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PRINCETON UNIV N J DEPT OF CHEMICAL ENGINEERING  
INVESTIGATION OF THE T SUB LL (> T SUB G) RELAXATION IN HOMOPOL--ETC(U)  
DEC 77 J K GILLHAM, R F BOYER

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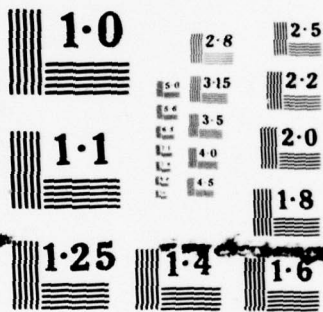


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INVESTIGATION OF THE  $T_{\alpha\alpha}$  ( $> T_g$ ) RELAXATION  
IN HOMOPOLYMERS AND BLOCK COPOLYMERS  
OF STYRENE BY TORSIONAL BRAID ANALYSIS

by

J. K. Gillham and R. F. Boyer

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ABSTRACT

Investigation of the  $T_{\ell\ell}$  ( $> T_g$ ) relaxation in amorphous polymers of styrene by the technique of torsional braid analysis has been reviewed. For the most part the relaxation behaves like the glass transition ( $T_g$ ) in its dependence on molecular weight, on average molecular weight in binary polystyrene blends, and on composition in a polystyrene homogeneously plasticized throughout the range of composition. Diblock and triblock copolymers also display a  $T > T_g$  relaxation above the  $T_g$  of the polystyrene phase.

Two results in particular suggest that the  $T_{\ell\ell}$  relaxation is molecularly based. 1) The temperature  $T_{\ell\ell}$  is determined by the number average molecular weight for binary blends of polystyrene when both components have molecular weights below  $M_c$  (the critical molecular weight for chain entanglements).

2) Homopolymers, and diblock and triblock copolymers of styrene, have a  $T > T_g$  relaxation at approximately the same temperature when the molecular weight of the styrene block is equal to that of the homopolymer.

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INTRODUCTION

The existence of a relaxation located above the temperature of the glass transition in amorphous polymers is a subject of controversy. Evidence for such a "transition" and the main features of its behavior have been summarized (1, 2). Since the transformation involves a change from one liquid state to another it has been designated  $T_{\ell\ell}$ .

Thermomechanical experiments above  $T_g$  for amorphous polymers are facilitated by using supported samples. One method employs a mixture of low molecular weight polymer in a matrix of the same polymer having high molecular weight. In this way, the dependency of a  $T > T_g$  relaxation on molecular weight has been studied for 1,4-polybutadiene (3). The dynamic mechanical experiment ( $\sim 50$  Hz) revealed the transition by a loss peak. Another approach investigates a composite specimen con-

sisting of polymer and inert glass substrate in a torsional pendulum experiment. The technique -- torsional braid analysis (4) -- has been employed to produce the results (2,5,6,7,8) which form the basis for the present article.

#### EXPERIMENTAL

##### *Torsional Braid Analysis (TBA)*

Experiments were performed using a fully automated torsional pendulum which operates at about 1 Hz throughout the range -195 to 500°C. A review (4) summarizes its development, application and experimental procedures.

The instrument generates a series of freely damped waves each of which is characterized by the period ( $P$ , sec) of oscillation and logarithmic decrement ( $\Delta = \ln A_i/A_{i+1}$ , where  $A_i$  is the amplitude of the  $i^{th}$  oscillation in a damped wave). A computer plots thermomechanical spectra of the specimen (in immediate time on an XYY plotter) which present the relative rigidity,  $1/P^2$ , which is directly proportional to the in-phase shear modulus ( $G'$ ), and logarithmic decrement,  $\Delta$ , which is directly proportional to the ratio of the out-of-phase shear modulus ( $G''$ ) to  $G'$ .  $G'$  and  $G''$  are material parameters which characterize the storage and loss of mechanical energy on deformation. Transition temperatures are assigned using peaks in the logarithmic decrement.

Temperature may be changed at controlled rates in both heating and cooling modes.

As an example of the thermomechanical spectra which were used to measure the  $T_g$  and  $T_{\alpha}$  transitions, Fig. 1 shows TBA data for a sample of polystyrene.

Specimens for TBA involving homopolymers were prepared generally from 10 percent solutions (g weight polystyrene/ml volume benzene) by heating the impregnated glass braid in the TBA apparatus to 200°C. Thermomechanical spectra were usually obtained in helium during cooling at 1.5°C/min from the maximum temperature used in preparing the specimen to below the glass transition and during subsequent heating at 1.5°C/minute. A set of TBA data for anionic polystyrenes of different molecular weights is shown in Fig. 2 (5).

#### *Materials*

A set of styrene homopolymer samples, obtained from the Pressure Chemical Co., Pittsburgh, Pa., had been synthesized by an anionic polymerization procedure which produces "monodisperse" material,  $\bar{M}_w/\bar{M}_n \approx 1.1$ . Thermomechanical TBA spectra have also been obtained using samples from fractionation of thermally polymerized styrene (5).

The plasticizer, m-bis(m-phenoxyphenoxy)benzene,  $[\text{C}_6\text{H}_5\text{OC}_6\text{H}_4\text{O}]_2\text{C}_6\text{H}_4$ ; MW = 446.5, BP 273-276°C (1 mm Hg pressure)] was obtained from Eastman Organic Chemicals, Rochester, N. Y. This was used as a plasticizer because of its similarity to polyphenylene oxide, which forms a homogeneous solution with polystyrene throughout the total range of composition, and because benzene could be removed from a braid impregnated

with a solution of polystyrene/plasticizer/benzene without removing plasticizer by heating to 175°C in flowing helium (7).

Details concerning the block copolymers of styrene are shown in Table 1 (8).

#### RESULTS AND DISCUSSION

##### *I. Homopolymers, Blends of Homopolymers and Plasticized Homopolymer.*

The  $T_g$  and  $T_{\ell\ell}$  transition temperatures for "monodisperse" anionic polystyrenes are plotted vs  $1/\bar{M}_n$  (Fig. 3), as is customary in investigating the influence of free volume. The curves were drawn using TBA data; DTA results were added (5). The  $T_g$  plot shows two regions, each of which follows the relationship  $T_g = T_{g^\infty} - K_g \bar{M}_n^{-1}$ . The plot of the  $T_{\ell\ell}$  transition temperature vs  $1/\bar{M}_n$  also displays two regions. Plots of  $T_{\ell\ell}$  and  $T_g$  vs  $1/\bar{M}_n$  for samples from fractionated thermal polystyrene were similar (5). The molecular weight at which the relationship changed corresponded approximately to the critical molecular weight for entanglements ( $M_c$ ).

The  $T_g$  and  $T_{\ell\ell}$  transition temperatures for "monodisperse" anionic polystyrenes are plotted vs  $\log \bar{M}_n$  (Fig. 4). The corresponding results for fractions of thermal polystyrene were similar (5). These plots are similar to isoviscosity plots relating temperature to molecular weight (Fig. 5).

Attempts have been made to distinguish between free volume and isoviscosity bases for the  $T_{\ell\ell}$  transition by examining binary blends of



"monodisperse" anionic polystyrenes (6). When both components had  $\bar{M}_n < M_c$ , both the  $T_g$  and  $T_{\ell\ell}$  transitions were averaged, and an equation similar to that used for averaging  $T_g$  was obeyed:

$$1/T_{\ell\ell} = W_A/A T_{\ell\ell} + W_B/B T_{\ell\ell}$$

where  $A T_{\ell\ell}$ ,  $B T_{\ell\ell}$  and  $T_{\ell\ell}$  are values of the  $T_{\ell\ell}$  ( $^{\circ}\text{K}$ ) transition for polymer A, polymer B and the blend of A and B, and  $W_A$  and  $W_B$  are the respective weight fractions of polymers A and B in the blend. Further, when both components of the blend had  $\bar{M}_n < M_c$ ,  $T_g$  and  $T_{\ell\ell}$  of the blends varied linearly with  $1/\bar{M}_n$  (Fig. 6). However, when one component had  $\bar{M}_n < M_c$  and the other  $\bar{M}_n > M_c$ , although the  $T_g$  was an averaged value (Fig. 7),  $T_{\ell\ell}$  transitions of the individual components were observed. The averaging equation and the dependence of  $T_{\ell\ell}$  on  $1/\bar{M}_n$  for blends suggest a free-volume basis for the  $T_{\ell\ell}$  transition (9).

It is interesting to note that the glass transition temperatures of blends (Fig. 7) and of "monodisperse" polymers (Fig. 3) are affected by entanglements.

Results (Figs. 8 and 9) on a plasticized anionic polystyrene show that the  $T_{\ell\ell}$  transition was observed throughout the range of composition and followed an equation of form (9) which again is similar to that used for  $T_g$ , i.e.

$$T_{\ell\ell} = A T_{\ell\ell} W_A + B T_{\ell\ell} W_B + K W_A W_B$$

where  $K$  is an empirical constant,  ${}_A T_{\ell\ell}$  and  $W_A$  are the  $T_{\ell\ell}$  transition and weight fraction of the pure polystyrene, and  ${}_B T_{\ell\ell}$  and  $W_B$  are the  $T_{\ell\ell}$  transition and weight fraction of the pure plasticizer, respectively.

$K = -59.6^\circ\text{K}$ ,  ${}_A T_{\ell\ell} = 424^\circ\text{K}$  and  ${}_B T_{\ell\ell} = 274^\circ\text{K}$  for the particular plasticizer/polystyrene. The corresponding values for the  $T_g$  transition are  $K = -111^\circ\text{K}$ ,  ${}_A T_g = 380^\circ\text{K}$  and  ${}_B T_g = 255^\circ\text{K}$ .

Another relaxation was observed (Fig. 8,  $T_{\ell\ell}' > T_{\ell\ell}$ ) which varied linearly with weight percentage composition with  ${}_A T_{\ell\ell}' = 484^\circ\text{K}$ ,  ${}_B T_{\ell\ell}' = 289^\circ\text{K}$  and the empirical constant  $K = 0$ .

A summary of the TBA data for homopolymers (5), polymer blends (6) and plasticized polymer (7) appears in Figure 10 (2) in which the temperatures  $T_{\ell\ell}$ ,  $T_{\ell\ell}'$  and  $T_{\min}$  ( $^\circ\text{K}$ ) are plotted versus  $T_g$  ( $^\circ\text{K}$ ) to explore relationships between the relaxations. It is apparent that the ratio  $T_{\ell\ell}/T_g$  is approximately constant over a wide range of temperature, except above  $M_c$  and at high plasticizer content.

## II. Block Copolymers of Styrene (8)

Tri- and diblock copolymers of styrene containing a rubber block (Table 1) display a relaxation in the TBA spectra at higher temperatures than the  $T_g$  of the polystyrene phase ( ${}_S T_g$ ). Thermomechanical spectra of three are shown in Figs. 11-13. Temperatures ( $^\circ\text{K}$ ) (Table 1) of the  $T > {}_S T_g$  and  ${}_S T_g$  relaxations vs a) MW of the styrene block, b) the sum of MWs of the styrene blocks per molecule, and c) MW of the block co-

polymers, are plotted in Figs. 14-16. Corresponding temperatures ( $^{\circ}\text{K}$ ) for anionic styrene homopolymers are included (lines only) in Figs. 14-16. It is apparent that the strongest correlation (i.e. that with the most monotonic variation) exists for the  $T > T_g$  and  $T_g$  temperatures vs the MW of the styrene end-block per molecule (Fig. 14). It is also apparent that the two processes of the block copolymers parallel those of the homopolymers and therefore that the  $T > T_g$  relaxations in block copolymers and homopolymers of styrene have a common origin.

#### CONCLUSIONS

Investigation of the  $T_{\ell\ell}$  ( $> T_g$ ) relaxation in amorphous polymers of styrene by the technique of torsional braid analysis has been reviewed. For the most part the relaxation behaves like the glass transition ( $T_g$ ) in its dependence on molecular weight, on average molecular weight in binary polystyrene blends, and on composition in a polystyrene homogeneously plasticized throughout the range of composition. Diblock and triblock copolymers also display a  $T > T_g$  relaxation above the  $T_g$  of the polystyrene phase.

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FIGURE CAPTIONS

- Fig. 1. Thermomechanical spectra [relative rigidity ( $1/P^2$ ) and logarithmic decrement ( $\Delta$ ) vs. temperature] of a polystyrene ("anionic",  $\bar{M}_n = 37,000$ ;  $\bar{M}_w/\bar{M}_n < 1.1$ ).
- Fig. 2. Thermomechanical spectra (logarithmic decrement vs temperature) of anionic "monodisperse" polystyrenes: effect of molecular weight ( $\bar{M}_n$ ). Curves have been displaced vertically by arbitrary amounts for purposes of clarification. Line drawings are shown for the decreasing temperature mode.
- Fig. 3. TBA and DTA. Anionic "monodisperse" polystyrenes:  $T_g$  and  $T_{\ell\ell}$  vs  $1/\bar{M}_n$ . (For DTA,  $T_g$  was defined as the peak of the endotherm.)
- Fig. 4. TBA and DTA. Anionic "monodisperse" polystyrenes:  $T_g$ ,  $T_{\min}$  and  $T_{\ell\ell}$  vs  $\log \bar{M}_n$  ( $T_{\min}$  is defined as the temperature of minimum damping between  $T_g$  and  $T_{\ell\ell}$ ).
- Fig. 5. Polystyrene. Zero-shear melt viscosity data from the literature: temperature vs log molecular weight for different iso-viscous levels. Data points and dashed lines are for  $T_{\ell\ell}$  and  $T_g$  of anionic "monodisperse" polystyrenes vs  $\log \bar{M}_n$ .
- Fig. 6. Blends of "monodisperse" anionic polystyrenes ( $\bar{M}_n^A = 2,050$ ;  $\bar{M}_n^B = 20,200$ ): effect of  $\bar{M}_n$  on  $T_g$  and  $T_{\ell\ell}$ .
- Fig. 7. Blends of "monodisperse" anionic polystyrenes ( $\bar{M}_n^A = 9,600$ ;  $\bar{M}_n^B = 111,000$ ): effect of  $\bar{M}_n$  on  $T_g$ .

Fig. 8. Thermomechanical spectra (logarithmic decrement vs temperature) of a plasticized polystyrene: effect of composition (weight percent plasticizer/weight percent polystyrene). Anionic polystyrene:  $\bar{M}_n = 37,000$ ;  $\bar{M}_w/\bar{M}_n < 1.1$ . Plasticizer:  $(C_6H_5OC_6H_4O)_2C_6H_4$ . Curves have been displaced vertically by arbitrary amounts for purposes of clarification.

Fig. 9. Plasticized polystyrene:  $T_g$ ,  $T_{\min}$ ,  $T_{\ell\ell}$  and  $T_{\ell\ell}'$  vs weight percent plasticizer. Anionic polystyrene:  $\bar{M}_n = 37,000$ ;  $\bar{M}_w/\bar{M}_n < 1.1$ . Plasticizer;  $(C_6H_5OC_6H_4O)_2C_6H_4$ .  $T_{\min}$  is the temperature of minimum damping between  $T_g$  and  $T_{\ell\ell}$  (5).

Fig. 10.  $T_{\ell\ell}$ ,  $T_{\ell\ell}'$ , and  $T_{\min}$  ( $^{\circ}K$ ) vs  $T_g$  ( $^{\circ}K$ ) for homopolymers, polystyrene/polystyrene blends, and plasticized polystyrene, by TBA (2).

Fig. 11. See Figure

Fig. 12. See Figure

Fig. 13. See Figure

Fig. 14. See Figure

Fig. 15. See Figure

Fig. 16. See Figure

TABLE I. BLOCK COPOLYMERS OF STYRENE

Polymer Structure*	MW ( $\times 10^{-3}$ ) of Blocks	$T > T_g$ (°K)	$T_g$ (°K)	$T_{max}^{**}$ (°C)
S/hyd-B/S	7.5/37.5/7.5	399	365	175
S/hyd-B/S	10/50/10	400	368	225
S/B/S	12/33/14	407	365	170
S/B/S	16/85/17	404	366	200
S/B/S	20/84/22	407	363	170
S/B	22/55	421	371	175
S/hyd-ip	37/65	442	379	175
S/B/S	44.3/108.4/44.3	436	375	175
S/B/S	45.7/113/45.7	434	373	175
S/DMS	52/117	441	380	175
S/B	91.5/114.6	440	373	200

\* S, B, hyd-B, hyd-ip, DMS  $\equiv$  polystyrene, polybutadiene, hydrogenated polybutadiene, hydrogenated polyisoprene, and polydimethylsiloxane, respectively.

\*\* Specimens were prepared by heating to temperature  $T_{max}$ .

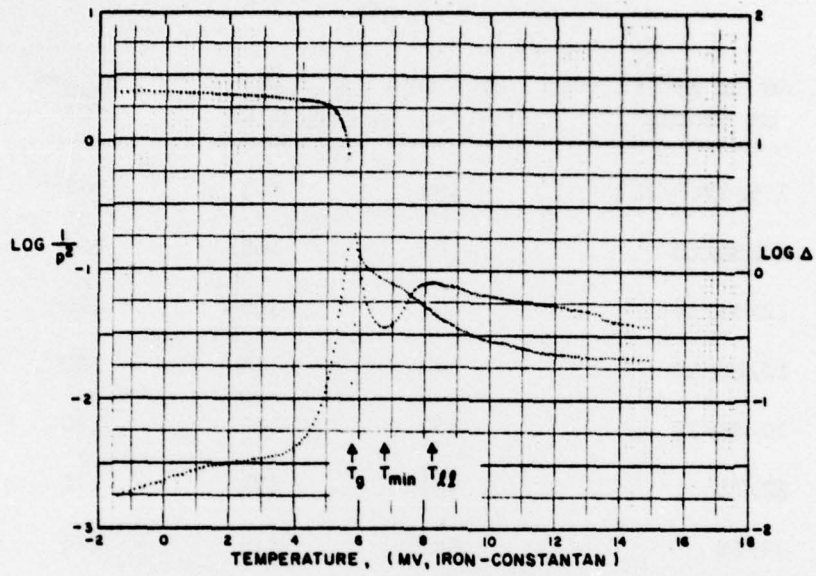


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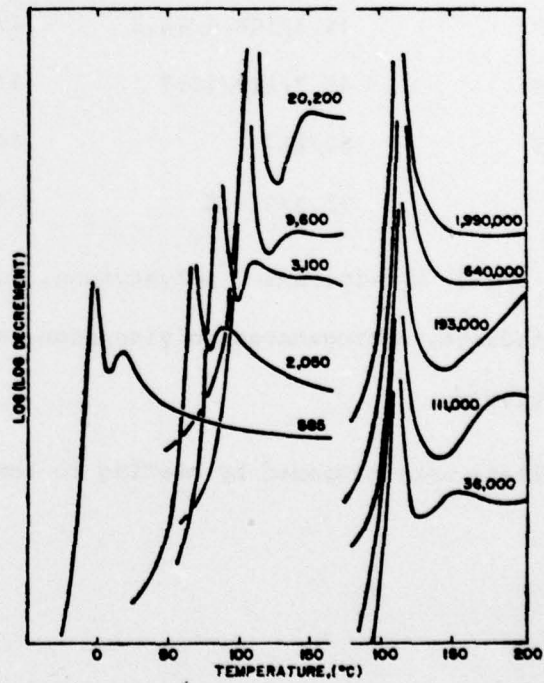


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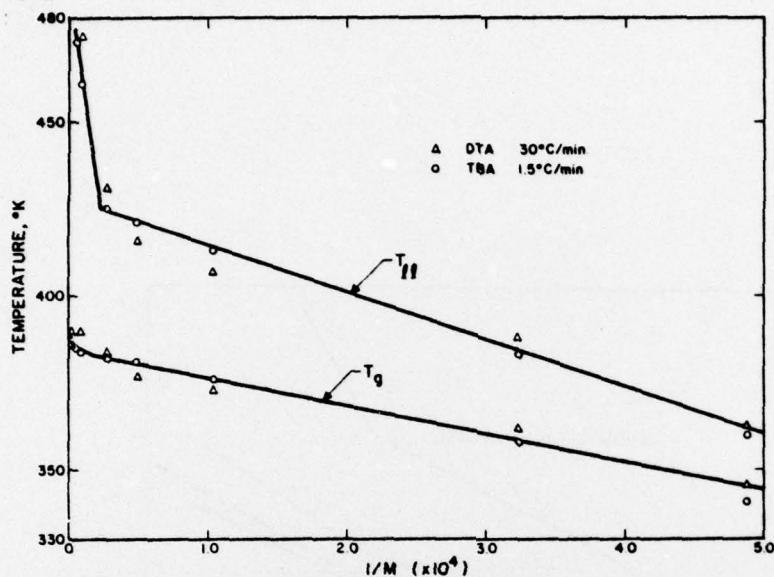


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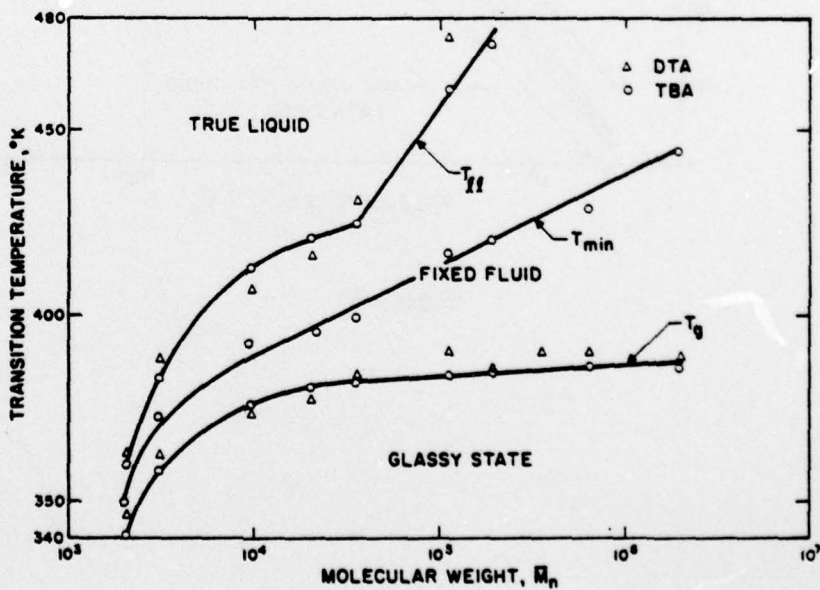


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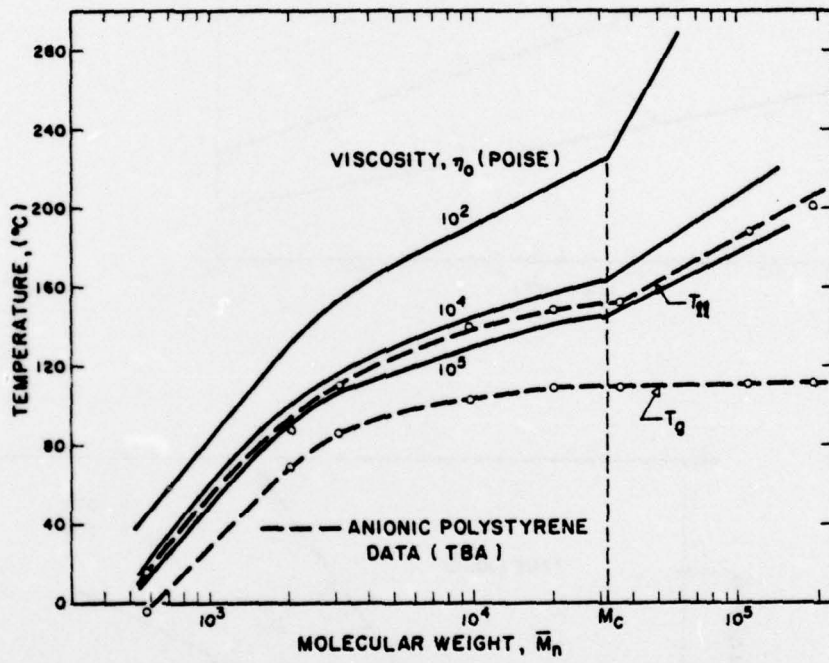


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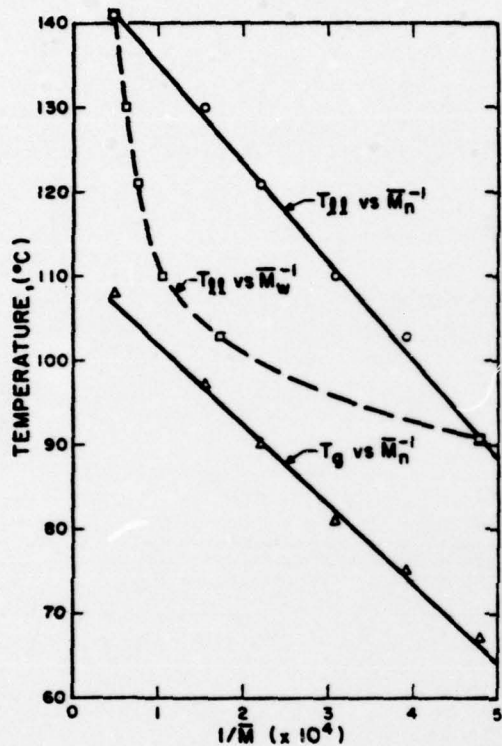
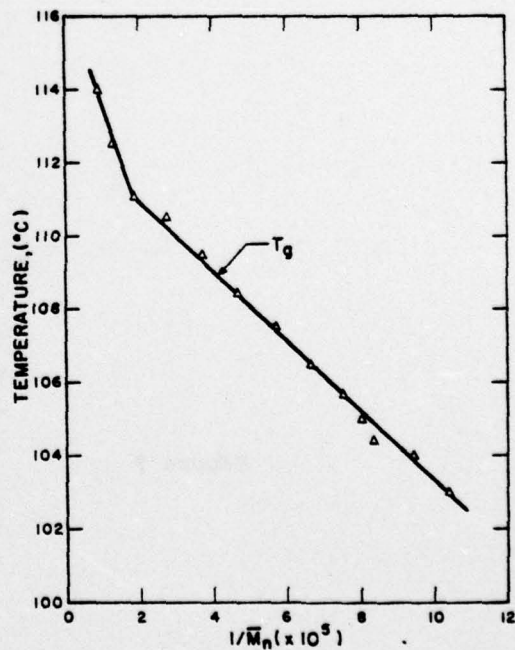


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Figure 7



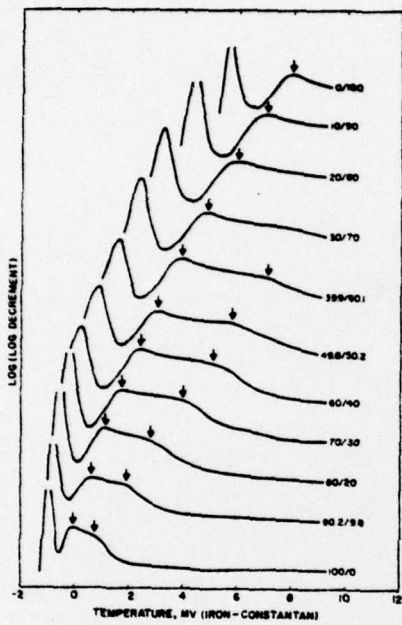


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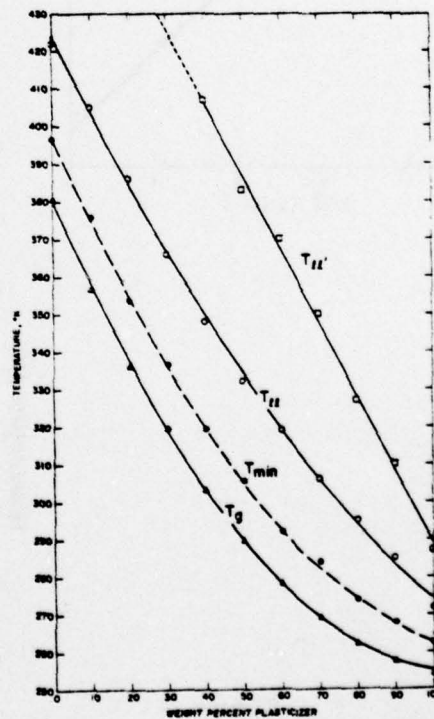


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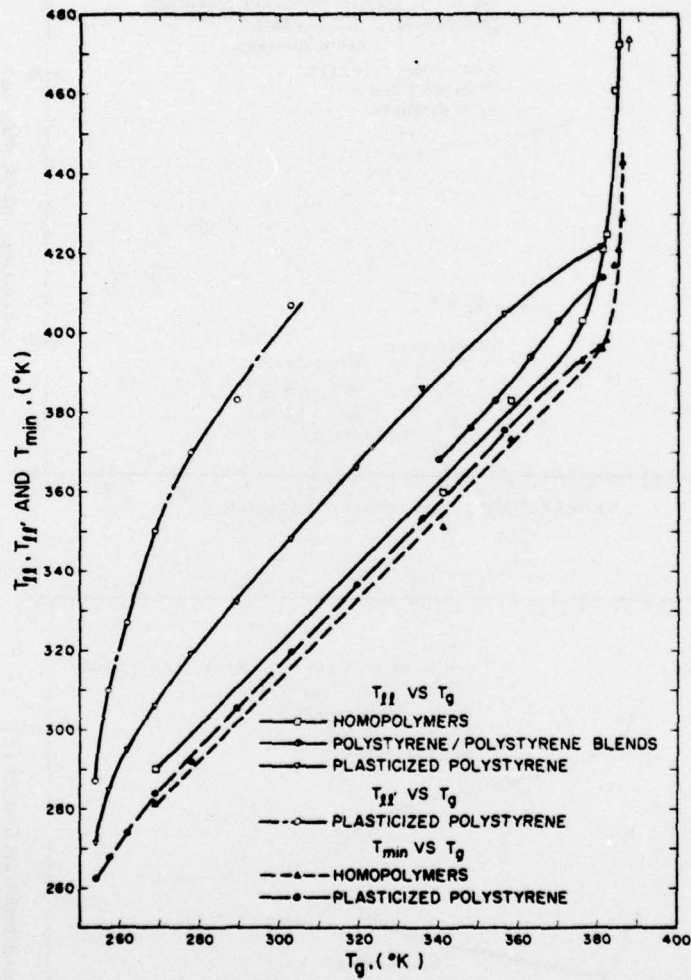


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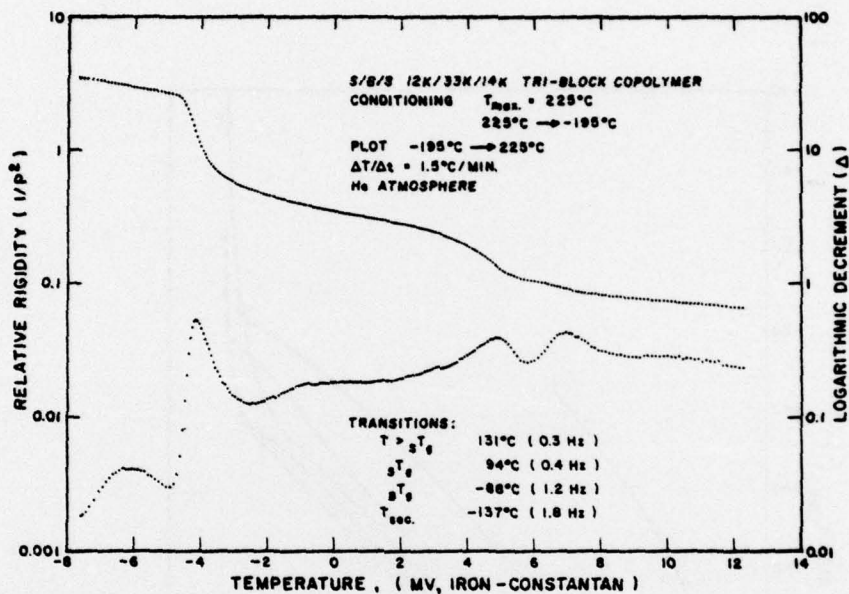


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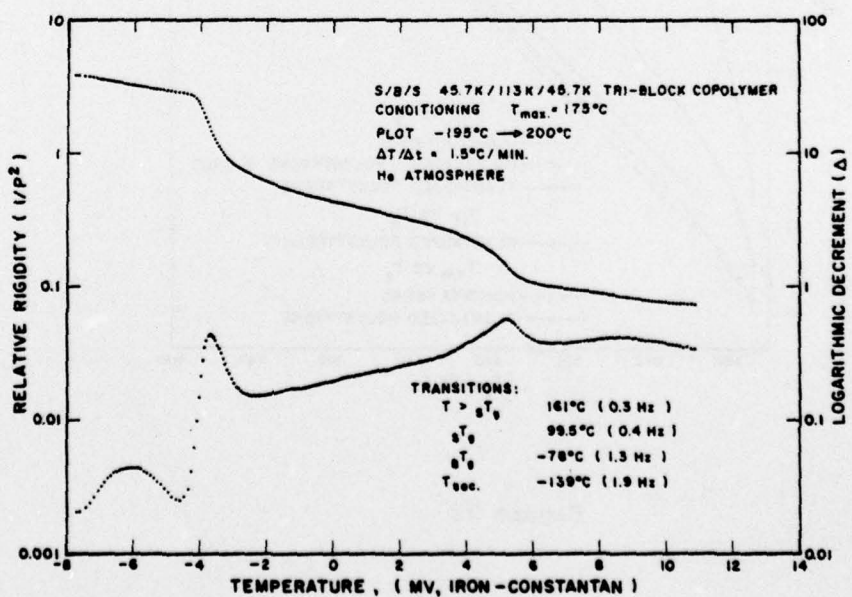


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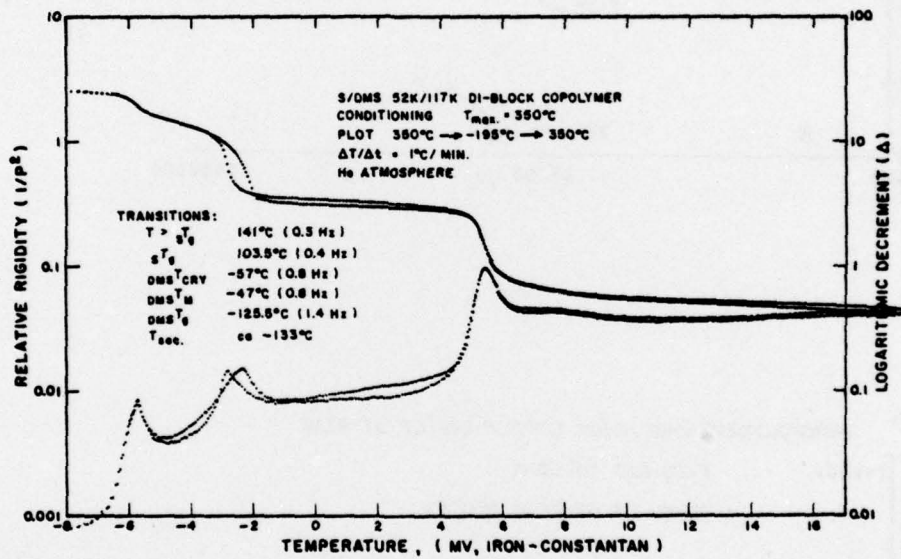


Figure 13

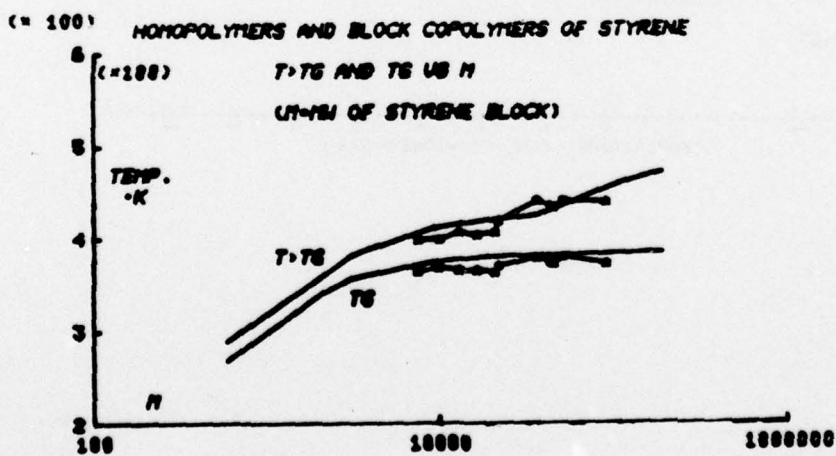
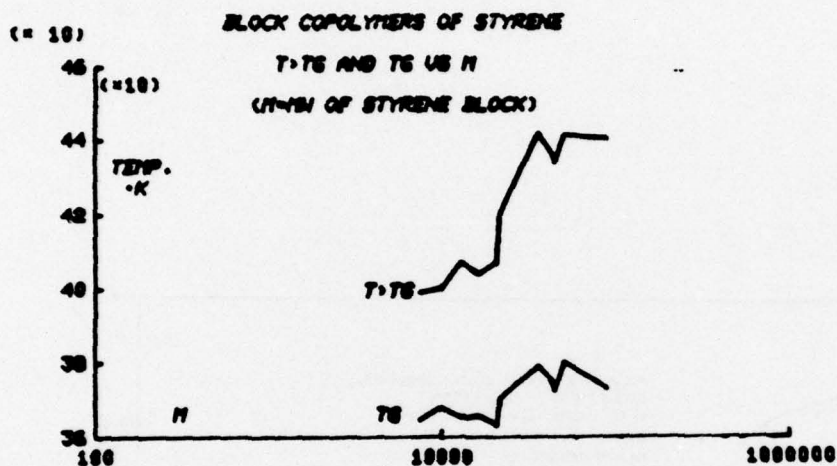


Figure 14



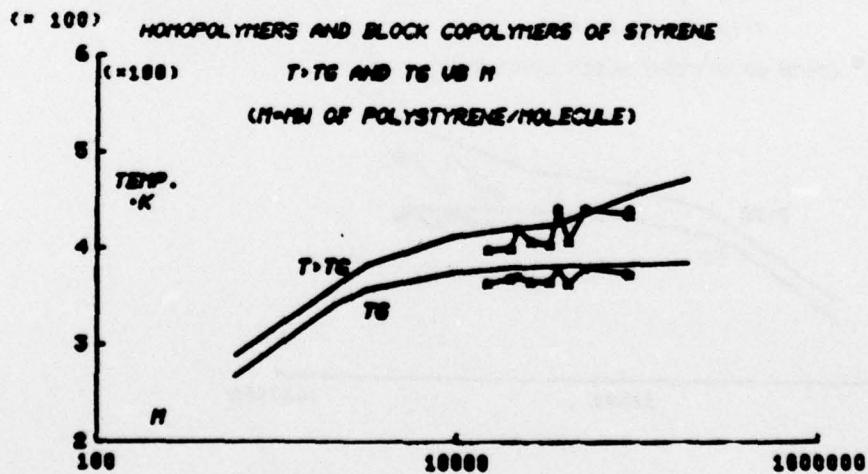
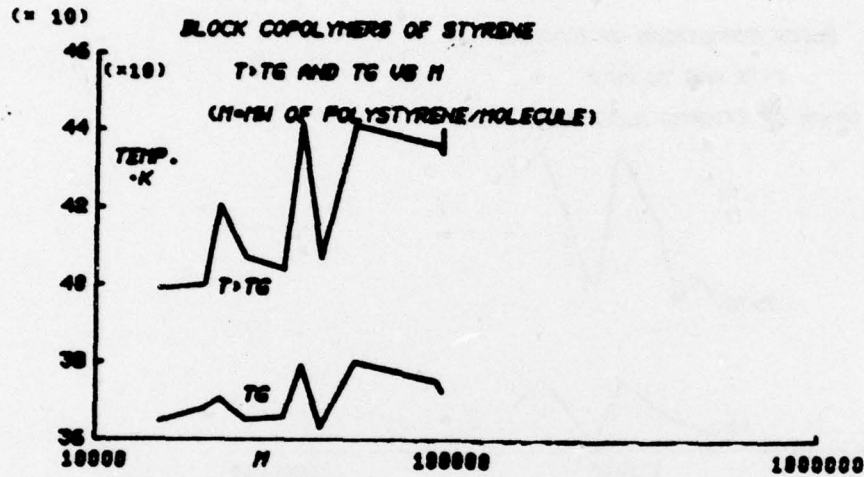


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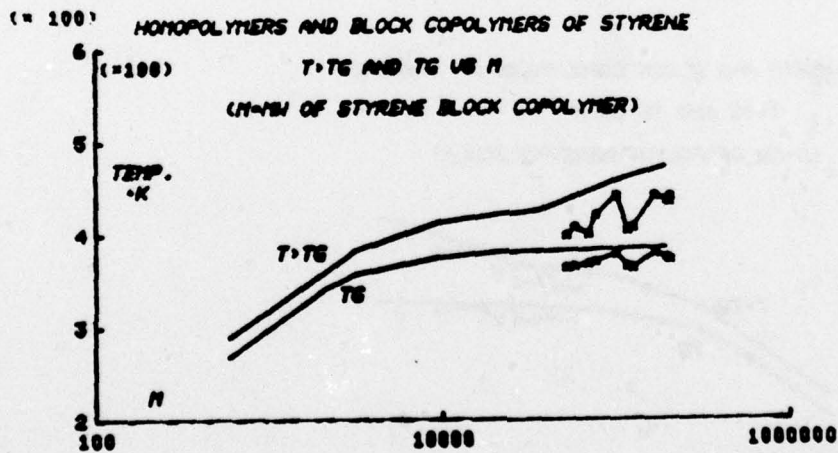
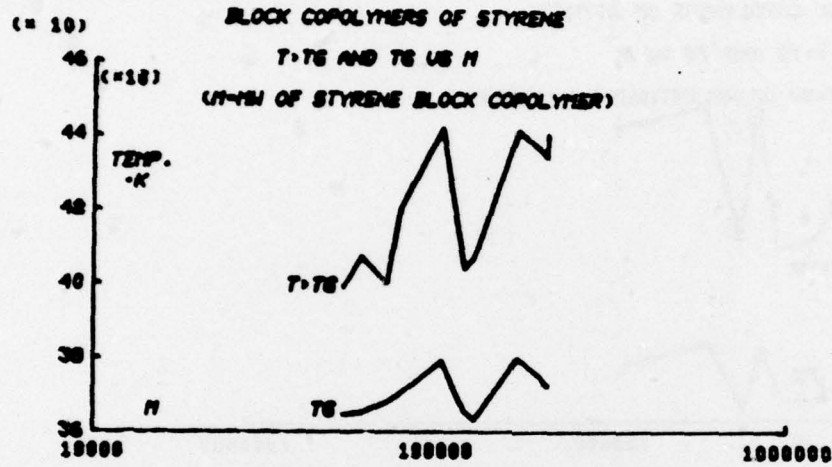


Figure 16

T sub ll      T sub g

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18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)  Polystyrene Transitions      sub ll Torsion Pendulum      sub g		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  Investigation of the $T_{ll}$ ( $> T_g$ ) relaxation in amorphous polymers of styrene by the technique of torsional braid analysis has been reviewed. For the most part the relaxation behaves like the glass transition ( $T_g$ ) in its dependence on molecular weight, on average molecular weight in binary polystyrene blends, and on composition in a polystyrene homogeneously plasticized throughout the range of composition. Diblock and triblock copolymers also display a $T > T_g$ relaxation above the $T_g$ of the polystyrene phase. (continued reverse)		

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Two results in particular suggest that the  $T_{gl}$  relaxation is molecularly based. 1) The temperature  $T_{gl}$  is determined by the number average molecular weight for binary blends of polystyrene when both components have molecular weights below  $M_c$  (the critical molecular weight for chain entanglements).

2) Homopolymers, and diblock and triblock copolymers of styrene, have a  $T > T_g$  relaxation at approximately the same temperature when the molecular weight of the styrene block is equal to that of the homopolymer.

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