

## Isochrone Based Mastercurves of Viscoelastic Functions

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### SUMMARY

Composite curves of the viscoelastic functions may be obtained not only by the usual shift of isotherme data along the frequency axis, but also by a shift of the respective isochrones along the reciprocal temperature axis. This shift along the  $1/T$  axis is equivalent to that of the isochrones of dynamic viscosity, along the slope of zero shear apparent activation energy of flow. It is demonstrated that both types of shift are related to this zero shear activation energy of flow, so that an unique shift mechanism is effective in both cases.

Isochrone based mastercurves are favourable for studies on polymer blends particularly, because the problematical choice of the reference temperatures of the components is circumvented.

### INTRODUCTION

Time and temperature dependence of the viscoelastic behaviour of polymers may be interpreted by the corresponding dependences of the relaxation spectra and by conformational changes within the macromolecular chains, consequently. The corresponding contributions to the viscoelastic functions are expressed by the frequency shift factor,  $a_T$

$$a_T = [a^2 \xi_0]_T \cdot T^0 / [a^2 \xi_0]_{T^0} \cdot T \quad , \quad (1)$$

which allows the superposition of viscoelastic isotherms to composite curves at  $T^0$ , the reference temperature. Temperature dependence is connected mainly to the translational friction coefficient per monomeric unit,  $\xi_0$ , although the mean-square end-to-end distance per monomeric unit,  $a^2$ , may vary significantly with temperature too for most polymers. In the terminal zone of the frequency scale, the shift factor is related to the dynamic viscosity,  $\eta'$ , according to

$$a_T = \eta' T^0 \rho^0 / \eta' T \rho \quad , \quad (2)$$

with  $\rho$  the density of the polymer. Neglecting the density correction temperature reduction of viscoelastic functions may be obtained, consequently, by plotting the moduli,  $G'_p = G' T^0 / T$  and  $G''_p = G'' T^0 / T$ , or the dynamic viscosity,  $\eta'_p = \eta' T^0 / a_T T$ , respectively, versus  $a_T \omega$ , with  $\omega$  the frequency of the dynamic stress.

### RESULTS AND DISCUSSIONS

For poly(methacryloyl- $\beta$ -hydroxyethyl-3,5-dinitrobenzoate) (DNBM)  $a_T$  shift master curves are shown in Fig. 1, for both  $G'$  and  $\eta'$  ( $\bar{M}_w = 12000$ ). It is evident that the relative position of the composite curves depends on the chosen reference temperature, as demonstrated in Fig. 2. Dynamic viscosity composite curves are constructed here for the dynamic viscosity of atactic head-to-tail and head-to-head poly(propylene)s in two different ways: Identical reference temperature for both

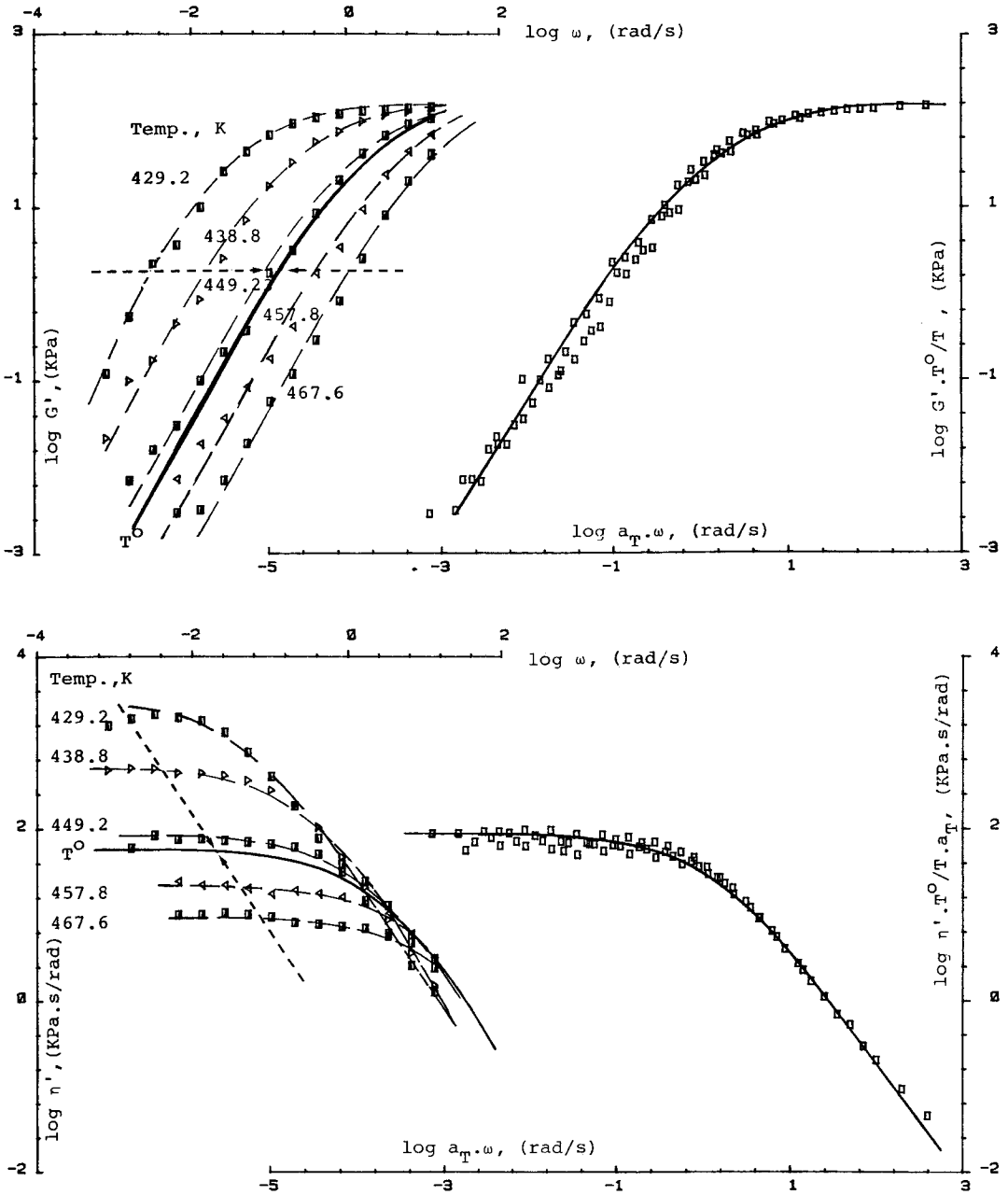


Figure 1: Isotherme based composite curves for poly(methacryloyl-β-hydroxyethyl-3,5-dinitrobenzoate),  $M_w = 12000$ .  $T^0 = T_g + 90$  K, temperature range  $T_g + 50$  K to  $T_g + 130$  K .

Upper diagram: Storage modulus  
 Lower diagram: Dynamic viscosity

the components, 330 K, and for  $T^0 = T_g + 75$  K for each of them. In order to avoid misinterpretation, composite curves have to be compared, consequently, at reference temperatures correlated to the respective  $T_g$ 's.

Fig. 1 evidences that significant a  $T$ -shift is operative mainly in the terminal zone of the frequency scale, e. g. when flow approaches Newtonian behaviour. At higher frequencies and at higher temperatures, respectively, this shift is less conspicuous. The experimental a  $T$ -shift factors will depend on the measuring range. The a  $T$ -shift in the terminal zone of frequency scale may be regarded as an upper limitation of the commonly applied shift factors. Consequently, apparent activation energies of flow as derived from the slope of curves  $\log a_T$  versus  $1/T$  will depend on both, temperature (FERRY, FITZGERALD 1953) and frequency range. They will approach, however, the activation energy of zero shear viscosity as the measuring range of the viscoelastic functions approximates the Newtonian range. As seen in Table I the concordancy of these values is satisfactory.

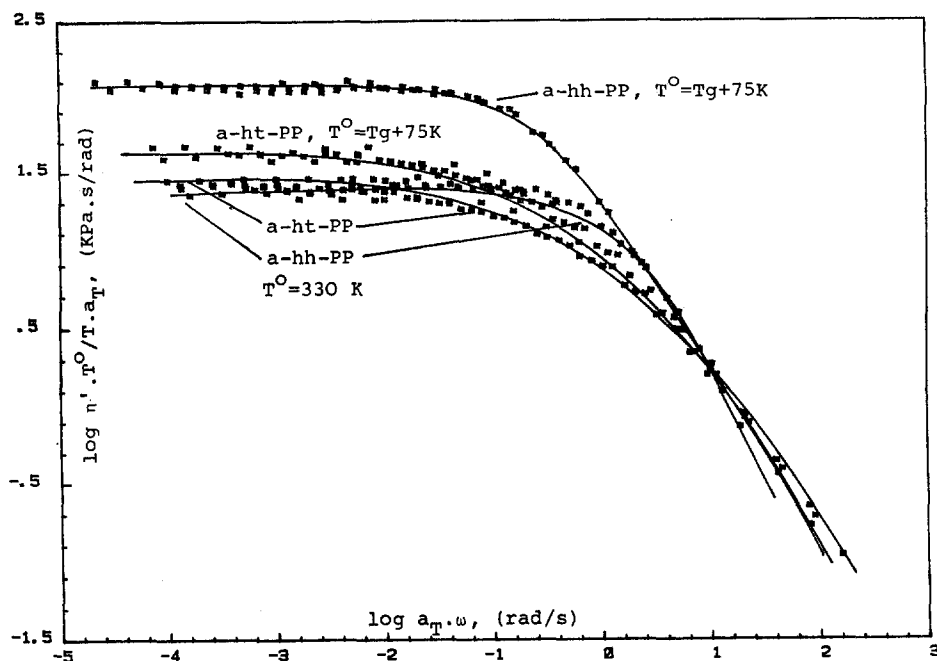


Figure 2: Dynamic viscosity mastercurves for atactic head-to tail poly(propylene)  $\bar{M}_w = 15500$ , and atactic head-to-head poly(propylene),  $\bar{M}_w = 16500$ . Reference temperature  $T^0 = 330$  K for both the components and  $T^0 = T_g + 75$  K for each of them.

Table I: Activation energies of polymer flow [KJ/mole], a  $T$ -values from isochrones

Polymer	$\bar{M}_w$	zero shear viscosity	a $T$ -values	a $F$ -values
a-ht-poly(PP)	15500	88.7	89.8	86.4
a-hh-poly(PP)	16500	82.1	81.8	85.2
poly(MMA)	45500	255.9	267.2	243.6
poly(BMA)	55000	148.4	160.3	151.2
poly(DNBM)	12000	238.8	242.3	248.8
poly(HECM) +	57000	252.3	262.7	280.3

+ poly(N-2-hydroxyethyl-carbazoloylmethacrylate)

For the temperature dependence of the dynamic viscosity two models generally are discussed. That of EYRING et al. (1941, HIRAI, EYRING 1959) assumes the overcoming of an energy barrier between holes in a liquid to be the rate determining step of viscous flow and applies transition state theory to explain the temperature dependence of viscosity

$$\eta = B' \exp(E_{\text{VISC}} / RT) \quad (3)$$

The preexponential constant  $B'$  includes both the molar volume of the liquid and the activation entropy of flow and is admitted constant generally. In contrast to this model that of DOOLITTLE (1952) supposes the formation of holes, i. e. the "free" volume as the rate determining step, introducing the expression

$$\eta = A' \exp(B v_0 / v_f) \quad (4)$$

with  $A'$  and  $B$  two constants, the latter of the order of unity, and  $v_0$  and  $v_f$  the occupied and the free specific volume of the liquid, respectively. The temperature dependence of the viscosity is explained by that of the volumes, and by rearranging the well known WLF - equation (WILLIAMS et al. 1955) is obtained

$$\log(\eta/\eta^0) \cong \log a_T = \frac{-C_{1,g}(T - T_g)}{C_{2,g} + (T - T_g)} \quad (5)$$

The constants,  $C_{1,g} = B / 2,303 f_g$  and  $C_{2,g} = f_g / \Delta\alpha_f$ , depend on the fractional free volume at  $T_g$ ,  $f_g = v_f / (v_0 + v_f) \cong v_f / v_0$ , where the viscosity is  $\eta^0$ , and on the thermal expansion coefficient of this fractional free volume,  $\Delta\alpha = (\alpha_L - \alpha_S)_{T_g}$ , as given by the difference between the thermal expansion coefficients of the liquid and of the glassy solid at  $T_g$ .

Expression (5) shows that the viscosity of a liquid at a given  $T$  equals the product between the viscosity at the reference temperature and the respective shift factor

$$\log \eta = \log \eta^0 \log a_T \quad (5a)$$

Usually a temperature above  $T_g$  is chosen as the reference temperature. The validity of the WLF - equation is limited, however, to temperatures not too far from  $T_g$ . The values of the WLF - constants depend on the chosen  $T^0$  and are interrelated by

$$C_{1,g} = C_1 C_2 / (C_2 + T_g - T^0) \quad C_{2,g} = C_2 + T_g - T^0 \quad (6)$$

With the observation that

$$T_g - C_{2,g} = T^0 - C_2 = T_u \quad (7)$$

expression (5) may be rewritten

$$\log a_T = C_1 (T - T^0) / (T - T_u) \quad (8)$$

where  $T_u$  is a fixed temperature (VOGEL temperature). Regardless of the arbitrary choice of  $T^0$ ,  $\log a_T$  becomes infinite at  $T_u$ , in accordance with equation (5).

Taking into consideration the rate determining steps assumed in both the theoretical approaches, the EYRING model will hold mainly at temperatures substantially higher than  $T_g$ , when sufficient holes already are present in the liquid, whilst the DOOLITTLE model works especially near  $T_g$ , when the creation of new holes to allow viscous flow evidently is the decisive factor.

Both equations (5) and (8) may be applied to calculate WLF - constants from ex-

perimental  $a_T$ -data. Iteration procedures may be recommendable until the respective computed  $C_1$ -constants are in accordance and the VOGEL temperature has a meaningful value. Fig. 3 presents final plots from this iteration procedure for some of the studied polymers. Using recalculated  $a_T$  shift factors instead of the experimental ones increased scattering of the data is observed, however, in the composite curves of the viscoelastic properties.

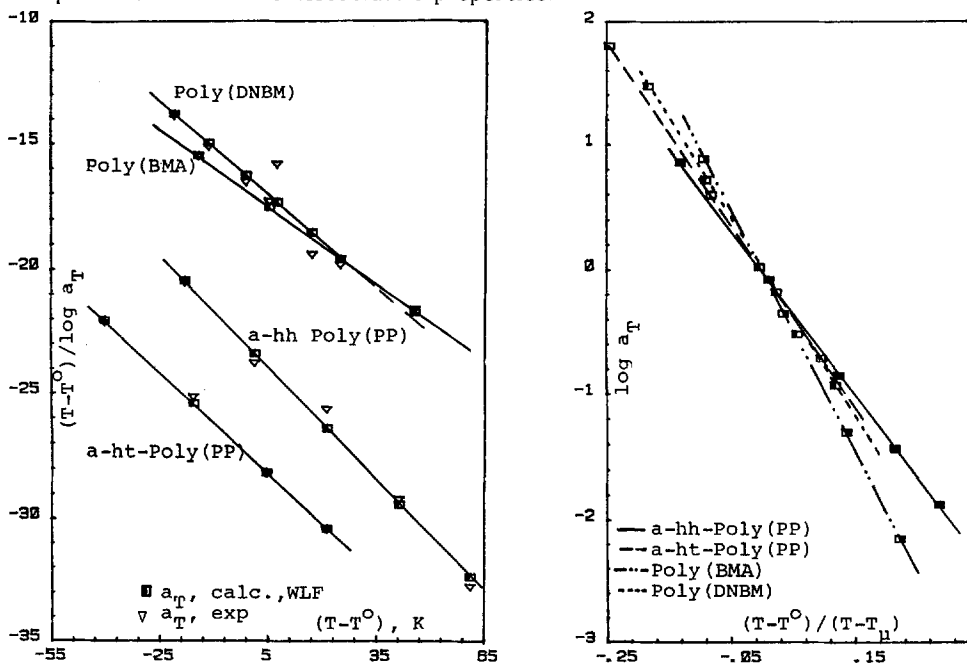


Figure 3: Calculation of the WLF-constants of polymers in Table II by the WLF - (left) and by the VOGEL - approach (right).

Table II gives WLF - constants derived by iteration. Although there is no strict correlation,  $C_1$  has the same trend as the apparent activation energy of flow.

Table II: WLF - constants and  $T_g$  of polymers.  $T^0 = T_g + 90$  K.

Polymer	$T_g$ / K	$C_1$		$C_2$	$T_u$	$C_{1,g}$
		WLF	VOGEL			
a-ht-poly(PP)	259.5	7.38	7.34	202.9	146.9	13.28
a-hh-poly(PP)	242.3	7.89	7.88	191.1	141.0	14.91
poly(MMA)	386.8	11.27	11.50	158.9	317.1	25.98
poly(BMA)	285.8	9.63	9.64	162.6	214.1	21.56
poly(DNBM)	359.7	8.13	8.05	132.5	317.2	25.35
poly(HECM)	415.9	10.57	10.49	179.5	307.8	19.38

$T_g$  's measured by DSC and extrapolated to zero heating rate

Isochrones have been plotted,  $\log \eta'$  versus  $1/T$ , in order to discuss the frequency dependence of the apparent activation energy of flow (upper diagram in Fig. 4). Evidently the deviation from linearity of the respective isochrones is more significant with increasing frequency, suggesting a corresponding "decrease" of the apparent activation energy of flow. Thus a frequency dependence of that activation energy is confirmed, although calculations basing on such non-linear curves are questionable.

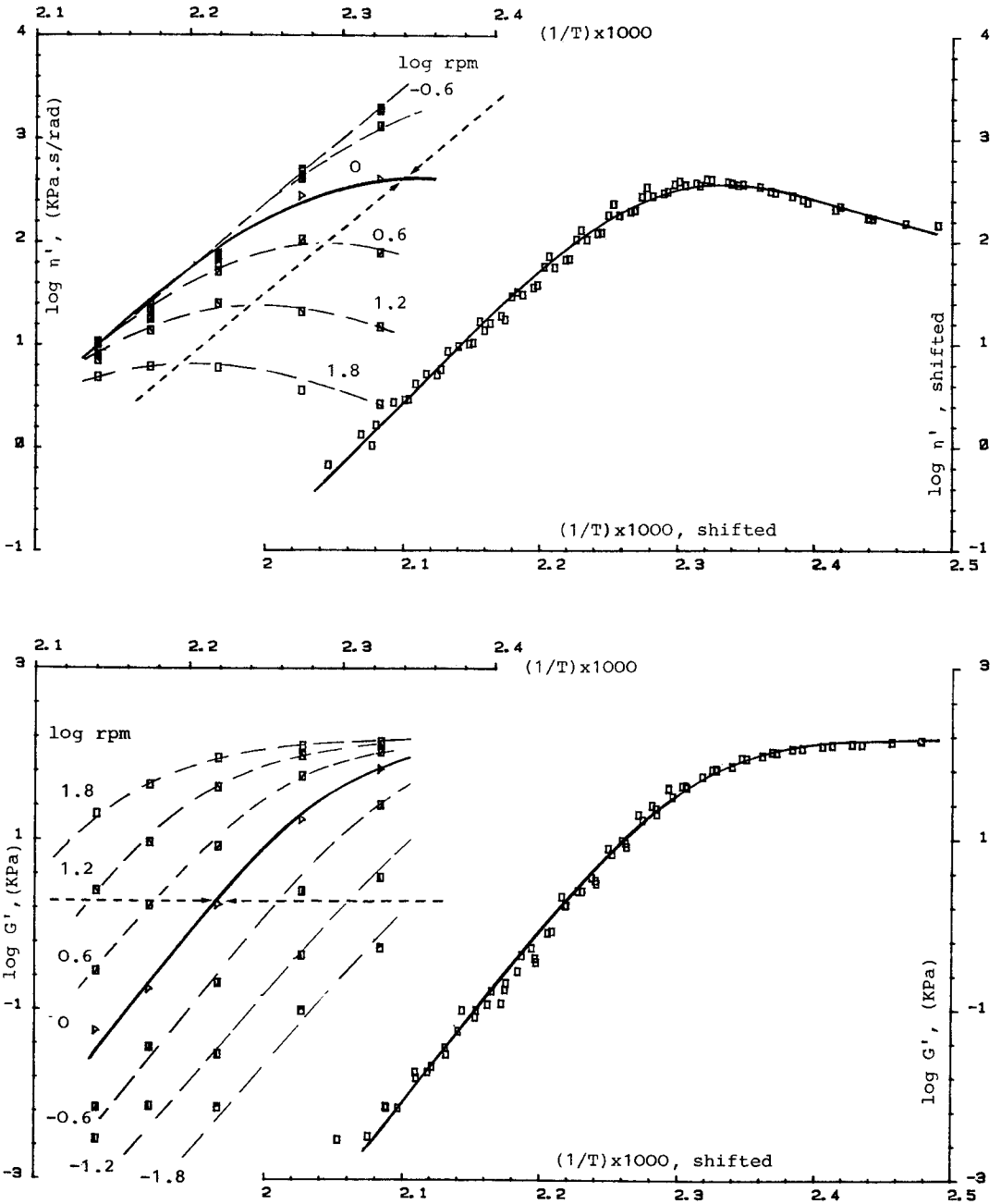


Figure 4: Isochrone type composite curves for poly(DNBM),  $\bar{M}_w = 12000$ .  
 Frequency range  $\log \text{rpm} = -2.1$  to  $2.1$ , reference frequency  $\log \text{rpm} = 0$ .  
 Upper diagram: Dynamic viscosity,  $1/T$ - shift =  $a_F \cos(E/T)$   
 $\eta' = \text{shift} = a_F \sin(E/T)$   
 Lower diagram: Storage modulus.

The attempt to realize a frequency reduction,  $a_T$ , along the slope of the zero shear activation energy of flow turns out to be a favourable approach, however, for the construction of an isochrone based mastercurve of the dynamic viscosity. By comparing Figs. 1 and 4 it is evident that both types of shift exhibit comparable accuracy. In a corresponding manner the isochrone curves of the storage modulus may be superposed to a master curve, by a horizontal  $\Delta(1/T)$ -shift along the  $1/T$ -axis (Fig. 4, lower diagram).

It may be mentioned that this horizontal shift of the isochrone storage modulus curves along the  $1/T$ -axis is identical with the horizontal shift,  $a_T \cos(E/R)$ , of the isochrone curves of dynamic viscosity along the  $1/T$ -axis. Thus an unique  $a_T$ -factor is applicable to shift isochrone viscoelastic data, just as an unique  $a_T$  is used to construct isotherme based mastercurves.

Figure 5 demonstrates that the same  $a_T$ -shift factor is obtained from both, experimental isochrone curves of dynamic viscosity and of storage modulus. The linear dependence between the  $a_T$ -shift factor and log frequency (Fig. 5) suggests that, consequently, the respective slope of the  $\Delta(1/T)$ -shift versus log frequency-curves may be applied to calculate an apparent activation energy of flow. The

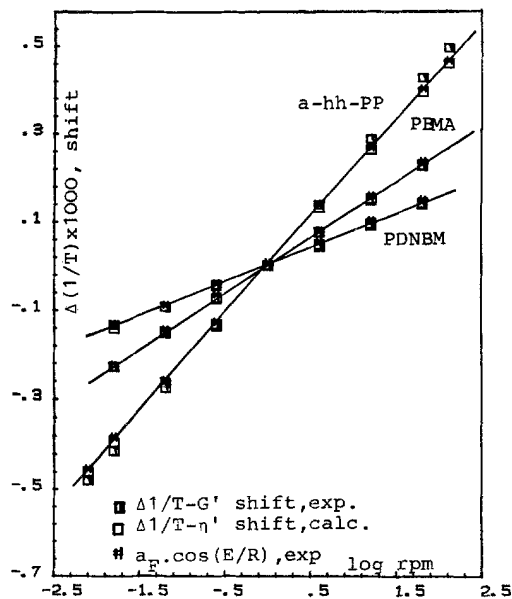


Figure 5: Verification of the applicability of the  $a_T$ -shift for dynamic viscosity and storage modulus.

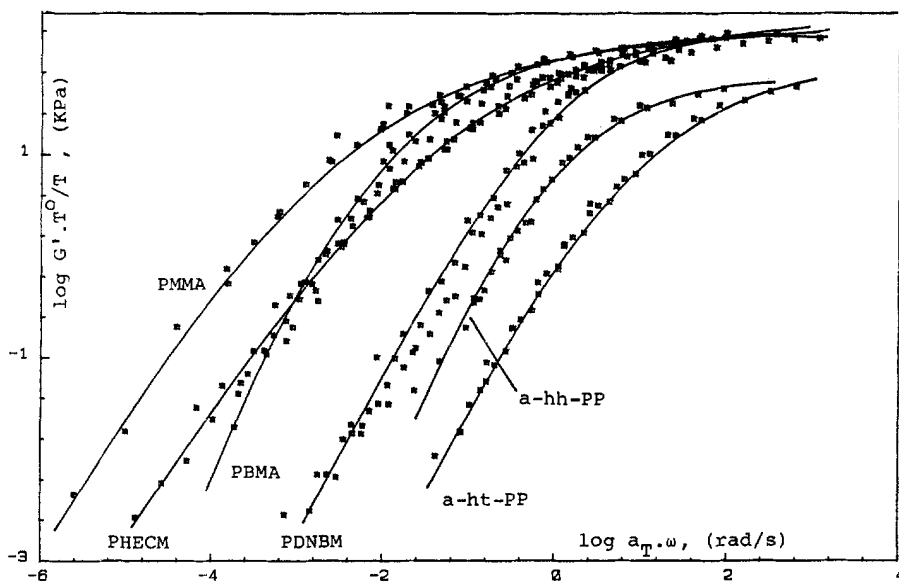


Figure 6: Isotherme based composite curves for the polymers in Tables I and II.  $T^0 = T_g + 90$  K, temperature range  $T_g + 50$  K to  $T_g + 130$  K.

obtained values are included in Table I. The agreement with the values computed from both zero shear viscosity and  $a_T$ -shift factors suggests that the same mechanism is responsible for both the shifts of the viscoelastic functions along the time as well as along the reciprocal temperature axis and that the activation energy of zero shear viscosity is related to this shift mechanism.

Finally, the isotherme based composite curves of the storage moduli are presented in Fig. 6, for the polymers listed in the Tables. Fig. 7 gives the respective isochrone based composite curves. The benefit of the isochrone based mastercurves is evident, when viscoelastic data of polymers with different glass transition temperatures have to be compared. The problematical choice of the reference temperature

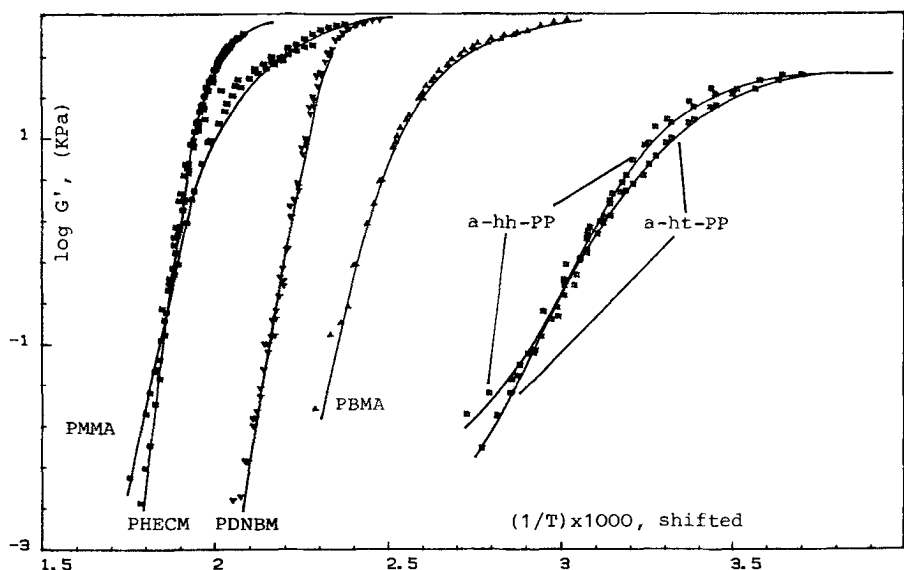


Figure 7: Isochrone based composite curves for the polymers in Tables I and II). Frequencies  $\log \text{rpm} = -2.1$  to  $2.1$ , reference frequency  $\log \text{rpm} = 0$ .

is circumvented. The isochrone based mastercurves are even more convincing for studies of composite systems, like incompatible or compatible polymer blends. The reference frequency - 1 rpm in the samples discussed in this paper - may be chosen according to the basic or to the applicational problem under study.

#### ACKNOWLEDGMENT

Financial support by DEUTSCHE FORSCHUNGSGEMEINSCHAFT and by BUNDES-MINISTERIUM FÜR FORSCHUNG UND TECHNOLOGIE is gratefully acknowledged.

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