

# The role of short chain molecules for the rheology of polystyrene melts.

## I. Molar mass dependent shift factors

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*Abstract:* Atactic polystyrenes of narrow molar mass distribution with average molar masses larger than the critical molar mass  $M_c$  were mixed with similar polystyrenes of molecular masses lower than  $M_c$ . Linear viscoelastic melt properties of these binary blends were measured with a dynamic viscometer of the concentric cylinder type. One of the experimental findings is that the time-temperature shift factors  $a_T$  are dependent on the composition of the samples. This can be understood, if free volume due to chain-ends is taken into account. A computer-fitted WLF-equation being modified in a proper way leads to the following results: At the glass-transition-temperature the fraction of free volume in polystyrene of infinite molar mass is only 0.015. At a temperature of 180 °C the mean value of the free volume at a chain end is 0.029 nm<sup>3</sup> for the polystyrene investigated.

*Key words:* Time-temperature superposition, free volume of chain ends, short chain polystyrene, melt rheology, complex modulus

### 1. Introduction

Most industrial polymers contain non-polymeric additives like processing aids (flow improvers, lubricants, release agents etc.) or agents influencing the properties of the final product (plasticizers, dyes etc. [1]). There is no question that these additives influence the flow properties of the melt. At first sight one is tempted to discern between two questions: The more comprehensive question is, how molecular interaction forces (Flory-Huggins interaction parameter) between polymer molecules and additive molecules influence melt properties. A less pretentious question, however, arises about those changes in flow properties which remain, if no differences in interaction forces between polymer and additive molecules are to be expected. The present paper is devoted to a special case of this latter question.

Molecules of polystyrene with a molar mass below  $M_c$  ( $\cong 33$  kg/mol) show an intermediate character between polystyrene molecules of a molar mass  $M > M_c$ , which actually contribute to the polymer network, and non-polymeric molecules of typical additives. For this investigation the addition of short molecules of the same polymer has a special advantage: The claim for the same interaction-forces between matrix polymer molecules and added molecules is

realized almost perfectly. Part I of this paper will particularly deal with the time-temperature superposition principle as influenced by the addition of polystyrene molecules with  $M < M_c$  to a polystyrene matrix with  $M > M_c$ . Part II will describe the pertinent changes in flow properties.

### 2. Basic considerations

Formally, the time-temperature superposition principle can be written as [2]:

$$G^*(\omega a_T, T_0) = G^*(\omega, T) \rho_0 T_0 / \rho T \quad (1)$$

where  $G^*$  is the complex modulus,  $a_T$  the time-temperature shift factor,  $\omega$  the circular frequency,  $T_0, T$  are temperatures and  $\rho_0, \rho$  the densities at  $T_0$  and  $T$ , respectively.

The right side of eq. (1) is called "reduced" complex modulus  $G_r^*(\omega, T)$  [2]. Obviously, the time-temperature shift factor  $a_T$  is determined by eq. (1) in such a way that the reduced complex modulus  $G_r^*(\omega, T)$  at frequency  $\omega$  and temperature  $T$  becomes equal to the complex modulus  $G^*(\omega a_T, T_0)$  at reference temperature  $T_0$  and frequency  $\omega a_T$ . By the factor  $\rho_0 T_0 / \rho T$  the volume changes of the melt due to thermal expansiveness and the proportionality of the complex modulus to the Boltzmann term  $kT$  are taken into account.

Practical experience shows that the linear-viscoelastic behaviour of a polymer melt can be described quite well by means of a set of Maxwell elements, where the distribution of molar masses is clearly reflected by the coefficients (weighting factors) of the individual elements [3]. Every Maxwell element stands, to a reasonable approximation, for an infinitesimal (monodisperse) fraction of uniform molar mass.

According to the current opinion the spring constants  $G_i$  of the Maxwell elements are all equal to the plateau modulus  $G_0$  of the entanglement network existing for  $M > M_c$ . Only recently, however, this view has been modified [4] without consequences for the basic assumptions of the time-temperature superposition principle. On the other side, the relaxation times  $\tau_i$  which are strongly dependent on the molar masses  $M_i$  ( $\tau_i \propto M_i^{3.4}$ ), also show a considerable temperature dependence. In fact, if eq. (1) is applied to a Maxwell element one sees that the shift factor  $a_T$  represents the ratio of the relaxation time  $\tau_i$  at temperature  $T$  to the relaxation time  $\tau_{i,0}$  at reference temperature  $T_0$ :

$$a_T = \tau_i / \tau_{i,0}. \quad (2)$$

For the relaxation time the validity of the Doolittle equation [5] is assumed:

$$\tau = C e^{B/f}. \quad (3)$$

The factor  $C$  is independent of temperature, in contrast to its strong dependence on molar mass. Parameter  $B$  is not only independent of temperature but also of molar mass. Usually, the fractional free volume  $f$  means the ratio of the free volume to the total volume of the polymer melt. It varies strongly with temperature. According to eq. (3) the relaxation time of a macromolecule is a function of molar mass and free volume and, because of the latter, an indirect function of temperature. Inserting eq. (3) into eq. (2) one arrives at the well-known relation\*):

$$\ln a_T = B(1/f - 1/f_0). \quad (4)$$

\*) According to the Maxwell-model one obtains for the zero-shear viscosity  $\eta_0$  of a monodisperse polymer melt the relation  $\eta_0 = G_0 \tau$ . Thus one can write down a Doolittle equation for the zero-shear viscosity:  $\eta_0 = A e^{B/f}$ . As  $A$  equals  $G_0 C$ , the value of  $A$  depends on the molar mass (due to factor  $C$ ) and on temperature (because of the plateau modulus  $G_0 = \rho RT/M_e$ , where  $M_e$  is the average molar mass between two adjacent entanglement-points of a polymer chain). If this temperature dependence of  $A$  is taken into account, the correction term  $\rho_0 T_0/\rho T$  mentioned in [6] in connection with eq. (4) must be omitted. Probably, the statement made in this reference, namely that the use of  $\tau$  instead of  $\eta_0$  causes a small variation of the quantity  $B$ , should be changed into the statement that  $B$  remains always the same whereas the temperature dependence of  $A$  cannot be disregarded

The fraction  $f$  of the free volume in the sample changes with temperature:

$$f = f_0 + \alpha_f(T - T_0) \quad (5)$$

where  $f_0$  refers to an arbitrary reference temperature  $T_0$  above glass temperature  $T_g$ , and  $\alpha_f$  means the thermal expansion coefficient of free volume. The coefficient  $\alpha_f$  is given by the difference of the thermal expansion coefficients above ( $\alpha_1$ ) and below ( $\alpha_g$ ) the glass-transition temperature where free volume is said to be "frozen in". It must be noted that the fraction  $f_g$  of free volume at the glass-transition temperature is dependent on the rate of cooling: the faster the melt is cooled down, the higher the percentage of free volume is in the vitrified sample. For this reason the determination of  $f_g$  has been standardized to a cooling-rate of 3 K/h. On the other hand,  $\alpha_g$  is not influenced by the cooling rate as long as this rate is large compared with the polymer specific ageing rate of the vitrified sample.

Inserting eq. (5) into eq. (4) one obtains the WLF-equation with an explicit representation of the well-known parameters  $c_1^0$  and  $c_2^0$ :

$$\log a_T = \frac{-\frac{B}{2.303 f_0}(T - T_0)}{f_0/\alpha_f + T - T_0}, \quad (6)$$

$$c_1^0 = B/(2.303 f_0), \quad (7)$$

$$c_2^0 = f_0/\alpha_f. \quad (8)$$

Because parameters  $B$  and  $\alpha_f$  are both independent of molar mass and temperature and form polymer specific constants, the product

$$c_1^0 c_2^0 = B/(2.303 \alpha_f) = c_1 c_2 \quad (9)$$

should be the same for all molar masses and reference temperatures [7].

### 3. Sample preparation and measurement [8]

The anionically polymerized standard polystyrenes with narrow molar mass distributions as used in this investigation, were purchased from Polymer Laboratories Ltd. (UK). Blends are made by putting together the dry components which are available in the form of powdery samples. After the dissolution of the powdery mixtures in cyclohexane at 70 °C the solvent is carefully distilled off and the remaining solid polystyrene foam is dried in vacuo at 100 °C for some days in order to remove all traces of solvent. The specimen is moulded to a hollow cylinder in a heated vacuum press, where temperature does not exceed 200 °C in avoiding thermal decomposition.

The dynamic viscometer used for the measurements is of the concentric cylinder type [9]. It was manufactured by Rodem Instrumentenfabriek (Netherlands). Several calibrated torsion wires are available. If required, torsion wires can be changed to achieve higher accuracies. Within usual error bonds measurements with a thicker and a thinner torsion wire agree sufficiently well. The measuring cell is immersed in a silicone oil bath, whose control system allows temperature adjustment with an accuracy better than 0.1 K.

To avoid inclusion of air at the walls of the measuring cell, the specimen is melted in a particular way. During the heating-up of the cell a temperature gradient with the highest temperature at the upper edge of the specimen is created. As a sign for the start of melting, one can see a sealing at the upper rim of the sample. At this moment the measuring cell is evacuated from below. After the melting front has travelled through the specimen, temperature is equalized everywhere in the cell.

#### 4. Analytical data

In table 1 the analytical data (weight average and number average molar masses  $M_w$  and  $M_n$ ) of the PS-standards and their blends are enlisted. To the data provided by the manufacturer for the samples with  $M_w > M_c$  a correction procedure was applied [10, 11]. For this purpose a comparative study of their complex moduli was carried out. For the standards with  $M_w < M_c$  data given by the manufacturer are directly used.

#### 5. Experimental results

A reference temperature of 180 °C was chosen for all measurements, because at this temperature measure-

ments are possible over a rather wide frequency-range without exchange of torsion-wires. As a consequence, the corresponding graph is suited very well as a basic section on which the other graphs are superimposed by shifting. See for example figure 1. In determining the master-curves with highest possible precision the use of an illuminated screen has proven a success. For the purpose, each graph (reduced complex moduli vs. circular frequency at corresponding temperature) is plotted on a separate sheet of graph-paper and superimposed on the basic graph on top of the said screen. By this method the shift-factors given in table 2 could be determined experimentally with an accuracy of about 0.015 (for  $\log a_T$ ).

#### 6. Evaluation of the experimental results

Looking at the shift factors of table 2 one notices that addition of short chain polystyrenes (of molar mass below  $M_c$ ) lowers the absolute values of the shift factors with respect to those determined for undiluted long chain standard samples. One can understand this tendency by assuming that the added polystyrene molecules with  $M < M_c$  cause an increase of the percentage of free volume in the sample. In fact, the closest package of chains is disturbed at the end points of the chains. Consequently, a certain amount of extra free volume must be assigned to the chain ends [12]. Since the number of ends is proportional to the number average  $M_n$ , one can use the formula

$$f = f_0 + A/M_n \quad (11)$$

Table 1. Analytical data of PS-standards and their blends

Standards		Blends			
$M_w$	$M_n$	$M_{w,2}/M_{w,1}$	( $w_2$ )	$M_w$	$M_n$
123	119	123/18	(0.80)	102	55
293	268	293/8	(0.90)	265	61
670	613	293/8	(0.80)	236	34.5
760	692	293/8	(0.67)	199	22
		670/8	(0.90)	604	69
8	7.7	670/8	(0.65)	438	21.5
18	17.3	670/18	(0.89)	598	128
		670/18	(0.80)	540	78
		670/18	(0.70)	474	54
		760/8	(0.67)	510	22.5

$M_w$ — weight average molar mass (kg/mol),  $M_n$ — number average molar mass (kg/mol),  $M_{w,2}/M_{w,1}$ — blend of a standard 2 with  $M_{w,2} > M_c$  and a standard 1 with  $M_{w,1} < M_c$ , ( $w_2$ ) weight fraction of the standard 2 ( $1/M_n = w_1/M_{n,1} + w_2/M_{n,2}$ )

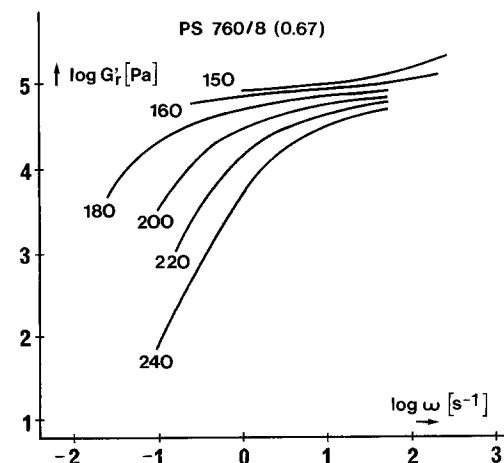


Fig. 1. Double-logarithmic plots of storage moduli  $G'$  as functions of circular frequency  $\omega$  at various temperatures (in °C) for the polystyrene blend 760/8 (0.67)

Table 2. Shift factors ( $\log a_T$ ) of PS-standards and their blends with respect to a reference temperature of 180 °C experimentally determined (exp.) and calculated with the aid of eq. (16) (calc.)

Sample	Temperature (°C)											
	150		160		200		220		230		240	
	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.
123		1.679	1.00	1.007		-0.719		-1.257		-1.479		-1.676
293	1.69	1.693	1.02	1.015	-0.72	-0.723	-1.27	-1.265		-1.487		-1.685
670		1.699	1.02	1.018	-0.72	-0.725	-1.26	-1.268		-1.491	-1.68	-1.690
760		1.700	1.02	1.019	-0.72	-0.726	-1.26	-1.268		-1.492	-1.68	-1.690
123/18 (0.80)		1.651	1.00	0.991		-0.709		-1.241		-1.461		-1.656
293/8 (0.90)	1.65	1.657	1.00	0.994	-0.71	-0.711		-1.244		-1.464		-1.659
293/8 (0.80)	1.62	1.621	0.98	0.974	-0.70	-0.699	-1.22	-1.224		-1.441		-1.634
293/8 (0.67)	1.56	1.576	0.96	0.949	-0.69	-0.683	-1.18	-1.199		-1.411		-1.601
670/8 (0.90)		1.662	0.99	0.997	-0.72	-0.713	-1.25	-1.247		-1.467	-1.67	-1.663
670/8 (0.65)		1.574	0.94	0.948	-0.69	-0.682		-1.197	-1.40	-1.410	-1.60	-1.600
670/18 (0.89)		1.681	1.00	1.008	-0.72	-0.719		-1.258	-1.48	-1.480		-1.677
670/18 (0.80)		1.667	0.99	1.000	-0.72	-0.714	-1.25	-1.250		-1.471	-1.67	-1.667
670/18 (0.70)		1.651	0.98	0.991	-0.72	-0.709	-1.24	-1.241		-1.460		-1.655
760/8 (0.67)	1.58	1.580	0.96	0.951	-0.69	-0.685	-1.19	-1.201		-1.414	-1.59	-1.604
$M_n \rightarrow \infty$		1.701		1.019		-0.726		-1.269		-1.492		-1.691

for the fraction  $f$  of free volume [2]. Parameter  $f_0$  stands for the fraction of free volume at reference-temperature  $T_0$  in a polystyrene sample of infinite molar mass. In other words:  $f_0$  is the fraction of  $f$ , which is not due to the contribution of chain ends. The parameter  $A$  has the dimension of a molar mass and can be interpreted as that mass of polymer, which is lacking in a volume occupied by one mole of the polymer (owing to the free volume at chain ends), when compared with the same volume occupied by a polymer of infinite molar mass. Thus,  $A$  is the product of the free volume at chain ends per mole  $v_e$  and density  $\rho$  of the polymer [13]. Accordingly, it is a temperature-dependent quantity.

This molar mass dependent form of  $f$  can be inserted into the WLF-equation. In this way one obtains a molar-mass-dependent shift factor related to reference temperature  $T_0$ :

$$\log a_T(T, M_n) = \frac{-B}{2.303(f_0 + A/M_n)} \frac{(T - T_0)}{(f_0 + A/M_n)/\alpha_f + T - T_0}, \quad (12)$$

$$c_1^0 = B/2.303(f_0 + A/M_n), \quad (13)$$

$$c_2^0 = (f_0 + A/M_n)/\alpha_f. \quad (14)$$

With this kind of molar-mass-dependent WLF-equation one can understand why usual WLF-plots [14] of the experimentally determined shift factors (see table 2) give separated straight lines with different slopes and

different intersections at the ordinate axis. Nevertheless, all these straight lines should furnish the same value of the product

$$c_1^0 c_2^0 = B/(2.303 \alpha_f). \quad (15)$$

This is expected, because – as stated before –  $B$  and  $\alpha_f$  have molar-mass-independent constant values.

One may try plots of  $1/c_1^0$  against  $1/M_n$  or  $c_2^0$  against  $1/M_n$ . It turns out that in these plots the general tendency is indicated in a correct way, whereas the value of  $A$  is subject to considerable deviations. The reason why such plots are not suitable is elucidated by the observation that the WLF-plot itself causes comparatively strong deviations in  $c_1^0$  and  $c_2^0$  when the corresponding shift factors are varied only to a relatively small extent. This statement is confirmed by the results presented below, where all shift factors being calculated with equal values of  $f_0$ ,  $A$  and the product  $c_1^0 c_2^0$  deviate less than 0.015 from measured shift factors. This deviation lies within the accuracy of the experimental determination of shift factors.

Looking at the values of  $c_1^0 c_2^0$  given in table 3 one cannot see a clear tendency. It may reasonably be assumed that deviations from the mean value  $c_1^0 c_2^0 = 600$  K are of a more random than systematic nature. This would be consistent with the independence of  $B$  and  $\alpha_f$  of molar mass. If one accepts the restrictive assumption that  $B/(2.303 \alpha_f)$  has a value of 600 K for all measurements, one has to realize that  $B$  and  $\alpha_f$  can no longer be chosen independently of each other. An

Table 3. Typical parameters of usual WLF-plots as calculated from the experimentally determined shift factors (see table 2) by least square fitting

Sample	$c_1^0$	$c_2^0$ (K)	$c_1^0 c_2^0$ (K)
293	5.045	119.4	602.3
670	4.965	117.5	583.6
760	4.965	117.5	583.6
293/8 (0.90)	4.975	120.0	597.0
293/8 (0.80)	4.899	120.3	589.5
293/8 (0.67)	4.783	120.6	576.9
670/8 (0.90)	5.076	122.1	619.8
670/8 (0.65)	4.879	123.1	600.5
670/18 (0.89)	5.082	121.5	617.4
670/18 (0.80)	5.076	122.1	619.8
670/18 (0.70)	5.112	123.8	632.7
760/8 (0.67)	4.774	119.8	572.1

Table 4. Values of  $\alpha_f$ ,  $B$  and  $f_g$  for polystyrene according to different references

Ref.	$\alpha_f \cdot 10^4$ (K <sup>-1</sup> )	$B$	$f_g$
7	3.92	0.331	0.01
14	4.8	—	0.025
17	5.42	1	0.028
18	3.1–3.7	—	0.028–0.035
19	3.03	$f_g/B = 0.025$ at $T_g = 100^\circ\text{C}$	—
20	4.0	0.574	0.019
21	4.5	—	0.025
22	3.0	0.53	0.025
2	3.7	0.59	0.019
12	3.0	0.91	0.029

experimental determination of  $\alpha_f$  (as the difference  $\alpha_1 - \alpha_g$  of heat-expansion coefficients above ( $\alpha_1$ ) and below ( $\alpha_g$ ) glass transition temperature) is not very difficult [12, 15–16]. In contrast, the parameter  $B$  is practically not accessible to direct measurements and shows considerable uncertainties. Taking a look at the literature one finds values for  $\alpha_f$ ,  $B$  and  $f_g$  as listed in table 4. The mean value of  $\alpha_f$ , given in this table, i.e.  $3.87 \cdot 10^{-4} \text{ K}^{-1}$  seems quite reliable and will be used in this paper. For  $B/(2.303 \alpha_f) = 600 \text{ K}$  and  $\alpha_f = 3.87 \cdot 10^{-4} \text{ K}^{-1}$  the value of  $B$  must be 0.535. Now we have to agree upon the value of  $A$  and  $f_0$  before we can insert them into the modified WLF-equation (eq. (12)). Unfortunately, quotations of values for  $A$  are rare in the literature [2, 13]. Apart from this one finds that only a very limited range of  $f_0$ -values allows good correspondence between measured and calculated shift factors [23]. It turns out, that on the basis of  $f_0$ -values as derived according to eq. (5) from the  $f_g$ -values quoted in table 4, no satisfying results can be achieved.

For this reason, a computer program was written, whose algorithm consisted in a simultaneous variation of the values of  $A$  and  $f_0$  within realistic limits and which enabled a calculation of corresponding shift factors for all fourteen samples and six measuring temperatures. This variation-algorithm was executed with the extra condition that the sum of the squares of the differences between experimentally determined and accordingly calculated shift factors became a minimum. The determination of the best-fitting  $A$ - and  $f_0$ -values from the forty-eight experimentally determined shift factors gives the following result:

$$A = 0.034 \text{ kg/mol and } f_0 = 0.046,$$

corresponding to  $f_g = 0.015$ .

Thus the molar-mass-dependent WLF-equation for polystyrene, as related to a reference temperature of  $180^\circ\text{C}$ , reads:

$$\log a_T(T, M_n) = \frac{-0.535}{2.303(0.046 + 0.034/M_n)}(T - 180) = \frac{-0.535}{(0.046 + 0.034/M_n)/3.87 \cdot 10^{-4} + T - 180} \quad (16)$$

Shift factors of polystyrene calculated in this way are given in table 2. The standard deviation between the calculated and the corresponding forty-eight measured values amounts to 0.0075. Deviations seem to be more accidental than systematic. If the value of  $f_g$  (resp.  $f_0$ ) is raised by no more than 0.001, one finds after a new least square adaptation of  $A$  that the standard deviation between measured and calculated values of the shift factors increases by a factor three. Such an increased deviation is certainly larger than the deviations experienced in the experimental determinations ( $A \log a_T \cong \pm 0.015$ ). A similar increase of the standard deviation is found when the value of  $f_g$  (resp.  $f_0$ ) is lowered with respect to its value quoted above. One can conclude that our measurements determine the value of  $f_0$  rather accurately if the validity of the proposed type of molar-mass-dependent WLF-equation is accepted. So the concept of varying  $A$  and  $f_0$  simultaneously instead of using separate values given by different authors is justified by the results achieved. Last not least one should mention that von Meerwall et al. [23] reported in their paper, which was devoted to the influence of free volume at chain ends to the diffusion of oligomers, that either  $\alpha_f$  or  $f_g$  must be fitted in order to reproduce the temperature dependence of measured data sufficiently well. Furthermore, they preferred to adapt  $f_g$ , because of  $\alpha_f$  being much better known than  $f_g$ . They also observed that the quality of fitting is significantly raised by a variation of  $f_g$  instead of a variation of  $\alpha_f$ .

Although the chosen value of  $\alpha_f$  ( $3.87 \cdot 10^{-4} \text{ K}^{-1}$ ) seems quite reliable, it remains worth mentioning how our results change if  $\alpha_f$  is given another value: For  $\alpha_f = 3.0 \cdot 10^{-4} \text{ K}^{-1}$  the computer algorithm gives the smallest standard deviations between measured and calculated shift factors, if a value of 0.0357 is attributed to  $f_0$  (corresponding to  $f_g = 0.0117$ ) and  $A$  is equal to 0.026 kg/mol. On the other hand, for  $\alpha_f = 4.5 \cdot 10^{-4} \text{ K}^{-1}$  the best fitting is obtained with  $f_0$  equal to 0.0535 (corresponding to  $f_g = 0.0175$ ) and  $A$  equal to 0.039 kg/mol.

Without having any notion of the precise error in  $f_0$  one can hardly give an estimate for the error of  $A$ . In fact, in the sum ( $f_0 + A/M_n$ ) an erroneous choice of  $f_0$  can, to some extent, be compensated by a readjustment of  $A$ . In this context it is worth noting that the term  $A/M_n$  is, in most cases, at least one decade lower than the value of  $f_0$ . For example, for a sample having a number average molar mass of  $M_n = 37 \text{ kg/mol}$ , the ratio  $f_0 : (A/M_n)$  amounts to about 50:1, which means that in this sample not more than one fiftieths of the free volume is due to the contribution of chain-ends. Calculating free chain-end-volume per mole ( $v_e = A/\rho$ , where  $\rho_{180} = 983 \text{ kg/m}^3$  is calculated with the aid of an equation given by Wales [24], i.e.  $\rho T = 400 + 0.82(T - 398)$ ) one finds that at a melt temperature of 180 °C as much as  $34.6 \text{ cm}^3$  of free volume must be ascribed to chain ends in one mole of our polystyrene samples. This corresponds to an averaged void volume of  $0.029 \text{ nm}^3$  per chain end, comparable with the volume of a cube having an edge length of 0.306 nm. Since this order of magnitude seems physically plausible and agrees well with that obtained in another measurement [13], the error of  $A$  may be within tolerable limits.

## 7. Discussion

By evaluating the molar mass dependence of the glass transition temperature Bueche [13] succeeds in finding a value for the free volume at chain ends. His method is based on the idea that during cooling the glass transition temperature is always reached, when  $f$  has acquired a certain fixed value  $f_g$ . At equal temperature a sample containing many chain ends (low molar mass sample) has a larger fraction of free volume than a sample containing few chain ends (high molar mass sample) [25]. Thus, a sample of low molar mass must be cooled to a lower temperature than a sample of high molar mass in order to reach the same value of  $f_g$ . From this consideration follows:

$$v_e = \alpha_f M_n (T_{g,\infty} - T_g) / \rho. \quad (17)$$

For polystyrene Orbon and Plazek [26] use the relation:  $T_{g,\infty} - T_g = 102/M_n$  ( $M_n$  in kg/mol). When this equation is inserted into eq. (17), a free volume per chain end of  $0.032 \text{ nm}^3$  is obtained. This value corresponds to the glass transition temperature. It is not sure whether a conversion to 180 °C is permissible. In fact, the free volume at chain ends may not have the same volume expansion coefficient as the ordinary free volume (which indeed can increase by the formation of new voids).

For sufficiently high values of the number average molar mass (e.g. for polystyrene standards with  $M_n = 613$  or  $692 \text{ kg/mol}$ ) the term ( $A/M_n$ ) can practically be neglected compared with  $f_0$ . So one can understand why all investigated polystyrene standards with  $M_n > M_c$  have nearly the same values of the shift factors. In the limit of  $M_n \rightarrow \infty$  the molar-mass-dependent WLF-equation becomes identical with the usual WLF-equation with shift factors given in table 2 (referred to a reference temperature of 180 °C). In this case the coefficients  $c_1^0$  and  $c_2^0$  assume the values 5.043 and 119 K.

As has been discussed before, our method permits a rather accurate fixation of the fraction of the free volume  $f_0$  (resp.  $f_g$ ) at the chosen reference temperature  $T_0$  (resp.  $T_g$ ). Looking at the values of  $f_g$  given in different references (table 4) one can notice an accumulation in the range of  $f_g = 0.025$ . With the assumption of a glass transition temperature of  $T_{g,\infty} = 100 \text{ °C}$  for polystyrene of infinite molar mass [19, 25, 27] our measurements result in a  $f_g$ -value of 0.015. This low value may be explained by the theoretical character of our derivation of  $f_g$ . Indeed, it is well-known that the fraction of "frozen in" free volume at the glass transition temperature depends on the rate of previous cooling. So one may suppose that experiments executed at cooling rates lower than the standardized cooling rate of 3 K/h will give lower values of  $f_g$  (resulting also in a lower value of  $T_g$ ). The value  $f_g = 0.015$  given in this paper corresponds to the limit of infinitely low cooling rate, which cannot be achieved experimentally. Moreover, an  $f_g$ -value of 0.015 refers to a polystyrene of infinite molar mass, whereas the measured values for real polymers are always influenced by the contribution of chain ends. In this respect a paper by Schwarzl and Zahradnik [7] should be mentioned: Using nearly the same expansion coefficient for the free volume of polystyrene these authors find a still lower value of 0.01 for  $f_g$ . It must be emphasized that the considerations given above refer to  $T_{g,\infty} = 100 \text{ °C}$  for polystyrene of infinite molar mass. But there are also indications that the value of  $T_{g,\infty}$  may be some-

what higher [26]. If one tries a value of  $T_{g, \infty} = 110$  °C, one obtains a  $f_g$ -value of 0.019.

Another interesting parameter is the Vogel-temperature  $T_{\infty}$ , i.e. the (theoretical) temperature at which the free volume vanishes entirely after an infinite time of cooling and ageing. Based on our measurements one can ascribe to a polystyrene of infinite molar mass a Vogel-temperature of 61.1 °C. Ferry quotes a Vogel-temperature of 50 °C for a polystyrene of finite molar mass [2]. Bearing in mind the shift of the glass-temperature due to the contribution of chain ends, one can conclude that there is no serious disagreement.

In any case the papers of Watanabe, Sakamoto and Kotaka must be mentioned [29]. The calculation of the molar-mass-dependent shift factors of these authors is based on a variation of the reference temperature in accordance with the experienced dependence of the glass transition temperature on the composition of the sample [14, 30]. The values of  $c_1^0$  and  $c_2^0$  remain unaffected. The basic idea of this approach is the iso-free-volume-concept, according to which a reference point for all different samples is not given by a certain reference temperature but by a state, in which all samples have the same fraction of free volume. This method can certainly be brought into line with the method used here.

The anionic, atactic polystyrene samples, as investigated in the present paper, have a butyl-group at one end (originating from the initiator) and a (1)- respective (2)-phenethyl-group at the other end. As a consequence, the value of the free volume determined in this paper must be considered as a mean value obtained for these different end groups. It must be noted that industrial polystyrenes, which are produced by radical polymerization, certainly have other end groups. With radical polymerization various initiators and modulators are in use. Pertinent end groups of varying sizes are attached to the chain ends. As it must be assumed that the size of the end group and the flexibility of the surrounding molecules are responsible for the value of free volume at the chain ends, an adjustment of the quantity  $A$  to each specific polymer seems to be inevitable.

The investigated polystyrene samples contain no additives. This is important as foreign molecules can strongly influence the results of the measurements. As an example it should be mentioned that the determination of the shift factors of an industrial polystyrene (PS N 7000 Hoechst) led to the conclusion that this polymer had a number average molar mass  $M_n$  of only about 25 kg/mol. In fact, Pfandl, Link and Schwarzl, who studied this polystyrene quite extensively [31], quoted a value of  $M_n$  equal to 170 kg/mol. As

this value had been determined by various techniques, it can be considered as rather safe. The reason for this discrepancy is that this industrial polystyrene contains small amounts of "white oil". This leads to a considerable increase of the free volume and, as a consequence to a change of the shift factors. Thus, one sees that non-polymeric substances which have been added to the samples in small amounts can readily be perceived by the observation of changes in the shift factors.

## Appendix

Our computations did not take into account the influence of entanglements on free volume. There are several research works [32, 33] on the influence of molecular weight on glass transition temperature (above and below  $M_c$ ) leading to the conclusion that entanglements lower the percentage of free volume in polymer solutions and melts. In considering the influence of entanglements on free volume one arrives at about  $0.014-0.019$  nm<sup>3</sup> for the mean value of free volume at one chain end of anionic polystyrene.

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(Received January 20, 1987)

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