Schönhals *et al.* **Reply:** The Comment by Cummins *et al.* [1] is concerned with the well-known fact that in low molecular glass forming liquids the temperature dependence of the α -relaxation times τ (or the viscosities) cannot be universally described by the empirical Vogel-Fulcher-Tammann (VFT) equation

$$\ln(f/f_0) = -B/(T - T_0) \tag{1}$$

 $(f = 1/2\pi\tau; f_0, B \text{ constants}, T_0 \text{ Vogel temperature}).$

Assuming a low temperature VFT equation, the deviations at high temperature can be described by an Arrhenius behavior in good approximation within experimental accuracy [2,3]. This approach was suggested by the observation that the temperature-viscosity relationship for liquids well above the melting temperatures follows the Arrhenius law [4–6].

The analysis of the temperature dependence of the relaxation time is complicated by the fact that the three parameters of the VFT equation cannot be uniquely determined from the activation plot. To overcome this difficulty Stickel [7] refined the data analysis by evaluating the difference quotient $\Delta \ln f / \Delta T$. From Eq. (1) it follows, under the assumption that f_0 does not depend on temperature, that the plot of the inverse square root $(\Delta \ln f / \Delta T)^{-1/2} = (T - T_0) / B$ versus temperature shows a straight line. As a result of dielectric measurements of glycerol (Fig. 1), we find a VFT behavior in the temperature range $T_g \leq T \leq T_g + 100$ K with $\ln(f_0/\text{sec}^{-1}) = 14.2$, B = 1040 K, and $T_0 = 127$ K in good agreement with Fig. 1(b) of the Comment. Above the melting point of glycerol $(T_m \approx 290 \text{ K})$ we find deviations from this VFT law with the same tendency as indicated in this figure. This behavior is opposite to the previous conclusion of Schönhals et al. [2] that above T_A Arrhenius behavior is observed.

The procedure described above was applied to a larger variety of glass forming liquids. Since salol was mentioned in the Comment, we show a similar plot for this



FIG. 1. Inverse square root of the difference quotient of the maximum position f_{max} vs temperature.



FIG. 2. Inverse square root of the difference quotient of the maximum position f_{max} vs temperature.

substance (Fig. 2). In contrast to glycerol the figure shows deviations from the VFT behavior at low temperatures. For about ten glass forming liquids studied so far, a behavior similar to that plotted in Fig. 2 was observed.

Since the activation plot $\ln f(T)$ is a continuously decreasing function in all cases, it is difficult to recognize characteristic temperatures by an unbiased evaluation of those data. The method of Stickel described above, however, shows a clear change of the temperature dependence of the difference quotient at certain temperatures. A detailed report about these results is in preparation [8].

This work was supported by SFB 262.

F. Stickel,¹ E. W. Fischer,¹ A. Schönhals,² and F. Kremer³

¹Max-Planck Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Federal Republic of Germany ²Zentrum für Makromolekulare Chemie, Rudower Chaussee 5, D-12484 Berlin, Federal Republic of Germany ³Universität Leipzig, Linnèstrasse 5, D-04103 Leipzig,

Federal Republic of Germany

rederar Republic of Germa

Received 2 May 1994 PACS numbers: 64.70.Pf, 64.70.Dv, 66.20.+d

- [1] H.Z. Cummins *et al.*, preceding Comment, Phys. Rev. Lett. **73**, 2935 (1994).
- [2] A. Schönhals et al., Phys. Rev. Lett. 70, 3459 (1993).
- [3] E. W. Fischer, Physica (Amsterdam) 201A, 183 (1993).
- [4] P.A. Egelstaff, An Introduction to the Liquid State (Clarendon, Oxford, 1992), 2nd ed.
- [5] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, London, 1965), 2nd ed.
- [6] E. N. C. Andrade, Philos. Mag. 17, 698 (1934).
- [7] F. Stickel, PhD thesis, Mainz, (to be published).
- [8] F. Stickel and E. W. Fischer, (to be published).