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INVESTIGATION OF THE T(LL) (> T(G)) RELAXATION OF HOMOPOLYMERS --ETC(U)  
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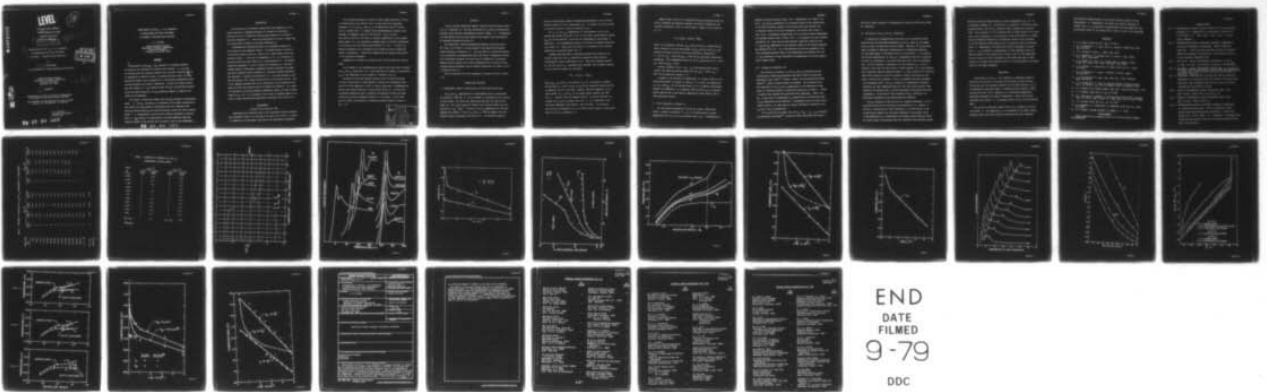
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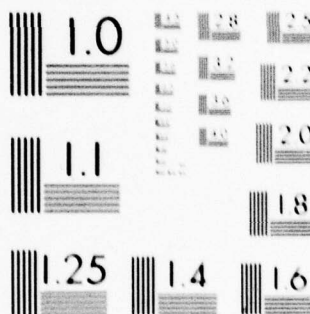
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6 Investigation of the  $T_{\alpha\alpha}$  ( $> T_g$ ) Relaxation  
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INVESTIGATION OF THE  $T_{ll}$  ( $> T_g$ ) RELAXATION  
 OF HOMOPOLYMERS AND BLOCK COPOLYMERS  
 OF STYRENE BY TORSIONAL BRAID ANALYSIS

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ABSTRACT

Investigation of the  $T_{ll}$  ( $> T_g$ ) relaxation in amorphous polymers of styrene by the technique of torsional braid analysis is 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. Unlike the glass transition, the  $T_{ll}$  relaxation appears to depend on the nature of the substrate.

Two results in particular suggest that the  $T_{ll}$  relaxation is molecularly based. 1) The  $T_{ll}$  temperature 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). Since the transformation involves a change from one liquid state to another it has been designated  $T_{ll}$ .

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 (2). The dynamic mechanical experiment ( $\sim 50$  Hz) revealed the relaxation by a loss peak. Another approach investigates a composite specimen consisting of polymer and inert (generally glass) filaments in a torsional pendulum experiment. The technique -- torsional braid analysis (3) -- has been employed to produce the results (4-11) which form the basis for the present article. Use of the composite specimen adds to the controversy in that mechanical loss peaks can arise from relative motion of polymer and substrate. As a basis for discussion the loss peak observed immediately above  $T_g$  by TBA is designated the  $T_{ll}$  (or  $T > T_g$ ) relaxation since values so obtained appear to be equal to those obtained using quasi-static techniques such as DTA (1,4).

## 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 (3) 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  $i^{\text{th}}$  oscillation in a damped wave). A computer plots thermomechanical spectra of the specimen (in immediate time on an  $XY$  plotter) which present the relative rigidity,  $1/P^2$  which is directly proportional to the in-phase shear modulus ( $G'$ ), and logarithmic decrement 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 is 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  $T_{ll}$  relaxations, Fig. 1 shows TBA data for a sample of polystyrene.  $T_{\text{min}}$  is the temperature of the minimum of  $\Delta$  between  $T_g$  and  $T_{ll}$ .

Specimens for TBA were prepared generally from 10 percent solutions (g weight polystyrene/ml volume benzene) by heating the impregnated glass braid in the TBA apparatus to  $200^\circ\text{C}$  in flowing helium gas. Thermomechanical spectra were usually obtained in helium during cooling at  $1.5^\circ\text{C}/\text{min}$  from the maximum temperature used in preparing the specimen to below the glass transition and during subsequent heating at  $1.5^\circ\text{C}/\text{minute}$ . A set of TBA data for anionic polystyrenes of different molecular weights is shown in Fig. 2 (4).

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### 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 (4).

The plasticizer, *m*-bis(*m*-phenoxyphenoxy)benzene,  $[(C_6H_5OC_6H_4O)_2C_6H_4]$ ; 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 (6).

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  $T_{\ell\ell}$  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 (4). The  $T_g$  plot shows two regions, each of which follows the relationship  $T_g = T_{g^\infty} - K \bar{M}_n^{-1}$ . The plot of the  $T_{\ell\ell}$  temperatures 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 (4). The molecular weight at

which the relationships changed corresponded approximately to the critical molecular weight for chain entanglements ( $M_c$ ). (It appears that TBA provides a convenient method for obtaining estimates of  $M_c$ .)

The  $T_g$ ,  $T_{\ell\ell}$  and  $T_{\min}$  temperatures for "monodisperse" anionic polystyrenes are plotted vs  $\log \bar{M}_n$  in Fig. 4. (The direct proportionality between  $T_{\min}$  and  $\log \bar{M}_n$  above  $\bar{M}_n = 10,000$  for the "monodisperse" polystyrenes is noteworthy.) The corresponding results for fractions of thermal polystyrene were similar (4). 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  $T_{\ell\ell}$  relaxation by examining binary blends of "monodisperse" anionic polystyrenes (5,10). When both components had  $\bar{M}_n < M_c$ , both the  $T_g$  and  $T_{\ell\ell}$  relaxations 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  $T_{\ell\ell}$  ( $^{\circ}\text{K}$ ) 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),  $T_{\ell\ell}$  relaxations of the individual components were observed (data not shown). The averaging equation and the dependence of  $T_{\ell\ell}$  on  $1/\bar{M}_n$  for blends suggest a free-volume basis for the  $T_{\ell\ell}$  relaxation (12).

Results (Figs. 8 and 9) on a plasticized anionic polystyrene show that the  $T_{ll}$  relaxation was observed throughout the range of composition and followed an equation of form (12) which again is similar to that used for  $T_g$ , i.e.

$$T_{ll} = T_{A ll} W_A + T_{B ll} W_B + K W_A W_B$$

where  $K$  is an empirical constant,  $T_{A ll}$  and  $W_A$  are the  $T_{ll}$  temperature and weight fraction of the pure polystyrene, and  $T_{B ll}$  and  $W_B$  are the  $T_{ll}$  temperature and weight fraction of the pure plasticizer, respectively.

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

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

A summary of the TBA data for homopolymers (4), polymer blends (5) and plasticized polymer (6) appears in Figure 10 (7) in which the temperatures  $T_{ll}'$ ,  $T_{ll}$  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  $T_{ll}'/T_g$  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 ( $T > T_g$ ) in the TBA spectra at higher temperatures than the  $T_g$  of the polystyrene phase ( $T_g$ ). 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) molecular weight of the styrene block, b) the sum of molecular weights of the styrene blocks per molecule, and c) molecular weight of the block copolymers, are plotted (full lines) in Figs. 14-16. Corresponding temperatures ( $^{\circ}\text{K}$ ) for anionic styrene homopolymers are included (dashed lines) in Figs. 14-16. It is apparent that the strongest correlation (i.e. that with the most monotonic variation) exists for the  $T > S T_g$  and  $S T_g$  temperatures vs the molecular weight 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  $T > S T_g$  relaxations in block copolymers and homopolymers of styrene probably have a common origin.

### III. Influence of Substrate (10)

The influence of substrate on the  $T_{ll}$  and  $T_g$  relaxations has been investigated by examining homopolymers and binary blends of polystyrene supported by glass, Nomex<sup>(R)</sup> (duPont), carbon, and polytetrafluoroethylene (Teflon<sup>(R)</sup>, duPont) braided strands of filaments. The influence of the four substrates on the  $T_{ll}$  and  $T_g$  temperatures of the homopolymers using glass as a reference material is summarized numerically in Table 2. Figure 17 presents data obtained with glass and Teflon substrates. Table 2 and Fig. 17 show that for homopolymers  $T_{ll}$  temperatures are affected more than the  $T_g$  temperatures by the substrate. Corresponding data for binary blends (Table 3 and Fig. 18) again show the greater influence of substrate on the  $T_{ll}$  than on the  $T_g$  temperatures.

It is noted (data not shown) that the  $T_{ll}'$  ( $T_{ll}' > T_{ll} > T_g$ ) relaxation is discernible using Nomex<sup>(R)</sup>, carbon and Teflon substrates even though it

may not be readily apparent in thermomechanical spectra obtained using glass as a substrate.

#### IV. The Nature of the $T_{\beta\beta}$ and $T_{\beta\beta}'$ Relaxations

In general the thermomechanical TBA spectra for low molecular weight materials show two loss peaks designated  $T_{\beta\beta}$  and  $T_{\beta\beta}'$  above  $T_g$ , the temperatures of which increase with molecular weight. Similarly, as the molecular weight increases on isothermal polymerization of thermosetting materials, two loss peaks appear in TBA spectra prior to vitrification. It is apparent, and has been demonstrated (11) that  $T_{\beta\beta}'$  corresponds to the first relaxation and that  $T_{\beta\beta}$  corresponds to the second relaxation which occur on isothermal cure. The first process on isothermal cure, and therefore  $T_{\beta\beta}'$ , are considered to occur when the fluid attains a fixed viscosity, as in the determination of gelation times by rheological means. At lower viscosities the substrate moves freely relative to the fluid, whereas at higher viscosities the substrate and fluid move together -- the  $T_{\beta\beta}'$  relaxation loss peak represents the intermediate state. The  $T_{\beta\beta}$  relaxation in thermoplastics therefore represents the lower temperature limit for free flow just as gelation time represents the similar limit in time for processing thermosetting materials isothermally. On the basis of this reasoning the  $T_{\beta\beta}'$  relaxation is a macroscopic phenomenon of the polymer/substrate composite.

The  $T_{\beta\beta}$  relaxation of TBA may also be a composite phenomenon (7,13,14) which may account for the influence of the substrate on it. However, in addition to correlations by other techniques (1), two TBA results in particular provide support for a molecular mechanism of the polymer itself.

1) The temperature  $T_{\beta\beta}$  is determined by the number average molecular weight for binary blends of polystyrene when both components have molecular weights

below the critical molecular weight for chain entanglements ( $M_c$ ). If, as is generally accepted (15), the viscosity is a function of the weight average molecular weight, then the  $T_{\ell\ell}$  relaxation cannot represent an isoviscous state. The occurrence (2) of a relaxation peak in binary blends of low molecular weight polybutadiene in high molecular weight polybutadiene at a temperature and frequency determined by the molecular weight and not the amount of the low molecular weight species also is inconsistent with an isoviscous state. 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. That the viscosity of block copolymers is much higher than that of homopolymers of the same total molecular weight (15) also precludes an isoviscous state for the common phenomenon.

#### 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.

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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## ACKNOWLEDGMENT

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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",  $\bar{M}_n = 37,000$ ;  $\bar{M}_w/\bar{M}_n < 1.1$ ). Data:  $200^\circ\text{C} \rightarrow -50^\circ\text{C}$ ,  $\Delta T/\Delta t = 1.5^\circ\text{C}/\text{min}$ , helium atmosphere.
- 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  $T_{ll}$  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  $T_{ll}$  vs  $\log \bar{M}_n$ . Note the three distinct states of amorphous thermoplastics, i.e. glassy state, fixed fluid and true liquid (see reference 1), separated by  $T_g$  and  $T_{ll}$ .
- Fig. 5. Polystyrene. Zero-shear melt viscosity data from the literature: temperature vs log molecular weight for different isoviscous levels. Data points (TBA) and dashed lines are for  $T_{ll}$  and  $T_g$  of anionic "monodisperse" polystyrenes vs  $\log \bar{M}_n$ .
- Fig. 6. Blends of "monodisperse" anionic polystyrenes ( $\bar{M}_A = 2,050$ ;  $\bar{M}_B = 20,200$ ): effect of  $\bar{M}$  on  $T_g$  and  $T_{ll}$  (5).
- Fig. 7. Blends of "monodisperse" anionic polystyrenes ( $\bar{M}_A = 9,600$ ;  $\bar{M}_B = 111,000$ ): 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:  $(\text{C}_6\text{H}_5\text{OC}_6\text{H}_4\text{O})_2\text{C}_6\text{H}_4$ . Curves have been displaced vertically by arbitrary amounts for purposes of clarification.

Fig. 9. Plasticized polystyrene:  $T_g$ ,  $T_{min}$ ,  $T_{ll}$  and  $T_{ll}'$  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  $T_{ll}'$ .

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

Fig. 11. S/B/S 12K/33K/14K Tri-block copolymer.

Fig. 12. S/B/S 45.7K/113K/45.7K Tri-block copolymer.

Fig. 13. S/DMS 52K/117K Di-block copolymer.

Fig. 14.  $T > T_g$  and  $T_g$  vs molecular weight of styrene block.

Fig. 15.  $T > T_g$  and  $T_g$  vs molecular weight of polystyrene per molecule.

Fig. 16.  $T > T_g$  and  $T_g$  vs molecular weight of styrene block copolymer.

Fig. 17. Anionic "monodisperse" polystyrenes: effect of substrate on  $T_g$  and  $T_{ll}$  vs  $1/\bar{M}_n$ . Glass  $\blacktriangle \bullet$ , Teflon<sup>(R)</sup>  $\triangle \circ$

Fig. 18. Blends of "monodisperse" anionic polystyrenes ( $\bar{M}_A = 2,050$ ;

$\bar{M}_B = 20,200$ ): effect of substrate on  $T_g$  and  $T_{ll}$  vs  $1/\bar{M}$

Data Glass  $\blacktriangle \bullet$ , Nomex<sup>(R)</sup>  $\triangle \circ \square$ , matching data  $\triangle$ .

Other polystyrene binary blends, from left to right, ( $\bar{M}_A =$

$9200 + \bar{M}_B = 15,200$ ), ( $\bar{M}_A = 3100 + \bar{M}_B = 36000$ ), ( $\bar{M}_A = 2100$

$+ \bar{M}_B = 3100$ ), +.

TABLE 1. BLOCK COPOLYMERS OF STYRENE

Polymer Structure*	MW ( $\times 10^{-3}$ ) of Blocks	$T > S T_g^{**}$ ( $^{\circ}\text{K}$ )	$S T_g^{**}$ ( $^{\circ}\text{K}$ )	$T_{\text{max}}^{***}$ ( $^{\circ}\text{C}$ )
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.

\*\*  $S T_g$  and  $T > S T_g$   $\equiv$  temperature of peak of  $\Delta$  associated with the  $T_g$  of the polystyrene phase and with a relaxation above  $S T_g$ , respectively.

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

TABLE 2. INFLUENCE OF SUBSTRATE ON  $T_g$  AND  $T_{ll}$  TEMPERATURES OF HOMOPOLYMERS

Homopolymer $\bar{M}_n$	$\Delta T_g$ ( $^{\circ}\text{C}$ )				$\Delta T_{ll}$ ( $^{\circ}\text{C}$ )			
	Glass*	Nomex (R)	Carbon	Teflon (R)	Glass*	Nomex (R)	Carbon	Teflon (R)
585	0	-0.5	+2.5	+5.5	0	+1.5	-	-9.0
2,050	0	-0.5	+2.5	-1.5	0	-1.0	-5.5	-12.5
3,100	0	+1.0	+2.0	-0.5	0	-1.5	-6.0	-12.0
9,168	0	0	-0.5	-3.0	0	-1.5	-5.0	-18.0
15,100	0	+1.5	0	-3.0	0	-5.0	-8.5	-27.0
20,200	0	-0.5	0	-4.5	0	-1.0	-4.0	-19.5
36,000	0	+1.0	-0.5	-4.5	0	+6.0	-8.0	-16.0
51,150	0	+0.5	-1.0	-2.5	0	+11.0	-7.0	-10.0
71,000	0	+1.0	+0.5	-2.5	0	+11.0	-1.5	-16.0
111,000	0	+1.5	+0.5	-2.5	0	+12.5	+14.5	-8.5
147,000	0	+1.0	+0.5	-2.0	0	+11.0	+13.5	-15.0
193,000	0	+0.5	+2.0	-3.0	0	-	-	-16.0
350,000	0	+0.5	+1.5	-3.5	0	-	-	-26.0
640,000	0	+0.5	+1.5	-1.5	-	-	-	-
$1.9 \times 10^6$	0	+0.5	+1.5	+0.5	-	-	-	-
Avg. $\Delta T_g$ :	0	+0.53	+0.86	-1.97				

\*Reference

TABLE 3. INFLUENCE OF SUBSTRATE ON  $T_g$  AND  $T_{ll}$   
TEMPERATURES OF BINARY BLENDS

Blend $\bar{M}_n$	$\Delta T_g$ ( $^{\circ}\text{C}$ )		$\Delta T_{ll}$ ( $^{\circ}\text{C}$ )	
	Glass*	Nomex <sup>(R)</sup>	Glass*	Nomex <sup>(R)</sup>
20,200	0	+0.5	0	-4.5
10,710	0	+1.0	0	-4.0
7,290	0	+2.0	0	-4.0
5,530	0	0	0	-3.0
4,450	0	+3.5	0	-6.0
3,720	0	0	0	-4.5
3,200	0	+1.0	0	-3.0
2,810	0	+1.5	0	-3.0
2,500	0	+1.5	0	+2.5
2,250	0	+2.0	0	+2.0
2,050	0	+0.5	0	+1.5
Avg. $\Delta T_g$ :		+1.5	Avg. $\Delta T_{ll}$	-2.36

\* Reference

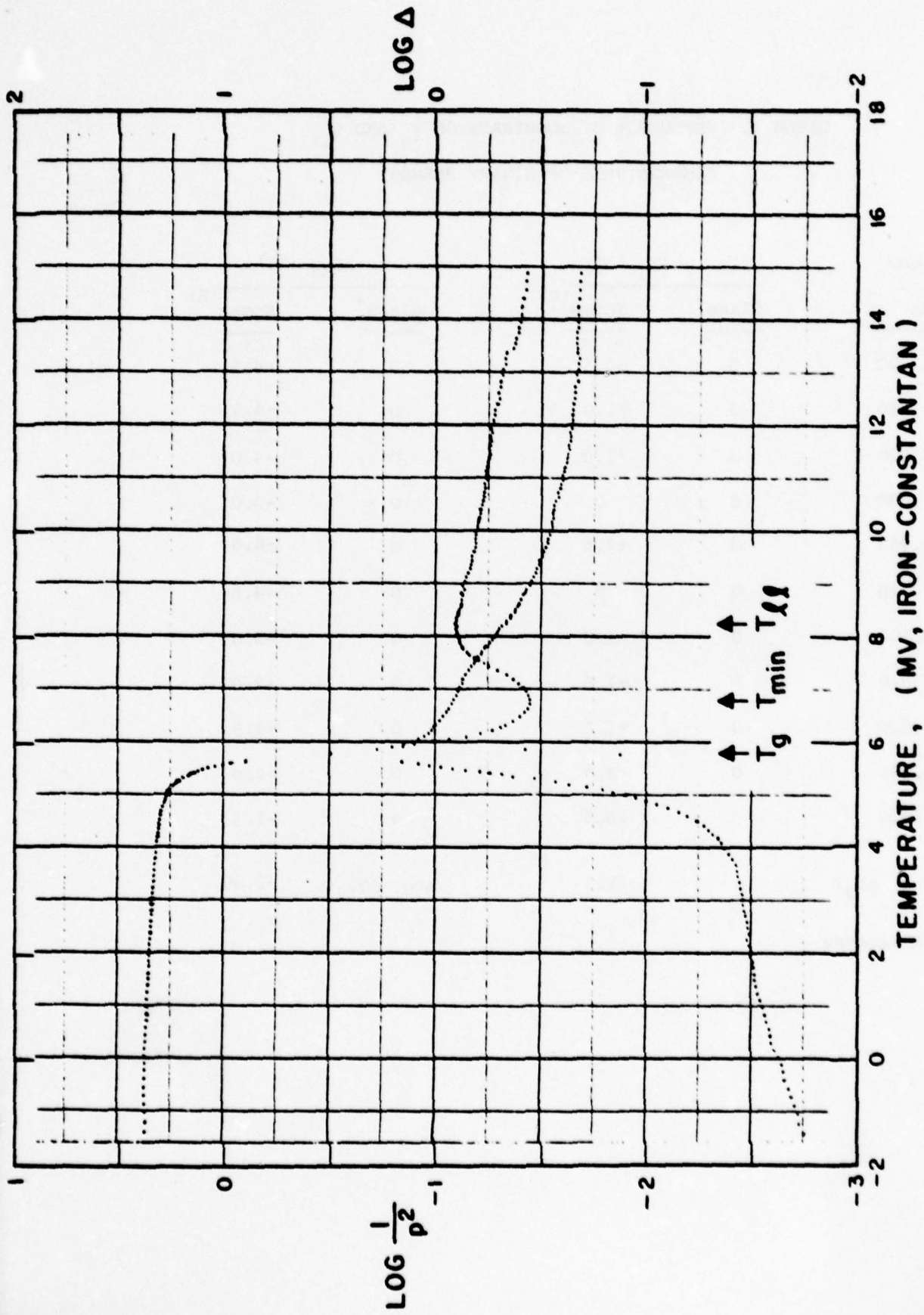


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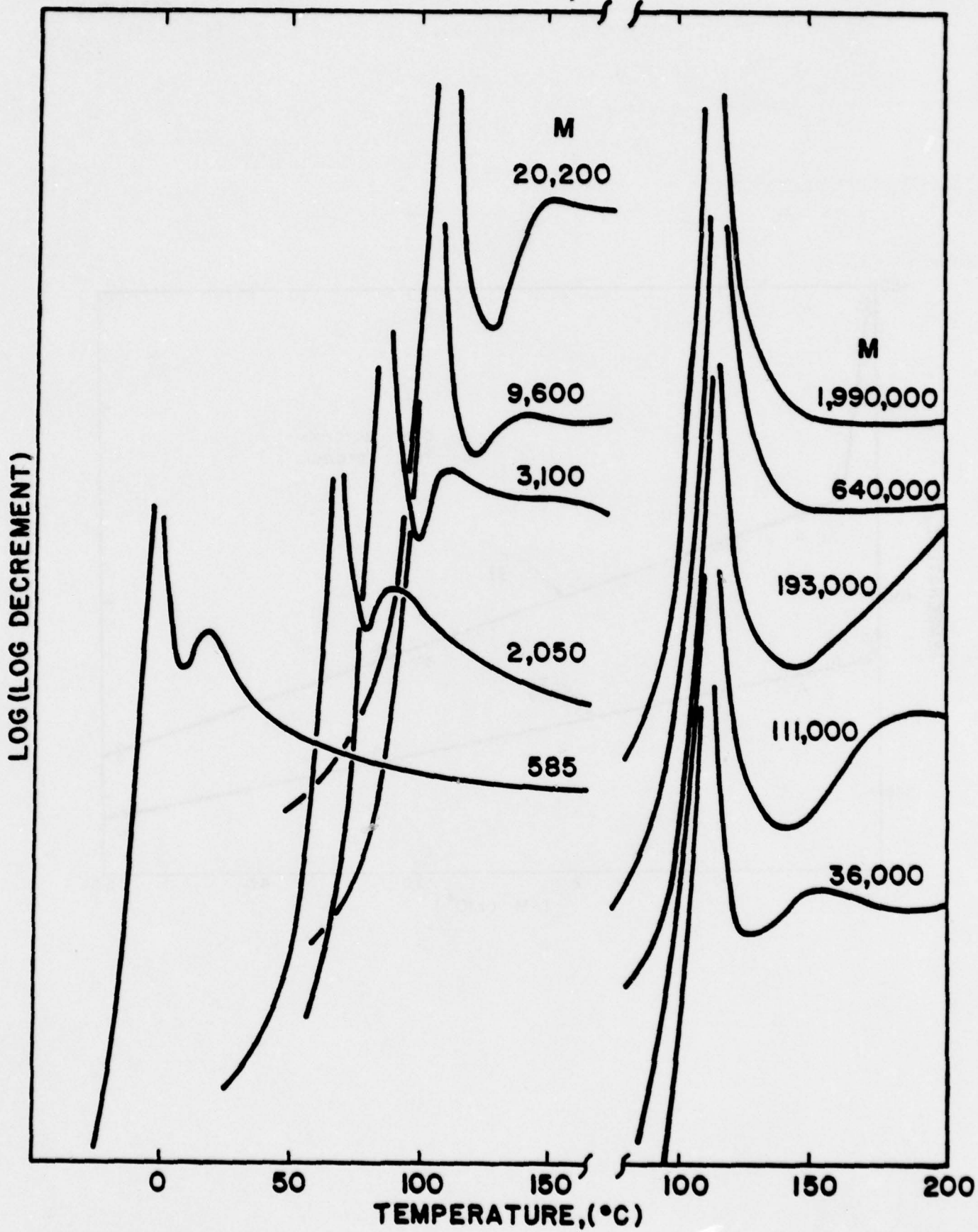


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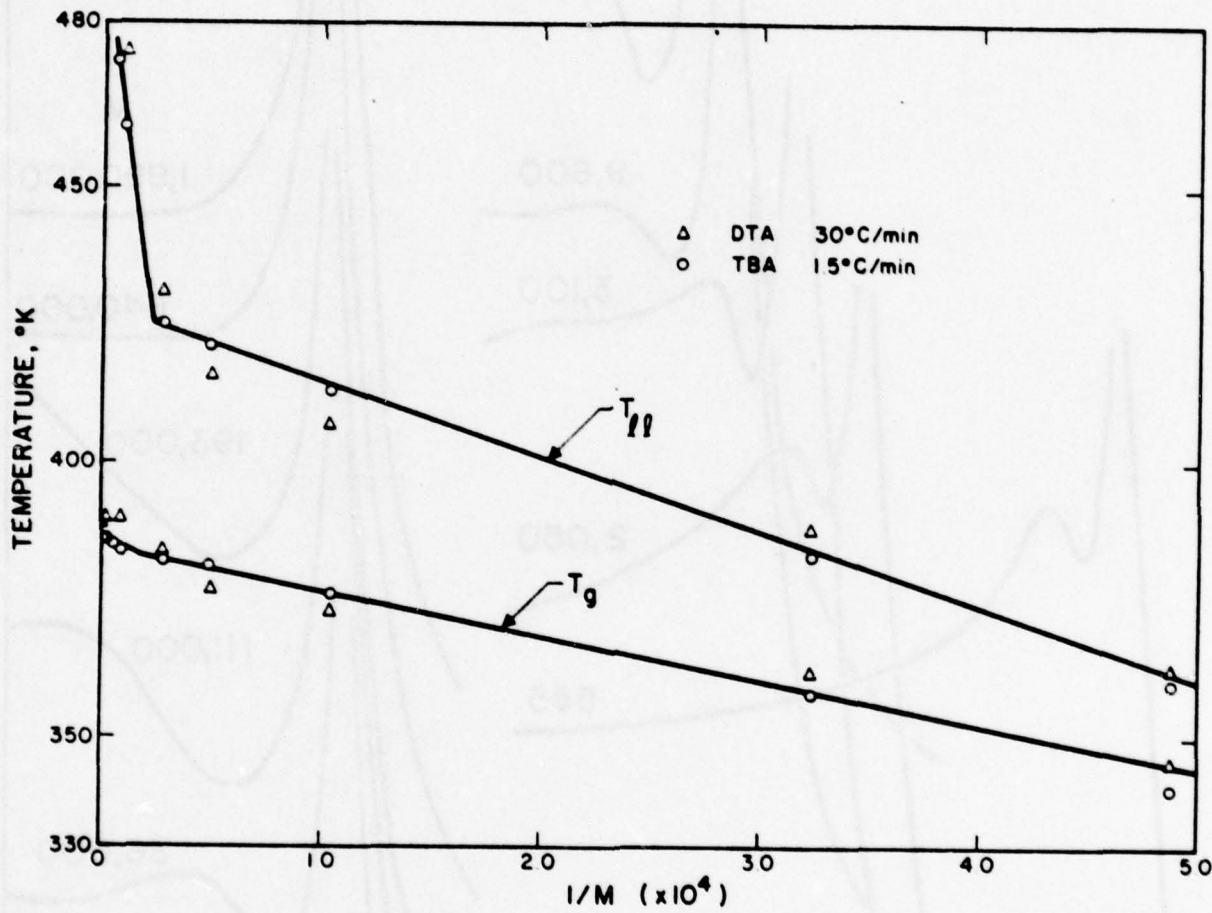


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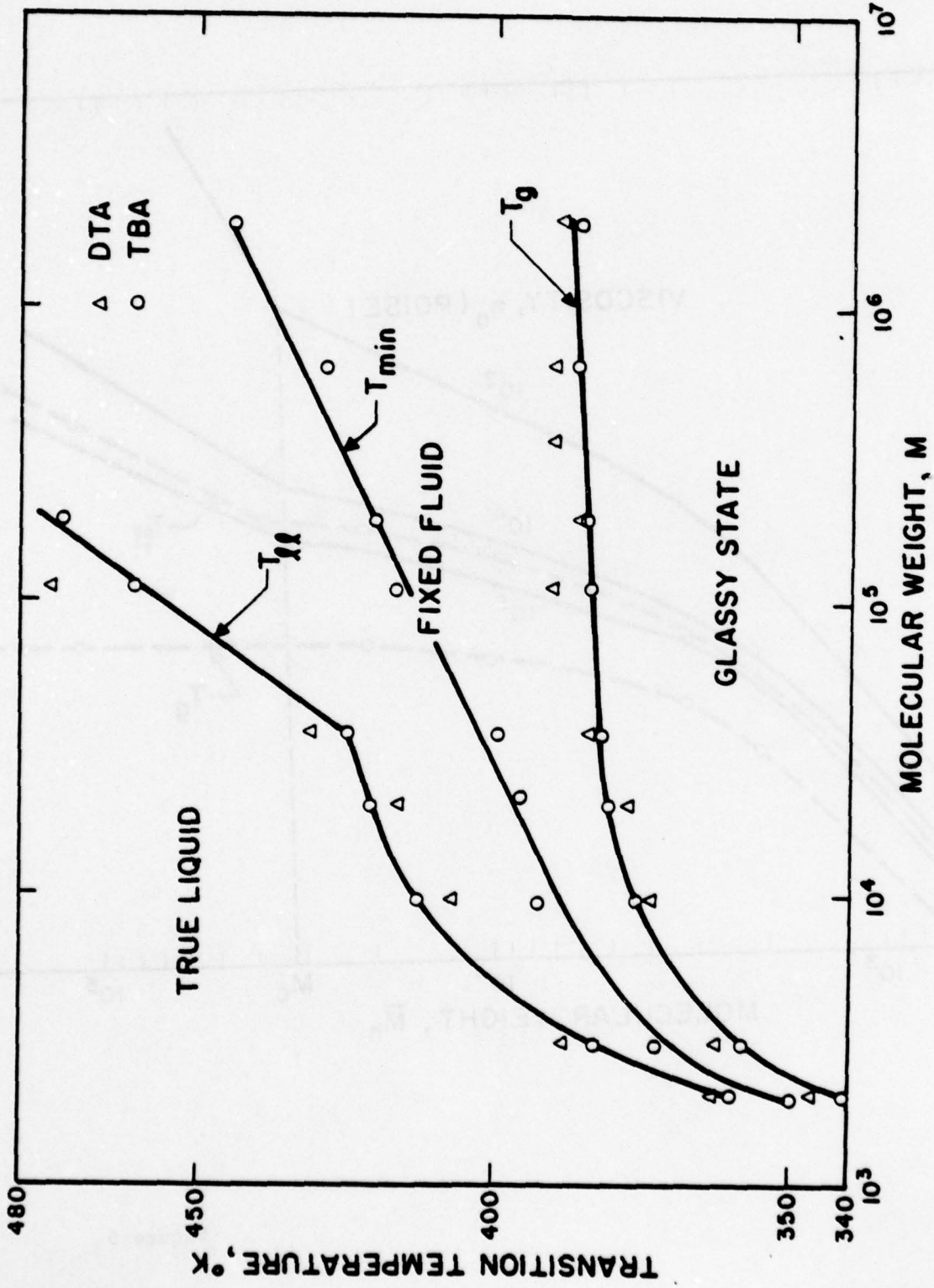


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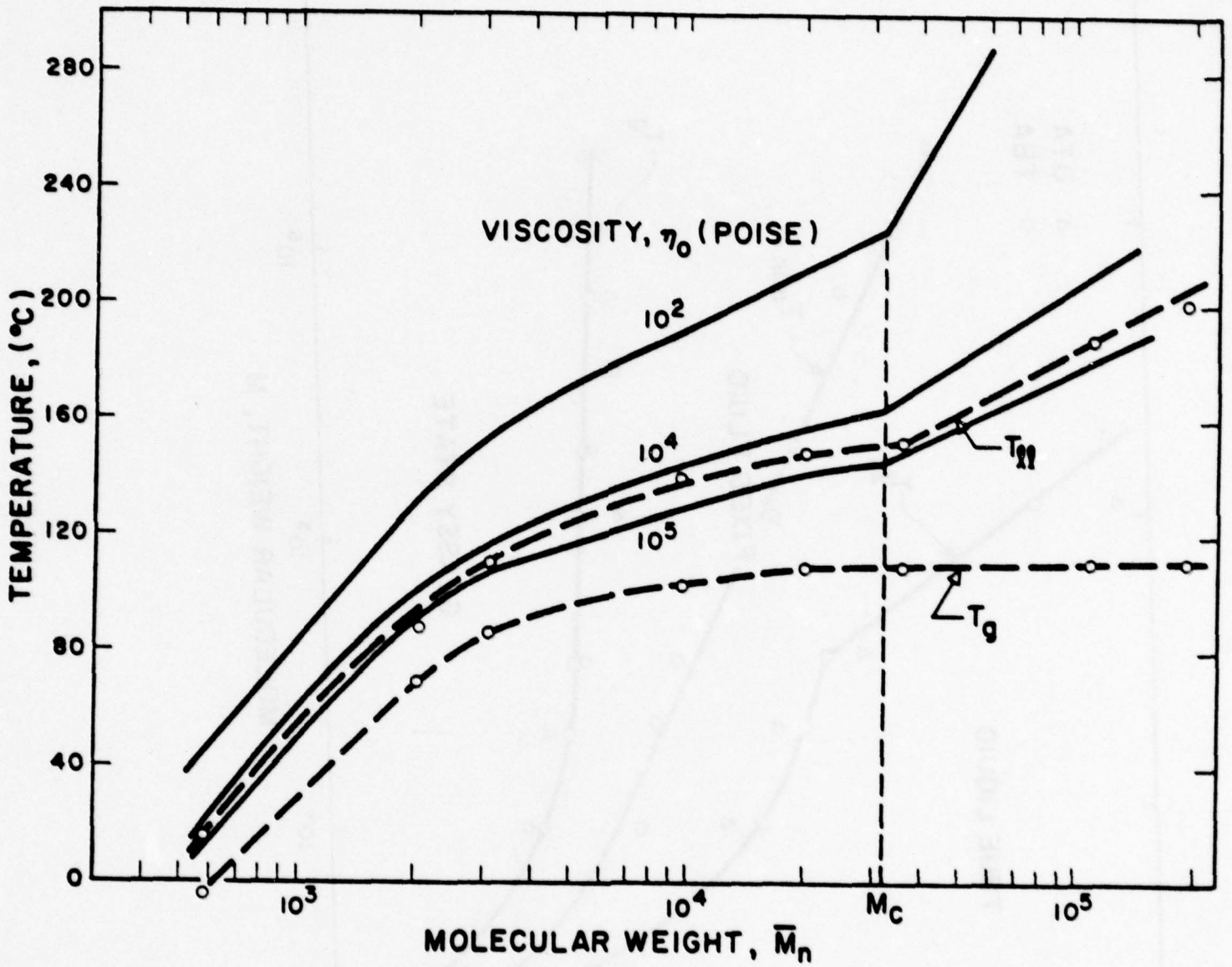


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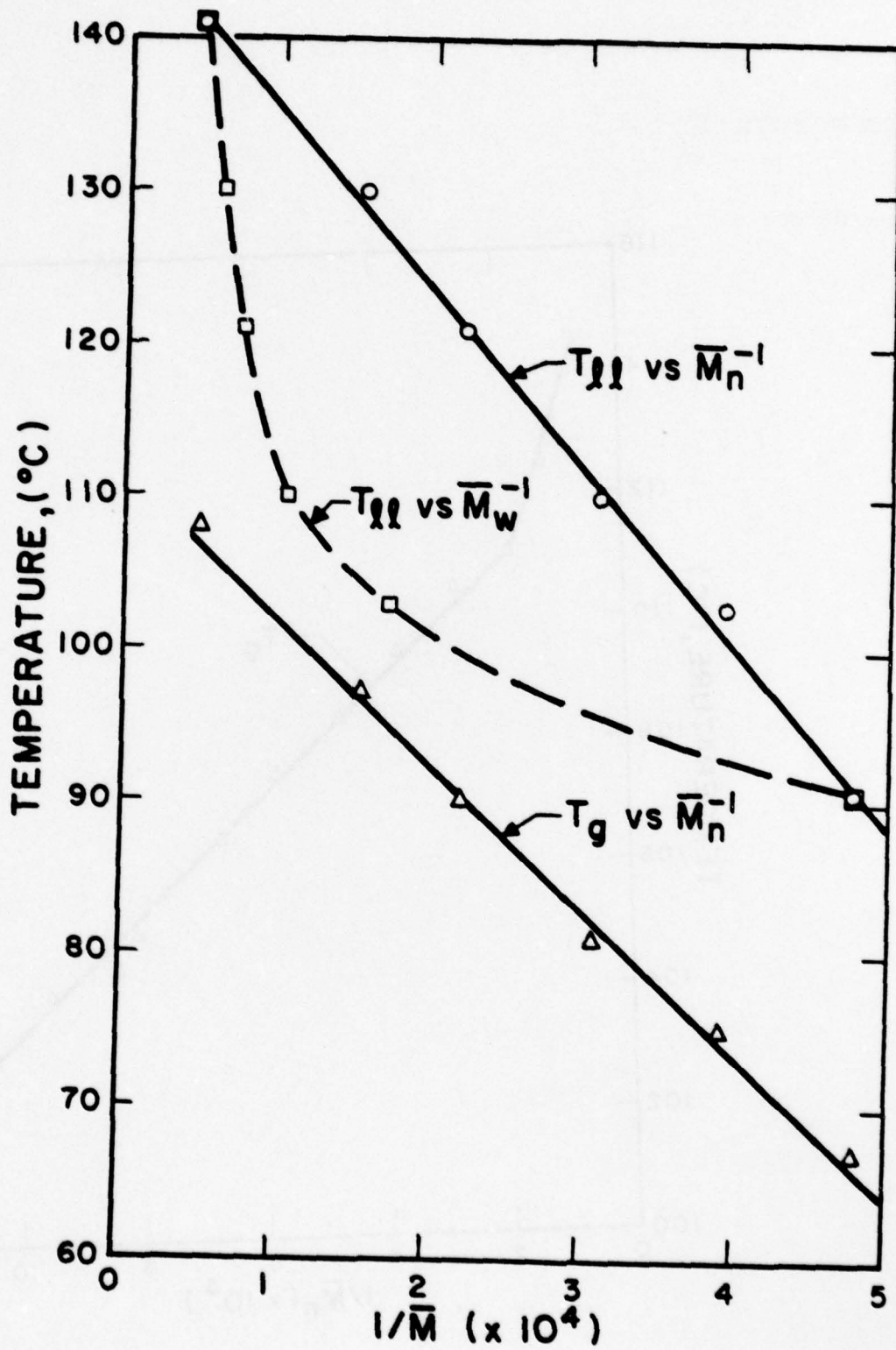


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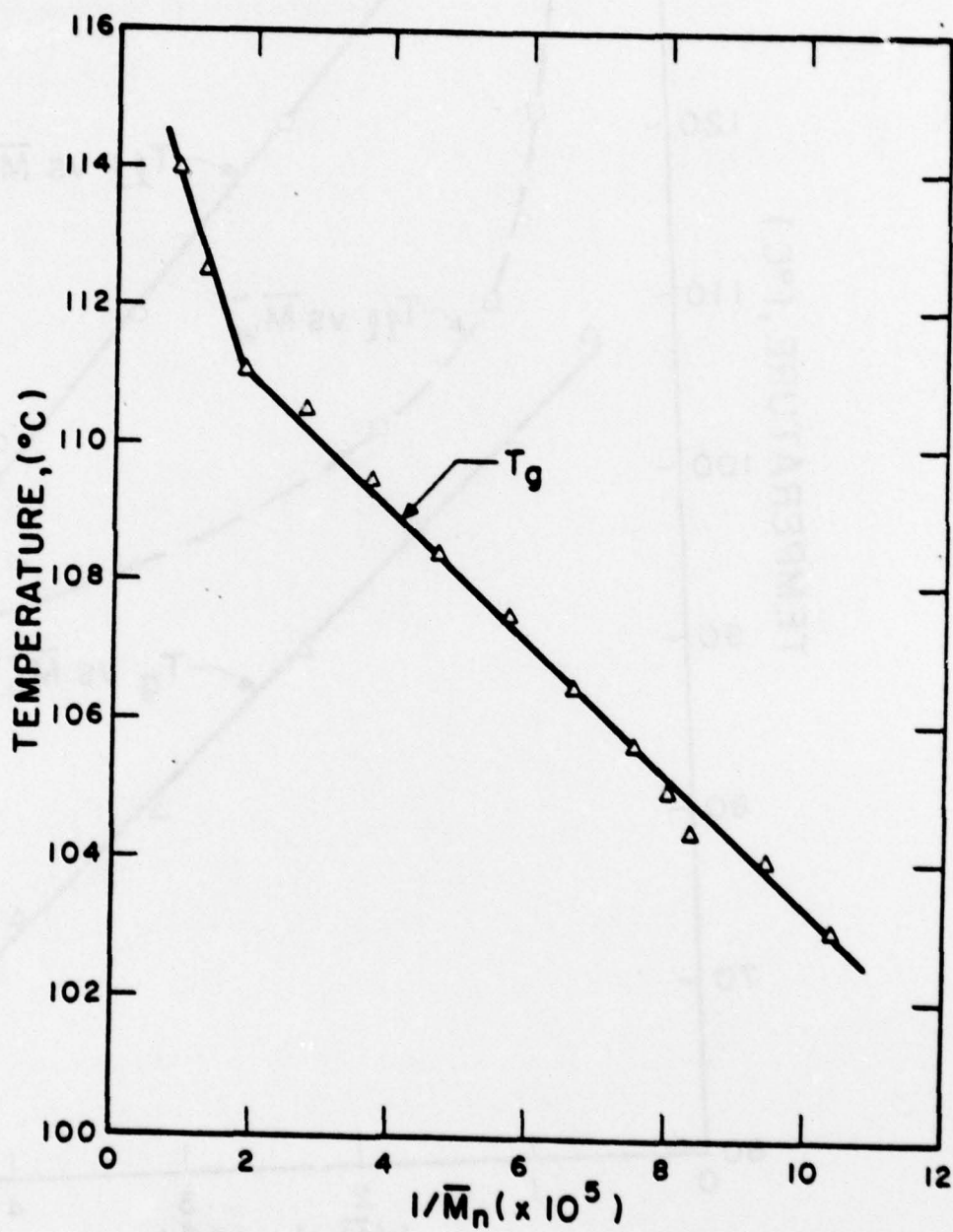


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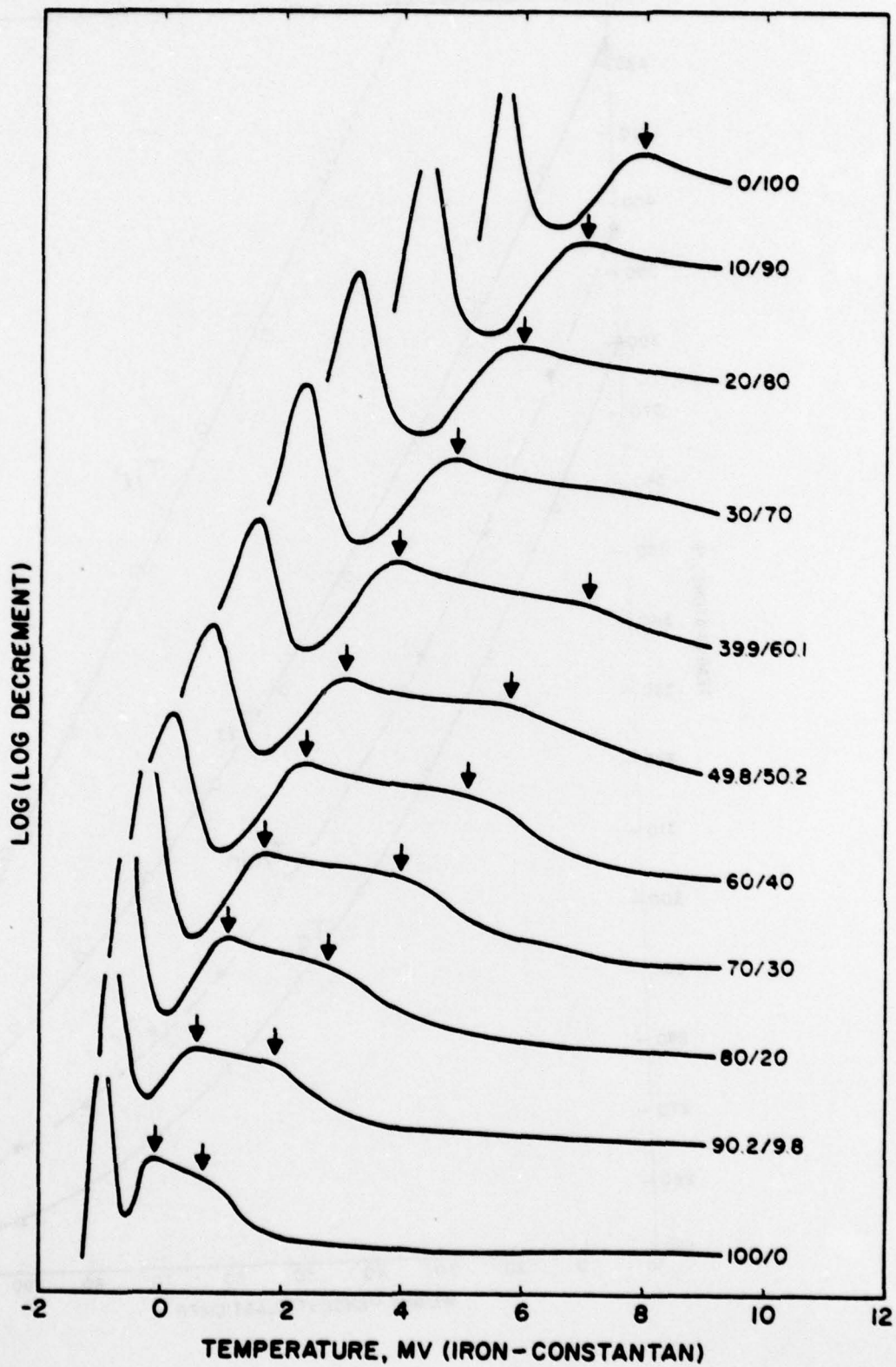


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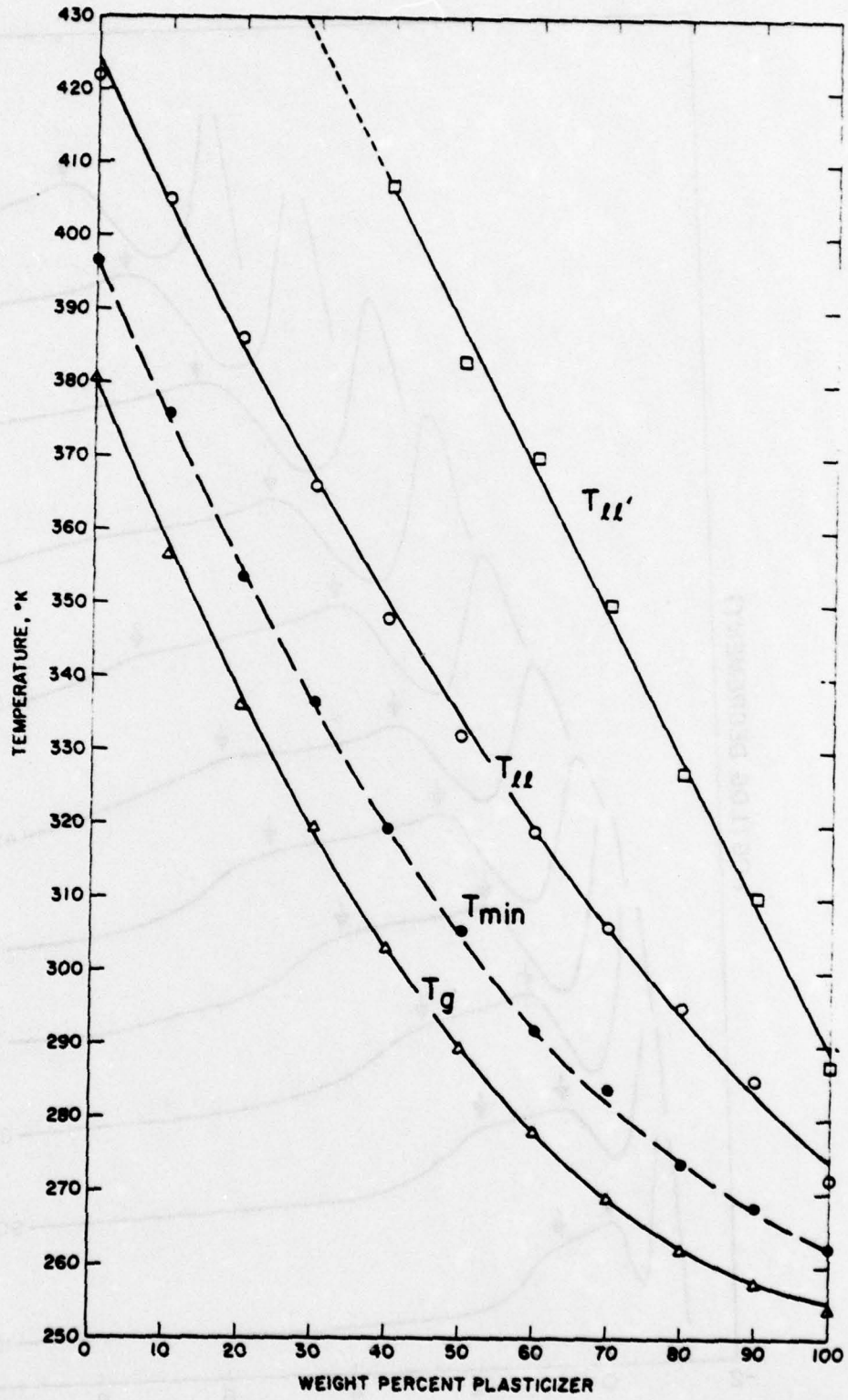


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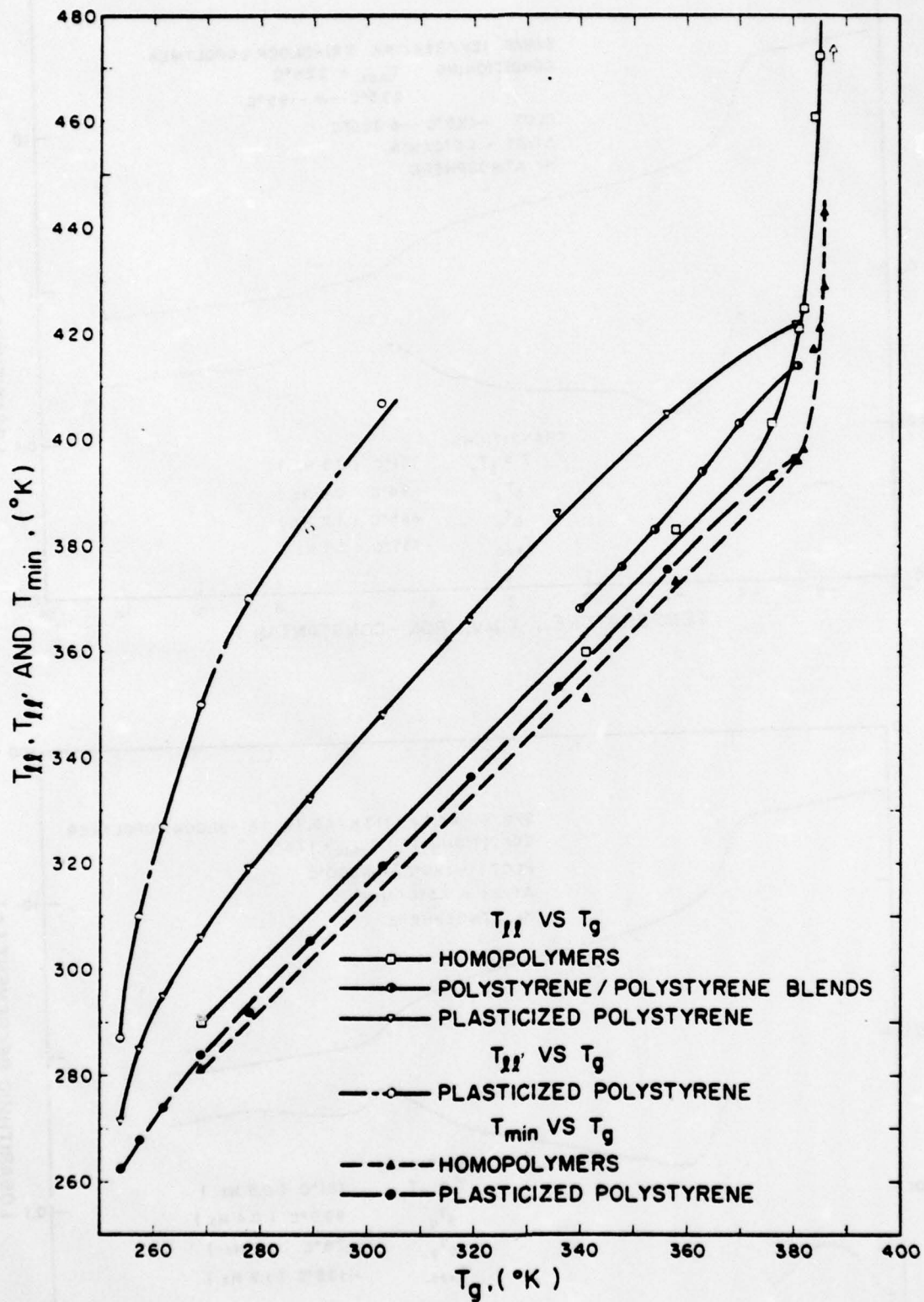


Figure 10

Figure 11

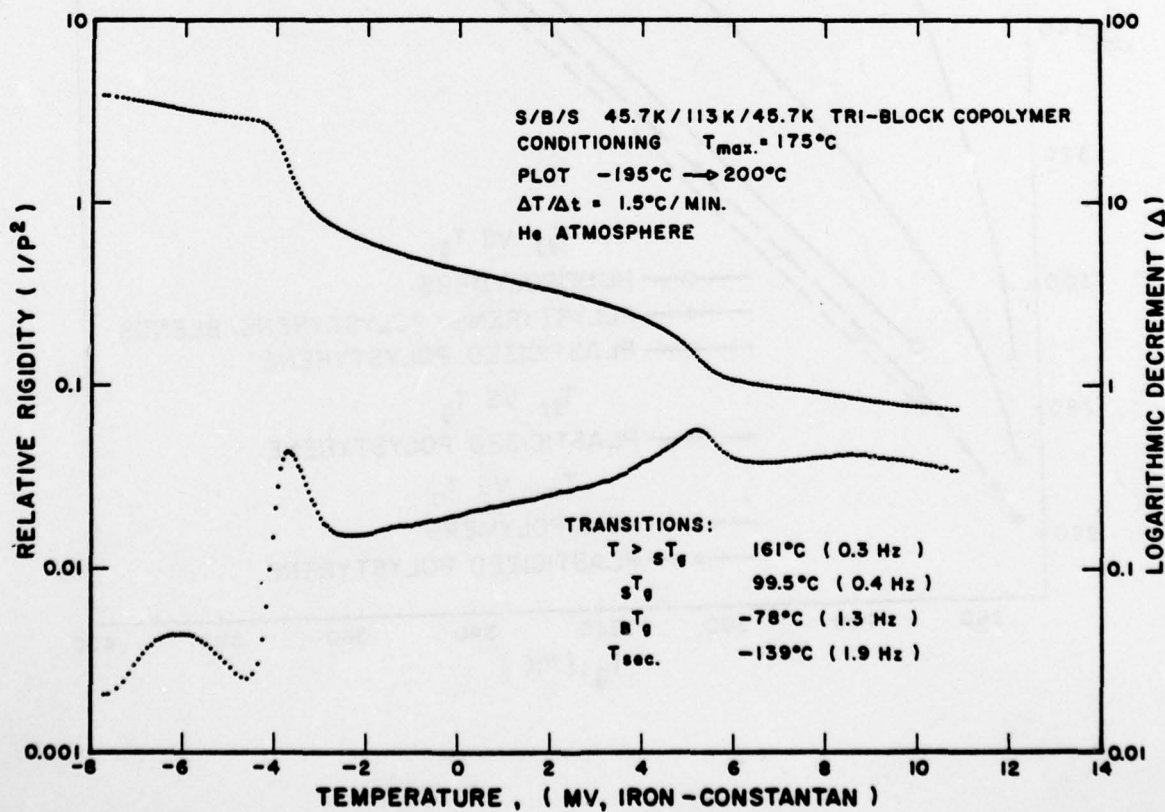
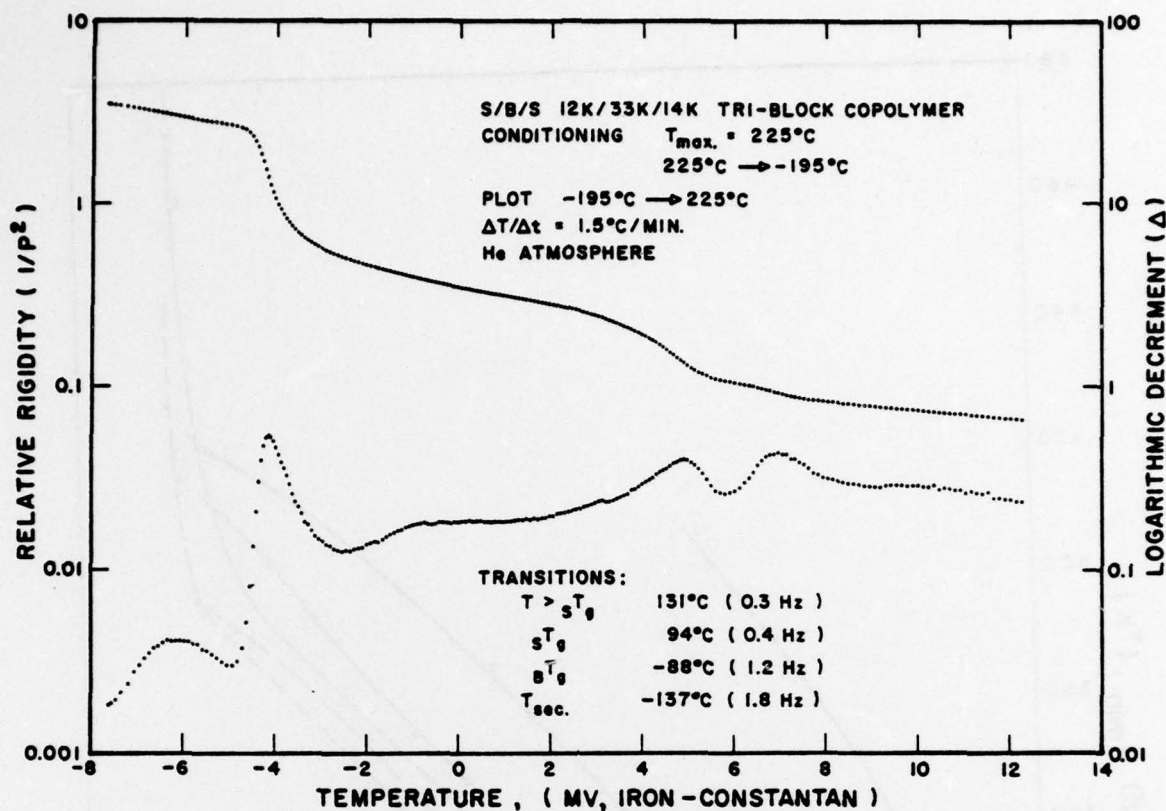


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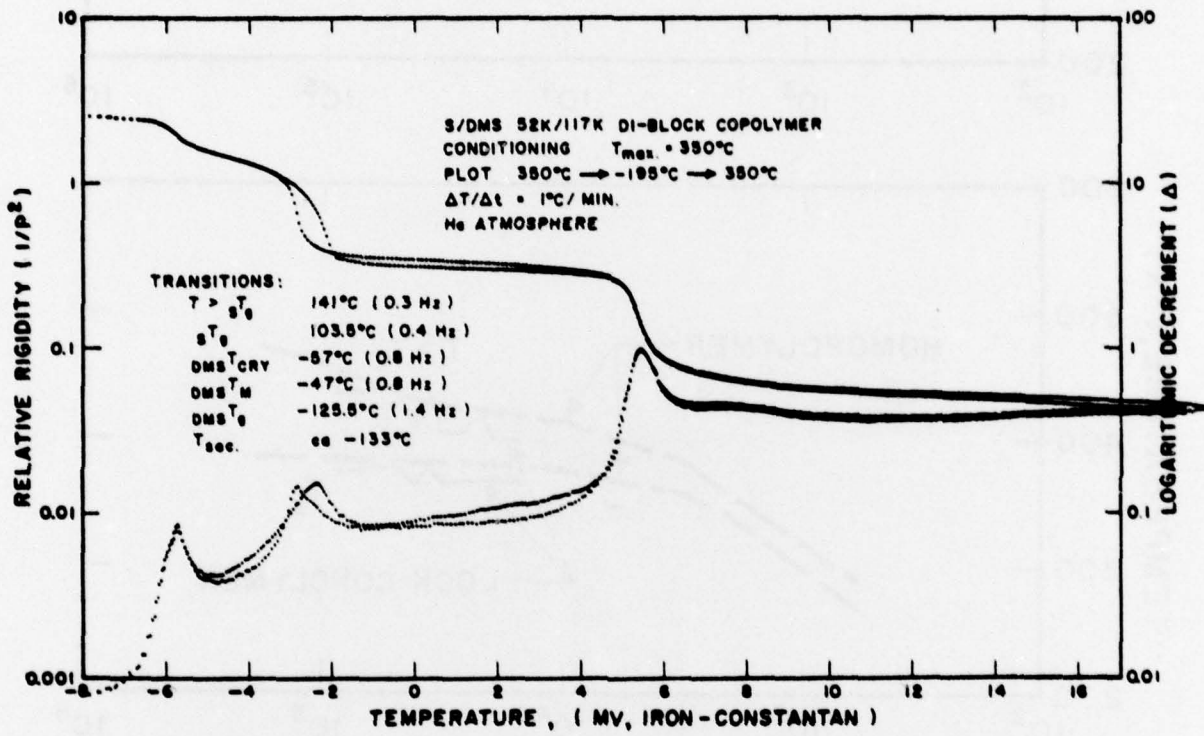


Figure 13

Figure 14

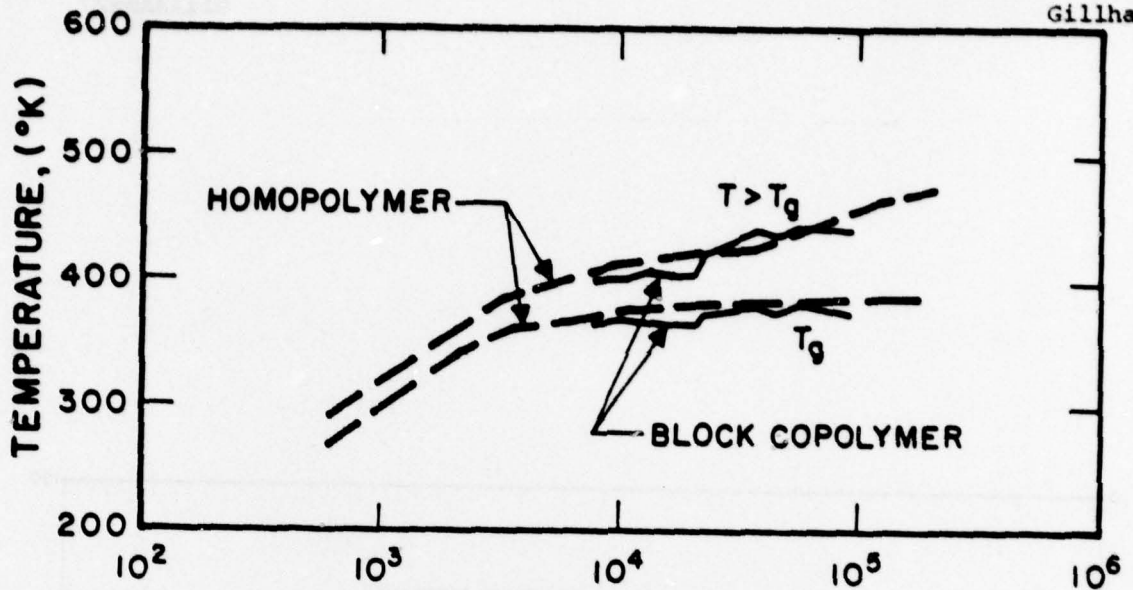


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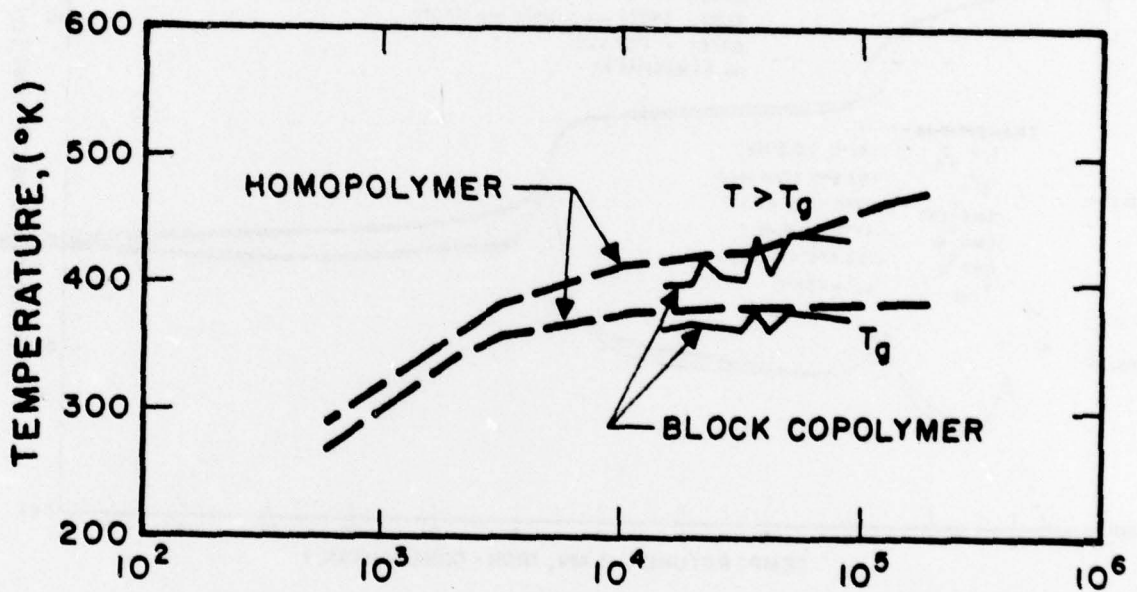
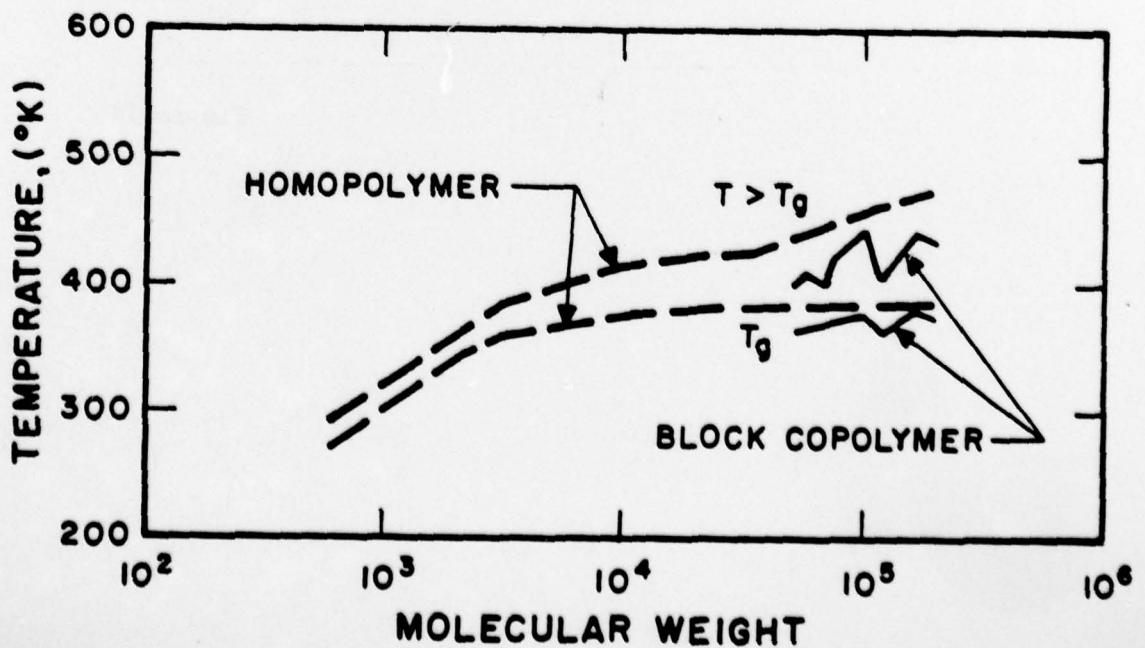


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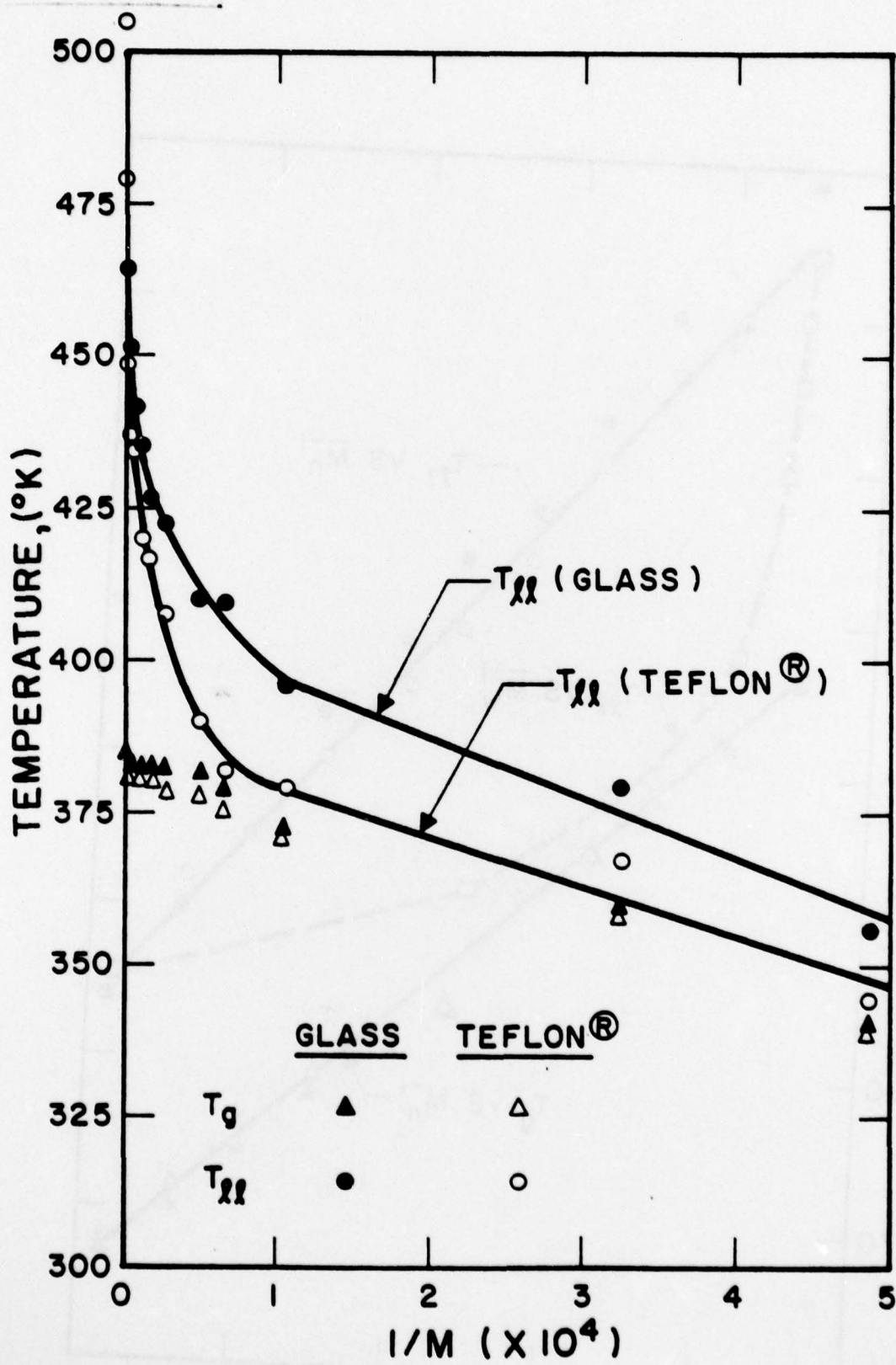


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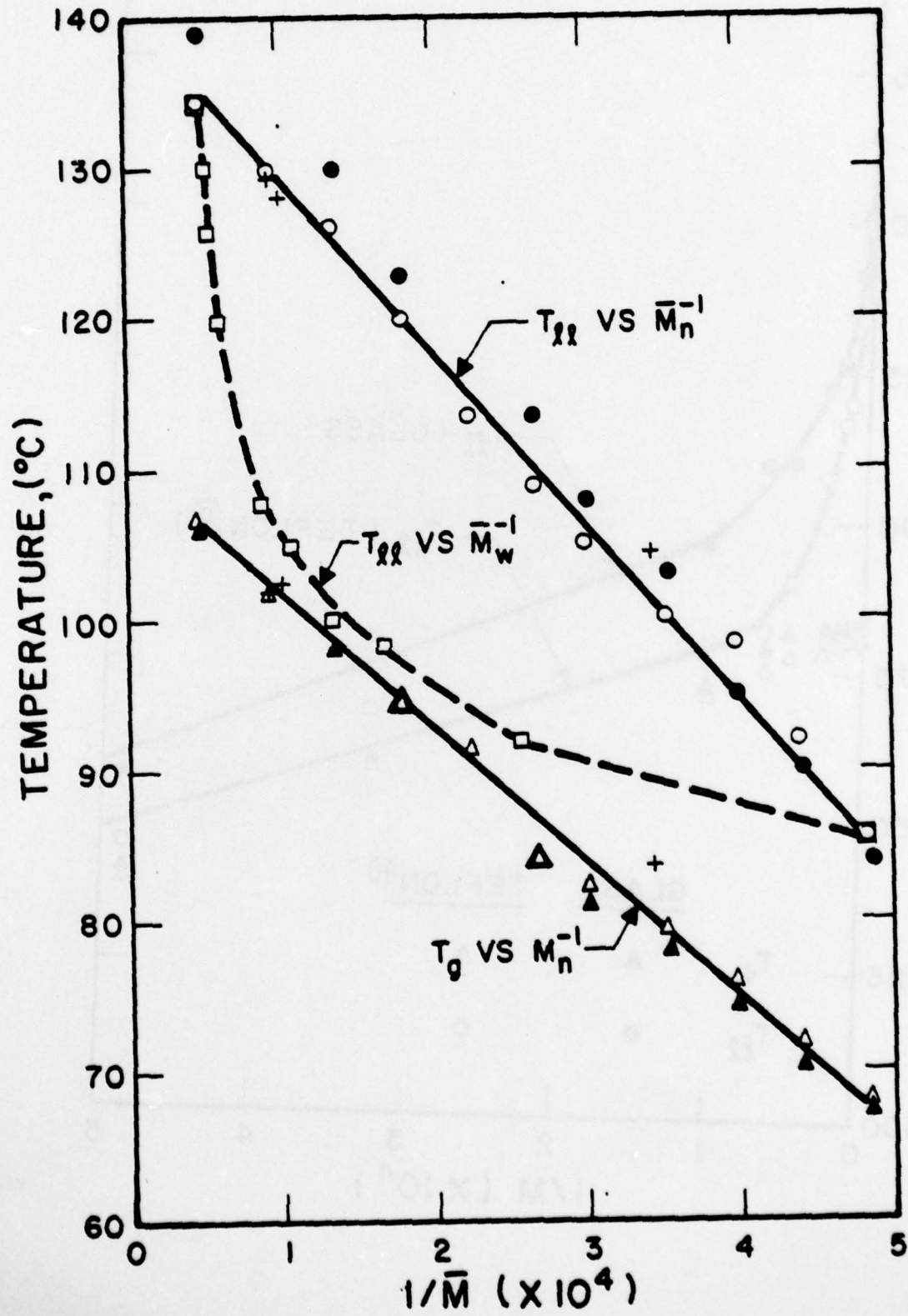


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19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Torsional Braid Analysis Transitions Polystyrene		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Investigation of the $T_{11}$ ( $> T_g$ ) relaxation in amorphous polymers of styrene by the technique of torsional braid analysis is 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. Unlike the glass transition, the (over)		

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$T_{\beta\beta}$  relaxation appears to depend on the nature of the substrate.

The results in particular suggest that the  $T_{\beta\beta}$  relaxation is molecularly based. 1) The  $T_{\beta\beta}$  temperature 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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