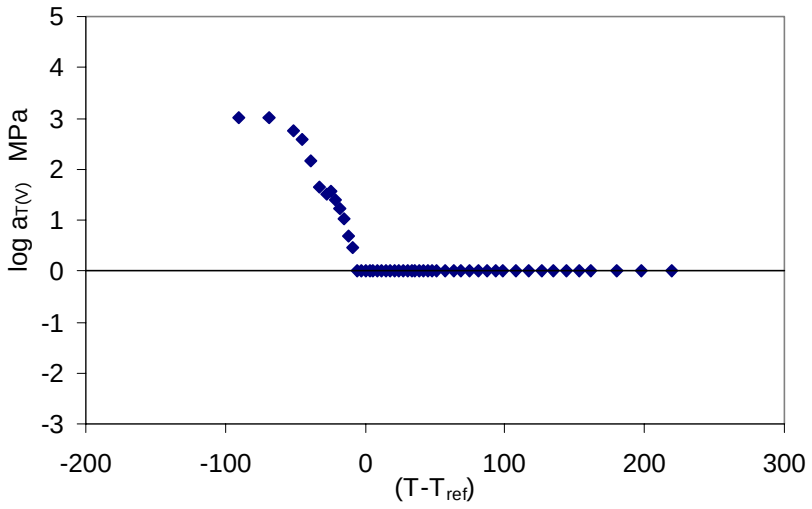
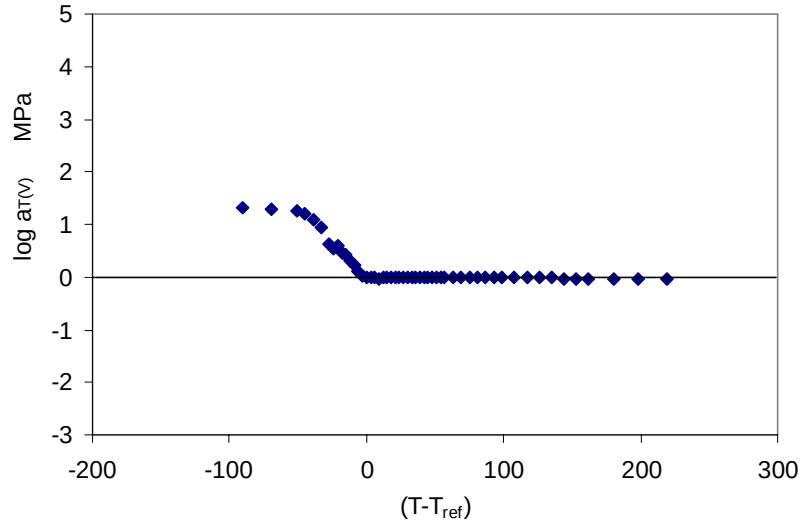
# Appendix K

## Vertical Shifts from Dynamic Mechanical Behavior

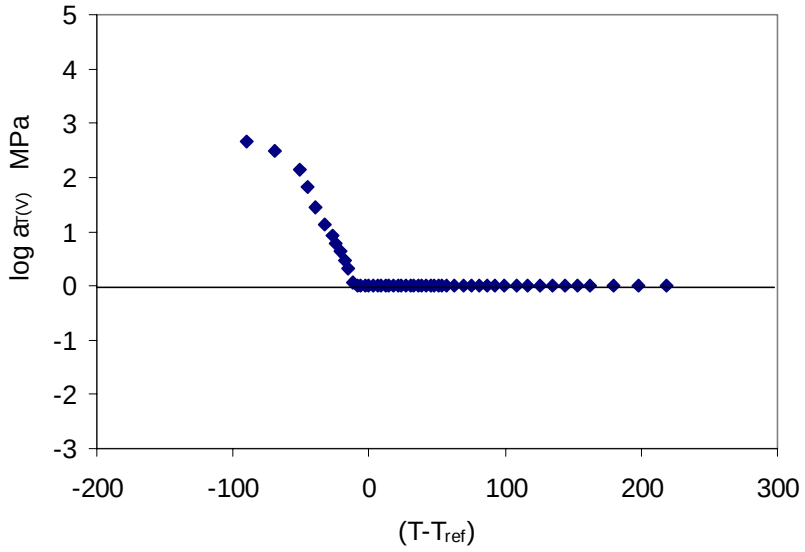
Examples of vertical shifts (log $a_{T(H)}$) obtained from the construction of frequency-temperature master curves described in Chapter 6 are given below.



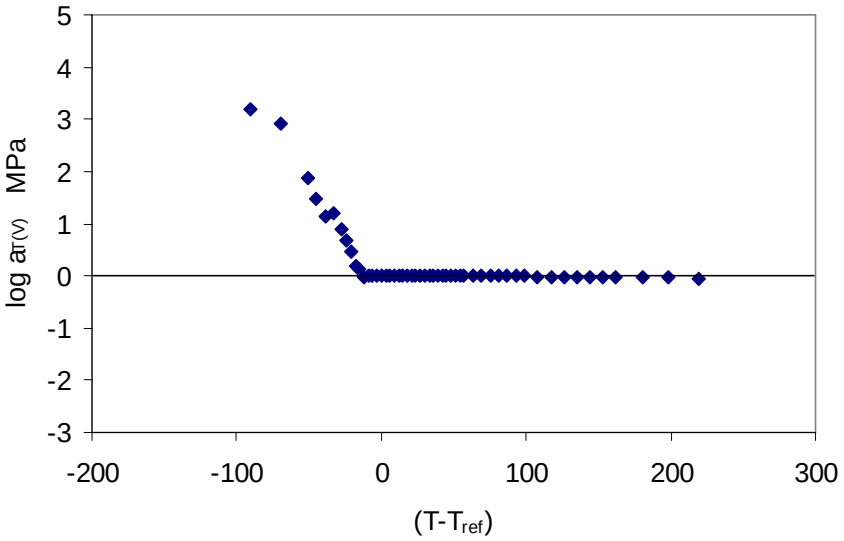

Vertical shifts (log $a_{T(V)}$) for a polymer film exposed to *decane* for $10^5$ minutes




Vertical shifts (log $a_{T(V)}$) for a polymer film exposed to *decane* for $10^{3.70}$ minutes



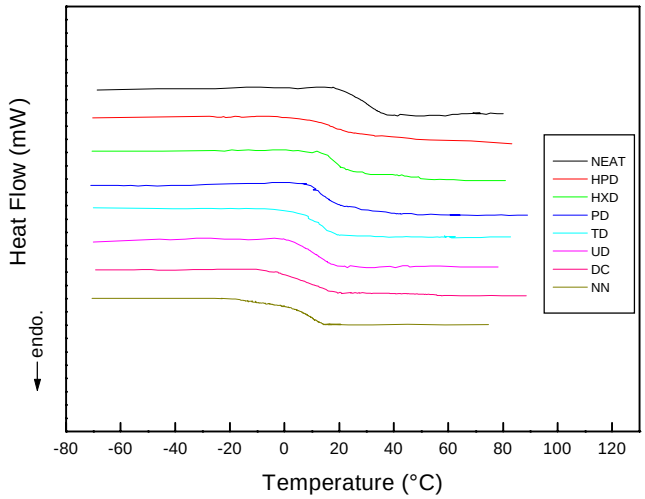

Vertical shifts (log $a_{T(V)}$) for a polymer film exposed to *ethyl undecanoate* for $10^3$ minutes



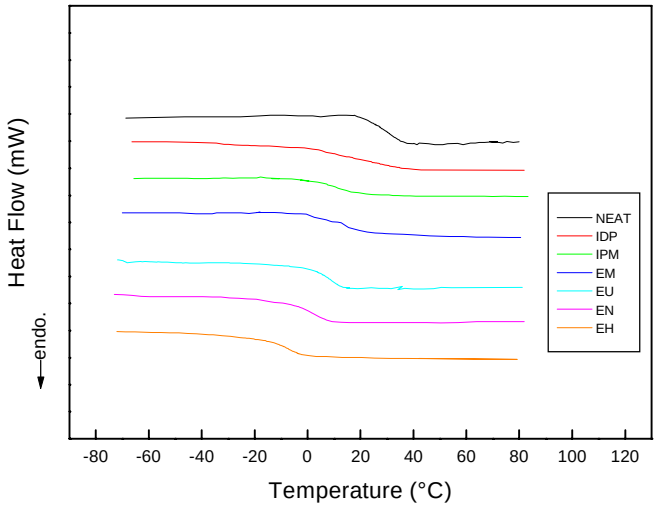

Vertical shifts (log $a_{T(V)}$) for a polymer film exposed to *decane* for $10^{4.60}$ minutes

**Investigation of Low Temperature Polymer-Penetrant Behavior via DSC**

Differential scanning calorimetry (DSC) was performed on samples that had been fully imbibed with penetrant. Tests were done using a TA 2920 MDSC from –75°C to 80°C at a heating rate of 10°C/min. No melting endotherm was observed below the polymer $T_g$ for any of the penetrants, indicative of non-clustering of penetrant within the polymer.



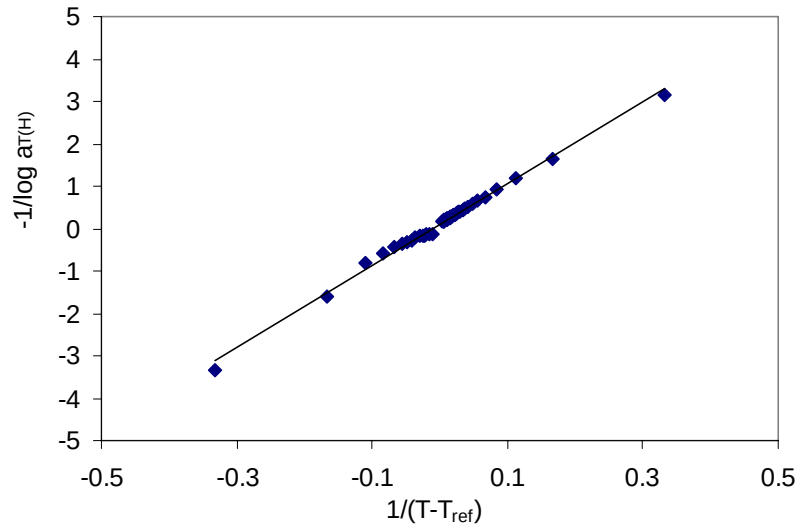

DSC thermogram for polymer films saturated with *n*-alkane penetrants



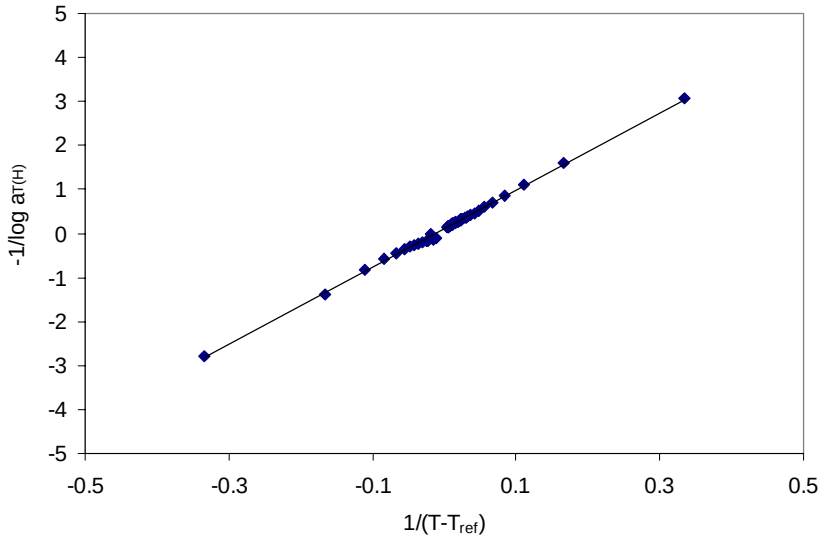

DSC thermogram for polymer films saturated with *ester* penetrants

**Determination of WLF Constants**

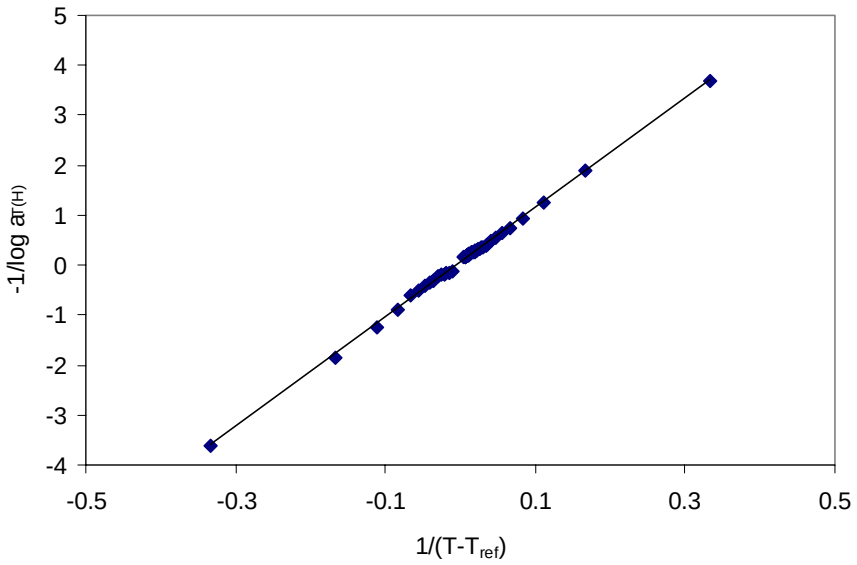
Example plots from the evaluation of $C_1$ and $C_2$ WLF constants are shown below depicting the linearized form of the WLF equation. The slope is proportional to $C_2/C_1$ and the y-intercept is $1/C_1$.



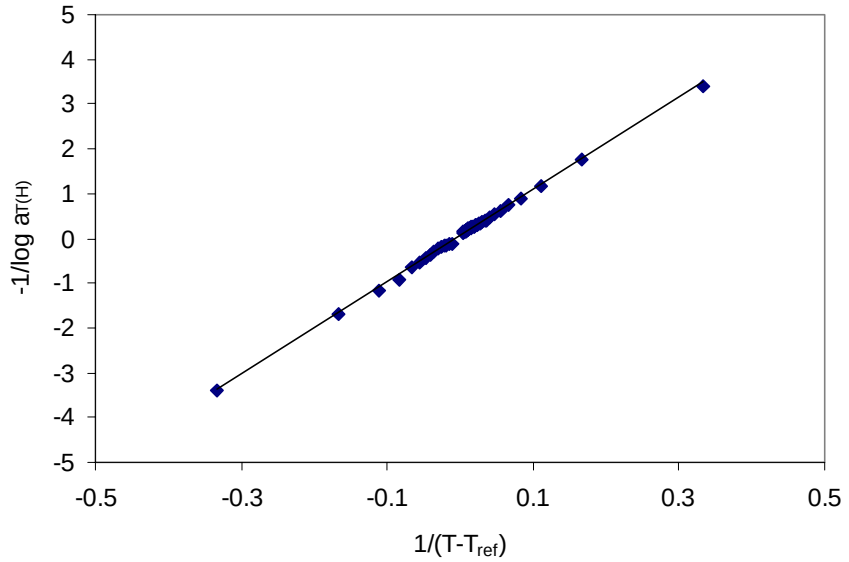

Plot of linearized WLF equation for polymer exposed to *decane* for $10^5$ minutes
($C_1$ =7.71 ; $C_2$ =71.0°K ; $r^2$=0.9995)




Plot of linearized WLF equation for polymer exposed to *decane* for $10^{3.70}$ minutes
($C_1$ =9.51 ; $C_2$ =84.4°K ; $r^2$=0.9995)



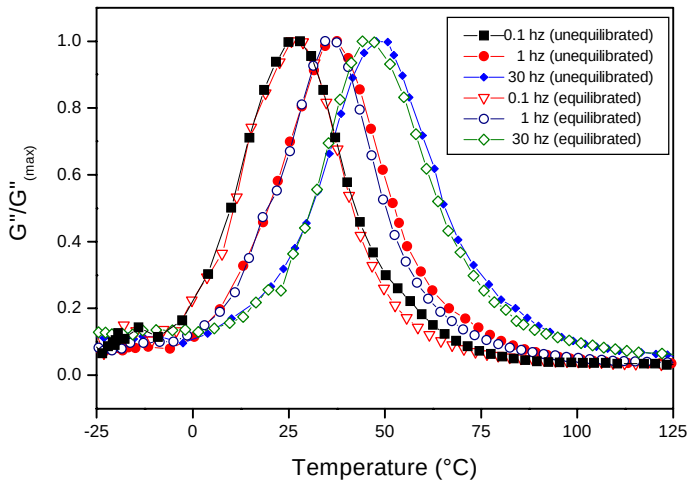

Plot of linearized WLF equation for polymer exposed to *ethyl undecanoate* for $10^3$ minutes ($C_1$ =11.1 ; $C_2$ =113°K ; $r^2$=0.9951)



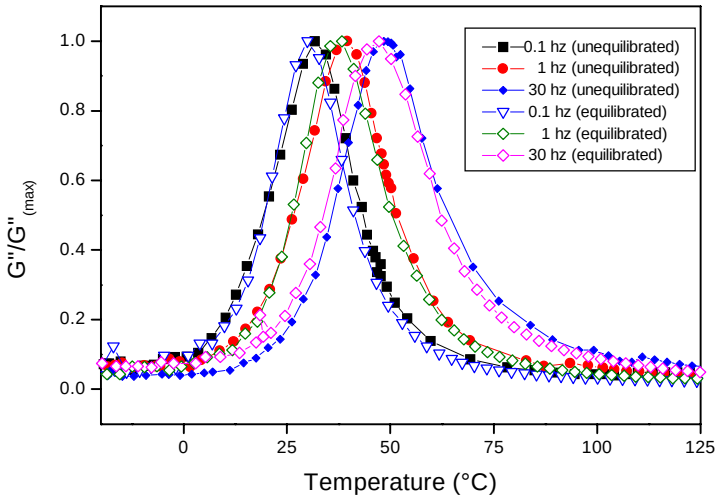

Plot of linearized WLF equation for polymer exposed to *ethyl undecanoate* for $10^{4.60}$ minutes ($C_1$ =10.9 ; $C_2$ =103°K ; $r^2$=0.9979)

**Investigation of Gradient Effects**

The effects of penetrant gradients on the observed dynamic mechanical response was investigated by comparing exposed polymer films that have been allowed to equilibrate (become homogeneous) to identical films that have not. Equilibrated and unequilibrated samples exhibited identical dynamic mechanical behavior, indicating that the assumption of a "homogenous" dispersion of penetrant, with respect to the mechanical behavior, is valid.




Dynamic mechanical behavior of an equilibrated (30 hours) and unequilibrated sample of a polymer film that had been exposed to *decane* for $10^2$ minutes.
(frequencies shown are 0.1, 1, and 30 hz)




Dynamic mechanical behavior of an equilibrated (1 month) and unequilibrated sample of a polymer film that had been exposed to *isodecyl pelargonate* for $10^3$ minutes.
(frequencies shown are 0.1, 1, and 30 hz)