

## PRESSURE DEPENDENT STUDIES OF PHOTON CORRELATION RELAXATION TIMES OF BULK POLYMERS

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### Abstract

The correlation times obtained from photon correlation spectroscopy at different temperatures and at pressures up to  $2 \cdot 10^8$  Pa are analyzed in view of separating the effect of temperature and volume on the segmental mobility.

### INTRODUCTION

The molecular motion in bulk polymers has been fruitfully studied by a number of techniques each presenting its particular practical importance and theoretical value. The relation between the results obtained by such different techniques as dielectric loss, mechanical relaxation and viscoelastic behaviour is however very difficult to establish because of the complexity both of the system and of the different measuring processes. In order to make a comparison of such dynamical properties of polymers which can be measured in time ranges

between  $10^{-11}$  to  $10^2$  seconds it is essential to have overlapping time scales obtained by more than one technique. This again raises the question of the reduction of data obtained in a given temperature and pressure range to other ranges of these state variables. The time-temperature reduction of dynamical data is being currently performed successfully by means of the empirical WLF equation (1,2). However, the time-temperature-pressure reduction is still in a less developed stage mainly because of the lack of high pressure static and dynamical data. This contribution deals with the question of the time-temperature-pressure reduction of photon correlation data which have been recently obtained on some bulk polymers at different temperatures above the glass point and at pressures between  $10^5$  and  $2 \cdot 10^8$  Pa. The discussion will be mainly phenomenological because it is important to achieve phenomenological consistency before entering into the discussion of molecular models.

The present discussion will be restricted to the correlation times of polymethyl acrylate (PMA), polyethyl acrylate (PEA) where only one process is monitored by photon correlation spectroscopy (3,4), polyphenylmethyl siloxane (PPMS) where a second process could be unambiguously separated from the main relaxation process (5) and finally to polystyrene (PS) where the separation of the two processes is as yet tentative (6). In spite of the problems associated with the second process in PS, which is still under study, the data have been included in this discussion because of the wealth of the existing PVT and viscoelastic data under pressure for this polymer which allow a more detailed discussion of the pressure dependence of the observed correlation times.

### PHOTON CORRELATION IN BULK POLYMERS

In a photon correlation experiment the light of a laser source is scattered by a polymer sample and is collected at a preset scattering angle. The scattering volume which is defined by the collecting optics must be sufficiently small to ensure that the light impinging on the detector comes from a coherent region of the illuminated sample. If this is the case, then the intensity fluctuations monitored by the detector can be analyzed by a correlator which will give a correlogram characteristic of the evolution of the fluctuations of the local optical density of the sample. On the molecular level the correlation function will reflect the various inter- or intramolecular motions of the polymer. The measured correlogram  $G^{(2)}(t)$  is connected to the correlation function of the scattered electric field  $G^{(1)}(t)$  by the relation:

$$G^{(2)}(t) = A (1 + b |G^{(1)}(t)|^2) \quad (1)$$

A is the baseline and b is a parameter depending upon the geometry of the optics used in the experiment. Both parameters are obtained by a fit of the experimental correlograms to eq. (1). Since  $G^{(1)}(t)$  is the field correlation function which is immediately connected to the monitored process this quantity is calculated in the first stage of the data analysis. In the case of bulk polymers above the glass temperature it has been shown that  $G^{(1)}(t)$  reflects a local segmental motion of the polymer chain (7).

The correlation functions of bulk polymers are generally non exponential and in most cases their shape can be described by the Williams-Watts correlation function (8).

$$|G^{(1)}(t)|^2 = b \exp(-2(t/\tau_0)^\beta) \quad (2)$$

The width parameter  $\beta$  is in many cases independent of the temperature (and pressure) (9) and is used to characterize the width of the distribution of relaxation times. The mean correlation time  $\tau$  is calculated by means of the following relation:

$$\tau = (\tau_0/\beta) \Gamma(\beta^{-1}) \quad (3)$$

where  $\Gamma(\beta^{-1})$  is the gamma function.

In some cases there has been evidence of the presence of two overlapping relaxation processes leading to an unresolved correlogram with a very small value of  $\beta$  (10). In such a case the correlation time obtained formally by eq. (3) should be considered with great caution. In some other cases the application of high pressure has led to the separation of two processes which could thus be described by two distributions of relaxation times (11,12). In spite of this observation a separation of this kind always implies a delicate curve fitting procedure and the correlation times obtained for each process may be somewhat contaminated by the other. The situation is more favorable in dielectric relaxation where the separation of an  $\alpha$ - and a  $\beta$ -process has been unambiguously performed in many cases (13,14). Despite some uncertainties connected to the interpretation of the photon correlation data it is safe to say that the processes observed are in many cases basically the same as the ones observed by dielectric or mechanical data. It is however possible that, due to the different point of view of the light scattering process, the correlation times obtained by this method reflect the different components of the complex molecular motion with different weight factors. One indication for this is that, although the temperature dependence of the process observed is the same as found by dielectric relaxation, the values of the mean relaxation times may be quite different (12).

#### THEORETICAL

The use of both temperature and pressure as variables offers the unique possibility to disentangle the effects of thermal energy and volume requirements upon the mobility of polymers. The following equations provide the framework for this kind of analysis.

Relaxation time data obtained under conditions of constant temperature on the one hand and constant pressure on the other can be transformed so as to give the temperature and the volume coefficients of the relaxation time. Equation (4) illustrates the relation between the isochoric and the isothermal coefficients of the relaxation time which can be calculated if the three quantities on the rhs. of this equation are known:

$$(\partial\tau/\partial T)_V / (\partial\tau/\partial T)_T = (k^T - k^V) \cdot \beta^V \cdot T \quad (4)$$

The quantities  $\alpha^V$  and  $\beta^V$  are the thermodynamic coefficients of thermal expansion and the compressibility is defined as follows:

$$\alpha^V = 1/V (\partial V/\partial T)_P \quad (5a)$$

$$\beta^V = -1/V (\partial V/\partial T)_T \quad k^V = \alpha^V/\beta^V \quad (5b)$$

The isokinetic coefficient:

$$k^T = (\partial P/\partial T)_\tau \quad (6)$$

is defined as the slope of an isokinetic curve i.e. the locus of equal relaxation times in the P-T plane. The isokinetic coefficient is a measure of the effect of pressure changes upon a given relaxation time as compared to the effect of a change in temperature.

The access to the isochoric quantities via high pressure measurements is important in view of the widespread use of free volume concepts in the interpretation of relaxation processes in

polymers (2,15). Thus the free volume  $V_f$  displays a thermal expansion and a compressibility which will be indicated here by the index  $f$ :

$$\alpha^f = 1/V_f (\partial V_f / \partial T)_P \quad (7a)$$

$$\beta^f = -1/V_f (\partial V_f / \partial T)_T \quad (7b)$$

In analogy to the isochoric and the isokinetic coefficients it will be useful to use the iso-free-volume coefficient:

$$k^f = (\partial P / \partial T)_f = \alpha^f / \beta^f \quad (8)$$

where the index  $f$  indicates that the expression is calculated under conditions of constant free volume.

We can derive some simple relations for the free volume if we make the following assumptions:

- The relaxation time is a function of the free volume and the temperature:  $\tau(f, T)$
- The free volume is a function of the total volume and the temperature, its pressure dependence being implicit in the pressure dependence of the total volume:  $V_f(V, T)$ .
- the total volume i.e. the sum of the free volume and an occupied volume  $V_0(P, T)$  is a function of the pressure and the temperature:

$$V(P, T) = V_0(P, T) + V_f(P, T) \quad (9)$$

In treating the three quantities  $V, V_f, \tau$  as state functions we find:

$$k^f = k^V + (\partial V / \partial T)_f / V \beta^V \quad (10)$$

Equations (4) and (10) provide useful connections between the thermodynamic quantity  $k^V$  and the corresponding quantities  $k^f, k^\tau$  for the free volume and the observed relaxation process respectively. Under the assumption that a given relaxation process is determined, as far as its volume requirements are concerned, only by  $V_f$  we can identify the iso-free-volume coefficient  $k^f$  to the corresponding isokinetic coefficient  $k^\tau$ .

Since the expression  $(\partial V / \partial T)_f$  is positive we would expect that the isokinetic coefficient is always larger than the corresponding isochoric coefficient  $(\partial P / \partial T)_V$ . The differences are a measure of the properties of the free volume with respect to changes of pressure and temperature. Since the free volume is not directly accessible by experiment we can use the assumption underlying eq. (10) and thus identify the iso-free-volume coefficient with the isokinetic coefficient which can be obtained experimentally.

The relations derived above can be applied to the shear viscosity of a polymer and a comparison of the iso-viscous coefficient:

$$k^\eta = (\partial P / \partial T)_\eta \quad (11)$$

with the isochoric and the isokinetic coefficients pertaining to other relaxation processes can be very instructive. Equation (12) relates  $k^\eta$  to the isochoric coefficient:

$$k^\eta = k^V + (\partial V / \partial T)_\eta / V \beta^V \quad (12)$$

The activation enthalpies  $H_p^\#$  for a particular motion in a polymer are defined and usually measured under conditions of constant pressure. A separation of the energy requirements to overcome a constant potential barrier determined by the conformation of the polymer from the total effect of temperature change is generally more instructive than the consideration of the effect of both the thermal energy and the free volume change contained in  $H_p^\#$ . For this purpose the activation energy at constant volume  $E_v^\#$  is more amenable to theoretical model considerations. Equation (13) relates the activation energies, under conditions of constant pressure and constant volume respectively, to the activation volume  $V^\#$  and the equilibrium P-V-T data of the polymer.

$$H_p^\# - E_v^\# = (\partial P / \partial T)_V T V^\# \quad (13)$$

The activation volume is obtained from pressure dependent kinetic data by means of eq. (14):

$$V^\# = (\partial \ln \tau / \partial P)_T RT \quad (14)$$

The isochoric coefficient in eq. (12) does not pertain to the volume which determines  $\eta$ , but to the total volume of the liquid. If we consider only the free volume eq. (13) should read

$$H_p^\# - E_v^\# = k^f T V^\# \tag{15}$$

As will be seen below this would lead to a decrease of the difference  $H_p^\# - E_v^\#$  by roughly a factor of two for the two acrylates PMA and PEA.

STATIC PROPERTIES AND DYNAMICS OF POLYSTYRENE

The P-V-T data of polystyrene have been measured by Hellwege et al. (16) and Quach and Simha (17) in a temperature range above and below the glass temperature  $T_g$  and in a pressure range from atmospheric pressure up to  $2 \cdot 10^8$  Pa. Figure 2 illustrates the data displayed in the V-T plane for six isobars for a sample of polystyrene with a molecular weight of 100000. The glass temperature is well characterized by a break indicating a discontinuity of the

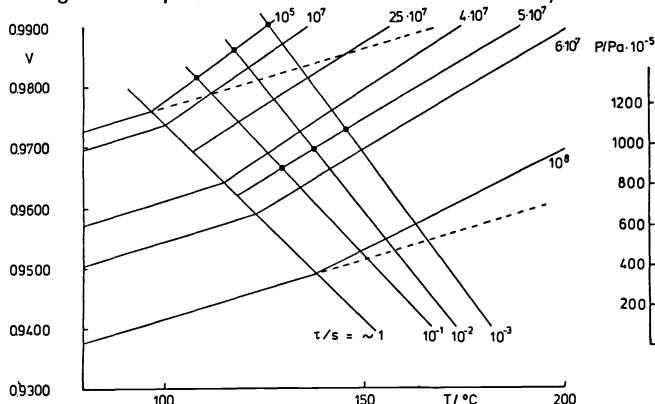


Fig. 1: V-T curves and lines of constant relaxation times in PS.

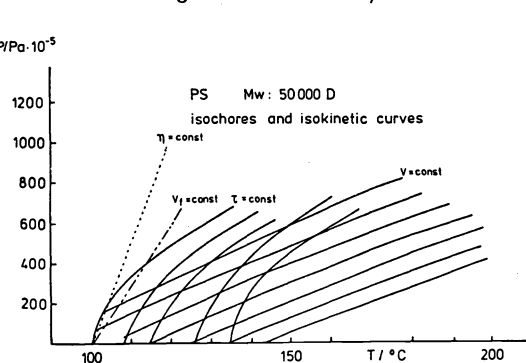


Fig. 2: Isochores and lines of constant relaxation times in PS.

thermal expansion coefficient at this temperature. According to this criterion the difference between the glass and the liquid is less sharp at higher pressures. The points corresponding to the glass temperature lie on a straight line illustrating a significant shift of  $T_g$

higher values with increasing pressure. If we assume that the glass point is an iso-free-volume state and that its pressure dependence simply reflects the decrease of free volume with increasing pressure, then the line joining the glass points at the different pressures should be a line of equal free volumes. In order to assess the validity of this assumption we can use the relaxation times obtained from photon correlation measurements.

This illustrated in the Fig. 1 where the points corresponding to relaxation times of  $10^{-3}$ ,  $10^{-2}$ ,  $10^{-1}$  seconds at pressures of  $10^5$  and  $5 \cdot 10^7$  Pa were joined by straight lines indicating the loci of equal relaxation times. The photon correlation data have been obtained on a 50 000 molecular weight sample. Despite the difference in molecular weight of the sample used for light scattering and the one used for the P-V-T data it was shown (18) that at molecular weights above 10 000 the free volume is no more a function of  $M_w$ . An

extrapolation of the relaxation data to longer times shows that the glass temperature would correspond roughly to relaxation times of the order of a few seconds. The Figure illustrates the displacements of the isokinetic lines in a systematic way in the V-T plane. We can conclude that indeed the glass points are points of equal relaxation times irrespective of the temperature and the pressure.  $T_g$  is obviously not a point of equal specific volume or density since at higher pressures the glass point occurs at lower values of the specific volume. Furthermore, if we can associate the relaxation times to a free volume then  $T_g$  is also an iso-free-volume state, a conclusion which was drawn already by Fox and Flory as early as 1949 (15) by very persuasive arguments. This result was verified by Williams, Landel and Ferry (1) and specified in a more detailed way by Boyer (18). This entails also the conclusion that the relaxation times observed in the present photon correlation experiment are directly connected to the modes which freeze in at the glass point. This does not exclude, as we shall see below, that other modes like the so-called secondary relaxation processes do not follow the changes of this particular kind of free volume.

We can obtain a more quantitative picture of the situation if we use, in connection to the

relations exposed in the theoretical section, a representation in a P-T plane. This is illustrated for polystyrene in Fig. 2. The nearly parallel family of curves with the smaller slope are isochores and the family of curves crossing the isochores are isokinetic, i.e. lines of equal relaxation times. The former display only small variations in slope with increasing temperature/pressure whereas the slope of the isokinetic curves decreases by more than a factor of two in the pressure range between  $10^5$  and  $6 \cdot 10^7$  Pa. The values of the slopes, i.e. the respective coefficients and their variation range for the two families of curves are displayed in the first and second columns of Table 1. Column three gives the iso-free-volume line according to eq. (16) below. The figure also displays an isoviscous line, and two iso free-volume lines according to the phenomenological definition of eq. (16) below.

TABLE 1. Dynamic and static coefficients in  $\text{Pa K}^{-1} 10^{-5}$  of PS in the P-T plane.

$k^v$	$k^\tau$	$k^f$	$k^\eta$	$k^g$
8-10	40-20	33	53	33

The values of the isoviscous coefficient, which does not change much over the pressure range between  $10^5$  to  $10^8$  Pa, is given in column four of Table 1. The column five of the table gives the value of the glass point coefficient:

$$k^g = (dP/dT_g) \quad (16)$$

The differences between the isochoric and the isokinetic coefficients illustrated in Table 1 are not unexpected; they are actually a consequence of eq. (10). They simply illustrate that the second rhs. term in eq. (10) is rather significant in the case of polystyrene of that particular molecular weight. If the dynamics reflected in the observed relaxation times, in the freezing of mobility at  $T_g$  and in the viscosity were identical, then we would expect the three corresponding coefficients to be equal. This is the case for the relaxation times and the glass point, but the isoviscous coefficient is significantly larger. Thus the values displayed in Table 1 support the conclusion drawn above that the glass points are isokinetic points and that they are not isoviscous points. In other words, although the macroscopic viscosity increases dramatically at temperatures near the glass point and is presumably determined by the volume available to particular molecular deformation modes, it is not determined by the same free volume as the relaxation time and the vitrification process. Actually, according to eq. (10) and the results illustrated in Table 1 the free volume manifested in viscous flow is characterized by a much larger value of  $(\partial P / \partial T)$ . This means that the free volume responsible for the relief of macroscopic shear stress is less compressible and/or has a larger thermal expansion than the free volume allowing for the segmental mobility of the polymer chain observed in light scattering. A purely hypothetical interpretation of such an observation could be that the latter is mainly determined by rotational isomerization of short chain segments, whereas the motion which a polymer molecule undergoes in the stress gradient of the viscosimeter contains another component which is not monitored to the same extent in the light scattering experiment. However, as the present experiments do not yet allow such detailed interpretations this can be only considered as a working hypothesis for future experiments. Boyer and Simha (18,20) have given a definition of free volume at  $T_g$  widely used and adopted here which depends only upon the thermodynamic

quantity  $\alpha^v$  and which gives the following expression for the free volume at constant pressure above  $T_g$ :

$$V_f = \Delta \alpha^v T \quad \text{for } T > T_g \quad (17)$$

$\Delta \alpha^v$  is the difference of the thermal expansion coefficients between the glass and the liquid. The value of the iso-free-volume coefficient according to the above equation displayed in column three of Table 1 is found to be very close to the isokinetic and to the glass point coefficients for polystyrene at pressures lower than  $5 \cdot 10^7$  Pa. This is a remarkable result since it confirms and extends the free volume concept of Simha and Boyer which was developed without considering such correlation times as obtained by light scattering techniques. When used in interpreting high pressure data the free volume definition must be extended to include changes of free volume with pressure. This is done in the same spirit of the above definition used for temperature changes only by postulating:

$$V_f(T,P) = \Delta \alpha^v T + \Delta \beta^v P \quad (18)$$

The inclusion of compressibility requires measurements of this quantity in the temperature and pressure range in question since  $\beta^V$  is not as constant as the thermal expansion coefficient.

The decrease in the slope of the isokinetic curves, illustrated by the decrease in the isokinetic coefficient in Table 1 by almost 65 % from  $10^5$  to  $10^8$  Pa is an indication of a change in the character of the motion monitored by the light scattering experiment in polystyrene with increasing pressure. Such a drastic change is not observed in  $(\partial P / \partial T)_V$ . On the other hand the free volume also decreases by approximately 30 % in the same pressure range entailing a similar change in  $(\partial P / \partial T)_g$ . At this stage however, one cannot exclude the possibility that the experimental relaxation times contain a component from the second observed mode which varies with increasing pressure. More experiments are in progress to clarify this point.

TIME-TEMPERATURE-PRESSURE REDUCTION OF THE CORRELATION TIMES OF PMA, PEA AND PPMS

The pressure and temperature dependence of relaxation data of polymers can be treated in several ways. The data analysis to be used is a question of the adequacy in view of the pressure and temperature ranges, the nature of the data available and the aim of the analysis. We owe the most widely and successfully used procedure to Williams, Landell and Ferry (1,2). Their shift factor  $a_T$  enables us to reduce relaxation data with respect to the temperature to a single master curve. The WLF equation:

$$\log a_T = c_1(T-T_0)/(c_2 + T - T_0) \tag{19}$$

is a purely empirical relation between the relaxation times at different temperatures. The equation contains three constants which can be fitted to experimental relaxation data. It was developed mainly to perform reduction for mechanical and dielectric loss data. Due to the close connection between various relaxation processes the WLF equation was also used to represent other relaxation data. Since the temperature  $T_0$  is arbitrary the two coefficients  $c_1$  and  $c_2$  are also arbitrary insofar as they are chosen so as to reduce the relaxation data from  $T_0$  to the temperature  $T$ .

In this section a data analysis is presented which does not start with a given equation, but on the contrary, the correlations between the data leads to an expression for the temperature and pressure dependence of  $\log \tau$ . The equation thus obtained is not derived from a model but it represents the simplest possible data reduction scheme in view of the given quality of the data.

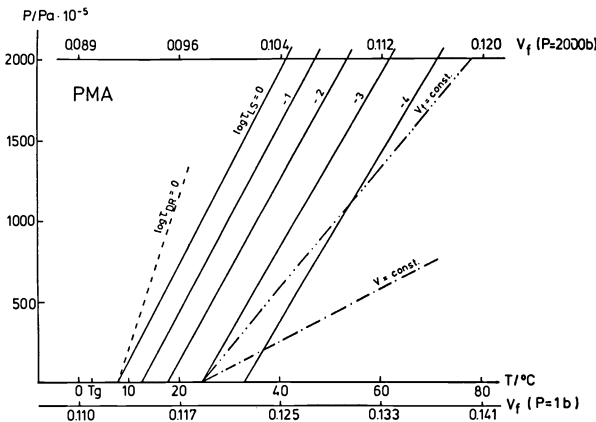


Figure 3: Isokinetic curves for PMA compared to isochores. LS refer to light scattering relaxation times and DR to dielectric relaxation times. The free volumes are indicated for two pressures.

Figure 3 displays the isokinetic curves for PMA in the P-T plane for the relaxation times  $\log \tau = 0, -1, -2, -3, -4$ . The difference between the isokinetic and the iso free-volume lines shows that the free volume calculated on the basis of eq. (18) does not represent the quantity which must be used to reproduce this particular motion.  $V_f$  as calculated by eq. (18) is more pressure dependent and/or less temperature dependent than . On the other hand the dielectric relaxation data display larger slopes i.e. this relaxation time is less pressure dependent and/or more temperature dependent than the light scattering correlation times. The experimental points for PMA illustrated in Fig. 3 give excellent fits with a linear equation:  $P = A + B T$ . The following linear expressions are thus obtained :

$$P_0 = -486 + 60.2 T \quad (20a)$$

$$P_{-1} = -733 + 57.9 T \quad (20b)$$

$$P_{-2} = -1024 + 56.3 T \quad (20c)$$

$$P_{-3} = -1378 + 54.1 T \quad (20d)$$

$$P_{-4} = -1730 + 52.4 T \quad (20e)$$

The indices indicate the value of  $\log \tau$  for which the isokinetic line is calculated. It can be easily seen that the two coefficients of the linear forms (20a-e) are functions of the logarithm of the relaxation time. This suggests the use of linear equations to fit the two quantities as a function of  $\log \tau$ . The fits are again excellent and the following equations are obtained by this procedure:

$$A = -16840 - 216 \log \tau \quad (21a)$$

$$B = 60 + 1.94 \log \tau \quad (21b)$$

Inserting these equations in the linear equation for P we obtain:

$$P = -16840 - 216 \log \tau + (60.1 + 1.94 \log \tau) \cdot T \quad (22)$$

This equation can be cast in a form giving  $\log \tau$  as a function of temperature and pressure:

$$\log \tau = (8680 - 31 T + 0.52 P) / (T - 111) \quad (23)$$

$\log \tau$  is thus expressed as a function of P and T with four parameters which have been calculated by the fitting procedure described:

$$\log \tau = (K_1 + K_2 T + K_3 P) / (T - K_4) \quad (24)$$

The procedure is based upon the observed linearity of the isokinetic curves and the fit is unique insofar as the three sets of data fitted by linear functions, as described, are linear within experimental precision. Thus the form of eq. (24) results from this linearity. The use of another form which might be theoretically better founded and is not borne out by the data includes the risk of overinterpretation. The best we can do in this situation is to express the coefficients of the theoretical model with the four constants of eq. (24). Figure 4 gives a master correlogram of PMA in which three correlograms obtained from photon correlation spectroscopy at three different temperatures and two different pressures have been included after reduction by eq. (24). The quality of the master curve illustrates

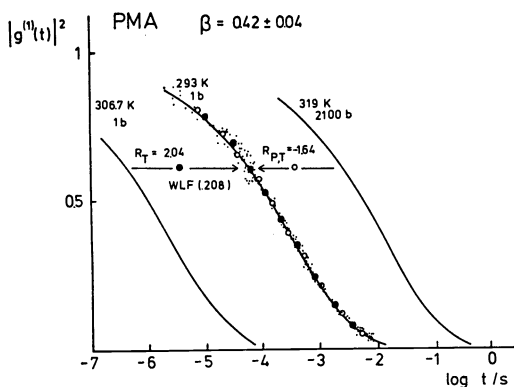


Figure 4: A master curve for the light scattering data of PMA obtained by a time temperature-pressure shift. The shift factors are  $R_T$  and  $R_{T,P}$  respectively.

that the calculated data are free from systematic errors and that the shape of the correlograms is independent of the temperature and the pressure in the range covered by the present experiments. Especially the width parameter  $\beta$  of the correlation functions thus appears to be independent of temperature and pressure. This was already observed for dielectric relaxation of PMA (9). In the case of the  $\alpha$ -relaxation of polystyrene, in contrast to the few other bulk polymers studied up to now by photon correlation spectroscopy under high pressure, the isokinetic curves are not linear, as illustrated in Fig. 2, and thus the described data reduction scheme and hence eq. (24) cannot be used in this simple form.

The eq. (24) is isomorphous to the WLF equation if we restrict it to the temperature dependence by setting  $P=0$ . In this case we can calculate the coefficients  $c_1$  and  $c_2$  and  $T_0$  of the WLF eq. (17) from  $K_1$ ,  $K_2$  and  $K_4$  of eq. (24) as follows:

$$c_1 = K_2 \tag{25a}$$

$$c_2 = K_4 - K_1/K_2 \tag{25b}$$

$$T_0 = - K_1/K_2 \tag{25c}$$

The WLF coefficients thus obtained for PMA differ drastically from the ones published in the literature (21,22). Actually the WLF equation which has been successfully used to reduce the mechanical data of PMA does not provide quite the same quality of temperature shift as eq. (24) for the present data. Table 2 illustrates the difference of the WLF coefficients from the literature (2) and as calculated from eq. (25) both sets being based upon a value of  $T_0=324K$ . The difference between the two shift factors displayed in columns four and five of

TABLE 2. Comparison of the WLF coefficients of PMA (2) and the coefficients obtained by means of eq. (23) from the light scattering data. In both cases the reference temperature was  $T_0 = 324K$ .  $a_T$  is the WLF shift factor and  $R_T$  the factor obtained from eq. (23)

	$c_1$	$c_2$	$a_T$	$R_T$
WLF	8.86	101.6	-3.91	
eq. (25)	24.3	213		-4.13

the table is rather large. The most obvious difference is observed at lower temperatures where the divergence of eq. (24) with  $K_4 = 111K$  leads to much higher values for  $\log a_T$ . The difference of the two sets of constants can be now understood if we take into account that the increase in  $c_1$  is compensated by a decrease in  $c_2$ . If the scatter of the data between 10 and 60°C exceeds the deviation of the two curves then either form can be used to reduce the data and differences of the parameters as large as the ones reported here do not entail drastic differences of the shift factors. However, as shown in Table 2, the shift factors for the shift from 324 to 293K differ significantly. Thus it is safe to say that between 10 and 60°C the procedure leading to eq. (24) is somewhat more adequate for this kind of data. Furthermore, it appears that, in view of the form of the WLF equation, and for that matter of eq. (24), which allow for drastic changes of the parameters as a consequence of rather small deviations of the data we should be careful in ascribing a physical meaning to their actual values as obtained from a fit.

On the other hand the isomorphism between eq. (24) and the WLF equation is remarkable and it provides a simple extension of the latter to deal with the pressure dependence of relaxation times. Actually, as illustrated by the master curve in Fig. 4, the pressure dependence of PMA, and also of the other two polymers discussed below can be described by eq. (24) which is much simpler than other equations proposed (23,24).

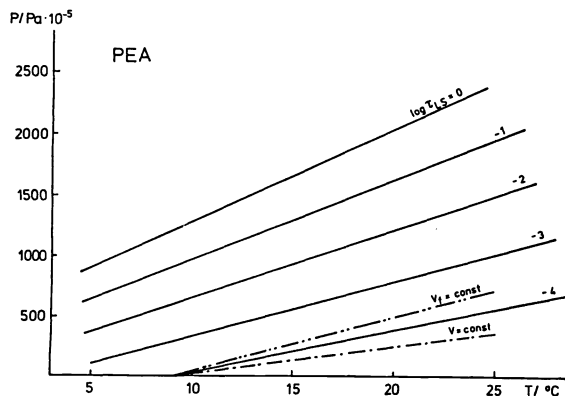


Figure 5: Isokinetic lines and isochores of PEA.

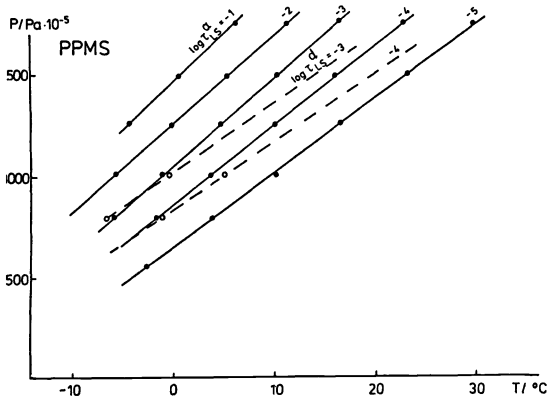


Figure 6: Isokinetic lines for PPMS. Note the difference between the two modes observed by light scattering.



It is interesting to compare high pressure dielectric relaxation data with the present photon correlation data on the basis of eq. (24). For this purpose the dielectric relaxation data for PMA of Williams (9) are used which lie in the range of 15 to 90 °C and 1 to 3.10<sup>3</sup> atm. Figure 5 shows also one isokinetic curve from the data of Williams which displays a clearly larger slope than the photon correlation data. The fit of eq. (24) to these data consequently yields coefficients which differ from the results obtained from photon correlation spectroscopy as illustrated in Table 3. It should be noted, that eq. (24) fits the dielectric relaxation results without any systematic deviation extremely well.

The relaxation data obtained by temperature and pressure dependent photon correlation spectroscopy of polyethyl acrylate PEA (4) and polyphenylmethyl siloxane PPMS (5) have been processed according to the scheme outlined above and the results are included in Table 3. In the case of PPMS two relaxation processes could be observed and separated. The corresponding relaxation times have been analyzed separately and have been included in the Table as d- mode values. Column 9 displays the calculated temperature at which log  $\tau = 0$  at atmospheric pressure. It coincides within experimental error with the measured value.

TABLE 3. Coefficients of the temperature and the pressure dependence of the relaxation times. For PMA the dielectric data of Williams have been recalculated by the procedure described. For PPMS the observed modes have been treated separately.  $T_1 = (K_4 + K_1)/K_2 + 1$  and  $T(0) = -K_1/K_2$ .

Substance	Technique	Mode	$K_1/K$	$K_2$	$K_3/K$	$K_4/K$	$T_1/K$	$T(0)/K$	Tg/K	ref.
PMA	LS	$\alpha$	8640	-31	0.52	111	273	280	222	3
	DR		3780	-11.85	0.13	282	300	319	.	9
PEA	LS	$\alpha$	2000	-7.47	0.098	257	266	268	213	4
PPMS	LS	$\alpha$	4310	-17.96	0.36	200	237	240	207	5
	LS	d	11700	-51	1.43	18.6	225	229	.	5

The behaviour of PEA is similar to that of PMA with the difference that the iso-free-volume line has a larger slope than the isokinetic lines in contrast to PMA. The result for the two modes of PPMS is also remarkable, since the d-mode appears to correspond to a smaller free volume than the  $\alpha$ -mode. This entails a larger pressure dependence and/or a smaller temperature dependence. The different nature of the d-mode is also illustrated in the small value of  $K_4$  for this mode as compared to the  $\alpha$ -mode value.

The reduced data in Table 3 allow the calculation of the activation energy and activation volume as well as their ratio and the isokinetic ratio by means of the following relations:

$$H^\# = RT (K_2 K_4 + K_1 + K_3 P) T / (T - K_4) \quad (26a)$$

$$V^\# = R K_3 T / (T - K_4) \quad (26b)$$

$$H^\# / V^\# = ((K_2 K_4 + K_1) / K_3 + P) T / (T - K_4) \quad (26c)$$

$$(\partial P / \partial T)_\tau = ((K_2 K_4 + K_1) / K_3 + P) / (T - K_4) \quad (26d)$$

The temperature dependence of these quantities are determined by the expression  $T / (T - K_4)$  or  $(T - K_4)^{-1}$ . The pressure enters the equations as a linear term. The numerical expressions for the three polymers displayed in Table 3 are the following.

$$\text{PMA: } H^\# = R (5200 + 0.52P) T / (T - 111)^2$$

$$V^\# = R 0.52 T / (T - 111)$$

$$H^\# / V^\# = (10000 + P) T / (T - 111)$$

$$(\partial P / \partial T)_\tau = (10000 + P) / (T - 111)$$

$$\text{PPMS } H^\# = R (715 + P) T / (T - 207)^2$$

$$V^\# = R \cdot 0.36 \cdot T / (T - 207)$$

$$H^\# / V^\# = (2000 + P) T / (T - 207)$$

$$(\partial P / \partial T)_\tau = (2000 + P) / (T - 207)$$

$$\text{PEA: } H^\# = R (80 + P) T / (T - 257)^2$$

$$V^\# = R 0.098 T / (T - 257)$$

$$H^\# / V^\# = (816 + P) / (T - 257)$$

$$(\partial P / \partial T)_\tau = (816 + P) / (T - 257)$$

On the basis of the data presented we can calculate the dynamics of PMA as a function of temperature under isochoric conditions and as a function of volume under isothermal conditions by the use of eq. (4). As the ratio  $(\partial \tau / \partial \ln T)_V / (\partial \tau / \partial \ln V)_T$  is temperature and

pressure dependent it was calculated for 20°C and 10<sup>5</sup> Pa corresponding to a relaxation time of approximately 10<sup>-3</sup> s as can be seen from Figure 3. The result is:

$$(\partial\tau/\partial \ln V)_T = 2.2 (\partial\tau/\partial \ln T)_V \quad (27)$$

This means that under the P-T conditions chosen the effect of a relative change of the volume is more than twice as large as the effect of the same relative change of the temperature. This result underlines the importance of the volume in determining the relaxation time of polymers.

By means of eqs. (26, 13, 14) the activation volume and the activation energy under constant pressure and under conditions of constant volume were calculated. Since the temperature enters the equations via the expression  $T/(T-111)$  the calculations were performed for T=50°C where the temperature factor is nearly constant. Physically this is the region where the concept of an activation energy makes more sense than at lower temperatures where the deviations from the Arrhenius equation are extremely large. The results for PMA are shown in Table 4:

TABLE 4. Activation parameters of PMA under isobaric and isochoric conditions.

$V^\#/\text{cm}^3 \text{mol}^{-1}$	$H_p^\#/\text{kJ mol}^{-1}$	$E_v^\#/\text{kJmol}^{-1}$
99.5	100	52

The comparison of the activation energy and enthalpy illustrates that the energy required to activate the molecular motion under conditions of constant volume is by 50% smaller than the energy required to achieve the same effect under conditions of constant pressure. The observed ratio  $E_v^\#/H_p^\# = 0.5$  is in agreement with what is observed in most polymers. This again stresses the important role of volume/free-volume restrictions in determining molecular mobility in bulk polymers.

#### CONCLUSION

The analysis of the temperature and pressure dependence of the relaxation times obtained by photon correlation spectroscopy has proved a useful approach to study the connection between the molecular mobility and the free volume of bulk polymers above the glass transition. The analysis was based upon the different coefficients describing the relative effect of pressure and temperature upon various dynamic quantities. The free volumes calculated from static considerations do not adequately describe the dynamic properties. It is probable that we require different values and hence different definitions of the free volume to describe different dynamic properties of bulk polymers above  $T_g$ .

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