

# Correlation of Normal Stresses in Polystyrene Melts and Its Implications

KUNIO ODA,\* JAMES L. WHITE, and EDWARD S. CLARK

*Polymer Engineering  
The University of Tennessee  
Knoxville, Tennessee 37916*

It is found that the principal normal stress difference,  $N_1$ , in commercial polystyrene melts is a unique function of shear stress  $\sigma_{12}$ , independent of temperature and molecular weight. An empirical expression representing this relationship is developed. The functional dependence reported does not represent data for narrow molecular weight distribution polystyrenes, generally significantly overpredicting  $N_1$  values. The basis for this behavior is discussed. The implications of the  $N_1 - \sigma_{12}$  relationship to some rheological and processing problems are described.

## INTRODUCTION

Laminar shear in a polymer melt can be represented by the expression:

$$V_1 = \dot{\gamma} \cdot X_2, V_2 = V_3 = 0 \quad (1)$$

where 1, 2, and 3 refer to orthogonal directions. This type of motion yields both shearing stresses  $\sigma_{12}$  and unequal normal stresses,  $\sigma_{11}$ ,  $\sigma_{22}$ , and  $\sigma_{33}$ . Generally these normal stresses are represented in terms of differences:

$$N_1 = \sigma_{11} - \sigma_{22}, N_2 = \sigma_{22} - \sigma_{33} \quad (2)$$

where  $N_1$  is the first and  $N_2$  the second normal stress differences.

Normal stresses have been studied for 30 years dating back to the work of Weissenberg (1). Except for early studies by Pollett (2), most published work until the last decade involved polymer solutions, primarily of polyisobutylene (3).

Beginning about 1970 there have been extensive experimental studies of normal stresses in polymer melts (4-14) including work in our laboratories. Generally to the present, no correlations have been developed for normal stresses in terms of shear stresses or shear rate which would allow a polymer engineer to determine normal stresses in melts without directly measuring them. Such a development would be of great practical interest. Some years back Tanner (3) found it possible to bring together almost all of the polyisobutylene solution normal stress-shear stress-concentration data in the literature in a single correlation. In this paper we present a study of the relationships between  $N_1$  and  $\sigma_{12}$  for polystyrene melts.

## SOURCES OF DATA

A summary of available data for normal stress behavior in polystyrene melts is summarized in *Table I* including polymer types, molecular weight ( $\bar{M}_w$ ), molecular weight distribution (MWD), instruments used, and temperature of the measurement. The data are obtained from four research groups: Xerox (4), University of Tennessee (5, 7-10, 12, 13), Polytechnic Institute of New York/New Jersey Institute of Technology (6, 14), and Northwestern University (11). The greatest quantity of data is admittedly from our own laboratories. The data were obtained using three instruments: (a) Weissenberg rheogoniometer (4-12), (b) mechanical spectrometer (13), and (c) slit/capillary rheometer (14). Each of the four groups separately used the rheogoniometer. The broad distribution polystyrenes were obtained variously from Arco, Dow, Monsanto, Hercules, Shell and Cadillac Plastics as commercial or experimental materials. One sample of the broad distribution polymers was prepared by blending (4). Two narrow molecular weight distribution polystyrene samples have also been studied (11).

## COMMERCIAL AND BROAD DISTRIBUTION POLYSTYRENES

The influence of temperature on the  $N_1 - \sigma_{12} - \dot{\gamma}$  interrelationship is seen in *Fig. 1*, where  $N_1$  is plotted as a function of  $\dot{\gamma}$  in *Fig. 1a* and of  $\sigma_{12}$  in *Fig. 1b*. Clearly *Fig. 1b* shows an excellent fit for a single curve indicating no temperature dependence.

The effect of comparing data from several laboratories with different polymers of different molecular weight is seen in *Fig. 2*. Considering the diversity of investigators, instruments and materials, the agreement is remarkable. The data for each sample were weighted

\*Permanent address: Ube Industries, Hirakata Plastics Laboratory, Hirakata, Osaka, Japan.

Table 1. Sources of Polystyrene Normal Stress Data

Codes	Polystyrene types	$M_w \times 10^3$	$M_w/M_n$	Instruments†	Temp (°C)	Reference
A	*	98	—	WR	185	(4)
B	Dow Styron 666	229	2.7	WR	160, 180, 200	(5)
C	Dow Styron 686	289	2.8	WR, SC	200	(6, 14)
D	Cadillac PS	295	3.3	WR	160, 180, 200	(7)
E	Shell TC 3-30	312	5.3	WR	160	(8)
F	Picco. D150	75	18.0	WR	160	(8)
G	Cadillac PS	295	3.3	WR	160	(9)
H	Dow Styron 678	215	3.3	WR	180	(10)
I	Dow Styron	220	—	WR	159	(11)
J	Dow Styron	261	—	WR	157-190	(11)
K	**	97	—	WR	142, 168	(11)
L	**	160	—	WR	169	(11)
M	*** (Arco)	350	2.7	WR	180	(12)
N	*** (US Steel)	329	3.0	WR	180	(12)
O	Cadillac PS	295	3.3	WR	180	(12)
P	*** (Monsanto)	262	3.2	WR	180	(12)
Q	Dow Styron 678	215	3.3	WR	180	(12)
R	*** (Arco)	88	2.4	WR	180	(12)
S	Picco. D150	75	18.0	WR	180	(12)
T	*** (Dow)	61	5.3	WR	180	(12)
U	Dow Styron 678 U	215	3.3	MS	180	(13)

\* Blended sample of narrow molecular weight distribution polystyrenes.

\*\* Narrow molecular weight distribution sample.

\*\*\* Experimental sample prepared by free radical polymerization.

† WR Weissenberg rheogoniometer, MS mechanical spectrometer, and SC slit/capillary rheometer.

equally to derive the following relationship using a least squares statistical analysis:

$$N_1 = A \cdot \sigma^{a_{12}} \quad (3)$$

where  $A = (7.5 \pm 2.0) \times 10^{-4} \text{ (cm}^2/\text{dynes)}^{0.66}$  and  $a = 1.66$ .

Since Eq 3 is a purely empirical correlation, it should be used within the range of variables from which it was derived. The limits were (a) commercial and moderately broad distribution polystyrenes, (b)  $M_w$  varied from  $350 \times 10^3$  to  $61 \times 10^3$ , and (c) shear stress varied from  $5 \times 10^3$  to  $1 \times 10^6$  dynes/cm<sup>2</sup>.

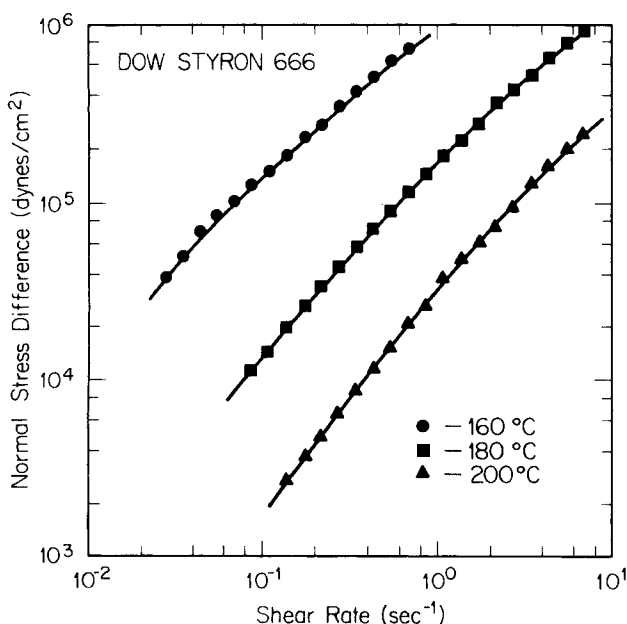


Fig. 1a. Principal normal stress difference  $N_1$  as a function of shear rate  $\dot{\gamma}$  and temperature for a polystyrene melt (after Chen (5)).

## ANIONIC POLYSTYRENES

Normal stress differences of narrow molecular weight distribution polystyrenes as a function of shear stress are shown in Fig. 3. The data for the blend of narrow molecular weight distribution polystyrenes and the correlation of the previous section are also plotted. The  $N_1 - \sigma_{12}$  data for the two narrow distribution polymers overlap. However, the values of  $N_1$  are significantly lower than for the commercial and broad molecular weight distribution polymers.

For the two narrow distribution polystyrenes, the form of Eq 3 remains valid. The quantities  $A$  and  $a$  have values:  $A = 1.4 \times 10^{-6} \text{ (cm}^2/\text{dynes)}$  and  $a = 2.0$ .

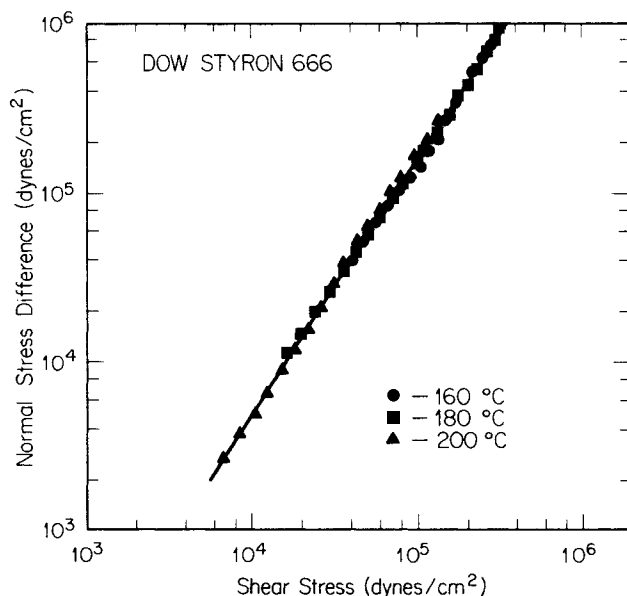


Fig. 1b. Principal normal stress difference  $N_1$  as a function of shear stress  $\sigma_{12}$  for the same polystyrene melt including 160, 180 and 200°C data.

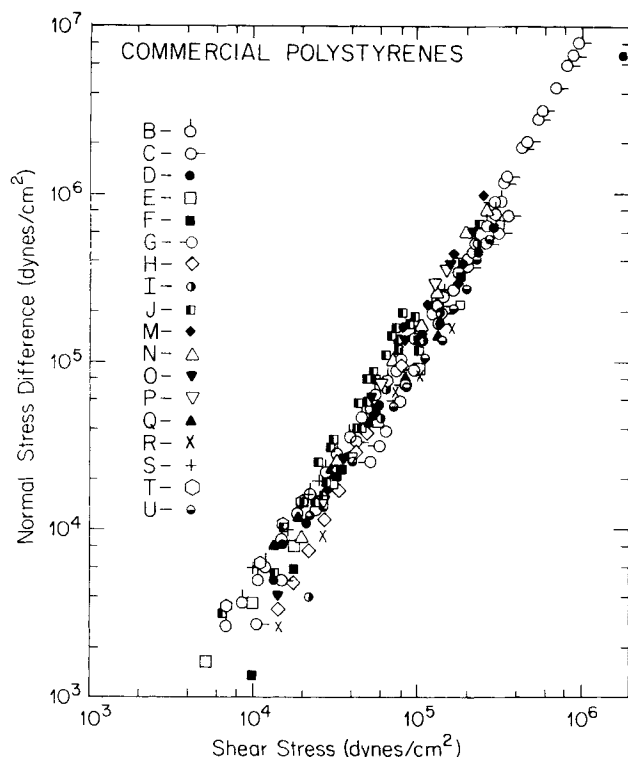


Fig. 2. General correlation of principal normal stress difference as a function of shear stress for commercial polystyrene melts.

### DISCUSSION

At low shear rates, the principal normal stress differences can be written in terms of the theory of second order fluids as (15, 16):

$$N_1 = \psi_{10} \cdot \dot{\gamma}^2 \quad (4a)$$

$$= 2 \cdot J_e \cdot \sigma_{12}^2 \quad (4b)$$

where  $\psi_{10}$  the principal normal stress difference coefficient is:

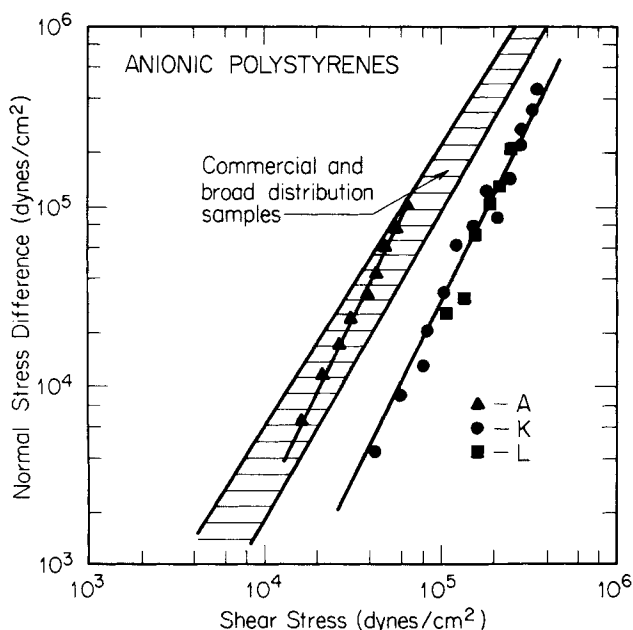


Fig. 3. Comparison of principal normal stress difference-shear stress relationships for narrow (anionic) and commercial and broad distribution samples.

$$\psi_{10} = 2 \cdot J_e \cdot \eta^2 \quad (5)$$

and  $J_e$  is the steady state compliance. Generally  $N_1$  should be proportional to the square of  $\sigma_{12}$  at low shear stresses.

The value of  $J_e$  may also be determined from recoil and linear viscoelastic dynamic measurements. Generally  $J_e$  is found to be independent of temperature. The influence of molecular weight and molecular weight distribution on the steady state compliance has been studied by Masuda, Onogi, and Kitagawa (17). They found no  $M_w$  dependence of  $J_e$  and for the case of narrow molecular weight distribution polystyrenes observed that if  $M_w$  is higher than a critical molecular weight ( $M_c \cong 4 \times 10^4$ ),  $J_e = 1.4 \times 10^{-6} \text{ cm}^2/\text{dynes}$  ( $M_w > M_c$ ).

For broader molecular weight distributions,  $J_e$  takes on larger values as shown by recoil and dynamic measurements (17). As indicated by Eq 4 this behavior of  $J_e$  can explain the larger values of  $N_1$  at fixed  $\sigma_{12}$  for the commercial and broader distribution melts. We must be a bit careful here because Eq 4 is restricted to the second order fluid range. Generally commercial polystyrenes possess similar molecular weight distributions and the agreement among different polymers is probably for this reason. Values of apparent  $J_e$  determined from  $N_1$  data as a function of shear stress are summarized in Fig. 4. This quantity decreases with increasing stress perhaps towards the narrow molecular weight distribution limit.

It is of interest to discuss what is known of second normal stress differences in polystyrene melts so that the possibility of complete specification of the stress ellipsoid may be pondered. Second normal stress difference measurements on polystyrene melts are limited. One experimental study using cone-plate and parallel disk modes in a rheogoniometer by Lee and White (2) suggests that  $N_2/N_1$  is small and negative ( $\sim -0.15$ ). A study by Han (14, 18) using the slit/

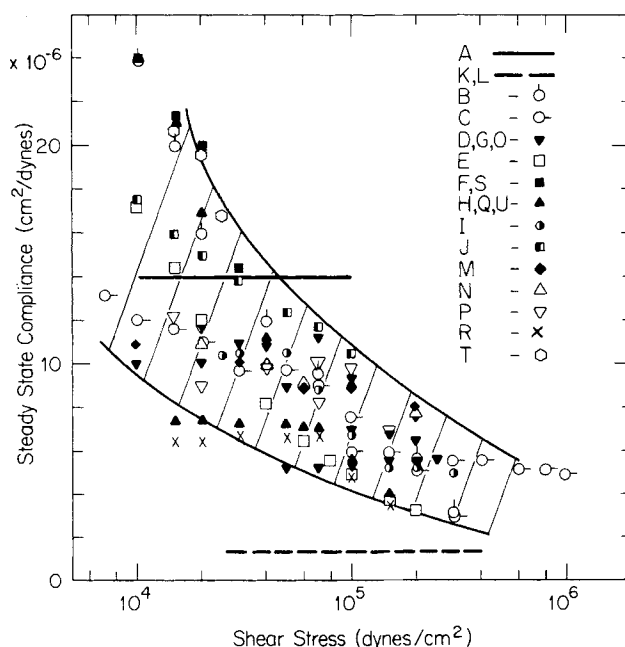


Fig. 4. Steady state shear compliance as a function of shear stress for commercial and narrow distribution samples.

capillary method indicates that  $N_2/N_1$  is negative and has value of (-0.45).

### IMPLICATIONS OF $N_1 - \sigma_{12}$ RELATION

There are many flow problems in polymer melt processing which one believes to be characterized by the ratio of the normal stress difference to shearing stresses in its role as a Weissenberg number  $N_{Ws}$  or elastic recovery (16, 19-21). As  $N_1$  is determined by  $\sigma_{12}$  and

$$N_{Ws} \cong \frac{N_1}{\sigma_{12}} = A\sigma_{12}^{a-1} \quad (6)$$

one would expect these phenomena to be correlated with  $\sigma_{12}$  alone. Some specific applications are discussed below.

Some obvious examples arise in extrusion. One would expect from considerations of extrudate swell,  $B$ , as unconstrained recovery for it to depend upon  $(N_1/\sigma_{12})_w$  (evaluated at the die wall) (21, 22) and from Eq 6 on  $(\sigma_{12})_w$  alone. From Fig. 3 one would further expect a stronger dependence on  $(\sigma_{12})_w$  for commercial polystyrenes than for narrow distribution polymers. This has been observed by Graessley, Glasscock and Crawley (22) in extrudate swell experiments on these two classes of polystyrene melts. They find  $B$  to be a unique but distinct function of  $(\sigma_{12})_w$  for commercial and anionic polystyrenes with the former systems showing a much stronger rate of increase of  $B$ .

A second application concerns die entry flow patterns (i.e., vortices) during extrusion. These have been observed in polystyrene by investigators at the University of Tennessee (5b, 12, 23, 24). White and Kondo (12) find that the vortex size depends on  $N_1/\sigma_{12}$  (evaluated at the die wall) alone for commercial polystyrene melts, when the normal stress-shear stress ratio is evaluated at the capillary wall. Clearly vortex size will also correlate with shear stress alone in the commercial polystyrene melts.

A third problem of interest involves the onset of extrudate distortion. This has been found to occur at a critical shear stress for polystyrene melts with some minor molecular weight dependence (25, 26). It has long been considered (16, 24) that the onset of extrudate distortion is determined by a critical Weissenberg number. If this is taken as  $(N_1/\sigma_{12})_c$  then the  $(\sigma_{12})$  criterion is to be expected. However, one would expect a molecular weight distribution dependence upon the value of the critical  $(\sigma_{12})$  which is greater than observed (24).

### ACKNOWLEDGMENT

We would like to thank Professor W. W. Graessley for

supplying the experimental data of reference (11). This research was supported in part by the General Electric Foundation and Ube Industries.

### REFERENCES

1. K. Weissenberg, *Nature*, **159**, 310 (1947); *Proc. 1st Int. Cong. Rheology*, **II**, 29 (1948).
2. W. F. O. Pollett and A. H. Cross, *J. Sci. Instr.*, **27**, 209 (1950); *Brit. J. Appl. Phys.*, **6**, 199 (1955).
3. R. I. Tanner, *Trans. Soc. Rheol.*, **17**, 365 (1973).
4. W. M. Prest, Jr., *J. Polym. Sci., A-2*, **8**, 1897 (1970).
5. (a) I. J. Chen, Ph.D. Dissertation, The University of Tennessee (1971);  
(b) T. F. Ballenger, I. J. Chen, J. W. Crowder, G. Hagler, D. C. Bogue, and J. L. White, *Trans. Soc. Rheol.*, **15**, 195 (1971).
6. C. D. Han, K. U. Kim, N. Siscovic, and C. R. Huang, *J. Appl. Polym. Sci.*, **17**, 95 (1973).
7. H. B. Dee, M.S. Thesis, The University of Tennessee (1973); J. L. White and H. B. Dee, *Polym. Eng. Sci.*, **14**, 212 (1974).
8. T. Takaki, M.S. Thesis, The University of Tennessee (1973); T. Takaki and D. C. Bogue, *J. Appl. Polym. Sci.*, **19**, 419 (1975).
9. B. L. Lee, Ph.D. Dissertation, The University of Tennessee (1974); B. L. Lee and J. L. White, *Trans. Soc. Rheol.*, **18**, 467 (1974).
10. J. F. Roman, M.S. Thesis, The University of Tennessee (1974); J. L. White and J. F. Roman, *J. Appl. Polym. Sci.*, **20**, 1005 (1976).
11. R. L. Crawley, M.S. Thesis, Northwestern University (1974).
12. A. Kondo, Ph.D. Dissertation, The University of Tennessee (1976); J. L. White and A. Kondo, *J. Non-Newtonian Fluid Mech.*, **3**, 41 (1977).
13. V. M. Lobe, Ph.D. Dissertation, The University of Tennessee (in progress).
14. C. D. Han, "Rheology in Polymer Processing," Academic Press, New York (1976).
15. B. D. Coleman and H. Markovitz, *J. Appl. Phys.*, **35**, 1 (1964).
16. J. L. White, *J. Appl. Polym. Sci.*, **8**, 2339 (1964).
17. T. Masuda, Ph.D. Dissertation, Kyoto University, Japan (1973); S. Onogi, T. Masuda and K. Kitagawa, *Macromolecules*, **3**, 109, 116 (1970).
18. C. D. Han, *Trans. Soc. Rheol.*, **18**, 163 (1974).
19. A. B. Metzner, J. L. White and M. M. Denn, *AIChE J.*, **12**, 863 (1966); *Chem. Eng. Prog.*, **62**, 12, 81 (1966).
20. D. C. Bogue and J. L. White, "Engineering Analysis of Non-Newtonian Fluids," NATO Agardograph 144, (1970).
21. R. I. Tanner, *J. Polym. Sci., A-2*, **8**, 2067 (1970).
22. W. W. Graessley, S. D. Glasscock, and R. L. Crawley, *Trans. Soc. Rheol.*, **14**, 519 (1970).
23. T. F. Ballenger and J. L. White, *J. Appl. Polym. Sci.*, **15**, 1949 (1971).
24. J. L. White in "U.S.-Japan Seminar on Polymer Processing and Rheology," edited by D. C. Bogue, M. Yamamoto, and J. L. White, *Appl. Polym. Symp.*, **20**, 155 (1973).
25. R. S. Spencer and R. E. Dillon, *J. Colloid Sci.*, **4**, 241 (1971).
26. J. Vlachopoulos and S. Lidorikis, *Polym. Eng. Sci.*, **11**, 1 (1971).