\bar{M}_n$  plot). Thus,  $T_g$  depends on  $1/\bar{M}_n$  only.

On the other hand, with respect to the  $T_{ll}$  transition, it is clear that there is no loss peak corresponding to the  $T_{ll}$  value for the "monodisperse" sample of molecular weight 70,000 (which would be around 182°C).

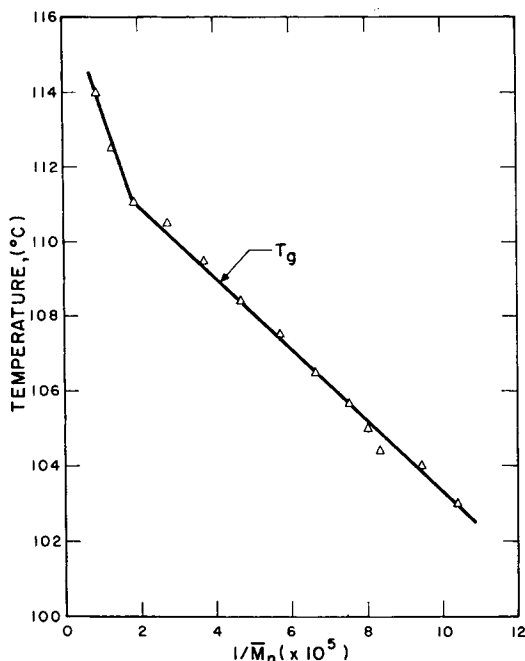


Fig. 8. Effect of  $\bar{M}_n$  on  $T_g$  for anionic polystyrene blends:  $(\bar{M}_n)_A = 9,600$ ;  $(\bar{M}_n)_B = 111,000$ .

Since the high molecular weight component has a value for  $T_{ll}$  higher than the range scanned in these experiments ( $200^{\circ}\text{C}$ ) and since the low molecular weight contributions are small (on a weight basis) or obscured by the averaged glass transition of the blends ( $_A\bar{M}_n = 3,100$ ,  $T_{ll} = 383^{\circ}\text{K}$ ;  $_A\bar{M}_n = 9,600$ ,  $T_{ll} = 413^{\circ}\text{K}$ ;  $_A\bar{M}_n = 20,200$ ,  $T_{ll} = 421^{\circ}\text{K}$ ;  $_B\bar{M}_n = 1,990,000$ ,  $T_g = 386^{\circ}\text{K}^1$ ), it is possible to account for the shape of the observed curves.

4. In this series, six blends were prepared from various "monodisperse" samples to give an  $\bar{M}_n = 8,000$  and  $\bar{M}_w/\bar{M}_n$  varying from 1.1 to 27.6. Three of these blends are made up from components both of which have molecular weights below  $M_c$ . It is seen in Figure 4 that these three blends have the same  $T_g$  and the same  $T_{ll}$ . This confirms the conclusion that  $\bar{M}_n$  determines the value of  $T_g$  and, in the absence of any chain entanglements, the value of  $T_{ll}$ . On the other hand, in those blends where the molecular weight of one of the components is around or above  $M_c$ , the  $T_{ll}$  shows the type of behavior where high and low molecular weight components can be considered to respond independently.

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