Dr. Andreas Schönhals

Rotational and Translational Diffusion in Polymeric Melts Studied by Dielectric Spectroscopy from 10^{-4} Hz to 10^{10} Hz

Recently investigations of diffusion in supercooled glass-forming melts near the glass transition temperature Tg has been received much attention /1/. Rössler /2/ found by a detailed analysis of literature data including different experimental techniques that near Tg the Stokes-Einstein relation

$$D_{Rot} = \frac{kT}{a\eta} \quad ; \quad \tau = \frac{v\eta}{kT} \quad (1)$$

is not valid independent of temperature (D_{Rot} - rotational diffusion coefficient, η - viscosity, τ -rotational relaxation time; a and v are constants depending on the
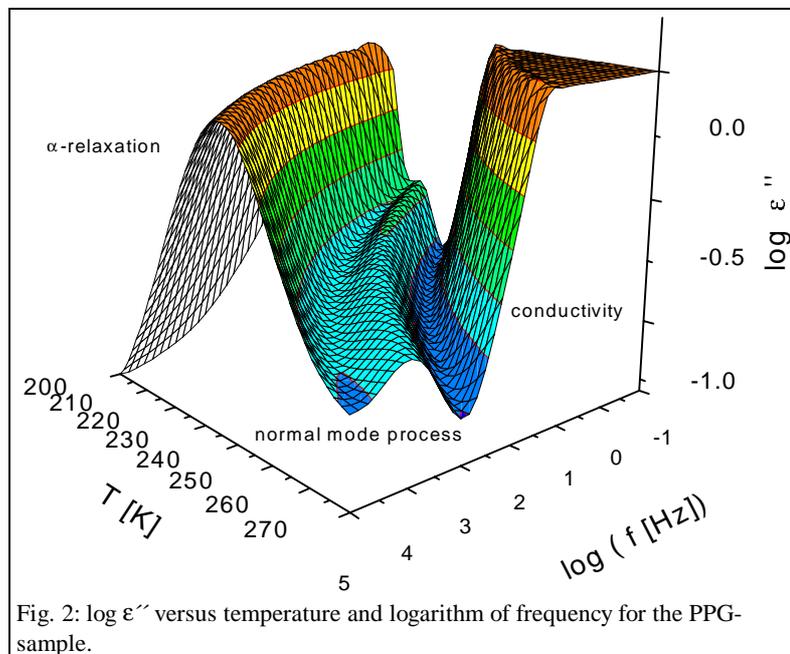
Fig. 2: log ε'' versus temperature and logarithm of frequency for the PPG-sample.

size of the diffusing molecule. kT has the usual meaning.). Sillescu and coworkers found a decoupling of the temperature dependence of translational and rotational diffusion in orthoterphenyl for a small probe molecule /1/ above but near T_g where the tracer diffusion was studied by a light scattering technique. No decoupling was found for the diffusion of large polystyrene spheres in an orthoterphenyl melt /1/. So one can speculate that the described effect depends on the size of the diffusing molecule. An understanding of this problem is closely related to the understanding of the glass transition phenomenon which true microscopic description remains an unsolved and actual problem of condensed matter physics /3/.

Fig. 1: Different geometric possibilities for the location of a molecular dipole moment with respect to the polymer chain.

Because in polymeric systems molecular dipole moments can be attached in different geometric

Fig. 3 Evaluation of data measured partly in time domain and in frequency domain for PPG at 202.15 K by fitting two HN- functions
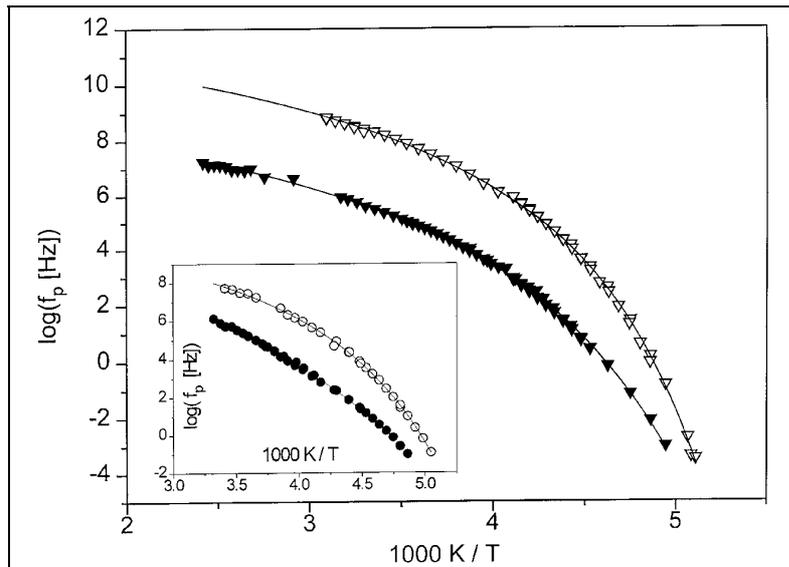
Fig. 4: log fp versus 1/T for the both relaxation processes. Open symbols : α-relaxation; Solid symbols - normal mode process; Triangels - PPG; Circles - Cis-1,4-polyisoprene, M_w=1400 g/mol. Lines are fits of the VFT-equation to the data.

orientations with respect to the main chain this problem can be also investigated by broadband dielectric spectroscopy.

According to Stockmayer /4/ (see Fig. 1), macromolecules with dipoles fixed parallel to the main chain are called Type A-polymers. The dipole moment for the whole chain is given by a summation over the individual dipole moments parallel to the chain backbone. So its time correlation function which can be measured by dielectric spectroscopy is proportional to the fluctuation of the end-to-end-vector $\langle r^2 \rangle$ of the chain /5/. The corresponding dielectric relaxation process, called normal mode relaxation, can be described by the Rouse theory of polymeric melts. It turns out that the frequency of maximal loss f_{pn} of the normal mode relaxation peak is related to the longest Rouse- time /5/

$$ \tau_n = \frac{1}{2\pi f_{pn}} = \frac{\zeta N^2 b^2}{3\pi^2 kT}, \quad (2) $$

where ζ is the monomeric friction coefficient and N is the number of statistical chain segments with the bond length b. Because the translational diffusion coefficient is given by

$$ D_{Trans} = \frac{kT}{\zeta N} \quad (3) $$

the combination of equation (2) and (3) gives ($\langle r^2 \rangle = b^2 N$)

$$ \tau_n D_{Trans} = \frac{\langle r^2 \rangle}{3\pi^2} \quad (4) $$

So D_{Trans} can be estimated from dielectric measurements if $\langle r^2 \rangle$ is known. On the other side D_{Trans} can be also measured directly for instance by field gradient NMR techniques. Recently equation (4) was proven by a combination of dielectric and NMR field gradient

measurements /6/. So one can be sure, that the dielectric normal mode relaxation is direct related to the translational diffusion of a polymer chain.

For type B-polymers the dipole moment is rigidly perpendicular attached to the chain skeleton (see Fig. 1). Conformational changes lead to a rotation of the molecular dipole vector around the chain. Generally it is believed that these motional processes are related to the dielectric α-relaxation process. For this reason the frequency of maximal loss of the α-peak is directly related to a rotational relaxation time or to D_{Rot}. Therefore for polymers having both type A and type B dipoles the temperature dependence of translational and rotational diffusion can be studied by only one method, by dielectric spectroscopy. So possible difficulties which can arise by a combination of methods such as plasticitation of the matrix by the tracer molecules or temperature shifts do not play a roll. Moreover the influence of the size of the diffusing molecule on the decoupling of rotational and translational diffusion can be studied very easily by a variation of the molecular weight of the
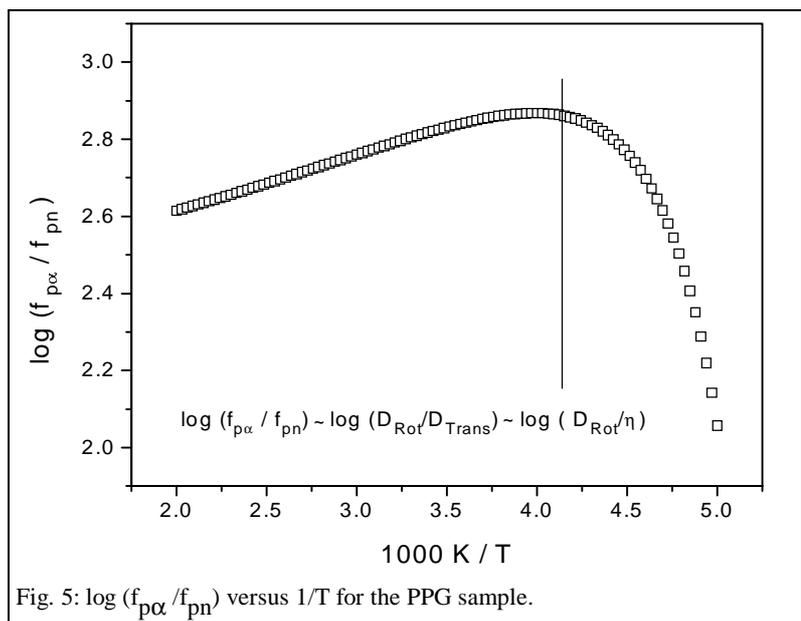
Fig. 5: log ($f_{p\alpha}$ /f_{pn}) versus 1/T for the PPG sample.

polymer chains (see Equation 4).

Just to maintain completeness it should be mentioned that polymers having the dipoles in a more or less flexible side chain are called to be from type C.

Examples for polymers having both type A and type B dipoles in the chain are polypropylene glycol and cis-1,4-polyisoprene /5/. For the first polymer a sample with nominal molecular weight of 4000 g/mol and for cis-1,4-polyisoprene different samples with molecular weights between 1000 g/mol and 10000 g/mol were studied.

To investigate the α- and the normal mode relaxation from temperatures close to the T_g up to high temperatures an extended frequency range for the dielectric measurements is necessary. For this reason the isothermal dielectric behavior, characterized by the complex dielectric permittivity $\varepsilon^*(f) = \varepsilon'(f) - i\varepsilon''(f)$ (f-frequency, ε'-real part, ε''-imaginary part, $i=\sqrt{-1}$) was measured in a frequency range from 10^{-5} Hz to 10^{10} Hz by combination of five different measuring systems /7/ : a time domain spectrometer presented elsewhere /8/ (10^{-5} < f/Hz < 1), a Schlumberger 1260 frequency response analyzer supplemented by a buffer amplifier of variable gain (10^{-2} < f/Hz < 10^6), HP four probe impedance analyzers (4192A, 4284A, 4285 A 10^2 < f/Hz < 10^7), a coaxial reflectometer using the HP 4191A device (10^6 < f/Hz < 10^9) and a coaxial reflectometer based on a HP 8510E network analyzer. ($5*10^7$ < f/Hz < $2*10^{10}$).The temperature of the sample was controlled by a custom made nitrogen gas jet heating systems. Fig. 2 shows the dielectric loss for the sample PPG-4000 versus temperature and log frequency. Clearly two relaxation processes can be observed. The relaxation process at high frequencies and low temperatures was assigned to the α-relaxation whereas the peak at

lower frequencies and higher temperatures was attributed to the normal mode relaxation.

To separate α- and normal mode-relaxation and to estimate f_p for both processes an evaluation method described elsewhere /9/ based on the model function of Havriliak and Negami /10/ (HN-function) was applied. By this method also measurements carried out partly in time and frequency domain can be analyzed in a consistent way. This is shown in Fig. 3 where the decomposition of the α- and normal mode relaxation measured both in time and frequency domain was carried out by fitting two HN-functions to the data.

Fig. 4 shows log f_p for both processes versus inverse temperature for PPG. In the inset the same is shown for a cis-1,4-polyisoprene sample with a molecular weight of 1400 g/mol. The relaxation rate of the α-relaxation as well as of the normal mode process shows a curved dependence on $1/T$ which can be well described by the empirical Vogel/Fulcher/Tammann equation /11/ (VFT-equation)

$$\log f_p = \log f_\infty - \frac{A}{T - T_0} \quad (5).$$

$\log f_\infty$ and A are constants and T_0 is the so called ideal glass transition temperature. The quality of the fits is demonstrated by the lines in Fig. 4. For the case that translational and rotational diffusion have same temperature dependencies at least T_0 should be the same for both processes. But as a first result it was found that for all investigated melts always the Vogel temperature for the α-process was higher than the value for the normal mode relaxation /12/.

By means of estimated VFT-parameters the ratio $\log(f_{p\alpha}/f_{pn})$ which is directly proportional to $\log(D_{Rot}/D_{Trans})$ was calculated and plotted versus inverse temperature. For the PPG-sample the result is given in Fig. 5. The temperature dependence of this ratio shows two regimes separated by a maximum. At high temperatures $\log(f_{p\alpha}/f_{pn})$ decreases with $1/T$ and at low temperatures $\log(f_{p\alpha}/f_{pn})$ decreases with inverse temperature. The maximum indicates a change in the mechanism of diffusion which corresponds directly to the decoupling of the temperature dependence of translatorial and rotational diffusion found by the Sillescu group /1/ or to the breakdown of the Stockes-Einstein relation near T_g found by Rössler
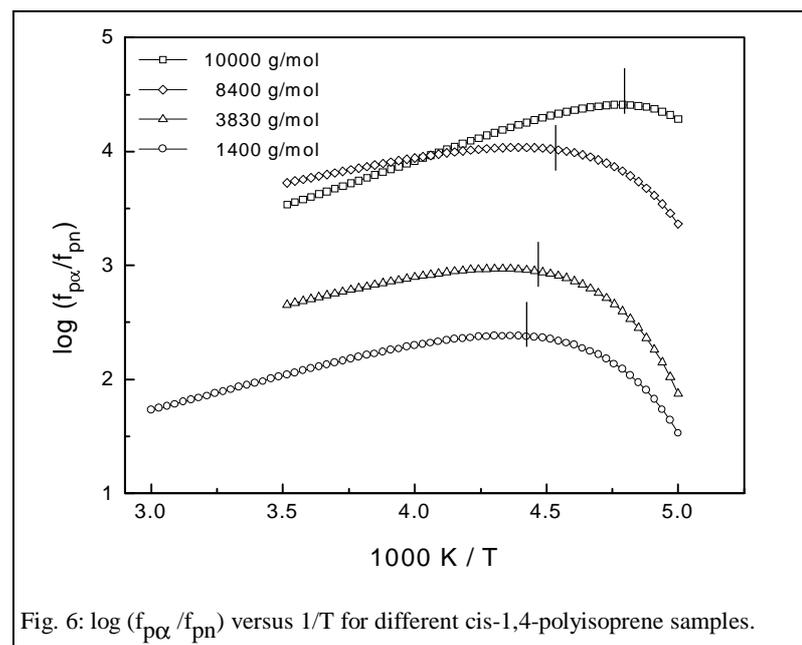
Fig. 6: log ($f_{p\alpha}$ /f_{pn}) versus 1/T for different cis-1,4-polyisoprene samples.

/2/. Fig. 6 shows the same behavior for the polyisoprene samples. In that case the temperature position of the maxima shifts to lower temperatures with increasing molecular weight. Because for oligomeric samples the glass transition temperature depends on the molecular weight, this shift is not a direct proof for a size dependence of the decoupling of translational and rotational diffusion. To settle this problem the maximum position of $\log(f_{p\alpha}/f_{pn})$ versus $1/T$ was taken from Fig. 6 for each molecular weight. After that with the estimated VFT- parameters for the α-relaxation of the respective melt an equivalent decoupling frequency f_{DC} can be calculated. This frequency can be compared for the different melts. Fig. 7 shows that log f_{DC} depends strongly on the molecular weight of the sample. So for the first time it was shown that the decoupling of temperature dependence of translational and rotational diffusion or the breakdown of the Stockes-Einstein relation depends on the size of the diffusing molecule. This experimental result can be regarded as an evidence for the cooperative nature of the molecular motions involved in the glass transition and that the extent of that cooperativity increases with decreasing temperature.

Fig. 7: decoupling frequency f_{DC} versus log M_W for the cis-1,4-polyisoprene samples.

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Broadband Dielectric Measurement Techniques - A Contest

Dielectric spectroscopy - in its modern form - requires broadband measurement systems with a large dynamic range in the determination of the dielectric loss. This is especially true for studies of the scaling of relaxation processes [1-8], where one is interested in as fundamental questions as the validity of the time - temperature - superposition, the occurrence of anomalies in the dynamic glass transition [2-5] or deviations of the high frequency wings of the dynamic glass transition from generalized relaxation functions. Of current interest is the molecular dynamics in confining geometries such as porous glass. Again Dielectric methods can give an important contribution [6-9]. In ferroelectric liquid crystals the dielectric losses are much stronger due to the cooperative character of the involved process [10]. A broad frequency window is required in order to study the collective and molecular dynamics. To cover a

frequency range as broad as 10^{-5} Hz to 10^{10} Hz different measurement techniques based on different measurement principles have to be combined :

In the frequency domain from 10^{-5} Hz to 10^{7} Hz : Frequency response analysis (e.g. using a Novocontrol Broadband Dielectric Converter BDC in combination with a Solartron SI 1260 gain-phase analyzer or with a Stanford Research Digital Lock-In Amplifier SR 830); from 20 Hz to 10^{6} Hz: AC-Impedance analysis (using a HP 4284A Impedance Bridge for instance); from 10^{6} Hz - $1.8 \cdot 10^{9}$ Hz : RF-Reflectometry (e.g. using a HP 4191A / resp. HP 4291A RF-Impedance Analyzer in combination with a Novocontrol RF-extension line and sample cell) and from 10^{7} Hz to 10^{10} Hz : Vectorial Networkanalysis (using for instance the HP 8510 Network Analyzer). The measurement techniques (beside network analysis) are discussed and outlined in detail in the March issue of the Novocontrol Dielectric Newsletter of 1994.

In the present article a comparison is made in which an identical dielectric sample is measured with the different measurement systems in order to demonstrate the strength and the limitations of the different dielectric spectrometers. In order to show the limitations of the systems an air capacitor was measured. The capacitor has a loss factor $\tan(\delta)$ below the accuracy limits of the tested systems and a constant capacity. The measured values for $\tan(\delta)$ and the deviations from the constant capacity show the system accuracy. As measured at the limit of accuracy the $\tan(\delta)$ curves show large scatter. All measurements were controlled and evaluated by the Novocontrol software WinDETA.

Measuring in the low frequency regime from 10^{-3} to 10^{7} Hz an air capacitor (two gold plate, polished
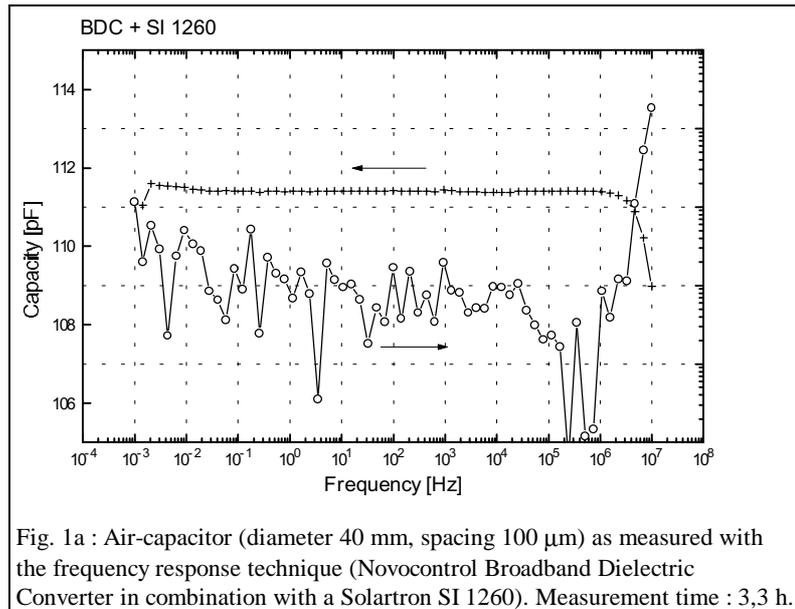
Fig. 1a : Air-capacitor (diameter 40 mm, spacing 100 μm) as measured with the frequency response technique (Novocontrol Broadband Dielectric Converter in combination with a Solartron SI 1260). Measurement time : 3,3 h.
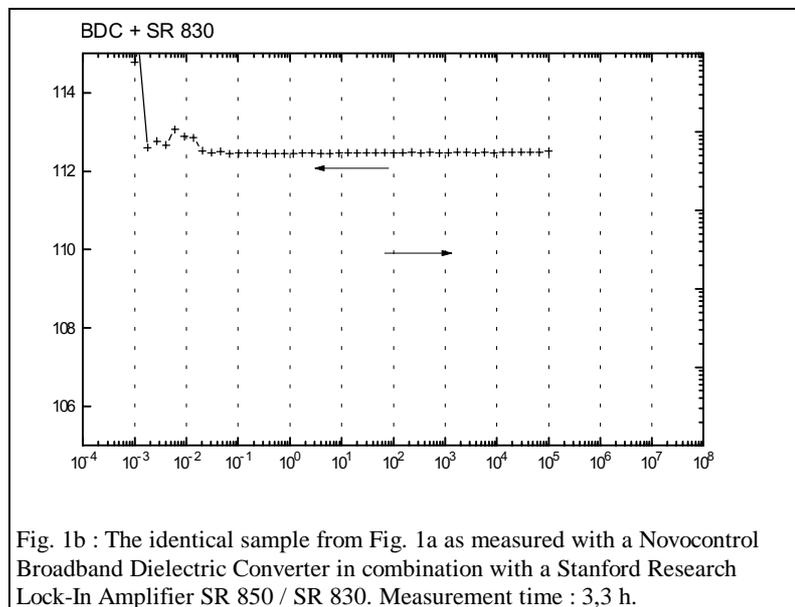
Fig. 1b : The identical sample from Fig. 1a as measured with a Novocontrol Broadband Dielectric Converter in combination with a Stanford Research Lock-In Amplifier SR 850 / SR 830. Measurement time : 3,3 h.
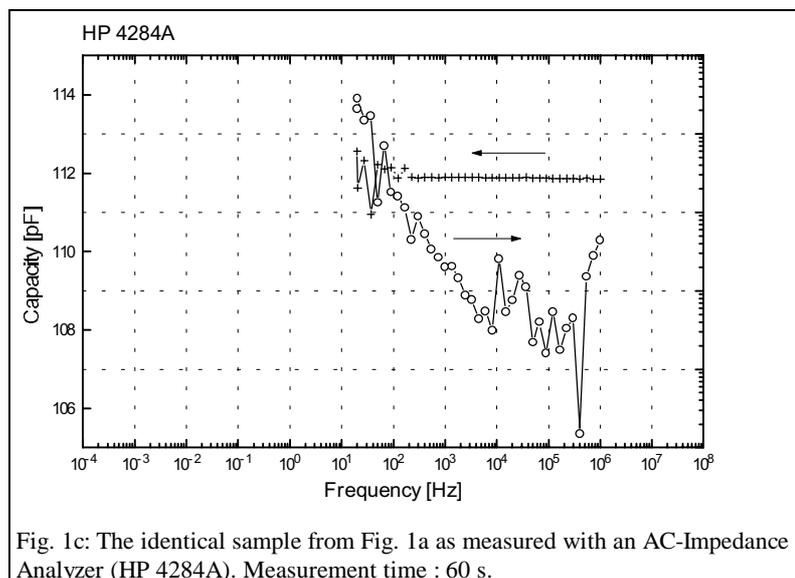
Fig. 1c: The identical sample from Fig. 1a as measured with an AC-Impedance Analyzer (HP 4284A). Measurement time : 60 s.

stainless-steel plates (diameter : 40 mm) being separated by two glasfiber spacers (thickness : 100 µm) shows the strength of the digital measurement technique (Fig. 1a/b) in comparison to the analog AC-impedance measurements (Fig.1c.). While the analog measurements become noisy for frequencies < 300 Hz the performance of the Dielectric Converter in combination with the digital Lock-In amplifier (Fig. 1b) or gain-phase analyzer (Fig. 1a) allows high precision measurements in the specified frequency range.

Only above 4 MHz artefacts are observed (Fig. 1a). In the frequency range from 10^6 Hz to 10^9 Hz resp. $1.8 \cdot 10^9$ Hz two RF-reflectometers are compared, the HP 4291A (Fig. 2a) and the HP 4191A (Fig. 2b). As sample capacitor two RF electrodes (diameter 5 mm, spacing 50 µm) were used and inserted in the Novocontrol sample cell BDS 2300 which was mounted on the RF extension line BDS 2000. It turns out that the newly developed reflectometer HP 4291A (Fig. 2a) is highly superior compared to the HP 4191A. (Fig. 2b). This is especially observable for frequencies between 10^6Hz and 10^7 Hz.

In summary, the experimental requirements of modern dielectric spectroscopy can be fulfilled by a combination of frequency response analysis (using a Novocontrol Broadband Dielectric Converter in combination with a gain phase analyzer) and reflectometry (using the new HP 4291 in combination with a Novocontrol RF-extension line and sample cell). This results in a frequency window from 10^{-5} to $1.8 \cdot 10^9$ Hz with a dynamic range from 10^{-4} to 10^3 in the dielectric loss.

Fig. 2a : Measurement of an air capacitor (diameter : 5 mm, spacing 50 µm) placed in the Novocontrol sample cell BDS 2300 with the RF-extension line BDS 2000. As RF-reflectometer the HP 4291A was used. Measurement time : 60s.
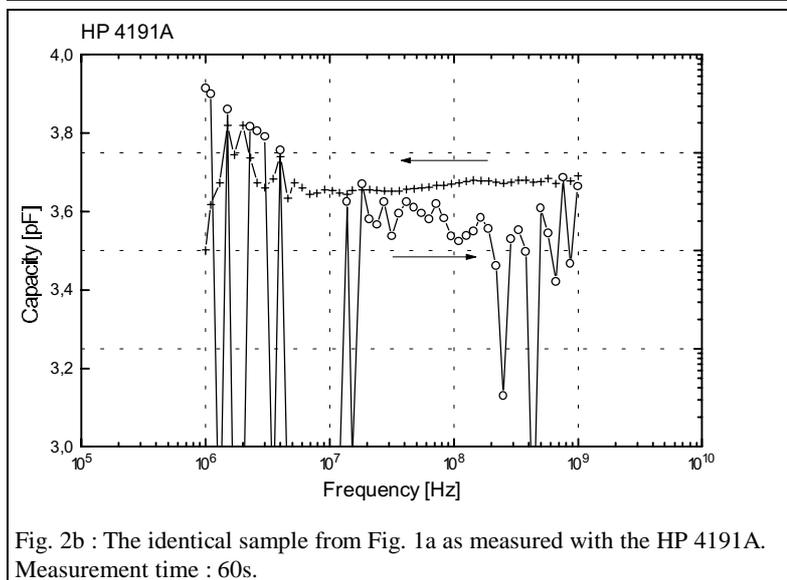
Fig. 2b : The identical sample from Fig. 1a as measured with the HP 4191A. Measurement time : 60s.

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NOVOCONTROL Cryo System for Dielectric Applications Improved by the New QUATRO 4.0 Controller

This article describes the NOVOCONTROL Cryo System for temperature control of dielectric measurements and the capabilities of the new QUATRO 4.0 controller. The QUATRO 4.0 controller is the successor of the QUATRO <= 3.5 controller series and was completely redesigned for optimal performance in combination with the NOVOCONTROL Cryo System. Compared to QUATRO <= 3.5 series, the QUATRO 4.0 offers the following advantages :

- reduces stabilization times typically by a factor of 2
- reduces nitrogen consumption typically by a factor of 3
- prevents the temperature from overshooting the setpoint typically by less than 0.2°C
- operates over the full temperature range from -160°C - +450°C with one factory set of PID parameters
- adapts automatically the nitrogen gas pressure in dependence of sample temperature
- finds automatically the PID parameters if connected to an unknown temperature cell (self-tuning)
- is easy to operate
- uses new nonlinear control algorithms
- uses an IEC port for data exchange with the PC

Temperature Control for Dielectric Measurements

Although the general purpose of any temperature control system is setting the actual temperature
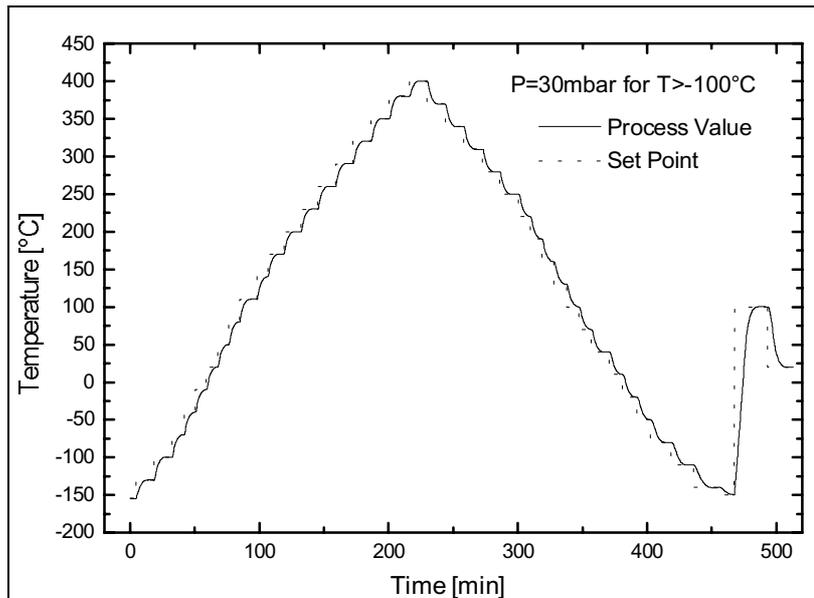
Fig. 1 : Temperature set point and sample temperature in dependence of time for the NOVOCONTROL Cryo System in combination with the new QUATRO 4.0 controller. Set point step after stabilization to 0.1°C and 0.1°C/min.

(process value) of a sample to a desired temperature (setpoint), there are some special requirements for systems used for dielectric measurements. An important requirement is fast temperature settling times, as these consume (for frequencies above 0.03 Hz) the major part of the measurement time and therefore are limiting the system performance. On the other hand, the dielectric response may depend very sensitive (e.g. in the region of phase transitions) on the temperature. Therefore for accurate measurements, a cryo system which is both fast and very accurate is required. A further requirement is, that after a setpoint step the sample temperature should approach the setpoint, but must not exceed it. This is important if samples are nearly measured a phase transition. The transition temperature must not be exceeded as the sample will change its structure or even become damaged in this case (e.g. melt).

The NOVOCONTROL Cryo System in combination with the new QUATRO 4.0 controller satisfies these three demands very well. A typical performance diagram of temperature frequency

measurement from -160°C to 400°C is shown in fig. 1. Typical stabilization times (for 0.1°C stability) are about 10 minutes per temperature step (20 minutes for 0.01°C). This means, that a two dimensional dielectric measurement with 12 frequency sweeps at 12 different temperatures will be performed in less than 2 hours. Moreover, from fig. 1 can be seen that the sample temperature practically follows the setpoint with no oscillations and without overshooting.

Set-up or structure of the NOVOCONTROL Cryo System

The Cryo System in combination with the QUATRO controller allows to automatically set the sample temperature. The structure is modular and may be combined with any NOVOCONTROL Dielectric Analysis System. The main parts of the system are the cryostat, the gas heating module, and the microprocessor QUATRO controller. The QUATRO has 4 independent loops controlling the sample temperature, the gas temperature (at the gas heater), the

temperature of the liquid nitrogen in the dewar, and the pressure in the dewar.

The liquid nitrogen evaporator heats the liquid nitrogen until a specified pressure in the dewar is reached. The actual pressure is controlled by the channels 1 and 2 of the QUATRO controller. The pressure is automatically adjusted for optimal performance depending on the setpoint of the sample temperature (high pressure at low temperatures, low pressure at high temperatures). Due to the pressure, the cold gas flows out of the dewar into the gas heating module. The line from the dewar to the gas heating module is vacuum isolated. The gas heater is controlled by channel 3 and 4 of the QUATRO controller in order to match the actual temperature at the sample to the desired temperature setpoint. After the gas heating module, the gas flows directly into the vacuum isolated sample cell volume in which the sample cell is mounted.

Due to the high stability of the gas pressure and the double control arrangement of the gas heating, the temperature stability is better than 0.01°C. Moreover, as the gas flows directly through the sample cell, this design allows a very fast and safe operation which is required for automatic controlled systems. Even if the sensors are damaged or the liquid nitrogen dewar becomes empty, there will be no damage at the system or the sample.

Setpoint Dependent Pressure Adaptation

The NOVOCONTROL Cryo System will reach its lowest temperature limit (-160°C) only if an appropriate pressure for the liquid nitrogen is applied. On the other hand, for higher temperatures only a lower pressure is necessary. In addition, there will not be enough heating power to reach the highest temperatures above 300°C at high pressure. Therefore, the new QUATRO 4.0 automatically
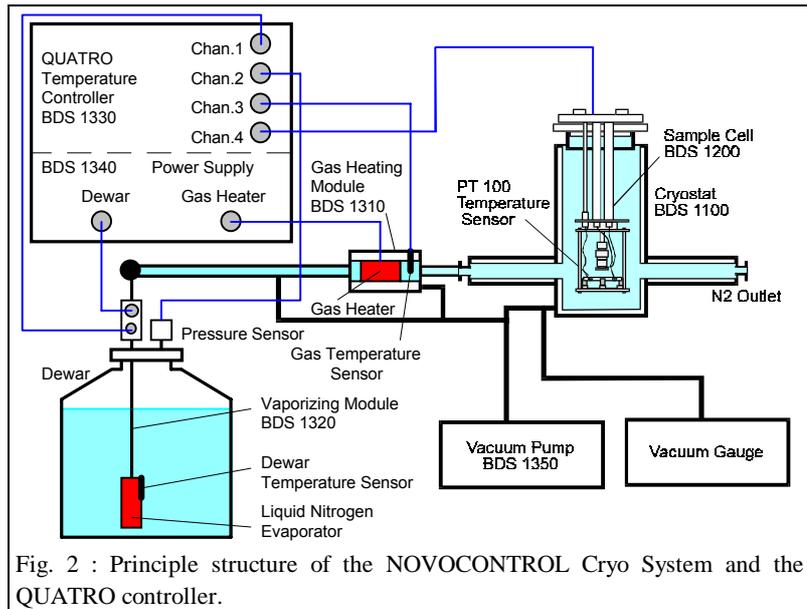
Fig. 2 : Principle structure of the NOVOCONTROL Cryo System and the QUATRO controller.

controls the pressure in dependence of the temperature setpoint as shown in fig. 3.
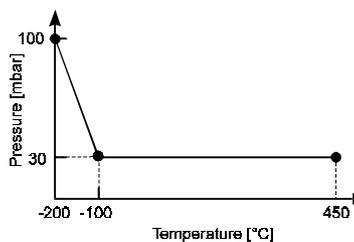
Fig. 3 : LN$_2$ pressure adaptation in dependence on temperature.

Due to the improved performance of the controller (see next paragraph), it is possible to reduce the pressure above -100°C to 30mbar without limitations in performance. Compared to the QUATRO<=3.5 controllers which are operated at a constant pressure of 100mbar, less than 1/3 of the liquid nitrogen is consumed. Moreover, due to the reduced stabilization times (typically by a factor of 2) there will be an additional saving of nitrogen. The pressure temperature dependence can be adjusted with 3 variable points. Fig. 3 shows the factory values for the NOVOCONTROL Cryo System.

Basics of Controller Operation

As shown in fig. 4, the actual temperature process value Tpv of the sample is measured by the temperature sensor. The second input is the temperature setpoint Tsp (the desired temperature) which is set by the user. The control deviation is calculated by $\Delta = Tsp - Tpv$. The purpose of the controller is to set the (formal) controller output temperature $Tout$ in such a way, that Δ becomes equal to zero in a time as short as possible without large oscillations or overshooting. In order to do this, Δ is processed further by the three independent PID parts, contributing to $Tout$ according to (1). The Temperature to Power Converter (DC power supply) converts $Tout$ to the power which is applied to the sample by the heater.

Nonlinear Controller Operation

As can be seen from (1), $Tout$ depends linear on Tsp and Tpv. Therefore, the performance of the controller will be good, if also the process is linear in temperature (if Tpv linear depends on $Tout$). Unfortunately this is only true for small values of Δ. For larger Δ, the

process becomes highly nonlinear. This is also due to the limitations of the Temperature to Power Converter (limits at zero power and maximum power). This non linearity affects the system in the following points

- The reaction of the temperature system to changes in *Tout* becomes slower. Hence, the control deviation Δ remains on large values for longer times then in the linear case. Due to the time integration, this causes a too strong response of the I part, resulting in overshooting or even instability of *Tpv*.

- If a large step in *Tsp* is selected, the controller will set the power to its maximum (or minimum value) for a long time. Hence, the time gradient of the temperature process value *dTpv/dt* will become quite large. If *Tpv* reaches the setpoint *Tsp*, there will not be enough cooling (or heating) power to slow down the fast changing temperature due to power limitations and *Tpv* will heavily overshoot the setpoint *Tsp*.

If a standard PID controller according to (1) is used, these effects can be partly compensated if the PID parameters are adjusted in such a way, that the response of the controller to changes in Δ becomes slower compared to the linear case. On the other hand, slowing down the controller response results in longer stabilization times and less accuracy. In addition, automatic PID parameter detection algorithms (selftune) generally provide the optimal parameters only for linear systems. Therefore, in practice even if selftune procedures are available, finding a PID parameter set working over a large Δ range often results in a cumbersome compromise between not to much overshooting, stabilization time and stability.

For this reasons, the new QUATRO 4.0 uses the standard PID algorithm only for $|\Delta|<2°C$

$$Tout(t) = \frac{100}{p}\left\{\Delta(t) + \frac{1}{ti}\int_{t_0}^{t}\Delta(t')dt' + td\frac{d}{dt}\Delta(t)\right\} \quad (1)$$

Fig. 4 : Components of the temperature controller and the temperature system
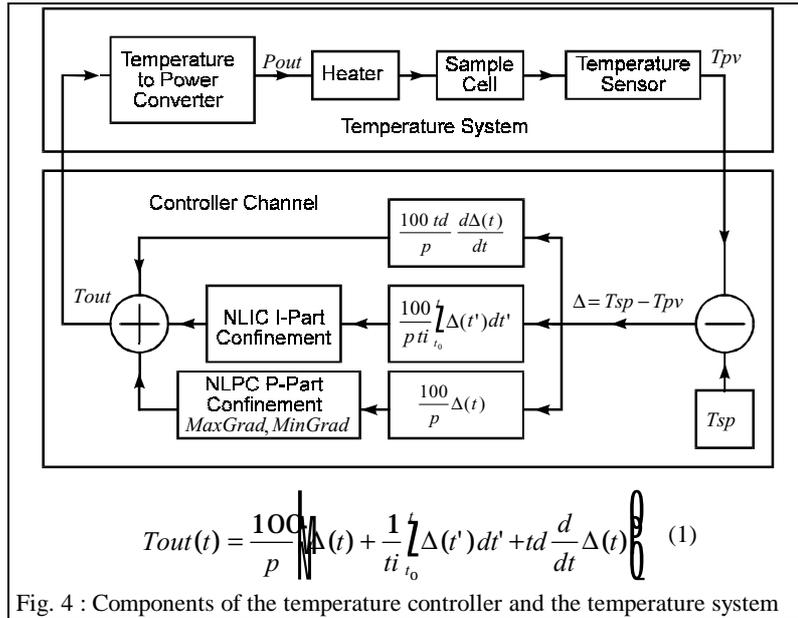
where the system surely is in the linear state. For $|\Delta|>2°C$ where non linearity may appear, the new nonlinear algorithms NLIC (NonLinear I-Part Confinement) and NLPC (NonLinear P-Part Confinement) controlling both temperature process value *Tpv* and its time derivation *dTpv/dt* as shown in fig. 4 are used. These algorithms determine the response of the I-part and the P-part in such a way that *dTpv/dt* does not exceed a specified value *MaxGrad* for large deviations Δ. In a second step, *dTpv/dt* is slowed down with an exponential behaviour until $|\Delta|<2°C$ is reached and the normal PID controller is activated. This procedure totally compensates the non linearity and prevents the system from overshooting by more than typically 0.2°C. Moreover, the PID parameters can be set to the fast values determined by selftune procedures for linear systems.

Selftune

The QUATRO 4.0 was designed to operate in combination with the Cryo System with high performance in any condition with the factory PID parameters. Nevertheless, if connected to a new (unknown) temperature system, or if something at the

NOVOCONTROL Cryo System was changed (e. g. a different sample cell is used), it may become necessary to determine a new set of PID parameters. In practice, such a set is often hard to find as the number of possible combinations is quite large. Therefore, the QUATRO has a selftune algorithm which can automatically adapt the PID parameters to the temperature system.

If the temperature system is linear and time invariant, the response of the process value *Tpv* to an arbitrary setpoint *Tsp* can be calculated by linear system theory. In this framework, the response of both, the temperature system and the controller can be described by two complex transfer functions in the frequency domain. The transfer functions give the response of the both system components to a harmonic input signal with frequency $\omega/2\pi$

$$Tout(\omega) = \Delta\exp(i\omega t)\cdot CTF(\omega) \quad (2)$$
and
$$Tpv(\omega) = Tout(\omega)\cdot STF(\omega) \quad (3)$$
where STF and CTF are the transfer functions of the process and the PID controller.

As the CTF only depends on the controller PID parameters it can be easily calculated by connection of (1) and (2). On the other hand the

STF depends on the physical properties of the process. The QUATRO selftune algorithm operates in two steps :

- Cryo system identification :

  After a setpoint step, the response of the actual temperature system (*Tpv* and *Tout*) is measured as function of time. From this measurement, the STF is calculated by a numerical Fourier Transform converting the time domain data into the frequency domain.

- Controller design : From the measured value of STF, a appropriate set of PID parameters is calculated according to several laws.

An example of a STF for the NOVOCONTROL Cryo System is shown in fig. 5. At low frequencies below 10^{-4} Hz, both the absolute value and the phase shift of the STF are nearly independent of frequency. This shows, that in this frequency range the process value *Tpv* follows the output of the controller *Tout* nearly without delay. At a frequency of $3 \cdot 10^{-3}$Hz, a phase shift of 180° is reached and the absolute value has dropped to less than 5% of its static value. At this frequency range, Tpv responds to changes in Tout in the opposite direction, which means that if *Tout* increases, *Tpv* will decrease. This situation causes overshooting or oscillations of *Tpv* if the controller PID parameters are not well adjusted. Therefore, the PID parameters have to be selected, that the response of the controller for frequencies with large phase in the STF is only weak.

The response of the controlled temperature system (controller connected to the process and activated) is determined by the TTF which is the product of the system transfer function and the controller transfer function (TTF = CTF·STF). According to the Nyquist laws, the QUATRO calculates the PID parameters in such a fashion , that
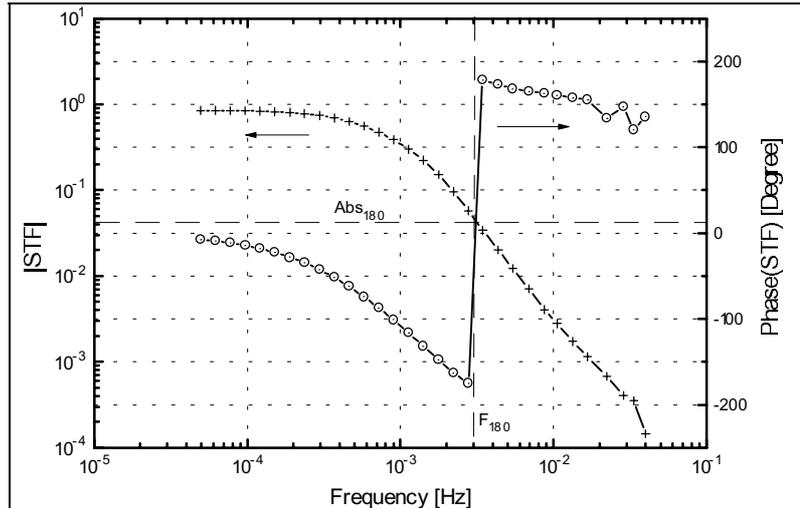
Fig. 5 : System Transfer Function (STF) of the NOVOCONTROL Cryo System determined by the QUATRO self tune function.

- the TTF will create no oscillations (|TTF| < 1 for phase shift < -180°)

but on the other hand

- the frequency where |TTF| becomes smaller than 1 is as high as possible which ensures fast settling times if the setpoint is changed.

In order to achieve this, the following two procedures can be applied :

- **NLIC** (NonLinear Integration Confinement) will calculate the PID parameters for optimal performance for the NOVOCONTROL Cryo System in combination with the NLIC control algorithm used by the QUATRO. This procedure uses all frequency points of the STF in order to calculate the PID parameters.

- **ZI-NI** will calculate the PID parameters according to the laws of Ziegler and Nichols. These are the standard laws for adjusting the parameters of PID controllers. The PID parameters are calculated from one point of the STF at the frequency F_{180} with 180° phase shift. Abs_{180} is the absolute value at F_{180} in the STF (see fig. 5).

$$p = \frac{100}{0.6} Abs_{180}, \quad ti = \frac{2}{F_{180}},$$

$$td = \frac{0.12}{F_{180}}$$

Conclusion

In order to install this new control software on existing QUATRO systems, a new microprocessor card and an IEC interface card must be mounted in the system. NOVOCONTROL is offering an upgrade-service for this at low cost.

Literature
Anderson, B.D.O. and J.B. More (1971). Linear optimal control. Englewood Cliffs: Prentice-Hall.

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NOVOCONTROL Worldwide

A short note to keep you informed about new affairs within the NOVOCONTROL organisation.

NOVOCONTROL has spent a lot of effort in development of new hardware and software for dielectric materials measurements

to satisfy the requirements of our customers worldwide.

Our international client list is increasing gradually and we wish to continue to offer our customers excellent support in every possible way.

For this reason NOVOCONTROL has recently entered an agreement with Jed Marson in England enabling him to distribute NOVOCONTROL products and services to scientific and industrial clients in the UK.

Our aim is to intensify the scope of our common activities also abroad.

Jed Marson is experienced in technical sales and marketing and has already been dealing with several NOVOCONTROL projects successfully.

In order to show this new partnership, Jed Marson is trading under the name NOVOCONTROL International.

Until recently the clients in North America and Japan had to contact our factory and head office at

Hundsangen/Germany for product information and prices. Now clients in the USA can contact directly Dr. Joachim Vinson, who is an expert on material analysis. Dr. Vinson will organize the participation of NOVOCONTROL to the MRS Fall meeting at Boston in November '95. Furthermore, we are happy to anounce, that we appointed as our agent in Japan : MORIMURA Bros. Inc. in Tokyo.

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Abstracts and papers are always welcome. We can publish max. 2 pages A4 on each subject. Please send your script to the editor.

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