

***Viscosity of Polystyrene Near the Glass Transition.***  
***Authors' Addition***

Some time ago the authors published a paper under the above title (*J. Appl. Polym. Sci.*, **13**, 2427 (1969)). This work has evoked wide attention and considerable correspondence—some of which may be of general interest for extension and clarification for studies of polymer flow.

In our previous work, frequency, shear rate, and pressure were considered as possible parameters which could cause a shift in the glass transition temperature,  $T_g$ . Such shifts could appreciably influence measured rheological responses. In this regard, we have previously discussed the interrelation of two established equations; the first, relating frequency of measurement and the apparent glass transition temperature; and the second, a relation between the glass transition temperature and viscosity (WLF equation). In the original paper of this series, cited above, we have noted that the combined equations do not provide a valid prediction of viscosity changes with frequency. This point is experimentally confirmed in the original manuscript. In this first paper we also indicated that the reason was not entirely clear why the calculated viscosity increases with frequency and shear rate were not experimentally observed. The following clarifying comments can be offered.

If the temperature of viscoelastic measurement is changed, the  $T_g$  will appear in a shifted position on the time or frequency scale. Lewis has presented such a correlation for polystyrene and for many other polymers.<sup>1</sup> The equation stating this relationship can be deceptive in that it implies that the  $T_g$  is a continuous function of frequency at a fixed temperature. From this equation, the calculated frequency necessary to observe the  $T_g$  at our test temperature lies much beyond the experimentally feasible range of frequencies. This is verified by our report that no viscosity increase was observed in the experimental data as a function of frequency or shear rate.

We wish to emphasize that the WLF and the corresponding Tammann-Hesse equations, in our best judgment, can be properly employed in the context of our studies. In the Tamman-Hesse equation,  $T_0$  is not, however, to be replaced by  $T_g$ . What can be assumed is a change in  $T_0$  equivalent to a change in  $T_g$ , as previously suggested by Miller.<sup>2</sup> Concerning the use which has been made of the WLF equation,  $T_0$  is the reference temperature and not  $T_g$ .

Our subsequent studies on pressure effects in polymer rheology have also extended and further clarified the presentation made in the original paper.<sup>3</sup>

**References**

1. A. F. Lewis, *J. Polym. Sci. B*, **2**, 649 (1963).
2. A. A. Miller, *J. Polym. Sci. A2*, **6**, 1161 (1968).
3. R. C. Penwell and R. S. Porter, *J. Polym. Sci.*, to be published.

RICHARD C. PENWELL  
ROGER S. PORTER

Polymer Science and Engineering  
University of Massachusetts  
Amherst, Massachusetts 01002

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