Colloid Polym Sci 274:105–111 (1996)

ORIGINAL CONTRIBUTION

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Stochastic theory for the glassy state

2. The pressure dependence of the glass transition temperature

Received: 10 January 1994
Accepted: 4 August 1995

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Abstract A stochastic theory presented earlier is applied to predict the glass transition temperature T_g for several amorphous polymers, as well as the pressure and cooling rate dependence of T_g and several thermal properties of the formed glass, such as relaxation behavior, thermal expansion and compressibility. In the theory a minimum number of input parameters is needed. All except one are equilibrium parameters, which can be determined independently from both equation of state behavior and bulk mobility data obtained in the equilibrium polymer melt. Assigning the only non-equilibrium parameter a universal value results in a good estimation of T_g, thus basing the prediction of T_g on equilibrium data only. It is realized that a good description of the pressure dependence of mobility is necessary to obtain a good pressure dependence of T_g. The use of a successful empirical equation that incorporates both pressure and temperature dependence of mobility significantly improves the agreement with experimental data on the pressure dependence of T_g, the mobility in the glassy state and the volumetric behavior during cooling and heating. It is also shown that the theory is widely applicable to amorphous polymers.

Key words Stochastic theory – glass transition – pressure dependence – amorphous polymers

Introduction

The non-equilibrium nature of a polymer glass hinders a thorough thermodynamic description of the glass. In particular the properties of a particular glass depend on the thermal history or formation route (i.e., time, temperature and pressure) and hence obviates the incorporation of parameters which characterize this formation history in the proper description of the glassy state. For many practical purposes, e.g., the simulation or prediction of injection molding processes, a prediction of the influence of the afore-mentioned effects is obligatory. With respect to the non-equilibrium state of a polymer, numerous theories have been proposed to describe isothermal relaxation phenomena, in particular at temperatures close to the T_g. For a recent review, the reader is referred to ref [1]. In particular, an important feature of successful theories is the assumption of a *distribution* of relaxation times. The KAHR model [2] is mentioned as a successful example of a phenomenological theory and the stochastic theory by Robertson, Curro and Simha (RCS) [3] as an example of a theory in which independently measured parameters (measured in the melt) are used. The use of independently determined parameters makes the RCS theory a promising starting point for the development of a truly predicting theory. Its potentials have been the reason to use the RCS theory and its assumptions in the development of a theory

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that incorporates the formation route dependence in the description of the properties of the glass. The use of a well defined free volume concept is also very appealing if quantification is pursued.

In part 1 of this series the stochastic theory [4] has been presented to predict for an amorphous polymer the existence of a transition to the glassy state. Furthermore, the proper location of the transition, its pressure and cooling rate dependence, the thermal properties of the ensuing glass and finally also the relaxation phenomena in the glassy state are obtainable from the theory. The theory is based on the assumption of a free volume distribution, and hence a mobility distribution. The free volume is identified with the order parameter h in the Holey Huggins (HH) cell fluid theory [5], being a modification of the SS theory [6]. Analysis of the equilibrium equation of state behavior yields the parameters that allow evaluation of the order parameter. Equilibrium mobility data (e.g., viscosity or dynamic mechanical shift factors) are used to relate free volume to mobility at each temperature and pressure. Finally the absolute time scale is fixed by fitting a single simulation to an experiment [4]. So far, good results have been obtained [4] for poly(vinyl acetate) (PVAC). Within the theory volume aging, the location and pressure and cooling rate dependence of T_g and thermal expansion and compressibility of the glass can be predicted. However, the pressure dependence of T_g is overestimated by the theory. It is shown that the mobility at high pressures is not predicted well by the aforementioned relation between free volume and mobility, based on ambient pressure data only [7]. As will become clear further on, a successful description of both pressure and temperature influence on the mobility of a polymer system is necessary. The well known Williams–Landel–Ferry (WLF) equation [8], which can be derived from the Doolittle equation [9], can describe the temperature dependence of mobility very well. In the theory as originally presented by Williams, Landel and Ferry [8] the free volume is assumed to vary linearly with temperature. This is somewhat in contradiction with the original work of Doolittle [9], where a non-linear temperature dependence was introduced to improve the description of viscosity data. Nevertheless, the WLF equation has proven to be very successful as an empirical equation. Even if another free volume concept is used, the WLF equation is still successful if the pertinent parameters are given other numerical values [3, 4, 10]. The influence of pressure on mobility has also been addressed extensively by Ferry [11] by extending the WLF equation. As in the original form, the dependence of free volume on pressure and temperature is again not defined explicitly. Nevertheless, the resulting phenomenological equations are valuable empirical tools. In our approach the free volume is defined independently (according to the HH theory [5]). Furthermore, we have chosen an empirical equation with a similar form as used in the above mentioned KAHR and RCS theories to incorporate both the temperature and pressure dependence [7]. This method was presented recently [7] using a modified Fulcher–Tammann–Hesse (FTH) equation. This equation differs on a crucial point from the equation used at low pressures and successfully incorporates the pressure dependence.

In this paper we will present results obtained with the use of the modified FTH equation in the stochastic theory. The influence on predictions at elevated pressure is shown for PVAC. To demonstrate the general character of the stochastic theory it is also applied to other amorphous polymers.

Theory

The framework of the stochastic theory is in essence identical to that proposed and used by Robertson, Curro and Simha [3]. Differences, however, exist in the choice of i) the underlying theory to predict the equilibrium thermal properties and ii) the particular empirical functional relationship to describe the polymer liquid mobility. But even more important in the present contribution is the application of the stochastic theory to predict the occurrence of a glass transition region, the equation of state behavior of the resulting glassy state and the dependence of these properties on the formation history.

The stochastic theory has been described in detail elsewhere [4]. A summary of the essentials is presented here. The theory is based on the assumption of a distribution of free volume in the polymer system. Thus the local free volume fluctuates. It was suggested by Robertson [3] that the local free volume is an appropriate parameter to describe the local segmental mobility and thus the rate of rearrangements. Hence the local free volume fluctuations result in local mobility fluctuations. Changes in the system consist of rearrangements of the free volume distribution.

The free volume is identified with the order parameter h in the HH theory [5]. The response of the system to a change in pressure and/or temperature is formed by a change of the actual free volume distribution to the new equilibrium. In the HH theory a partly filled lattice is assumed, with, as a central quantity the fraction occupied lattice sites $y = 1 - h$. The equation of state obeys a practical principle of corresponding states. The scaling parameters p^*, V^* and T^* are derived from simultaneously fitting experimental pVT data to the following equations

$$\frac{\tilde{p}\tilde{V}}{\tilde{T}} = \frac{1}{(1-\eta)} + \frac{2(1-\alpha)y}{(1-\alpha y)\tilde{T}(y\tilde{V})^2}\left[\frac{a}{(y\tilde{V})^2} - b\right] \qquad (1a)$$

and

$$1-\frac{1}{s}+\frac{1}{y}\ln(1-y)-\frac{z}{2y}\ln(1-\alpha y)-\frac{\alpha z}{2}$$
$$=c_s\left[\frac{(3\eta-1+\alpha y)}{(1-\eta)(1-\alpha y)}+\frac{(1-\alpha)y}{2\tilde{T}(1-\alpha y)^2(y\tilde{V})^2}\right.$$
$$\left.\times\left\{2b-\frac{3a}{(y\tilde{V})^2}+4\alpha y\left[\frac{a}{(y\tilde{V})^2}-b\right]\right\}\right], \tag{1b}$$

with $\eta=(2^{-1/6}(1-\alpha)y)/((y\tilde{V})^{1/3}(1-\alpha y))$, $\tilde{p}=p/p^*$, $\tilde{V}=V/V^*$, $\tilde{T}=T/T^*$, $a=1.011$, $b=1.0245$, $\alpha=(2/z)(1-1/s)$, where s is the number of lattice sites occupied by an s-mer, z the lattice coordination number and c_s = degrees of freedom per segment. Now, for a given polymer in the melt, the fraction occupied lattice sites y is fully determined by p and T. The method to determine the scaling parameters from $p-V-T$ data is described elsewhere [5].

The distribution in free volume h can be obtained from fluctuations in the fraction occupied lattice sites. According to fluctuation theory [12] the equilibrium fluctuations $\langle(\delta y_{\mathrm{eq}})^2\rangle$ in y in a domain containing N_s segments can be obtained from the second derivative of the free energy with respect to y

$$\langle(\delta h_{\mathrm{eq}})^2\rangle=\langle(h-\langle h\rangle_{\mathrm{eq}})^2\rangle=kT\left[\left[\frac{\partial^2 A}{\partial y^2}\right]_{\mathrm{N,T,V}}\right]^{-1} \tag{2}$$

with the explicit expression for the Helmholtz free energy A found in ref. [5]. Calculation of the second derivative in Eq. (2) results in

$$\langle(\delta h_{\mathrm{eq}})^2\rangle=\frac{1}{N_s y^2}\left\{1-\frac{1}{s}+\frac{1}{1-y}+\frac{2}{y}\ln(1-y)\right.$$
$$-\frac{\alpha z}{2}\left[1+\frac{1}{(1-\alpha y)}\right]-\frac{z}{y}\ln(1-\alpha y)$$
$$+c_s\left[1+\frac{\eta\{3\alpha y(1-\eta)+\frac{1}{3}(2+\alpha y)^2\}}{(1-\alpha y)^2(1-\eta)^2}\right.$$
$$-\frac{(2+\alpha y)\eta}{(1-\alpha y)(1-\eta)}+\frac{y(1-\alpha)}{(1-\alpha y)^3\,\tilde{T}(y\tilde{V})^2}$$
$$\times\left[\frac{(10\alpha^2y^2-15\alpha y+6)a}{(y\tilde{V})^2}\right.$$
$$\left.\left.\left.-2(4\alpha^2y^2+3\alpha y-1)b\right]\right]\right\}^{-1} \tag{3}$$

Having now expressions for both the average and width of the free volume distribution, the fluctuations can be defined.

Another important ingredient in the theory is the functional dependence of the polymer melt mobility on the parameters in the equilibrium theory. It has been shown by many authors that the mobility at atmospheric pressure can be described successfully based only on the order parameter h [7, 8, 11]. However it has been shown that at elevated pressure an accurate description based on the order parameter only is impossible [7, 35]. Different functional relationships are feasible, some using temperature and pressure as independent variables are described by Ferry [11]. In the context of the stochastic theory the order parameter h plays an important role and a few possible choices starting from this order parameter have been discussed elsewhere [7]. As best option the mobility μ in a region with a given free volume is assumed to depend on free volume and temperature by the empirical relation [7]

$$\mu=\exp\left[-2.303\frac{C_1}{h+C_{\mathrm{T}}T-C_2}\right]. \tag{4}$$

It was shown that this modified FTH equation relating the mobility to the structure parameter h and temperature describes the experimental data accurately. It should be clear that Eq. (4) is purely an empirical relation and no theoretical justification can be given. The choice of temperature as extra parameter seems physically intuitive as the mobility at constant temperature but at higher pressures decreases. A similar equation with pressure as extra variable leads to an increased isothermal mobility upon applying pressure which appears counter intuitive [7].

Equation (4) can be reduced to the Williams–Landel–Ferry (WLF) type of equation for $C_{\mathrm{T}}=0$ [7]. This WLF equation (Eq. (4) with $C_{\mathrm{T}}=0$) has been used previously and has been applied to PVAC [4]. However, for the description of polymer melt mobility data at elevated pressure, the temperature term in Eq. (4) is essential [7]. To determine the mobility parameters, different sets of experimental melt mobility data are fitted simultaneously to Eq. (3) [4]. The mobility is supposed to be reversely proportional to the melt viscosity, as well as to mechanical relaxation times measured in creep and stress relaxation. The free volume distribution, fully determined by Eqs. (1) and (3), can now be recalculated in terms of a mobility distribution by Eq. (4). By adapting the stochastic approach of Robertson et al. [3] to non-isothermal and/or non-isobaric conditions [4] the monitoring of the transient states in a polymer system is feasible. The calculations are based on a stochastic approach [3], in which the actual free volume distribution tends to equalize to the equilibrium distribution. In the case of changing pressure and/or temperature conditions this results in a change in the actual free volume distribution, and thus in macroscopic properties. This allows the simulation of, for example, a cooling experiment. The time scale of the simulations is fixed by fitting a single experiment. The choice of the type of experiment is not critical. One can, for example, use a relaxation experiment, but also the location of T_g at atmospheric pressure. Thus a compensation factor R for differences in global and local mobility is determined, by which the mobility calculated from Eq. (4) has to be scaled [4].

An experiment in which temperature and/or pressure changes in time is simulated by a series of small stepwise temperature and/or pressure changes. After each step the relaxation of the system is monitored as described above. At high temperatures (i.e., high mobility) following a step, the system will have reached the new equilibrium before the next step is made. At low temperatures (i.e., low mobility) the system will increasingly move away from equilibrium due to the relative fast changes of the imposed equilibrium situation, compared to the slow relaxation times of the system.

Results

In Table 1 the parameters p^*, V^* and T^* determined from *equilibrium* equation of state behavior, are listed for PVAC, polystyrene (PS), bisphenol-A polycarbonate (PC) and poly(methyl methacrylate) (PMMA). These are determined from measurements of the specific volume $v(p,T)$. Also the parameters C_1, C_2 and C_T which can be determined independently and which describe the pressure and temperature dependence of the polymer *equilibrium* (melt) mobility as function of free volume and temperature (Eq. (3)) are listed in Table 1 for the different polymers. As an illustration also the parameters determined from atmospheric pressure data (i.e. $C_T = 0$ [7]) are given. The way to determine the mobility parameters is described in ref. [4]. Finally, Table 1 lists the constant N_s, which is set equal to literature data [3] as far as possible, and the constant R, including the experiment from which it is determined. Thus R is the only parameter which is determined by data related to glass transition phenomena.

The predicted influence of pressure on the T_g of several polymers is compared to experimental data [13] in Fig. 1. In both the simulations and the experiments the polymers are cooled isobarically at a constant cooling rate.

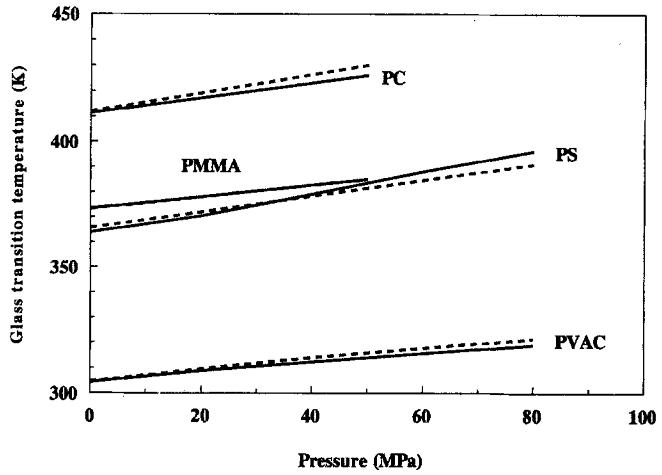

Fig. 1 Pressure dependence of the glass transition temperature T_g for the indicated polymers. Solid line, calculations; dashed line, experimental data (see Table 2 for references). The lines for PMMA completely coincide

Table 1 Parameters for various polymers used in the stochastic theory

	PVAC		PS		PC		PMMA	
p^*(MPa)	895.48		679.65		1000.47		888.17	
V^* (cm^3/g)	0.80627		0.94679		0.79675		0.81985	
T^* (K)	7988.0		9438.0		7928.5		8531.9	
ref. pVT data	[13]		[14]		[15]		[16]	
	$p = 0^a$	$p \geq 0^a$	$p = 0^a$	$p \geq 0^a$	$p = 0^a$	$p \geq 0^a$	$p = 0^a$	$p \geq 0^a$
C_2 (−)	0.0581	0.201	0.0518	0.140	0.0797	0.183	0.0646	0.211
C_1 (−)	0.392	0.785	0.156	0.315	0.358	0.558	0.309	0.561
$10^4 C_T$ (K^{-1})	0	5.52	0	2.70	0	2.93	0	4.25
R (s^{-1})	10^8	10^8	3.10^8	10^8	10^{10}	3.10^7	3.10^{11}	2.10^{13}
ref. mobility data	[17–19]	[20, 21]	[22–24]	[24, 25]	[24, 26, 27]	[24]	[22, 24]	[24, 28]
experiment used to determine R	temp jump 40 → 37.5 °C [29]		temp jump 91.8 → 90.7 °C [30]		T_g (0.1 MPa) [31]		T_g (0.1 MPa) [31]	
N_s (−)	26		50		26		26	

[a] $p = 0$ refers to the situation at atmospheric pressure, including only temperature dependence; $p \geq 0$ refers to both pressure and temperature dependence

The temperature of intercept of the tangents at the volume–temperature curves in melt and glass is taken as T_g. The mobility in the calculations is described with Eq. (4) with $C_T \neq 0$. It is clear that by including the pressure dependence of mobility the predictions of T_g at elevated pressures are improved considerably and coincidence with experimental data is good. With $C_T = 0$, i.e., the WLF type of description, higher values were obtained [4]. It should be noted that all mobility data used to obtain parameters C_1, C_2 and C_T in Eq. (4) are obtained from the polymer melt, i.e., only equilibrium data have been used. Furthermore, once determined, these parameters are not adjusted in further calculations.

The influence of pressure on the specific volume of a glass is shown in Fig. 2a. The simulated formation conditions are chosen to mimic the experimental formation conditions, pressure and cooling rate. The dependence of specific volume on temperature under isobaric cooling is depicted. The deviations in the glass can be largely explained by the behavior of the order parameter h during the glass formation, see Fig. 2b. In this figure the order parameter h is shown which forms the basis of the volume data presented in Fig. 2a by the use of Eq. (1a). It can be seen that the simulated glass freezes completely, i.e., the order parameter becomes constant at temperatures below T_g. From this it can be concluded that the change in specific volume in the glassy state is mainly due to changes in the lattice cell volume. This is in contrast with results obtained by Simha by extracting values for the order parameter from experimental specific volume data for a PVAC glass [33]. From this approach it was concluded that changes in h had to be assumed to describe the equation of state behavior of the glass. These findings are consistent with the too low a thermal expansion coefficient in the simulated glasses, see Table 2. From Fig. 2b it is also clear that in the simulations T_g is definitely not an iso-free-volume transition.

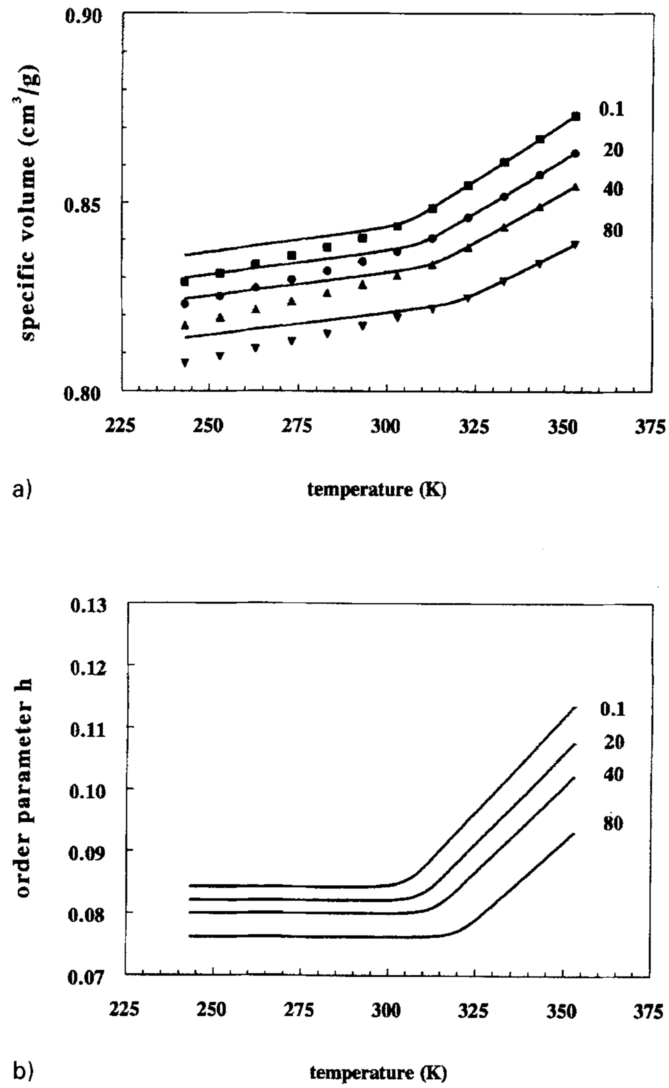

Fig. 2 Specific volume (a) and order parameter (b) versus temperature for the indicated pressures in MPa for PVAC during cooling at 5 K/h. Symbols, experimental data [13]; solid lines, calculations

Table 2 Comparison of predicted and experimental data for various polymers

	PVAC		PS		PC		PMMA	
	calc.	exper.	calc.	exper.	calc.	exper.	calc.	exper.
Glass transition temperature T_g (at 1 bar) (K)	304	305 [13]	364	366 [31]	412^a		373^a	
Pressure dependence of T_g dT_g/dp (K/MPa)	0.19	0.21 [13]	0.28	0.32 [14]	0.28	0.36^b [15]	0.22	0.24 [16]
Cooling rate dependence of T_g $dT_g/d(\log q)$ (K)	3.8	2.9 [32]	1.8	2.9 [31]	3.0	2.5 [31]	1.4	3.3 [31]
Thermal expansion α_g ($10^{-4}K^{-1}$)	1.58	2.86 [13]	1.47	1.97 [14]	1.56	2.55 [31]	1.51	1.93 [16]
Isothermal compressibility β_g ($10^{-4}K^{-1}$)	2.64	2.54 [13]	3.24	2.62 [14]	2.62	2.36 [15]	2.70	2.72 [16]

[a] The experimental value [31] is used to determine the parameter R.
[b] Interpolation between 0.1 and 180 MPa [15]

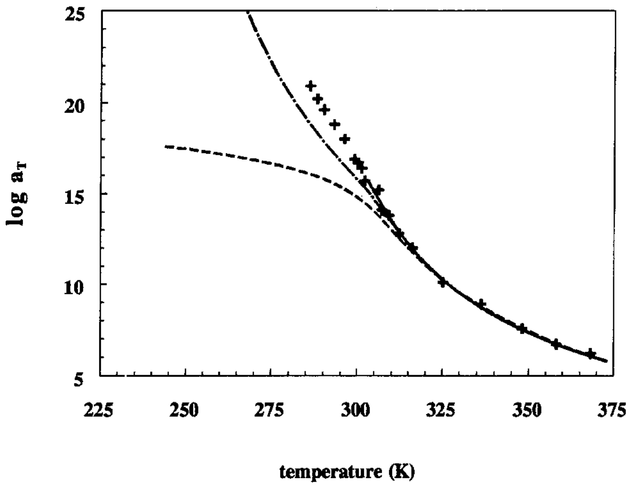

Fig. 3 Shift factors in the equilibrium and glassy state at atmospheric pressure for PVAC. Calculated with $C_T \neq 0$ (dash dotted line); with $C_T = 0$ (dashed line); equilibrium (solid line); experimental stress relaxation data [17] (symbols)

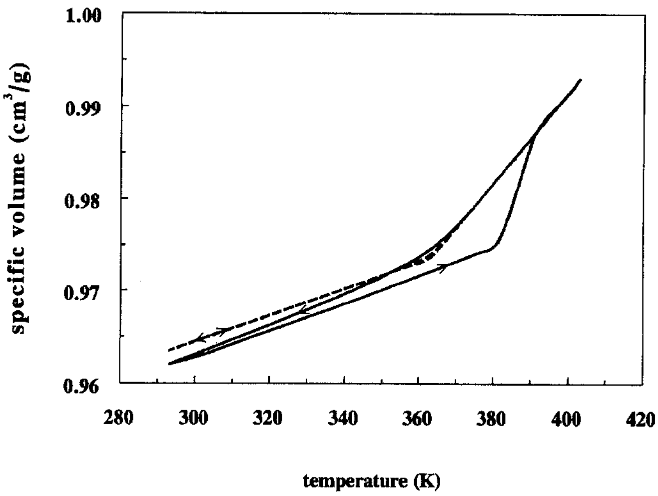

Fig. 4 Calculated specific volume versus temperature for PS during cooling and subsequent heating, both at 10 K/h. Calculated with $C_T \neq 0$ (dashed line); with $C_T = 0$ (solid lines)

To summarize the generality of the theory predictions and experimental data are compared in Table 2 for PVAC, PS, PC and PMMA.

It is now interesting to compare the predicted mobility in a simulated glass, calculated from the predicted value of h, using Eq. (4), with experimental data. By these simulations the merits of the model become clear. The predicted mobility, as defined by Eq. (4) for both cases $C_T = 0$ and $C_T \neq 0$ for a PVAC glass, is plotted in Fig. 3 together with experimental shift factors based on stress relaxation measured for a PVAC glass [17]. The use of the modified FTH equation (Eq. (4) with $C_T \neq 0$) instead of the WLF type (Eq. (4) with $C_T = 0$, i.e., Eq. (18) in ref. [4]) improves the agreement with experimental data. The use of atmospheric pressure melt mobility data results in significantly too low shift factors (too high mobility) in the glass. The use of mobility melt data at elevated pressure explicitly introduces the influence of temperature, resulting in close agreement with experiments. This is also illustrated in Fig. 4, where a polymer (PS) is cooled through its T_g, and subsequently heated at the same rate. In the case $C_T = 0$ the mobility in the glass is too high, resulting in distinct relaxation. By the time the polymer is heated to T_g relaxation times have increased so far that a large overshoot results, which is not found experimentally. This artefact is absent in the case $C_T \neq 0$ as can be seen from Fig. 4. By these examples it is demonstrated clearly that the extension of mobility description to elevated pressures enables the prediction of essential features of the glass.

Conclusions

The predicting power of the presented stochastic theory for the glass transition at elevated pressures is obtained by incorporation of the pressure dependence of mobility in polymer melts (characterized by a shift factor), cast in a modified FTH empirical relation. It is shown that the theory is applicable to various polymers, with close agreement with experiments, the more so if one considers the limited amount of input data. The relative insensitivity of the predicted T_g for R (e.g., T_g changes 3 K if R changes one order of magnitude for PVAC [4] and 1.5 K for PS [34]) offers in principle the possibility to estimate $R = 10^{10}$, making the use of experimental data to determine R almost redundant. For the four polymers presented, this estimation for R would have resulted in predictions for T_g at most 7 K apart from the experimental value. For these predictions then *only equilibrium data* (*pVT* and mobility) have been used.

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