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## *Behavior*

# Theoretical Approach to the Temperature Dependence of Local Flow in Polymer Systems

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**Herrn Prof. Dr. Dr. H. C. Mult. G. V. Schulz zu seinem 80. Geburtstag mit allen guten Wünschen gewidmet**

## Summary

Starting with the concept of temperature dependent apparent activation energy of flow as a specific temperature function of the considered polymer system a general appraoch is presented, which includes both the Arrhenius and the WLF behaviour. It is demonstrated how local flow can be characterized directly from mechanical measurements via temperature dependent apparent activation energy of flow, using two parameters only, the apparent activation energy of flow extrapolated to infinite temperature, and the Vogel temperature as obtained by extrapolation to infinite activation energy.

Examples are given in order to confirm the usefullness of these parameters for molecular interpretation of changes in the local flow mechanism as well as for clarification of the dependences between the polymer structure and the local flow process. As an unique effect it has been found that the energetic interaction of oligomeric polystyrene with poly(vinylmethylether) is much more pronounced than that with high molecular weight polystyrene. This findings may exhibit technical relevance.

## Introduction

Two models are most frequently used for the analysis of the temperature dependence of viscoelasticity of polymer systems. The one is the empirical Arrhenius law, supported by Eyring's rate theory [1], and the second is the empirical Williams-Landel-Ferry (WLF) equation [2] which is related to magnitudes implied in the free volume viscosity model of Doolittle [3].

A first attempt to deduce a general theoretical approach which combines both the models has been advanced by Macedo and Litovitz [4]. They started with the concept of a flow probability, defined by the product of two probabilities, the one determined by a potential barrier between molecular equilibrium positions and the second depending on the possibility of hole-forming, i. e. the creation of sufficient free volume in order to enable the local flow process. This concept results in an Arrhenius-like behaviour at high temperatures and a WLF behaviour near the glass transition temperature, $T_g$. This is in accordance with the limitation of the applicability of the WLF equation, i.e. from $T_g$ to about $T_g$+100 K. The difficulties in the application of the approach of Macedo and Litovitz are related with the relatively high number of variables and with the resulting complicated theoretical interpretation of the analyzed phenomenon.

The approach presented in this paper concerns also with a general conception on the local flow process. It enables the characterization of the local flow process of the considered system directly from viscoelastic measurements without any experimentally unaccessible parameter.

## Theory

### Basic Considerations

It has been already pointed out that the temperature dependent apparent activation energy of local flow, E(T), can be estimated directly from rheological data 5). E(T) represents a temperature function which is specific for the considered polymer system and which characterizes the local flow process. Recent papers have shown both the practical and the theoretical capabilities in using this temperature function for evaluation and interpretation of rheological data 6-10).

As the result from literature data of the last three decades, the temperature dependence of the viscoelastic behavior of polymer systems, i.e. the shift factor, $\log(a_T)$, is approached either by the empirical WLF equation

$$\log(a_T) = -c_1{}^g(T-T_g)/(c_2{}^g+T-T_g) \qquad (1)$$

or by the general Arrhenius law

$$\log(a_T) = C + E/2.3RT \qquad \text{with} \qquad C = -E/2.3RT_g \quad . \qquad (2)$$

Reports are also known concerning deviations from these regularities 11) 12). It has been shown that the shift factor is related with E(T) according to 5)

$$\log(a_T) = \int_{1/T_g}^{1/T} (E(T)/2.3R)\, d(1/T) \quad . \qquad (3)$$

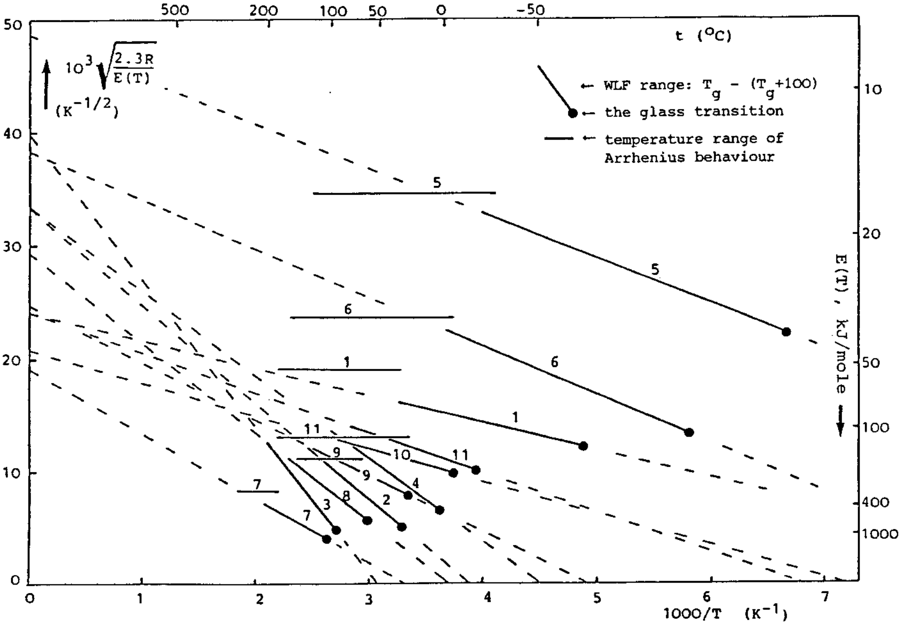

Figure 1: Plot of the temperature dependent activation energy of flow versus 1/T for WLF and Arrhenius behaviour

1.polyisobutylene 14-16); 2. poly(vinylacetate) 17)18); 3. polystyrene 19)20); 4. poly(methylacrylate) 21); 5. poly(dimethylsiloxane) 5); 6. polybutadiene 22); 7. poly(methylmethacrylate) 23)16); 8. poly(ethylmethacrylate) 24); 9. poly(n-butylmethacrylate) 25)16); 10. poly(n-hexylmethacrylate) 25); 11. poly(n-octylmethacrylate) 26

The latter equation supports that $\log(a_T)$ is always depending on an integration constant, whereas E(T) is not. Thus, E(T) only, as a derivative of $\log(a_T)$, really is characterizing the temperature dependence of the viscoelastic behaviour of polymer systems unequivocally. When E(T) is temperature invariant, it is identical with the apparent activation energy of the Arrhenius law, consequently.

For the case of WLF behaviour E(T) is given by

$$d(\log a_T))/d(1/T) = c_1^g c_2^g T^2/(c_2^g+T-T_g)^2 = E(T)/2.3R \; . \qquad (4)$$

Equation (5) follows if $c_1^g \cdot c_2^g = A$ and $c_2^g - T_g = -T_\infty = B$, with $T_\infty$ the Vogel temperature [13],

$$(2.3R/E(T))^{0.5} = 1/A^{0.5}(1+B/T) \qquad (5)$$

or

$$(E(T))^{-0.5} = A^* + B^*(1/T) \quad . \qquad (6)$$

These eqns. demonstrate that for WLF behaviour the plot of the $(E(T))^{-0.5}$ values versus 1/T approach an inclined straight line. In the same plot the Arrhenius behaviour appears as a horizontal straight line, corresponding to E(T) = constant.

Figure 1 presents an overview about temperature dependences of the viscoelastic behaviour reported in the last thirty years. It makes the differentiation between the two models evident. The plot visualizes also very clearly, if different temperature dependences of the viscoelastic behaviour of the polymer exist in different temperature ranges. Figure 2 illustrates such a case based on the data reported by Pfandl et al. [11] for polystyrene. The 'rubber transition' has been omitted because of the uncertainity concerning the validity of the time-temperature superposition principle in this range. It seems, however, possible that a continuous change of the temperature dependence in a certain temperature range might be approached also by two different straight lines as presented in Figure 2. Generally the question arises wether any temperature dependence does not appear to be linear for a sufficient small temperature interval of investigation. Thus the extent of the temperature interval of measurement is an important factor in order to detect deviations from regularities, i.e. changes in the parameters of the local flow process.

The recommended plot based on the determination of E(T), however, allows a realistic characterization of the local flow process, even if variations in the flow mechanism exist.

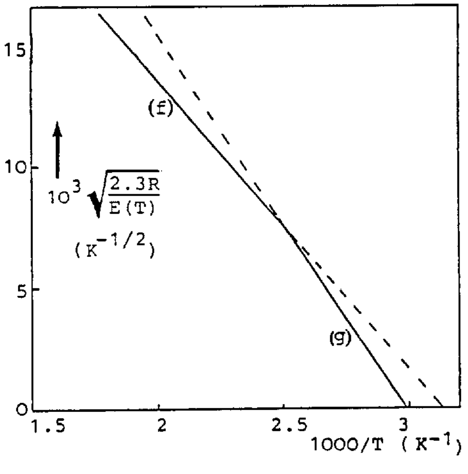

Figure 2:

Representation of the two WLF behaviours in different temperature ranges for polystyrene N-7000, according to the data of Pfandl[11].

(f) = terminal zone:
$c_1^g c_2^g$ = 706 K; $T_\infty$ = 45.7°C

(g) = glass transition region:
$c_1^g c_2^g$ = 459 K; $T_\infty$ = 60.7°C

## $T_\infty$ as Characteristic Temperature of the Local Flow

Introducing $T_g$ and $T_\infty$, eqns. (7) and (8), may be formulated in analogy to eqn. (5)

$$(2.3R/E(T))^{0.5} = (1/c_1^g c_2^g)^{0.5}(1-T_\infty/T) \qquad (7)$$

$$(2.3R/E(T))^{0.5} = (1/c_1^g c_2^g)^{0.5}(1-(T_g-c_2^g)/T) \quad . \qquad (8)$$

From these eqns. it is evident that the use of E(T) substitutes the WLF equation. The introduction of the constant $c_2^g$ - which distinguishes the WLF from the Tammann equation [27] -

$$\log(a_T) = C' + B'/(T-T_\infty) \qquad (9)$$

has been necessary only because Williams, Landel and Ferry have chosen $T_g$ or the higher $T_0$ temperature as a reference temperature for viscoelasticity. This choice becomes questionable, however, because the equations demonstrate that neither $T_g$ nor $T_0$ but only the Vogel temperature $T_\infty$ is a specific parameter for the temperature dependence of the local flow. Using the recommended plot, the problem of choice of a reference temperature is eliminated. In the following suplementary arguments are presented in order to demonstrate that $T_g$ has not to be used as a specific temperature of local flow processes .

## General Kinetic Description of the Temperature Dependence of Local Flow in Polymer Systems

Starting with the plots of Figure 1, the intersections of the straight lines with the ordinate and the abscissa, respectively, can be formulated as follows

$$(2.3R/E_\infty)^{0.5} = (1/c_1^g c_2^g)^{0.5} \qquad (10)$$

$$T = T_\infty \quad . \qquad (11)$$

The intercept corresponds to the apparent activation energy of flow extrapolated to infinite temperature, $E_\infty$ . It is also evident that $E_\infty$ is related with the product of the WLF constants. Such, the physical meaning of the constants is different from that which results from the free volume concept.

If the product of the WLF constants in eqn. (4) is substituted by $E_\infty / 2.3\ R$ and the integration is performed according to eqn. (3) with the integration constant $1/T_g$ one obtains the shift factor which is related with the relaxation times $\theta(T)$, by definition

$$\log(a_T)=-\log\ \theta_p(T_g)+\log\ \theta_p(T)=-(E_\infty/2.3R)/(T_g-T_\infty)+(E_\infty/2.3R)/(T-T_\infty)\ . \qquad (12)$$

This eqn. yields the following relations of the WLF and of the Tammann constants

$$c_1^g = E_\infty/(2.3R(T_g-T_\infty) \qquad c_2^g = T_g-T_\infty \qquad (13)$$

$$C' = -\ E_\infty/(2.3R(T_g-T_\infty)) \qquad B' = E_\infty/2.3R \quad . \qquad (14)$$

The kinetic character of these constants appears evident. Considering Eyring's definition of the relaxation times [1] and setting $P^* = (\lambda p/2\lambda)(h/k_B T \kappa)(Q\ /\ Q^{\#})$ the relaxation times in eqn. (12) may be defined as

$$\theta_p(T) = P^* \exp(E_\infty/R(T - T_\infty)) \qquad (15)$$

and $$\theta_p(T_g) = P^* \exp(E_\infty / R(T_g - T_\infty)) \quad . \qquad (16)$$

In this context P* is a specific constant of the relaxation process P, while the preexponential factor $(h / k_B T\kappa)(Q / Q^*)$ is considered to be invariant within the analyzed temperature interval.

The above formulated definition of the relaxation time as well as eqn. (12) show the similarity between the formulation derived from the empirical WLF equation and that from the Arrhenius formulation. As the only difference the Arrhenius law refers to 0 K, the other to $T_\infty$. This statement can be evidenced also by transforming eqn. (12) into

$$\log(a_T) = A + E_\infty / 2.3RT_\Delta \quad , \qquad (17)$$

with $T_\Delta = T - T_\infty$ or $T_\Delta = T - 0 = T$.

$E_\infty$ may also be expressed in terms of the classical Arrhenius approach

$$d(\log(a_T))/d(1/T_\Delta) = E_\infty / 2.3R \quad . \qquad (18)$$

Thus, the use of $T_\Delta$ instead of T enables a general formulation of temperature dependence of the local flow process, which includes both, the WLF and the Arrhenius behaviour, the latter one as a limiting case. The more the slope of the straight lines of Figure 1 approaches zero, the more the critical temperature $T_\Delta$ will be shifted towards 0 K.

In this context some remarks might be made:

- The local flow process exhibits more pronounced deviation from the Arrhenius behaviour for rigid polymers, because the number of degrees of freedom decreases. Consequently – from entropic considerations – the process will occur above 0 K.
- When the process becomes possible nearby 0 K it is difficult to differentiate between a dependence according to Arrhenius and one corresponding to eqns. (17) and (18).

## Applications

### Experimental

Blends of poly(vinylmethylether)-polystyrene have been analyzed. PVME (BASF) with $M_w$ = 73.000 has been choosen as the one component and PS with $M_w$ = 800, $M_w / M_n$ = 1.3, and with $M_w$ = 75.000, $M_w / M_n$ = 1.06, as the second one.

Mixtures with $PS_{800}$ have been prepared in melt under nitrogen , those with $PS_{75k}$ by freeze-drying from toluene solution. Mechanical measurements were carried out with the INSTRON 3250 Rheometer in cone-and-plate geometry, in the oscillating mode. The measurements have been performed within the same temperature range for all bends, and data range from the flow region through the rubber plateau up to onsetting the glass transition.

$T_g$ values have been determined with a PERKIN-ELMER DSC-2, the presented data being extrapolated to zero heating rate.

### Results and Discussion

Composition dependent changes in distribution of the relaxation processes with inclusion of the glass transition and the E(T)-data have been published already 9). The analysis of the E(T) data of blends according to the presented approach is the purpose of this paper.

Applying the recommended method, the parameters $T_\infty$ and $E_\infty$ have been determined for all blends. Figure 3 visualizes the determination of $T_\infty$. The deviations from linearity at high temperatures suggest a tendency towards Arrhenius behaviour.

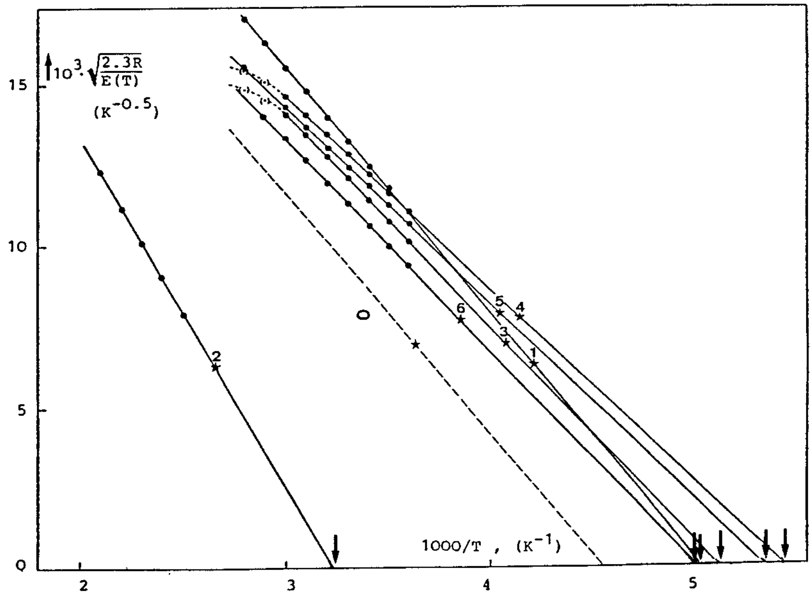

Figure 3: Plot of the E(T) values in order to characterize the local flow process in PS-PVME blends.

1 = PVME ; 2 = $PS_{75k}$; 3 = $PS_{75k}$-PVME (24.1 w.% PS) ; 4 = $PS_{800}$-PVME (8.6 w.% PS) ; 5 = $PS_{800}$-PVME (24.2 w.% PS) ; 6 = $PS_{800}$-PVME (75.4 w.% PS)

▬ ▬ local flow behaviour of $PS_{800}$ as derived from extrapolated $E_\infty$ and $T_\infty$ values; ○ value of E(T) of $PS_{800}$ determined experimental ; ―― inclined straight lines characterizing the local flow process ; (•) deviations at high temperatures, tendency for Arrhenius behaviour ; ● values of the E(T) function ; ✶ glass transition; ↓ estimated $T_\infty$ values

The obtained values for $T_\infty$ and $E_\infty$ are shown in Figure 4. Before analyzing the kinetic parameters of the local flow process it has to be pointed out that the Vogel temperature is depending on entropic factors, whilst $E_\infty$ is determined by energetic ones. $T_\infty$ has the same meaning as the $T_2$ temperature of the Gibbs and DiMarzio theory 28), which characterizes the equilibrium freezing in of any conformational change.

A fact wich has to be pointed out is the possibility to determine the kinetic parameters of $PS_{800}$ by extrapolation from those of the blends, as indicated in Figure 4. From direct measurements, feasible in a very small temperature range only, just a single value for the activation energy of flow can be computed. In Figure 3 the accordance of both the values seems to be satisfactory. A way to characterize experimentally unaccesible flow process data is offered in this manner.

Generally, Figure 4 shows that mixing of PVME with both the high molecular and the oligomer the rises the $E_\infty$ and lowers the $T_\infty$ values.

Comparing the behaviour of the blend of high molecular PS with that containing oligomer , it turns out that the composition dependences of $E_\infty$ and $T_\infty$ are much more pronounced in the case of the oligomer component.

Taking into account the interrelation of $E_\infty$ and $T_\infty$ with entropic and energetic factors, respectively, the following conclusions may be drawn:

- Higher $E_\infty$ of the blends suggest a more pronounced energetic chain interaction. It may be also correlated with a higher orientation effect, in accordance with the observations of Faivre et al.30) This effect is much more accentuated in blends with oligomeric PS.

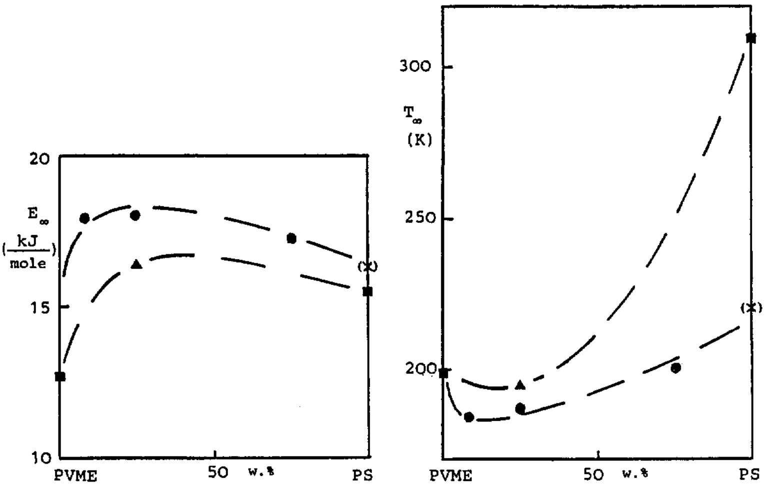

Figure 4: Composition dependence of kinetic parameters of local flow process
■ homopolymer ; • blends withs $PS_{800}$; ▲ blend with $PS_{75k}$; x extrapolated values of $T_\infty$ and $E_\infty$

- The lowering of $T_\infty$ , especially at low PS concentrations, indicates that mixing increases in paralell the degrees of freedom in the system. The greater decrease of $T_\infty$ by addition of oligomer PS to PVME indicates that the oligomer introduces more freedom, partly due to the influence of chain ends on free volume.

Considering the $T_g$ values of the blends as presented in Figure 5 it becomes evident that $T_\infty$ does not correlate with $T_g$. On the contrary, the differences between the $T_g$ of the blends have the tendency to correlate with the effects expected from the $E_\infty$ differences.

The difference between the thermal equilibrium chain motion - connected to $T_g$ - and the segmental chain motion implicated in the local flow process, - related with $T_\infty$ - has to be considered as an explanation. Whereas the overal motion is mainly influenced by energetic chain interaction, the segmental motion is considerably dependent on $T_\infty$, i. e. on entropic factors.

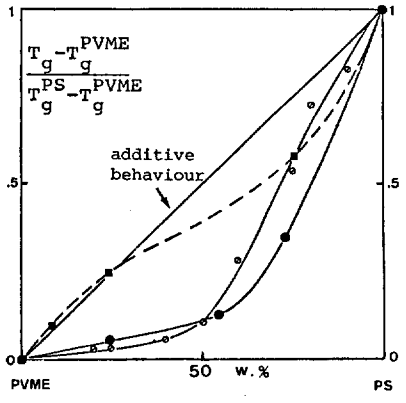

Figure 5:
Reduced $T_g$-data of PVME-PS blends
■ $PS_{800}$-PVME ; • $PS_{75k}$-PVME
∅ literature data of Bank[29]) for:
PS ($M_n$=150.000) - PVME ($M_n$=524.000, partially isotactic)

Taking into account that the two blends differ in the molecular weight of PS only, the influence of energetic interaction on the thermal chain motion might be interpreted as follows:

- The oligomer PS, because of smaller inertia, follows the motion of the PVME chain more consequently. The contact time between the components is enlarged. The oligomer PS may be assumed as a free chain segment of the high molecular PS. Thus, its interaction with the PVME chain is more effective than that of the high molecular PS.
- As a consequence, the PVME gets stiffer in the blend with oligomer PS and thus its thermal motion is more hindered. This may cause the pronounced increase of $T_g$ in those blends.

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