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Viscoelastic properties of solutions of polystyrene melts and carbon dioxide: Analysis of a transient shear rheology approach

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Abstract

In this work, the viscoelastic, thermal and diffusion properties of solutions of polystyrene melts and carbon dioxide (CO_2) were analyzed using plate-plate rheometry in the transient mode. The objective of this study was to evaluate a transient shear rheology approach for high viscosity polymer melts, to verify superposition principles for polystyrene/CO_2 solutions and to measure the glass transition temperature as a function of pressure and CO_2 concentration. Two different procedures of saturating polystyrene with carbon dioxide were applied, i.e. loading with the blowing agent below the glass transition temperature of polystyrene and at the measurement temperature. Stress-growth experiments in shear were performed in order to measure the transient viscosity of polystyrene/CO_2 solutions in the linear regime. A shift of the transient viscosity data to a mastercurve was applied in order to determine the shift factor of the viscosity and the average relaxation time. Our data indicate that the steady-state viscosity and the average relaxation time are proportional to the temperature-pressure-concentration shift factor $a_{T,p,c}$ within experimental scatter, and consequently a time-temperature-pressure-concentration superposition principle holds for polystyrene/CO_2 solutions. Whereas the viscosity of polystyrene strongly depends on the applied temperature and pressure, the elastic equilibrium compliance depicts only a weak dependence on temperature and pressure.

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Key words: Polystyrene/CO_2 solutions; superposition principles; transient shear rheology; diffusion.

I. INTRODUCTION

The rising technological relevance of polymer foams requires a profound understanding of processing and end-use properties of cellular polymers. Reduction of material cost and weight as well as good thermal insulation lead to an increasing interest in these materials. In foam extrusion a physical blowing agent (e.g., carbon dioxide or nitrogen) is homogeneously dissolved in the polymer melt. Optimization of processing parameters such as extrusion temperature, pressure and concentration of the blowing agent is highly relevant for an efficient preparation of polymer foams. In this context, the rheological and transport properties of solutions of polymer melts and physical blowing agents have attracted much attention. Accurate measurement techniques and determination of shift factors are the topics of several works [Han and Ma (1983a,b), Gerhardt et al. (1997, 1998), Royer et al. (2000, 2001, 2002), Kwag et al. (1999), Lee et al. (1999), Areerat et al. (2002), Park and Dealy (2006)]. In most experimental studies (e.g., in measurements using capillary rheometry), the authors focused on the stationary viscosity of the melt as a function of the concentration of the blowing agent. In contrast to the stationary viscosity, the time-dependence of the viscosity was studied to a much lesser extent, although investigations of the effect of a blowing agent on the transient rheological properties are of high relevance for foam extrusion. For example, strain-hardening of polymer melts in melt elongation is influenced by the ratio of the applied elongational rate to the average relaxation time. In addition to the rheological properties precise values of the diffusion coefficient and the solubility of blowing agents in polymer melts are of interest [Sato et al. (1999, 2001), Kundra et al. (2011)].

A large pressure is generally applied in order to dissolve the blowing agent in the polymer melt. Therefore several studies were devoted to the effect of pressure on the viscosity of molten polymers [Semjonow (1962), Hellwege et al. (1967), Christmann and Knappe (1976), Ramsteiner (1976), Goubert et al. (2001), Laun (2003, 2004), Park et al. (2006), Cardinaels et al. (2007), Park et al. (2008), Park and Dealy (2008), Aho and Syrjälä (2010), Kulisiewicz and Delgado (2010)]. These works generally confirmed the validity of the Barus equation at low pressures. Furthermore, it was shown that the pressure coefficient of polystyrene does not depend on the degree of branching and not significantly on the tacticity, either [Pantani and Sorrentino (2005)]. Most previous works on the rheology of solutions of a polymer melt and a blowing agent were devoted to shear flows [Royer et al. (2001), Choudhary et al. (2005), Park et al. (2006, 2008)]. In the work of Royer et al. (2000) the temperature dependence of the concentration shift

factor was discussed. The reduction of viscosity by the addition of a blowing agent is more pronounced at lower temperatures. Wingert et al. (2009) studied the steady state shear rheology of solutions of polystyrene and supercritical carbon dioxide. Recently, the extensional viscosity of polymer/blowing agent solutions was measured [Ladin et al. (2001), Sedlacek et al. (2004), Wang et al. (2008, 2010)]. The subject of these studies was the determination of the reduction of the steady-state viscosity through the addition of a blowing agent and the resulting superposition principles. These works revealed that flow curves (stationary viscosity η versus shear rate $\dot{\gamma}$) which were measured at different concentrations can be shifted to a mastercurve. Scaling concepts founded on thermodynamic principles (e.g., the equation of Chow (1980)) were established and the shift factors $a_{T,p,c}$ were calculated. However, flow curve measurements do not take into account the time-dependence of the viscosity (which is intimately associated with the distribution of the molar mass of the polymer) and therefore only give a partial insight on the viscoelastic properties of the polymer melt. Whereas for pristine polymer melts the shift factors determined by flow curve measurements and by measurements in the transient mode are identical, this equivalence needs to be verified for solutions of polymer melts and a blowing agent. Furthermore, experiments in the transient or in the dynamic mode are suited in order to determine the elastic properties of polymer melts, i.e. the elastic equilibrium compliance J_e^0.

The transient rheological properties of polymer melts at a high pressure can be measured using various rheometers. A sliding gap rheometer was developed by Koran and Dealy (1999) in order to measure the effect of pressure and blowing agent on the rheological properties. This rheometer was applied by Park and Dealy (2006) in order to determine the shift factor for solutions of polyethylene and supercritical fluids. Viscosity measurements of polystyrene/carbon dioxide solutions using a Couette geometry were performed by Wingert et al. (2009). Generally, a plate-plate or a cone-plate geometry is favoured for rotational rheometers, in particular for high viscosity polymer melts such as amorphous polymers in the vicinity of the glass transition T_g or filled polymers. The temperature range in the vicinity of T_g is of particular importance for foaming of polymers. Recently, a rotational rheometer was equipped with a pressure cell in order to determine the pressure dependence of the viscosity using a plate-plate geometry [Krebs and Wünsch (2010)]. Whereas these rheometers in principal allow one to perform measurements in the transient or in the dynamic mode, only a very few data in these modes have been published yet, see for instance the work of Koran and Dealy (1999). In this work, we apply the methods of rotational rheometry (parallel plates geometry) in order to

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investigate the viscoelastic properties of solutions of polystyrene and carbon dioxide. We focus on the effect of carbon dioxide pressure in the range from 1 bar to 50 bar. The objective of our study is to elucidate the time-dependent behaviour of solutions of polystyrene and carbon dioxide and to evaluate this procedure. Saturation of the polymer melt with the blowing agent is achieved via diffusion either in an autoclave (preloading below the glass transition temperature) or in the rheometer at measurement temperature. These two methods of saturation of polystyrene with carbon dioxide are compared.

In the work of Ouchi et al. (2008) rotational rheometry was applied for experiments in the dynamic mode (linear viscoelastic shear oscillations). The complex modulus G^* of linear low density polyethylene (LDPE)/CO_2 solutions was determined and time-temperature-pressure superposition was verified for this system at two temperature and two pressure values. In the dynamic mode, the ball bearing creates a drawback, namely a non-negligible residual torque which becomes highly relevant in the low frequency range corresponding to low stresses. In this work, we circumvent this drawback by performing experiments in the transient mode (start-up experiments with a constant shear rate) where the residual torque plays a minor role at large times because of the larger torque.

The paper is organized as follows: First, diffusion in a polymer sample for rheological measurements is discussed (Section II). In Section III the experimental set-up for our investigations is described. The results of our start-up experiments are presented in Section IV. Two different procedures of saturation of the polymer with the blowing agent are compared. The data allow one to determine the shift factors for concentration and pressure as well as the elastic equilibrium compliance. The temperature shift of the glass transition of polystyrene with pressure and concentration as determined by rheological measurements and by differential scanning calorimetry are compared. We also apply the rheological measurements in order to determine the diffusion coefficient in the polymer melt. A summary of results concludes our work.

II.   DIFFUSION OF CO_2 IN A POLYSTYRENE MELT

One method which is applied in this work consists of saturating a polymer melt with the blowing agent by placing the sample in the atmosphere under a certain gas pressure. In order to estimate the saturation time as a function of the geometry of the sample and to evaluate the experimental accuracy, we consider the time-dependent diffusion of a blowing agent in a cylindrical sample of a polymer melt. The radius of the cylindrical sample is denoted by R, and h is its thickness. The sample is placed between the two plates of

a plate-plate geometry of a pressure cell, see Fig. 1. The pressure cell is filled with the blowing agent (for example carbon dioxide) at a certain pressure p which is constant with time. Before the experiment, we assume that the polymer is not loaded with the blowing agent at all and that the concentration $c(r,t)$ of the blowing agent in the sample is zero ($c(r, t = 0) = 0$). Then the molecules of the blowing agent start to diffuse in the sample until a complete saturation of the polymer sample is achieved. Because of the cylindrical symmetry of the sample which is covered by the two plates, we assume that diffusion only takes place in the radial direction.

The concentration $c(r,t)$ of carbon dioxide (CO_2) into the polystyrene sample increases because of diffusion of CO_2 from the surrounding pressure atmosphere. The time-dependent concentration $c(r,t)$ follows from the diffusion equation in cylindrical coordinates

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} \right) \tag{1}$$

where D denotes the coefficient of diffusion. Because of symmetry, the concentration $c(r,t)$ does not depend on φ and z and thus has been dropped in Eq. (1). A convection term $-\vec{v} \cdot \vec{\nabla} c(r,t)$ on the rhs of Eq. (1) is not taken into account, since the velocity vector $\vec{v}$ in shear is perpendicular to the gradient of concentration which yields $\vec{v} \cdot \vec{\nabla} c(r,t) = 0$. The boundary conditions are $\partial c(r = 0, t)/\partial r = 0$ for $r = 0$ and $c(r = R, t) = p/k_p = c_0$ for $r = R$ with Henry's constant k_p. Then the solution of the diffusion equation for the initial condition $c = 0$ is given by [Carslaw and Jaeger (1940)]

$$c(r,t) = c_0 \left[1 - 2 \sum_{n=1}^{\infty} \frac{J_0\left(a_n r/R\right)}{a_n J_1(a_n)} \exp\left(-\frac{a_n^2 D t}{R^2} \right) \right] \tag{2}$$

where $J_0(x)$ and $J_1(x)$ denote the Bessel function of order 0 and 1, respectively. The number a_n is the nth positive zero of the Bessel function of the first kind $J_0(x)$.

The diffusion coefficient of carbon dioxide in polystyrene at $170\,^{\circ}\mathrm{C}$ is in the order of $D = 5 \times 10^{-10}\,\mathrm{m^2/s}$ [Sato et al. (1999, 2001)]. The evolution of concentration $c(r,t)$ with time is plotted in Fig. 2(a) for the parameters $D = 5 \times 10^{-10}\,\mathrm{m^2/s}$, $R = 8 \times 10^{-3}\,\mathrm{m}$ and $c_0 = 0.04$. The concentration $c(r,t)$ increases with r and t and attains its maximum at $r = R$, i.e. at the outer rim of the sample. If the radius R of the cylindrical sample is $R = 8 \times 10^{-3}\,\mathrm{m}$, an almost complete saturation of the sample is achieved at time $t \approx 43200\,\mathrm{s} = 12\,\mathrm{h}$. The average concentration $\langle c \rangle$ of the blowing agent in the polymer melt follows from integration:

$$\langle c \rangle = \frac{2}{R_2^2 - R_1^2} \int_{R_1}^{R_2} c(r,t) r \, dr \tag{3}$$

with $R_1 = 0$ and $R_2 = R$. Figure 2(b) presents the dependence of $\langle c \rangle$ on time for $D = 5 \times 10^{-10}\,\mathrm{m^2/s}$, $R = 8 \times 10^{-3}\,\mathrm{m}$ and $c_0 = 0.04$. The value of $\langle c \rangle$ rapidly increases in the beginning and continues to grow until an almost stationary value is attained at time $t \approx 43200\,\mathrm{s}$.

The zero shear rate viscosity η_0 of a solution of a polymer melt and a blowing agent decreases with $\langle c \rangle$. The concentration dependence of the viscosity was experimentally determined by Wingert et al. (2009) and is given for low concentrations by $\eta_0(\langle c \rangle) = a_c \eta_0(\langle c \rangle = 0)$ with the shift factor $a_c \approx \exp\left(-b_c \langle c \rangle\right)$ and the parameter b_c. In our experiments, the zero shear rate viscosity η_0 also depends on the radial position r for $0 < t < \infty$ because of the spatially non-uniform concentration $c(r,t)$. In order to give an approximation for the average viscosity $\langle \eta_0 \rangle$, this effect is neglected and we simply set $\langle \eta_0 \rangle = \eta_0(\langle c \rangle)$. At $T = 175\,^\circ\mathrm{C}$ the value of b_c for polystyrene/CO_2 solutions approximately is $b_c \approx 70$ [Kwag et al. (1999)]. Inserting these a_c and b_c values yields a sigmoidal function for the stationary viscosity $\langle \eta_0 \rangle = \eta_0(\langle c \rangle)$ as a function of time in a double-logarithmic scale, see Fig. 2(c). The viscosity steeply decreases in the interval between 100 and 40000 s and attains a steady-state value around 43200 s. The data clearly indicate that an analysis of saturation time is necessary in order to evaluate the experimental accuracy and to minimize polymer degradation.

The diffusion coefficient D and the radius R of the sample strongly influence the time of saturation of the sample. The solution Eq. (2) allows one to calculate the time which is necessary for saturation. The results of this calculation are presented in Fig. 3. The figure depicts the time (in units of L_c^2/D with the characteristic length $L_c = R$) which is necessary until $x\%$ of the blowing agent is dissolved in the polymer sample. The time of saturation is proportional to the inverse $1/D$ of the diffusion coefficient D and proportional to the square of the radius R of the sample. Therefore a smaller sample size reduces the time of saturation, but on the contrary **increases** the minimum stress which can be measured in the rheological experiments. The time t_{90} which is necessary in order to achieve a saturation of 90% is $t_{90} = 0.31792 R^2/D$. For $D = 5 \times 10^{-10}\,\mathrm{m^2/s}$ and $R = 8 \times 10^{-3}\,\mathrm{m}$ we find $t_{90} = 40694\,\mathrm{s}$. On the contrary, in case of pure one-dimensional diffusion along a simple rectangular geometry with an edge of size $2L_c$ one has $c(r,t) = c_0 - 4c_0 \sum_{n=1,n\,\mathrm{odd}}^{\infty} (n\pi)^{-1} \exp\left[-n^2\pi^2 Dt/(4L_c^2)\right] \sin\left[n\pi x/(2L_c)\right]$ and $t_{90} = 0.80944 L_c^2/D$, see Park et al. (2008) and Handge and Schmidheiny (2007).

For the sake of completeness we also mention the results for a Couette geometry where the inner cylinder consists of a porous material accelerating saturation [Wingert et al. (2009)]. The time of saturation can be calculated using the solution $c(r,t)$ for diffusion

in the gap of two concentric cylinders with the boundary conditions $c(R_1, t) = c_0$ and $\partial c(R_2, t)/\partial r = 0$. The solution of the diffusion equation in cylindrical coordinates for the initial condition $c(r, 0) = 0$ and an infinitely long cylinder is [Kneschke (1961)]

$$c(r, t) = c_0 + \pi c_0 \sum_{n=1}^{\infty} \frac{Y_1^2(\kappa b_n)}{Y_0^2(b_n) - Y_1^2(\kappa b_n)} \times \tag{4}$$
$$[Y_0(b_n)J_0(b_n r/R_1) - J_0(b_n)Y_0(b_n r/R_1)] \exp\left(-b_n^2 Dt/R_1^2\right)$$

with $\kappa = R_2/R_1$. In Eq. (4) $Y_0(x)$ and $Y_1(x)$ denote the Bessel function of the second kind (also called Neumann function) of order 0 and 1, respectively. The values b_n are the solutions of the equation $J_0(b_n)/Y_0(b_n) = J_1(\kappa b_n)/Y_1(\kappa b_n)$. Using Eqs. (3) and (4), the time t_x for partial saturation can be calculated, see Fig. 3. Figure 3 presents the value t_x in units of L_c^2/D and reveals that in this presentation the Couette geometry with $L_c = R_1$ and $\kappa = 1.1$ leads to the shortest saturation times because of the small gap. However, it has to be taken into account that the size of the sample strongly influences the time for saturation of the polymer sample with the blowing agent.

III. EXPERIMENTAL

A. Material

A commercial polystyrene (PS 158K) was supplied by BASF SE (Ludwigshafen, Germany) and used for the investigations of this study (lot no. 96707416K0). Polystyrene PS 158K is a polydisperse polymer with $M_w/M_n \approx 2.15$, see Table I. The pellets of PS 158K were dried in vacuum at $50\,^\circ$C for several hours. Cylindrical samples for rheological investigations were prepared by compression moulding pellets of PS 158K at $180\,^\circ$C for 8 min. The thickness of the samples was 1 mm, and the radius was 4 and 7 mm, respectively. Before the start of the experiments, the samples were dried again for at least 10 hours in vacuum.

B. Differential Scanning Calorimetry at High Pressure

The glass transition of pristine polystyrene and polystyrene loaded with carbon dioxide was studied using differential scanning calorimetry (DSC) at high pressure. A DSC device DSC27HP (Mettler-Toledo, Gießen, Germany) was used. The measurements were performed either in a nitrogen or in a carbon dioxide atmosphere. The mass of the sample was approximately 8 mg. The heating rate was 10 K/min and the temperature interval was $25\,^\circ$C to $180\,^\circ$C. In the first heating and the cooling cycle the pressure was

1 bar. The first heating and the cooling cycle were intended to eliminate the thermal history of the sample. Then the sample was heated up to a so-called equilibration temperature of 50 °C or 70 °C, respectively. At this temperature an interval of 10 min was chosen for thermal equilibration. Then the pressure was increased up to the measurement pressure. When the DSC chamber was filled with nitrogen, the sample was heated up to 180 °C with 10 K/min immediately after the increase of pressure. In case of carbon dioxide as pressurizing medium, an additional period of 30 min was chosen in order to guarantee saturation of the sample with carbon dioxide. The saturation time t_{sat} approximately is $t_{\mathrm{sat}} = h^2/D = 450\,\mathrm{s}$ with the thickness h of the sample $h = 300\,\mu\mathrm{m}$ and $D = 2 \times 10^{-10}\,\mathrm{m}^2/\mathrm{s}$. After approximately 2 minutes after the second heating ramp has been started, the concentration of carbon dioxide in the polystyrene sample corresponds to the saturation concentration at the actual temperature. This effect was checked by comparing the glass transition temperature as a function of the so-called equilibration temperature.

C.   Rheological Measurements

In order to determine the viscoelastic properties of PS 158K at normal pressure ($p = 1\,\mathrm{bar}$), a rotational rheometer RDA III (Rheometric Scientific, Piscataway (NJ), USA) was used. The measurements were performed at different temperatures between 120 °C and 210 °C. First strain sweeps were carried out in order to determine the linear viscoelastic regime. Then frequency sweeps at different temperatures were performed with an amplitude of strain $\gamma_0 = 4\%$. The data of the storage and the loss modulus were shifted to a mastercurve using the software LLSHIFT, and the relaxation time spectrum was calculated using the software NLREG [Freiburg Materials Research Center (2001)], see Honerkamp and Weese (1993a,b) for details of the software. Furthermore experiments with a constant shear rate $\dot{\gamma}_0$ (so-called start-up or stress-growth experiments) were carried out using the rotational rheometer RDA III at various temperatures. In both dynamic and stress growth experiments, a sufficient long time interval after loading of the sample was chosen in order to guarantee thermal equilibrium and relaxation of normal force.

Experiments at high pressure were performed using the rotational rheometer MCR 301 (Anton Paar, Graz, Austria). A scheme of the experimental set-up is presented in Fig. 4. This rheometer was equipped with a temperature control unit and a pressure cell which withstands a maximum pressure of 400 bar up to a temperature of 200 °C. A cylindrical plate is fixed to the shaft of the rotational axis. Furthermore, a cylindrical

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magnet is mounted on the axis, and the deformation and torque signals are transferred via a magnetic coupling to the transducer of the rheometer. In order to load the pressure cell, the sealed chamber was connected to a gas container with carbon dioxide. The use of a gas container limited the maximum gas pressure to 50 bar. The pressure cell allows one to carry out shear experiments in different modes with a plate-plate geometry and a plate diameter of 20 mm. In our experiments, first the sample was inserted in the rheometer at measurement temperature. Then the upper part of the pressure cell with the upper plate was placed in the rheometer. Since this construction does not allow one to control the gap setting, the thickness of the solidified sample was measured after the experiment and was taken as gap distance h. The volume reduction because of cooling to room temperature is in the order of 7% leading to a reduction of h of 2.2% (values for $T = 170\,°C$) which is negligible.

If Ω denotes the angular velocity of the plate, then the shear rate $\dot{\gamma}_0$ is given by

$$\dot{\gamma}_0 = \Omega R / h \tag{5}$$

with the thickness h of the sample and its radius R. The radius of the sample is determined as follows. Before the experiment the mass m of the sample is measured. Furthermore the relation $m/\rho_m = \pi R^2 h$ holds where ρ_m is the density of the sample at measurement temperature, see Table I. Consequently, we have $R = \sqrt{m/(\pi \rho_m h)}$ and thus

$$\dot{\gamma}_0 = \Omega \sqrt{m/(\pi \rho_m h^3)}. \tag{6}$$

The transient shear stress $\tau(t)$ for a plate-plate geometry follows from $\tau = 2M/(\pi R^3)$ with the measured torque $M(t)$. Then the transient shear viscosity $\eta(t) = \tau(t)/\dot{\gamma}_0$ is given by

$$\eta(t) = 2\pi \rho_m^2 h^3 M / (\Omega m^2). \tag{7}$$

If Ω_{rot} is the number of revolutions per time, we have $\Omega = 2\pi \Omega_{\mathrm{rot}}$ and therefore the relation $\eta(t) = \rho_m^2 h^3 M / (\Omega_{\mathrm{rot}} m^2)$ holds. At large times and low shear rates, the viscosity $\eta(t)$ attains a stationary value which equals the zero shear rate viscosity: $\lim_{t \to \infty} \eta(t) = \eta_0$.

Equation (7) implies that the measured value of the viscosity $\eta(t)$ depends on the density ρ_m at measurement temperature. Because of swelling, the density ρ_m is also influenced by the carbon dioxide concentration [Hilic et al. (2001), Nikitin et al. (2003)]. A volume change of 5% leads to a reduction of viscosity of approx. 10%.

In contrast to conventional rheometry at an ambient pressure of 1 bar, rheological experiments at higher pressures require a considerably larger effort. A main source of

error is a non-constant gap during the experiments because of a squeeze flow caused by the upper plate. Therefore care was taken by correctly tightening the upper part of the pressure cell.

In this work, two different procedures were applied in order to saturate the sample of polystyrene with the blowing agent, namely below (method A) and above (method B) the glass transition temperature of polystyrene. Both methods are described in a flow chart, see Fig. 5. These two methods were compared regarding their suitability for our purposes.

In the first method (A), an autoclave was applied in order to load the polystyrene sample. The cylindrical sample was preloaded with the blowing agent during six days at a temperature of $60\,°\mathrm{C}$ and a pressure of 10 bar. Then the sample was removed from the autoclave and rapidly inserted into the rheometer. The pressure was increased up to the test pressure, and then the temperature was increased. Thermal equilibration was verified by performing repeatedly stress-growth experiments and was achieved after the stationary viscosity (being measured in these tests) was constant. Method A is intended to be used for polymer melts with a very high viscosity (i.e. in the vicinity of the glass transition). Because of the very long relaxation times near T_g, experiments in the transient mode can be only performed after a drastic viscosity reduction which has been caused by the blowing agent.

Method B consisted of the following steps: The cylindrical sample was placed into the plate-plate geometry at test temperature. After thermal equilibration (i.e. after a constant value of the stationary viscosity), the pressure was increased up to the measurement pressure p. Then the sequence of stress-growth experiments was performed. This method is suited for polymer melts with a lower viscosity. Note that for both methods the sample mostly is in the quiescent state ($\dot{\gamma}_0 = 0\,\mathrm{s}^{-1}$) during the complete experiment, since shear is only applied in relative short intervals with respect to the total duration of the experiment.

The solubility of the blowing agent in the polymer sample at equilibrium strongly depends on the experimental parameters temperature and pressure. In this work, the solubility is calculated using the data of solubility measurements. In order to determine the concentration of the blowing agent in the polymer sample, data of solubility measurements of Sato et al. (2001) are used. The concentration c_0 of the blowing agent in the polymer sample at saturation is given by Henry's law. At given values of temperature T and pressure p the concentration is $c_0 = p/k_p$ where k_p denotes Henry's constant. Sato et al. (2001) experimentally determined the dependence of k_p on temperature which is given by the relation

$$\ln k_p = -6.400 - 2.537 \left(T_c/T\right)^2 \tag{8}$$

with the critical temperature $T_c = 304.12\,\mathrm{K}$ [Poling et al. (2001)]. In Eq. (8), the constant k_p is given in units of $\mathrm{kg\,MPa/cm^3(STP)}$, and the density of carbon dioxide at standard temperature and pressure (STP) is $1.977\,\mathrm{kg/m^3}$. In this work, Eq. (8) and Henry's law $c_0 = p/k_p$ are used for calculating the concentration of carbon dioxide in polystyrene at measurement temperature, see Fig. 6. The value of c_0 decreases with temperature and increases linearly with pressure in the presented range of parameters.

IV. RESULTS AND DISCUSSION

The complex modulus $G^* = G' + iG''$ of neat polystyrene PS 158K at $p = 1$ bar is plotted in Fig. 7(a). The data measured at different temperatures were shifted to a mastercurve at reference temperature $T_{\mathrm{ref}} = 170\,^\circ\mathrm{C}$. The different regimes (terminal zone, rubbery plateau and glass transition) can be clearly identified. Using the nonlinear regularization routine NLREG, the relaxation time spectrum $H(\tau)$ can be determined, see Fig. 7(b). The spectrum reveals that polystyrene PS 158K is a polydisperse polymer. The average relaxation time $\langle \tau \rangle$ can be estimated using the relation $\langle \tau \rangle = J_e^0 \eta_0$ where J_e^0 denotes the equilibrium compliance and η_0 the zero shear rate viscosity. At $T_{\mathrm{ref}} = 170\,^\circ\mathrm{C}$ the average relaxation time is approximately $\langle \tau \rangle = 31\,\mathrm{s}$. The average relaxation time depends on temperature and increases up to $\langle \tau \rangle = 487\,\mathrm{s}$ for the test temperature of $T_{\mathrm{ref}} = 150\,^\circ\mathrm{C}$, see Table II. Table II also indicates that the elastic equilibrium compliance J_e^0 only moderately depends on temperature, see also Resch et al. (2009). The horizontal and vertical shift factors a_T and b_T which will be used in the analysis are listed in Table III.

In order to check the accuracy of the pressure cell, in particular for time-dependent measurements, the transient shear viscosities using a conventional rheometer and a rheometer with the pressure cell were compared. The measurement temperature was $170\,^\circ\mathrm{C}$. The results of the measurements with the two different rheometers are compared in Fig. 8 for two different shear rates. The results of the apparatus with the pressure cell are in good agreement with the data of the conventional rheometer. In particular, the time-dependence of the viscosity was accurately measured. The transient viscosity of polystyrene increases with time and achieves a stationary value around $40\,\mathrm{s}$ for $T_{\mathrm{ref}} = 170\,^\circ\mathrm{C}$. Lower measurement temperatures yield a longer time until a steady-state value of the viscosity is achieved.

Figure 9(a) presents the effect of pressure on the transient viscosity $\eta(t)$ of polystyrene. These experiments were carried out using helium which is nearly insoluble in polystyrene. The Barus equation is often applied in order to describe the dependence of the shift factor

a_p on pressure p:

$$a_p = \exp\left[\beta(p - p_{\text{ref}})\right] \tag{9}$$

with the pressure coefficient $\beta = (1/\eta_0)d\eta_0/dp$ and the reference pressure $p_{\text{ref}} = 1$ bar. The pressure coefficient β for polystyrene is in the order of $\beta = 2 \times 10^{-8}$ Pa^{-1} [Sorrentino and Pantani (2009)]. Figure 9(a) reveals that the steady-state value of the viscosity increases with pressure. The increase of viscosity with pressure allows one to calculate the value of the pressure coefficient which is given by $\beta = (6.00 \pm 0.16) \times 10^{-8}$ Pa^{-1} in our experiments. The influence of carbon dioxide at a pressure of 50 bar on the viscosity η is shown in Fig. 9(b). The value of η increases at short times after the increase of pressure p, when the effect of diffusion of carbon dioxide into the polystyrene sample can be neglected. The analysis of the data in Fig. 9(b) yields the pressure coefficient $\beta = 6.15 \times 10^{-8}$ Pa^{-1}.

Figure 10 presents the results of our transient shear viscosity measurements. After thermal equilibration, the transient shear viscosity agrees with the data obtained by the conventional rheometer. Then the pressure was increased up to a constant value of 50 bar. The increase of the pressure led to a rapid increase of the transient viscosity, see Fig. 9(b). Because of diffusion of carbon dioxide into the polystyrene sample the viscosity decreased with increasing time of measurement t_{measure}, see Figs. 10(a) and (b). At time $t_{\text{measure}} \approx 43200$ s. the viscosity became stationary. Since the time of saturation is proportional to the square of the characteristic length L_c of the sample, saturation of the sample proceeds more rapidly for smaller samples which has been verified in our experiments (Fig. 10(c)). The minimum torque which can be measured also increases with sample size, an effect which has to be taken into account since the addition of a low amount of blowing agent drastically reduces the viscosity. The determination of the molar mass of the polystyrene sample after the experiment led to $M_n = 111\,000$ g/mol and to $M_w = 231\,800$ g/mol which shows that in the case of polystyrene PS 158K the effect of degradation is negligible (cf. Table I).

In this work, the influence of the loading procedure (methods A and B) was evaluated. Figure 11 presents the relative steady state viscosity $\eta_{\text{stat}}(t_{\text{measure}})/\eta_{\text{stat}}(t_{\text{measure}} = 0)$ as a function of measurement time t_{measure}. Preloading clearly reduces the time of saturation. However, a complete saturation is not achieved via preloading even for six days, and an additional time after insertion of the sample into the rheometer is needed until a complete saturation of the polymer sample is attained. Although the preloading procedure yields a shorter time until saturation is achieved, in the following we used unloaded samples

for the experiments at temperatures of 150 °C and more because of simplicity. At lower temperatures, the preloading procedure has the advantage that transient shear experiments could be directly performed. Unloaded polystyrene of the grade under investigation had too long relaxation times below 150 °C such that transient experiments could not be performed at a pressure of 1 bar and below 150 °C.

In principal, an infinite period is needed in order to saturate the polymer sample completely. However, the experiment is stopped when the steady-state viscosity does not change anymore with measurement time t_{measure} within experimental scatter. In this study, we assume that this time is given by t_{95}, see Fig. 3. Measuring the value of t_{95} allows one to calculate the coefficient of diffusion D of the blowing agent in the polystyrene melt. In this study the diffusion coefficient was evaluated as a function of temperature and pressure. The evaluation of Eqs. (2) and (3) yields $t_{95}D/R^2 = 0.42415$. Setting $t_{\mathrm{saturation}} = t_{95}$, we find

$$D = 0.42415R^2/t_{\mathrm{saturation}}. \tag{10}$$

The measured values of D are listed in Table IV. The average value of D is $6.10 \pm 2.26 \times 10^{-10}\mathrm{m}^2/\mathrm{s}$ which is in good agreement with literature data [Sato et al. (2001)]. The scattering of the data in Table IV is possibly caused by the combined effect of scattering in rheological data and the determination of t_{95} using Eq. (10) which also is an approximation.

The average relaxation time and the stationary viscosity decrease with increasing fraction of carbon dioxide. The results of different measurements are shown in Fig. 12(a). In this study, we applied a time-pressure-concentration shift in order to verify superposition principles regarding time and temperature, pressure and concentration. We introduce the shift factor $a_{T,p,c} = a_{T,p,c}(T_{\mathrm{ref}}, p_{\mathrm{ref}}, c_{\mathrm{ref}})$ which describes the decrease of viscosity and the decrease of the average relaxation time. The set of reference parameters $(T_{\mathrm{ref}}, p_{\mathrm{ref}}, c_{\mathrm{ref}})$ is given by $(T_{\mathrm{ref}} = T_g(p = 10^5\,\mathrm{Pa}, c = 0), p_{\mathrm{ref}} = 10^5\,\mathrm{Pa}, c_{\mathrm{ref}} = 0)$. A time-pressure-concentration superposition principle can be formulated using the relation

$$\eta_{T,p,c}(t) = a_{T,p,c}\eta_{T_{\mathrm{ref}},p_{\mathrm{ref}},c_{\mathrm{ref}}}(a_{T,p,c}t), \tag{11}$$

where we use for simplicity $c \equiv c_0$ from now on. This superposition principle implies the same scaling factor $a_{T,p,c}$ for all relaxation times τ:

$$\tau(T, p, c) = a_{T,p,c}\tau(T_{\mathrm{ref}}, p_{\mathrm{ref}}, c_{\mathrm{ref}}). \tag{12}$$

Our data can be indeed superimposed to a master curve, see Figs. 12(b) and (c). The shift behaviour Eq. (11) is a straight-forward generalisation of the time-temperature superpo-

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sition principle. Such a universal scaling behaviour was also observed in dielectric measurements [Matsumiya et al. (2007, 2009)]. The shift factors $a_{T,p,c}$ are listed in Table V as a function of temperature and pressure. Generally, the shift factor for polystyrene/CO_2 solutions is much lower than for linear low density polyethylene/CO_2 solutions [Ouchi et al. (2008)].

Time-dependent shear experiments and linear viscoelastic shear oscillations allow one to determine the viscous and the elastic properties of polymer melts. In this work, we extracted the elastic creep compliance J_e^0 using the transient viscosity data. The relation between zero shear viscosity η_0, elastic creep compliance J_e^0 and average relaxation time $\langle \tau \rangle$ is given by $\langle \tau \rangle = J_e^0 \eta_0$. Hence we have

$$J_e^0 = \langle \tau \rangle / \eta_0. \tag{13}$$

The value of $\langle \tau \rangle$ was determined by the t value where the transient shear viscosity $\eta(t)$ fulfills $\eta(t) = 0.9 \times \eta_0$. Such a simplified approach is admissible, since the time-temperature-pressure-concentration principle is valid. A more sophisticated analysis implies the calculation of the relaxation time spectrum or creep recovery experiments in shear [Triebel et al. (2010)]. The results of Eq. (13) are shown in Fig. 13. The values of J_e^0 for $p = 1\,\mathrm{bar}$ and the data measured at larger pressures are constant within experimental scatter and do not show an obvious trend. The data indicate that the elastic equilibrium compliance does not depend on temperature and pressure and hence not on the concentration of carbon dioxide. Scattering at larger temperatures is more pronounced than at lower temperatures, since the viscosity η_0 and the average relaxation time $\langle \tau \rangle$ decrease with T which yields a lower resolution at larger T.

Furthermore our rheological data allow one to determine the glass transition $T_g(p,c)$ of polystyrene as a function of pressure p and concentration c of carbon dioxide. The WLF equation yields

$$\ln a_{T,p,c} = -\frac{c_1[T - T_g(p,c)]}{c_2 + T - T_g(p,c)} \tag{14}$$

with the parameters $c_1 = 17.44$ and $c_2 = 51.6\,\mathrm{K}$ for polystyrene. The value of $T_g(p,c)$ was determined as follows. The temperature shift factor $a_T = a_{T_g,p=10^5\,\mathrm{Pa},c=0}$ for an unloaded sample $c = 0$ at a pressure of 1 bar was calculated using the measurement temperature and $T_g(p = 10^5\,\mathrm{Pa}, c = 0) = 103\,°\mathrm{C}$. Then the shift factor $a_{T,p,c}$ is the product of this shift factor $a_T = a_{T_g,p=10^5\,\mathrm{Pa},c=0}$ and the decrease of the viscosity at measurement temperature by the addition of a blowing agent. Therefore the value of $a_{T,p,c}$ is given by

$$a_{T,p,c} = a_{T,p,c}(T_\mathrm{ref} = T_\mathrm{measurement}, p_\mathrm{ref} = 10^5\,\mathrm{Pa}, c = 0)a_{T_g,p=10^5\,\mathrm{Pa},c=0}.$$ Inserting this

shift factor into Eq. (14) allows one to calculate the shifted glass transition temperature $T_g(p, c)$. The value $T_g(p, c)$ as determined by the WLF equation is plotted in Fig. 14. The shift of glass transition temperature T_g with pressure p can be also measured using high pressure differential scanning calorimetry (DSC) measurements. The concentration at saturation of the DSC sample was determined using Eq. (8) and Henry's law. In Fig. 14 the results of the shift procedure based on Eq. (10) and of the DSC measurements are compared. The prediction of Chow (1980) for a pressure of p

$$\ln\left[T_g(p, c)/T_g(p, c = 0)\right] = \tilde{\beta}\left[(1 - \theta)\ln(1 - \theta) + \theta\ln\theta\right] \tag{15}$$

with the parameters $\tilde{\beta} = zR/(M_p\Delta C_{p,T_g})$ and $\theta = M_p c/[zM_d(1 - c)]$ is also plotted. Here M_p is the molar mass of the monomer, M_d the molar mass of the diluent and z is the coordination number. Furthermore $\Delta C_{p,T_g}$ is the excess transition isobaric specific heat of polystyrene and R the universal gas constant. The following data for polystyrene/carbon dioxide solutions were used, see also Wingert et al. (2009): $M_d = 44\,\text{g/mol}$, $M_p = 104.15\,\text{g/mol}$, $R = 8.3145\,\text{J/(K\,mol)}$, $\Delta C_p = 0.3209\,\text{J/(g\,K)}$, $T_g = 103\,^\circ\text{C}$ and $z = 3$. The results of the two measurement techniques which correspond to different concentration regimes complement each other. Since the DSC experiments are performed non-isothermally, only approximate values of the carbon dioxide concentration can be given for these experiments. The rheological measurements are performed at constant temperature such that a complete saturation of the sample can be achieved. The data shown in Fig. 14 agree well with the equation of Chow (1980) for $T = 160\,^\circ\text{C}$ and $z = 3$ and pressures lower than or equal to 30 bar.

Our rheological results indicate that the change of temperature, pressure and concentration of the blowing agent yield the same effect, i.e. the scaling of the relaxation time spectrum with the shift factor. The shift of the relaxation time spectrum with p and c corresponds to a shift of the glass transition temperature T_g. Whereas the rheological measurements give information on the temperature dependence of the dynamics of polymer chains, the DSC measurements detect the change of heat flow. The scaling of the relaxation time spectrum with p and c implies that the relaxation times are associated with the dynamics of single polymer chains. The effects of T, p and c on the rheological properties of polystyrene are coupled, possibly via their influence on the monomeric friction coefficient. Our measurements indicate that the whole relaxation time spectrum scales with the shift factor $a_{T,p,c}$.

V. CONCLUSIONS

In this work, we quantitatively evaluated an approach which is based on the measurement of the transient shear viscosity in order to investigate the influence of carbon dioxide on the viscoelastic properties of polystyrene. In contrast to previous works, we focused on the time-dependence of the viscosity in order to determine both viscous and elastic properties. Stress-growth experiments using a plate-plate geometry were performed and the transient shear viscosity in the linear viscoelastic regime was measured. In these experiments, the influence of residual torque is less pronounced than in linear viscoelastic shear oscillations. The effect of diffusion of the pressurizing medium into the sample was quantitatively considered in order to optimize the experimental accuracy. This approach allows one to measure the decrease of the average relaxation time as a function of applied pressure and concentration of the blowing agent.

Our analysis reveals that the effects of diffusion and solubility as a function of the thermodynamical parameters (temperature, pressure) have to be taken into account carefully for rheological and differential scanning calorimetry experiments in order to minimize effects of degradation and to optimize the experimental accuracy. The measurement procedure which was outlined here can be applied to a large variety of polymeric materials. It is ideally suited for the investigation of high viscosity polymer melts. The tests in the transient mode allow one to measure the time-dependent viscosity (and thus the shift factor and the glass transition temperature), the elastic equilibrium compliance J_e^0, the pressure coefficient and the diffusion coefficient in a single experiment.

The reduction of the viscosity which was caused by the blowing agent agrees with data of related works. The transient shear viscosity in the linear regime was shifted to a master curve which indicates that a time-temperature-pressure-concentration principle is valid for solutions of polystyrene and carbon dioxide. Consequently, in transient experiments (stress-growth tests) and flow curve measurements the same superposition principle holds. Hence temperature, pressure and concentration of the blowing agent equally influence all relaxation times. The elastic equilibrium compliance only weakly depends on temperature, pressure and carbon dioxide concentration. These results imply that temperature, pressure and concentration of carbon dioxide mainly influence the monomeric friction coefficient.

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ACKNOWLEDGMENTS

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Table captions

Table I: Glass transition temperature T_g at a pressure of 1 bar (determined by differential scanning calorimetry), number and weight average M_n and M_w of the molecular weight (results of gel permeation chromatography) and density ρ of polystyrene PS 158K (BASF SE, Ludwigshafen, Germany) at different temperatures.

Table II: Rheological properties of PS 158K at different temperatures. The data were obtained by analysis of G' and G'' using the software NLREG [Freiburg Materials Research Center (2001)]. The zero shear rate viscosity is denoted by η_0, the elastic equilibrium compliance by J_e^0 and the average relaxation time by $\langle \tau \rangle$.

Table III: Horizontal (a_T) and vertical (b_T) shift factors of polystyrene PS 158K at $T_{\mathrm{ref}} = 170\,^\circ\mathrm{C}$ and $p = 1\,\mathrm{bar}$. The standard deviation is denoted by Δa_T and Δb_T, respectively.

Table IV: Diffusion coefficient D of carbon dioxide in a quiescent ($\dot{\gamma}_0 = 0\,\mathrm{s}^{-1}$) polystyrene melt as a function of temperature.

Table V: Shift factor $a_{T,p,c}$ for polystyrene/carbon dioxide solutions (a) as a function of temperature T for a pressure p of $p = 40\,\mathrm{bar}$ and (b) as a function of pressure p for $T = 160\,^\circ\mathrm{C}$.

	T_g	M_n	M_w	M_w/M_n	ρ at 25 °C	ρ at 150 °C	ρ at 160 °C	ρ at 170 °C
	(°C)	(g/mol)	(g/mol)		(g/cm^3)	(g/cm^3)	(g/cm^3)	(g/cm^3)
PS 158K	103	114 100	244 800	2.15	1.050	0.995	0.989	0.983

Table I

U.A. Handge and V. Altstädt

Journal of Rheology

T	η_0	J_e^0	$\langle \tau \rangle$
(°C)	(Pa s)	(Pa^{-1})	(s)
130	1.57×10^8	1.69×10^{-4}	26505.2
140	1.77×10^7	1.65×10^{-4}	2913.7
150	3.43×10^6	1.42×10^{-4}	487.3
160	8.08×10^5	1.31×10^{-4}	105.6
170	2.32×10^5	1.34×10^{-4}	31.2

Table II

U.A. Handge and V. Altstädt

Journal of Rheology

T	a_T	Δa_T	b_T	Δb_T
(ºC)				
130	8.556×10^2	4.588×10^1	7.886×10^{-1}	1.359×10^{-2}
140	9.375×10^1	4.526×10^0	8.128×10^{-1}	1.283×10^{-2}
150	1.514×10^1	5.029×10^{-1}	9.798×10^{-1}	1.341×10^{-2}
160	3.410×10^0	8.291×10^{-2}	1.021×10^0	1.266×10^{-2}
170	1.000×10^0	0.000×10^0	1.000×10^0	0.000×10^0

Table III

U.A. Handge and V. Altstädt

Journal of Rheology

T	D
(ºC)	(m^2/s)
130	4.5×10^{-10}
140	9.6×10^{-10}
150	4.2×10^{-10}
160	5.1×10^{-10}
170	7.1×10^{-10}

Table IV

U.A. Handge and V. Altstädt

Journal of Rheology

(a)

T	p	$a_{T,p,c}$
(°C)	(bar)	
140	40	0.069
150	40	0.094
160	40	0.177
170	40	0.299

(b)

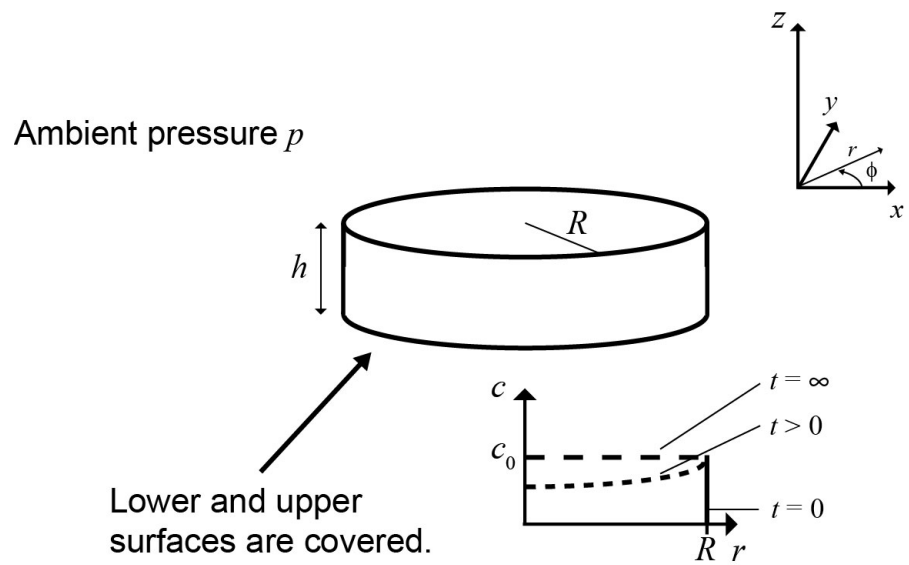| T	p	$a_{T,p,c}$
(°C)	(bar)	
160	30	0.340
160	40	0.177
160	47	0.115

Table V

U.A. Handge and V. Altstädt

Journal of Rheology

Figure captions

Figure 1: Diffusion of a blowing agent into a polymer sample of cylindrical shape. The ambient pressure in the gas atmosphere of the blowing agent is p. The radius of the sample is denoted by R and its thickness by h. Since the sample is confined between the two plates of the rotational rheometer, we assume that diffusion only takes place in the radial direction.

Figure 2: Concentration of the blowing agent in a cylindrical polymer sample, cf. Eqs. (2) and (3). (a) Concentration $c(r, t_{\text{measure}})$ after different times of diffusion t_{measure}. (b) Average concentration $\langle c \rangle$ as a function of t_{measure}. (c) Zero shear rate viscosity η_0 as a function of t_{measure}. The parameters are $D = 5 \times 10^{-10}\,\text{m}^2/\text{s}$, $R = 8 \times 10^{-3}\,\text{m}$, $c_0 = 4\%$ and $b_c = 70$.

Figure 3: (a) Dimensionless time Dt/L_c^2 in order to achieve a partial saturation (in units of $x\%$) of a blowing agent in a polymer sample. The measurement geometry (plate-plate, Couette or sliding plate) is indicated. The parameter L_c is the characteristic length of the geometry (edge length of sliding plate $2L_c$, plate-plate $L_c = R$ and Couette $L_c = R_1$). Moreover $\kappa = 1.1$ holds for the Couette geometry.

Figure 4: (a) Scheme and (b) photograph of the set-up for rheological experiments using a plate-plate geometry at a high pressure.

Figure 5: Protocol for determination of the transient shear viscosity $\eta(t)$ of a polystyrene melt saturated with a blowing agent at high pressure.

Figure 6: Solubility of carbon dioxide in polystyrene at different temperatures and pressures. The solubility is calculated based on Henry's law using Eq. (8) and data of Sato et al. (2001).

Figure 7: Mastercurve for polystyrene PS 158K at $T = 170\,^\circ\text{C}$ and an ambient pressure of $p = 1\,\text{bar}$. (a) Storage modulus G', loss modulus G'' and absolute value of the complex viscosity η^* versus angular frequency ω. (b) Relaxation time spectrum $H(\tau)$ calculated using the data of G' and G''.

Figure 8: Comparison of the transient shear viscosity $\eta(t)$ measured using a conventional rotational rheometer and the rheometer adapted with the pressure cell, respectively. The linear viscoelastic prediction (LVE) is also shown. The test temperature was $T = 170\,°C$. The shear rate is (a) $\dot{\gamma}_0 = 0.05\,s^{-1}$ and (b) $\dot{\gamma}_0 = 0.30\,s^{-1}$.

Figure 9: Effect of pressure p on the transient viscosity of polystyrene PS 158K. The measurement temperature was $T = 170\,°C$. (a) Time-dependent shear viscosity $\eta(t)$ for different values of pressure p using helium as pressurizing medium ($\dot{\gamma}_0 = 0.023\,s^{-1}$). (b) Time-dependent shear viscosity $\eta(t)$ using carbon dioxide as pressurizing medium. The pressure was $p = 50\,bar$ and the shear rate $\dot{\gamma}_0 = 0.059\,s^{-1}$.

Figure 10: Results of stress-growth experiments at $T = 170\,°C$ and $p = 50\,bar$. (a) Transient shear viscosity $\eta(t)$ after different times of diffusion $t_{measure}$. (b) Relative steady-state viscosity $\eta_{stat}(t_{measure})/\eta_{stat}(t_{measure} = 0)$ as a function of $t_{measure}$. (c) Effect of sample size on the duration until complete saturation of the polystyrene sample with carbon dioxide is achieved ($T = 150\,°C, p = 40\,bar$).

Figure 11: Influence of loading procedure (methods A and B) on the time of saturation of a polystyrene melt with carbon dioxide. The parameters are $T = 170\,°C$ and $p = 50\,bar$.

Figure 12: (a) Transient viscosity $\eta(t)$ of unloaded polystyrene and completely saturated polystyrene at $T = 160\,°C$ and three different values of pressure. (b) Mastercurve based on the data of (a). (c) Mastercurve based on experiments at different temperature and pressure values.

Figure 13: Elastic equilibrium compliance J_e^0 as a function of temperature for solutions of polystyrene and carbon dioxide.

Figure 14: Influence of pressure p on the glass transition temperature T_g of polystyrene. The estimated CO_2 concentration for the rheological experiments is indicated. The results were obtained using rheological and DSC measurements under high pressure, respectively. The prediction of Eq. (15) for $T = 160\,°C$ is also plotted.

Ambient pressure p

R

h

Lower and upper
surfaces are covered.

z

y

r

ϕ

x

c

c_0

$t = \infty$

$t > 0$

$t = 0$

$R \quad r$

Fig. 1

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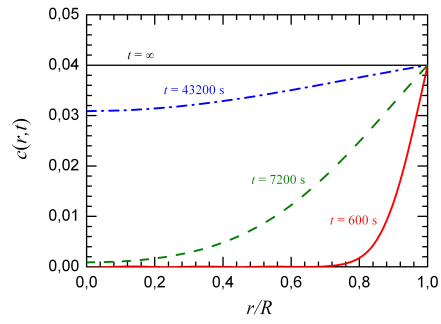
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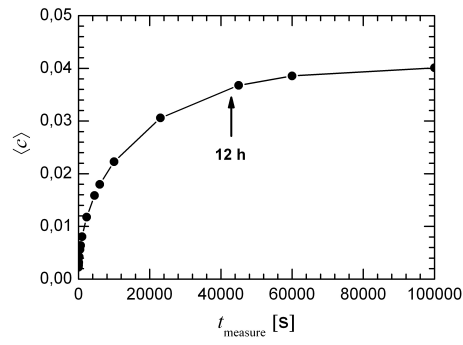
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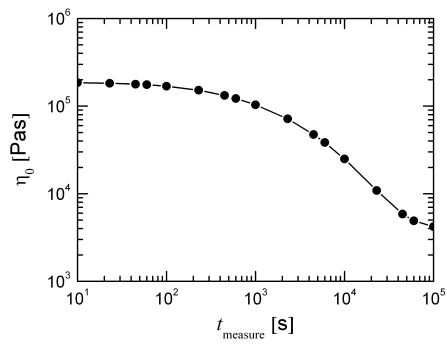
(c)

Figs. 2(a)-(c)

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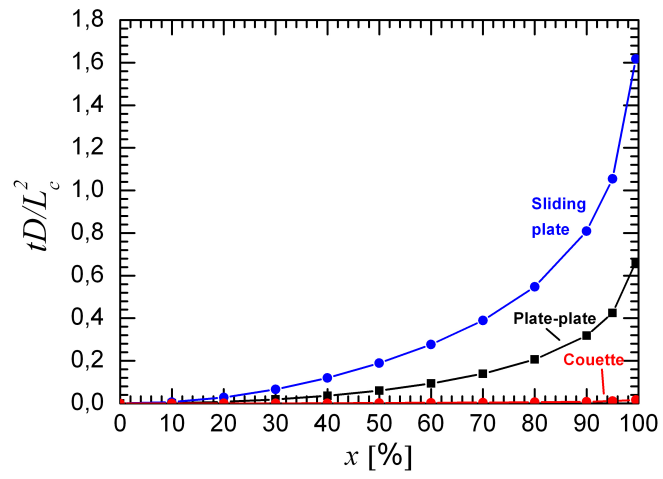Fig. 3
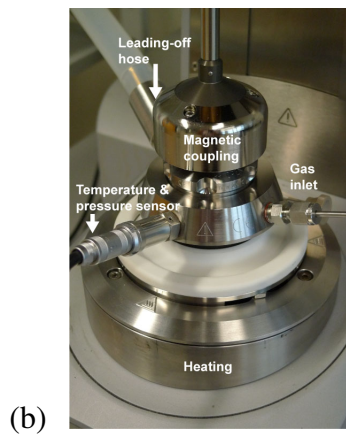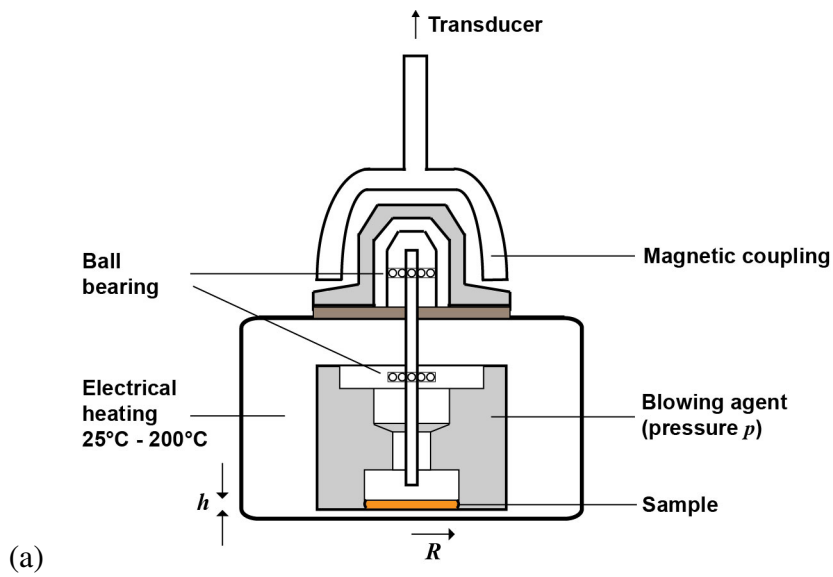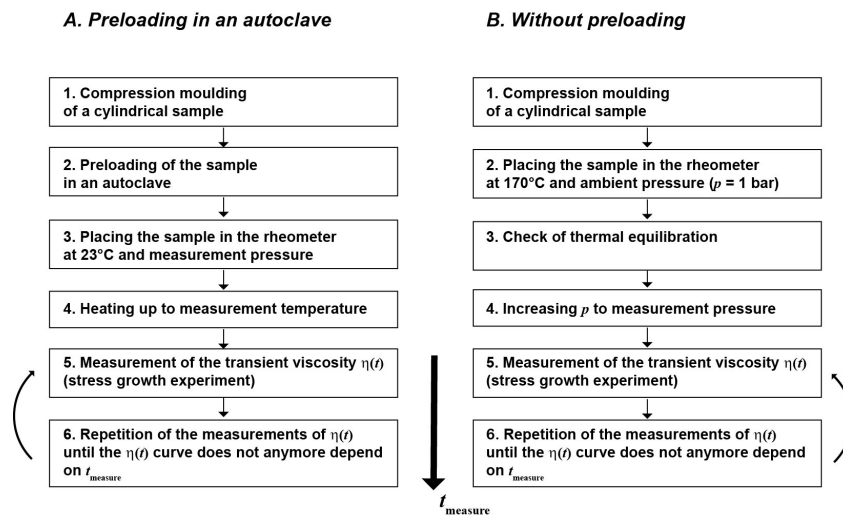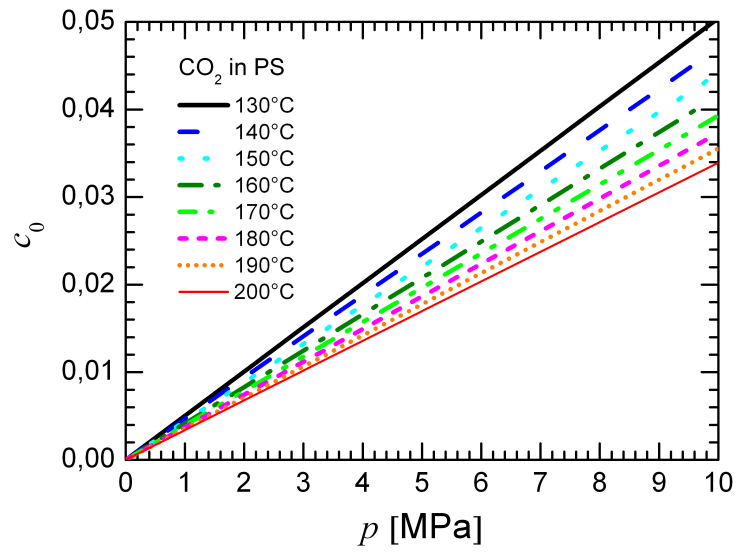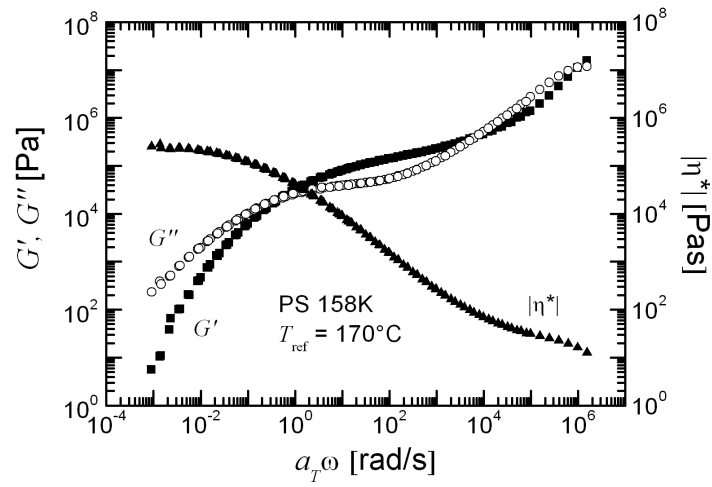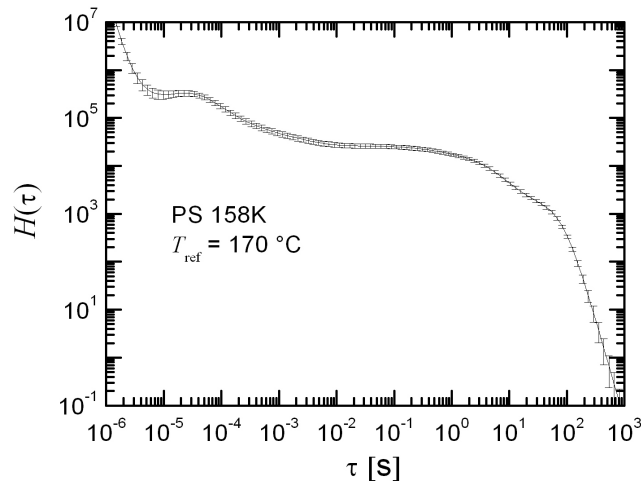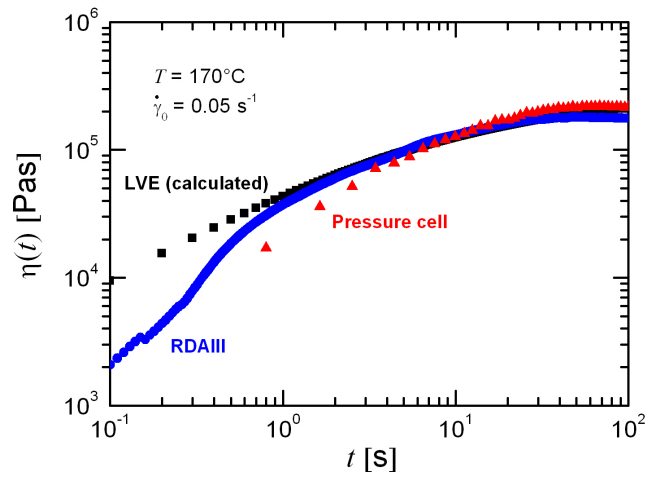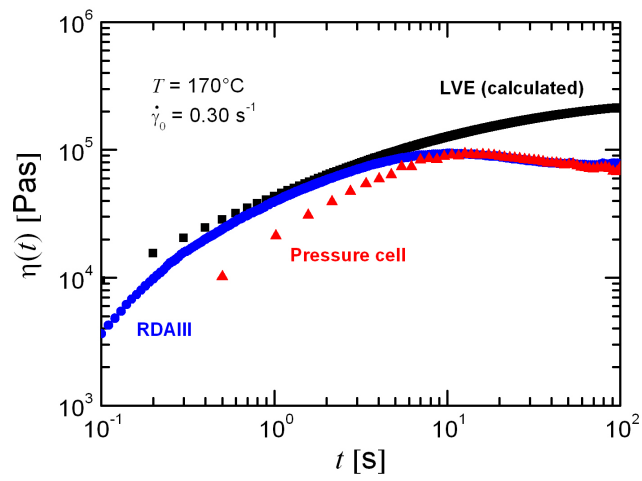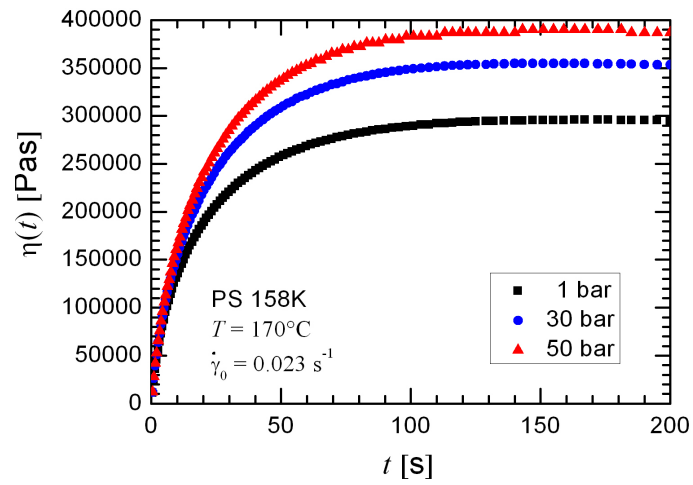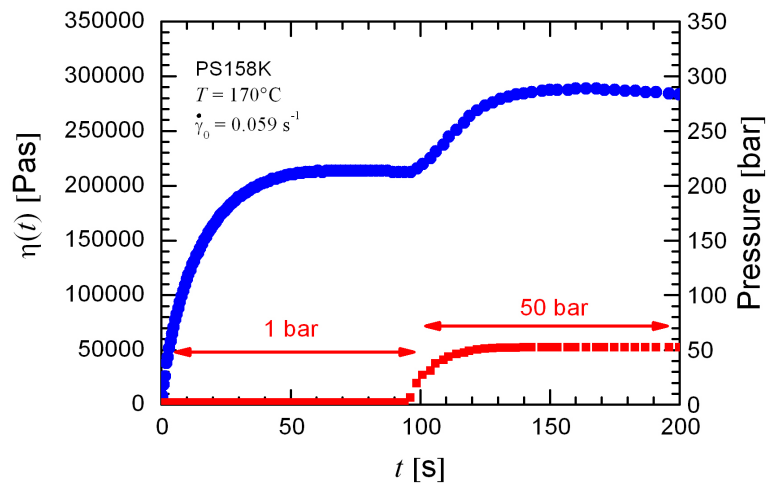
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(a)

(b)

Figs. 4(a) and (b)
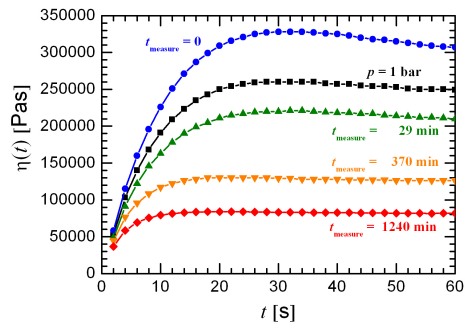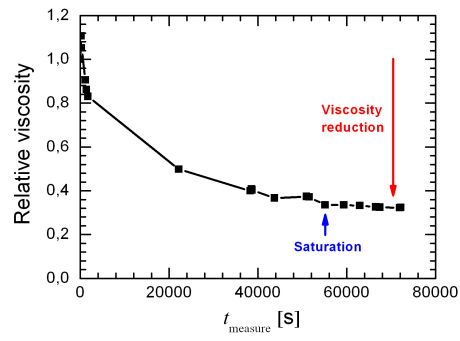
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A. Preloading in an autoclave　　　　　**B. Without preloading**

A. Preloading in an autoclave
1. Compression moulding of a cylindrical sample
2. Preloading of the sample in an autoclave
3. Placing the sample in the rheometer at 23°C and measurement pressure
4. Heating up to measurement temperature
5. Measurement of the transient viscosity $\eta(t)$ (stress growth experiment)
6. Repetition of the measurements of $\eta(t)$ until the $\eta(t)$ curve does not anymore depend on $t_{measure}$

B. Without preloading
1. Compression moulding of a cylindrical sample
2. Placing the sample in the rheometer at 170°C and ambient pressure (p = 1 bar)
3. Check of thermal equilibration
4. Increasing p to measurement pressure
5. Measurement of the transient viscosity $\eta(t)$ (stress growth experiment)
6. Repetition of the measurements of $\eta(t)$ until the $\eta(t)$ curve does not anymore depend on $t_{measure}$

$t_{measure}$

Fig. 5

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Fig. 6

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(a)

(b)

Figs. 7(a) and (b)

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(a)

(b)

Figs. 8(a) and (b)

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(a)

(b)

Figs. 9(a) and (b)
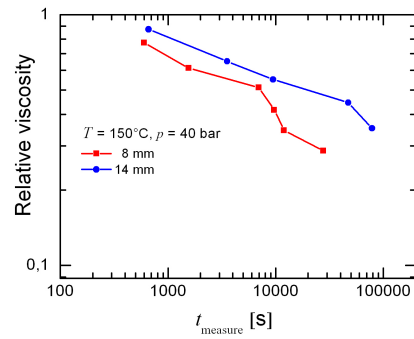
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(a)

(b)

(c)

Figs. 10(a) to (c)

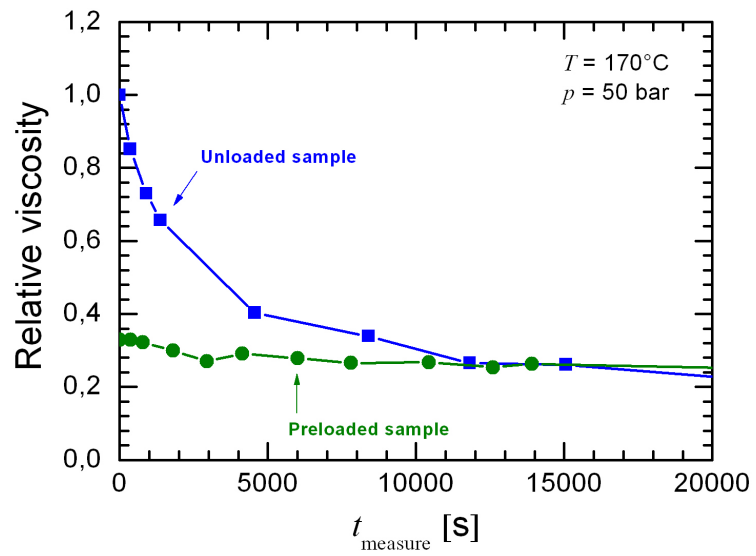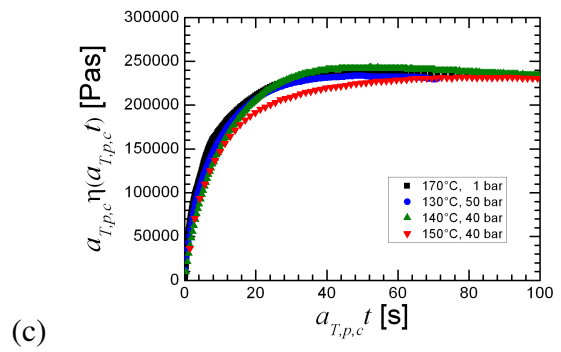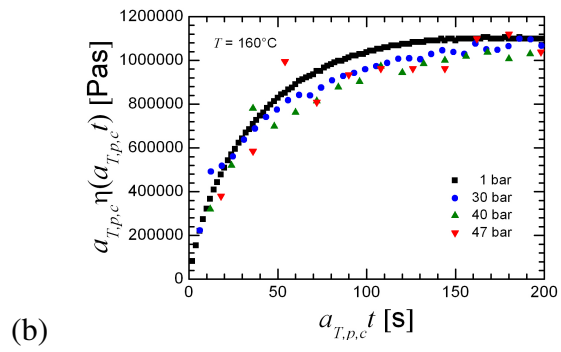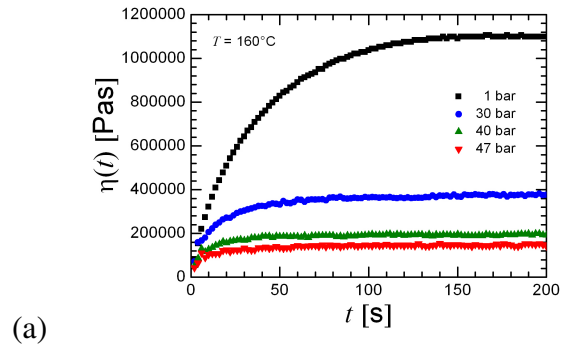U.A. Handge and V. Altstädt

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Fig. 11

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(a)

(b)

(c)

Figs. 12(a) to (c)

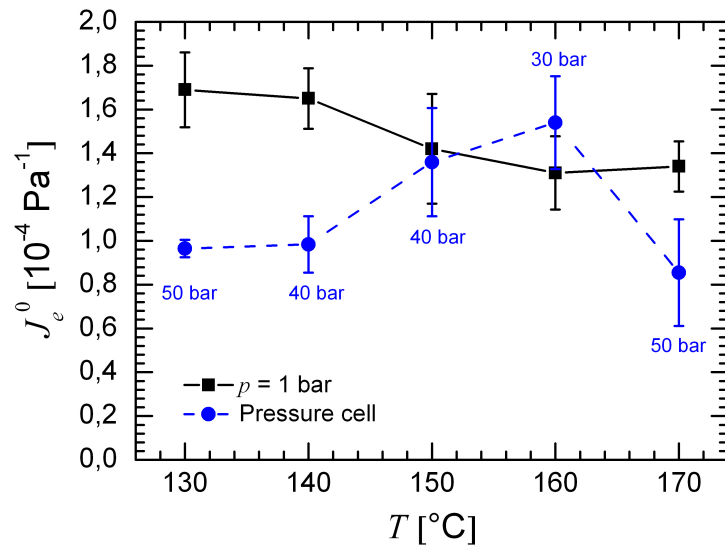U.A. Handge and V. Altstädt

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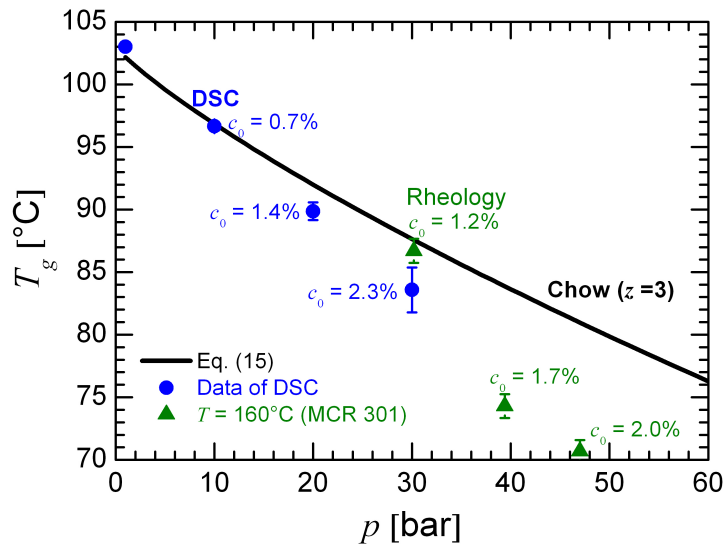
Fig. 13

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Fig. 14

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