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Effect of Pressure on the Side-Chain Crystallization of Poly(N-Octadecyl Methacrylated) Studied by Dielectric Spectroscopy

Introduction

It is well known [1][2] that complete specification of the dynamic state of amorphous polymers requires knowledge of the relaxation times as a function of temperature (T) and pressure (P). We have recently studied the effect of pressure on (i) the relaxation modes of the type-A polymer polyisoprene (PI) and (ii) on the dual segmental relaxation of an athermal poly(isoprene-*b*-vinylethylene) (PI-PVE) diblock copolymer melt using dielectric spectroscopy. For the polyisoprene the effect of pressure on the segmental and longest normal modes was investigated [3] [4] as a function of chain length for M/M_e ratio's: 1/5, 1/2, 2/3, 2 and 5. We found that the spectral shape of the segmental and normal modes is invariant under temperature and pressure variations but the time-Pressure superposition fails as a consequence of the stronger P -dependence of the segmental mode. The corresponding failure with decreasing temperature under isobaric conditions is well known [5]. The segmental mode activation volume for the different molecular weights was found to scale with the

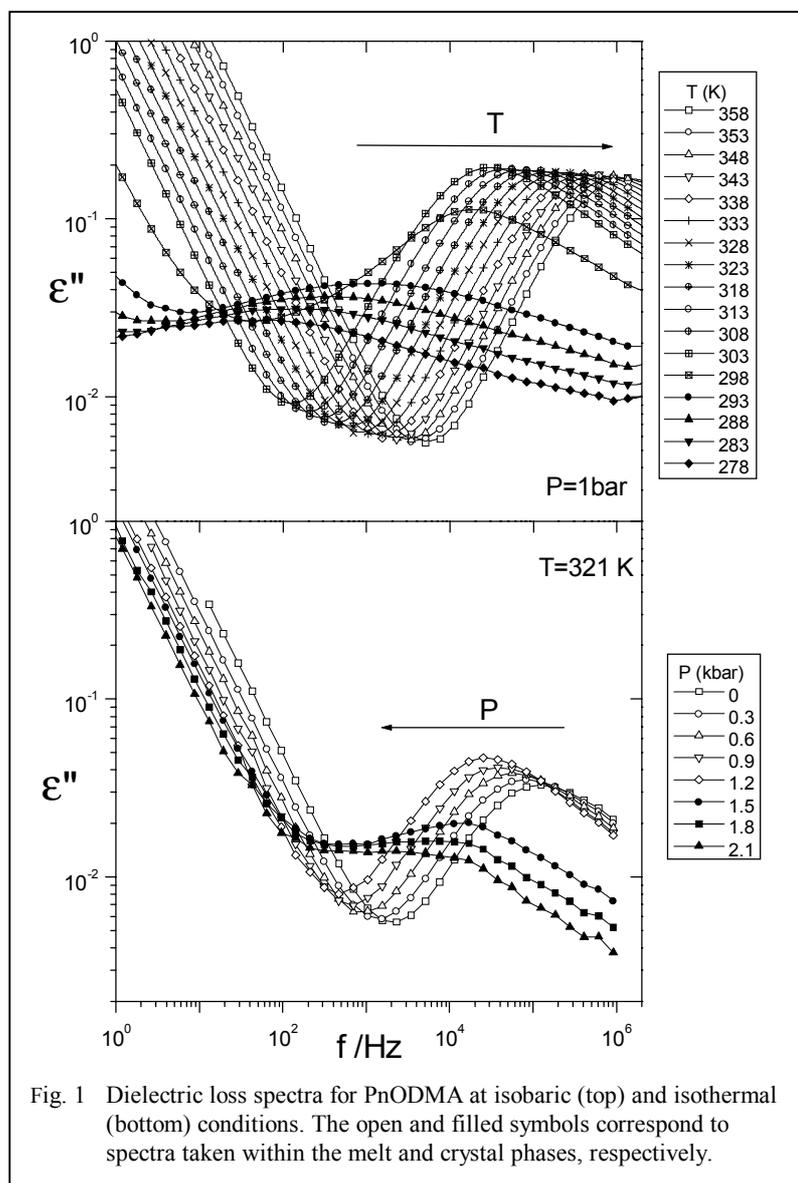


Fig. 1 Dielectric loss spectra for PnODMA at isobaric (top) and isothermal (bottom) conditions. The open and filled symbols correspond to spectra taken within the melt and crystal phases, respectively.

temperature difference from the respective glass transition temperature. Pressure is found to slow-down both modes in a quantitative similar way irrespective of chain length, implying that M_e is largely independent of pressure. In the case of the athermal PI-PVE diblock copolymer, the quantity $(\partial \log \tau / \partial P)_T$ was employed as a probe of the state of dynamic miscibility in the

system. We found that pressure – unlike temperature – induces dynamic homogeneity [6].

Although the effect of pressure on the segmental relaxation of amorphous polymers has been investigated the effect on the complex relaxation spectra of semicrystalline polymers remains totally unexplored. Herein we briefly report on the effect of pressure on the crystallization of

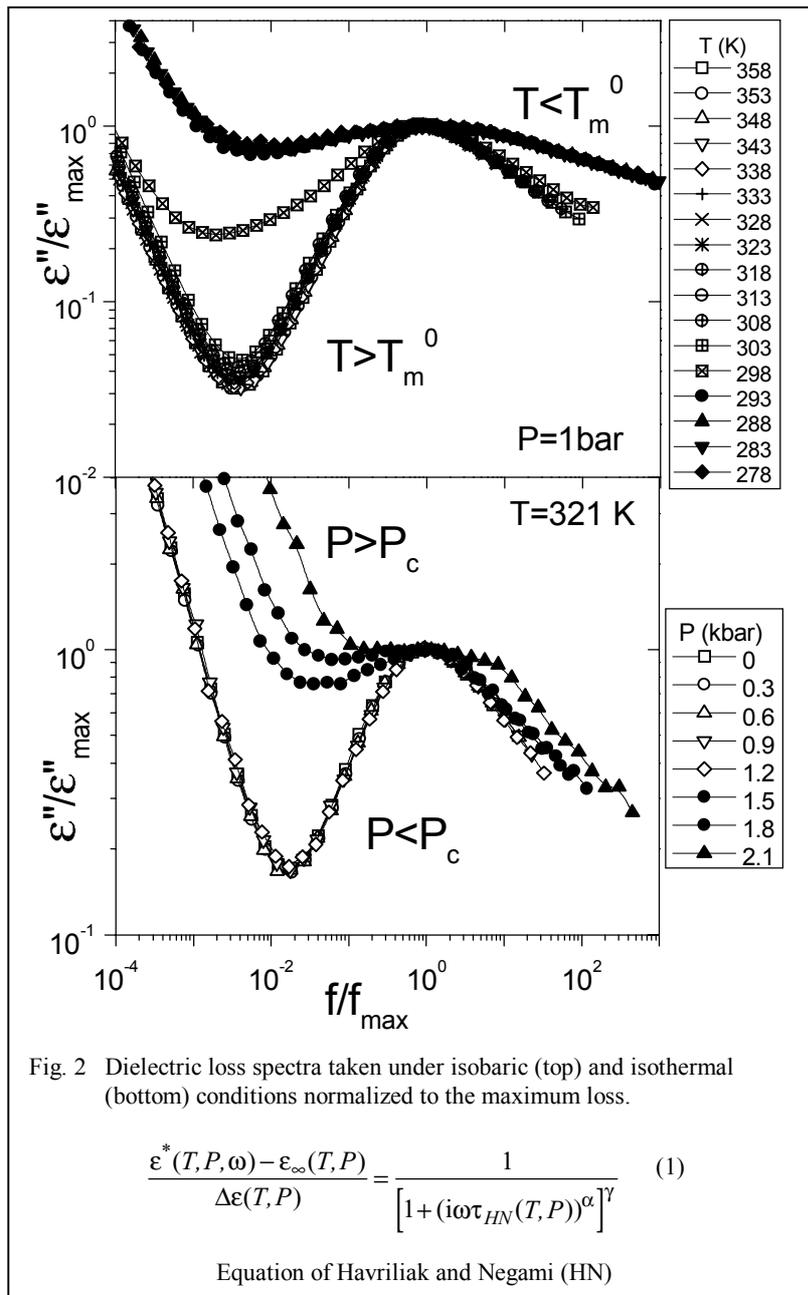


Fig. 2 Dielectric loss spectra taken under isobaric (top) and isothermal (bottom) conditions normalized to the maximum loss.

$$\frac{\epsilon^*(T, P, \omega) - \epsilon_\infty(T, P)}{\Delta\epsilon(T, P)} = \frac{1}{[1 + (i\omega\tau_{HN}(T, P))^\alpha]^\gamma} \quad (1)$$

the semicrystalline polymer poly(*n*-octadecyl methacrylate) (PnODMA) and more details can be found elsewhere [7]. For this purpose we have used static (WAXS, DSC) and dynamic probes (Dielectric Spectroscopy, DS). Earlier IR [8] and the present WAXS measurements have shown that - at atmospheric pressure - part of the side-chains composed of about 10 CH₂ units crystallize in a lattice with a hexagonal symmetry. We find that pressure has a strong influence on the side-chain crystallization of PnODMA by increasing the number the crystallizing CH₂ units.

experiment

The PnODMA had a molecular weight of 1.43×10^5 with a polydispersity of 2.4. The set-up for the pressure dependent dielectric measurements [9] consisted of the following parts: temperature controlled sample cell, hydraulic closing press with pump and pump for hydrostatic test pressure. Silicon oil was used as the pressure transducing medium. The sample cell consisted of two electrodes with 20 mm in diameter and the sample with a thickness of 50 μm. The sample capacitor was sealed and placed inside a teflon ring to

separate the sample from the silicon oil. The dielectric measurements were made at different temperatures in the range 253 to 363 K, for pressures in the range from 1 bar to 3 kbars, and for frequencies in the range from 10^{-2} to 10^6 Hz using a Novocontrol BDS system composed from a frequency response analyzer and a broad band dielectric converter. The complex dielectric permittivity $\epsilon^* = \epsilon' - i\epsilon''$, where ϵ' is the real and ϵ'' is the imaginary part, is a function of frequency ω , temperature T and pressure P , $\epsilon^* = \epsilon^*(\omega, T, P)$. In Figure 1 representative dielectric loss spectra for the PnODMA are shown under isobaric ($P=1$ bar) and isothermal ($T=321$ K) conditions. Both sets of spectra display a single mode which becomes slower with increasing pressure and decreasing temperature. There exist a particular critical temperature (T_m^0) and a critical pressure (P_c) below and above which, correspondingly, the polymer undergoes side-chain crystallization. The melt to crystal transition is indicated by the loss of intensity and slower relaxation of dipoles within the restricted amorphous phase.

In the analysis of the DS spectra we have used the empirical equation of Havriliak and Negami (HN) (1) where $\tau_{HN}(T, P)$ is the characteristic relaxation time in this equation, $\Delta\epsilon(T, P) = \epsilon_0 - \epsilon_\infty$ is the relaxation strength of the process under investigation and α , γ describe, respectively, the symmetrical and asymmetrical broadening of the distribution of relaxation times. In the fitting procedure we have used both the ϵ' and ϵ'' values at every temperature and pressure. The complete P - and T -dependence of the dielectric strength and of the local field is discussed in ref[7]. The rise of the ϵ'' at lower frequencies is caused by the conductivity ($\epsilon'' \sim (\sigma_0/\epsilon_0)\omega^{-1}$, where σ_0 is the dc-conductivity and ϵ_0 is the permittivity of free space) which has been included in the fitting procedure.

results and discussion

Below the melting temperature (T_m^0) for a given pressure or above the critical pressure (P_c) at a given temperature, upon crystallization, the dielectric spectra undergo considerable changes: first they shift to lower frequencies and broaden considerably towards the lower frequency side. The loss of the crystal phase intensity relative to the melt which is both T- and P-dependent and the broadening of the spectra originate from the T- and P-dependent number of dipoles within the restricted amorphous phase. There is also a weak T- and P-dependent intensity in the melt state reflecting decreasing pair correlations with increasing T and decreasing P. In Figure 2 the spectra of Figure 1 have been normalized to the maximum dielectric loss and reveal that the time-Temperature-superposition (tTs) and the time-Pressure-superposition (tPs) works well in the melt state but only approximately in the crystal state. Figure 3 gives the dependence of the relaxation times at the maximum of the loss peak as a function of applied pressure for different temperatures. Within the

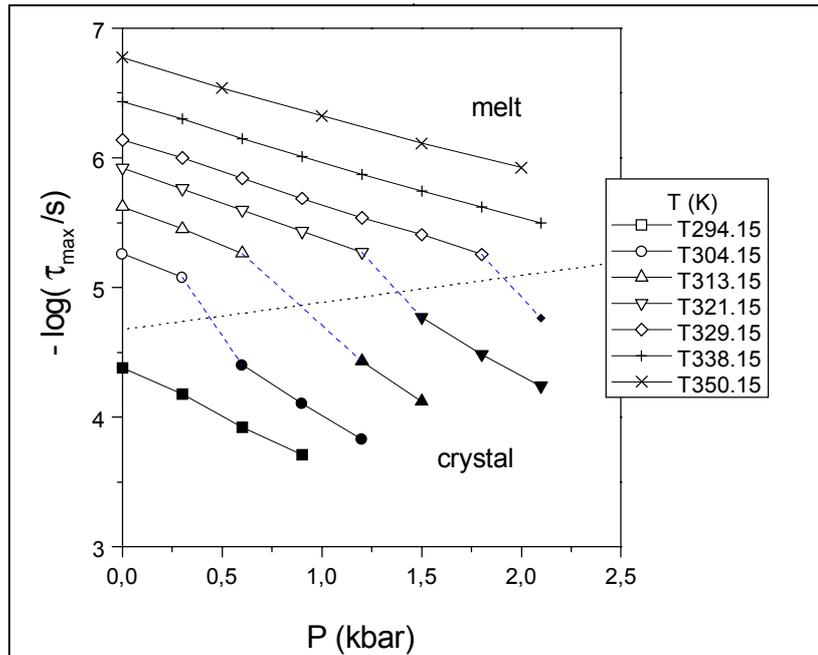


Fig. 3 Pressure dependence of the relaxation times corresponding to the melt (open symbols) and crystal (filled symbols) states.

investigated pressure range both relaxation times, in the crystal and melt states, display a nearly linear dependence on pressure, but the dependence is stronger in the crystal state. For a purely activated process we can define an activation volume as $\Delta V = 2.303RT(\partial \log \tau / \partial P)_T$ and this is always higher in the crystal state as compared to the melt. At the same time the apparent activation energy at a constant

pressure $Q_p = -2.303 RT^2(\partial \log \tau / \partial T)_P$ is also higher in the crystal as compared to the melt state. The higher activation volume and apparent activation energies in the crystal phase are suggestive for a more cooperative relaxation within the restricted amorphous phase. Furthermore, from the dependence of the relaxation times on density we found considerable differences between the melt and crystal states: first, T is more effective than P in shifting the relaxation times but, within the measured T-range melts with the same density differ in their relaxation times by 2 decades while in the crystal state they differ by 4 decades. This results mainly from the much higher activation energy in the crystal as compared to the melt state.

The critical crystallization temperature T_c was found to increase linearly with P as shown in Figure 4. Since the crystallization/melting process is a first order transition we can employ the Clausius-Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \quad (2)$$

where ΔH is the latent heat of the transition and ΔV the change in volume. Using $dP/dT = 0.0579$ kbar/K, $\Delta V = 0.0574$ cm³/g and

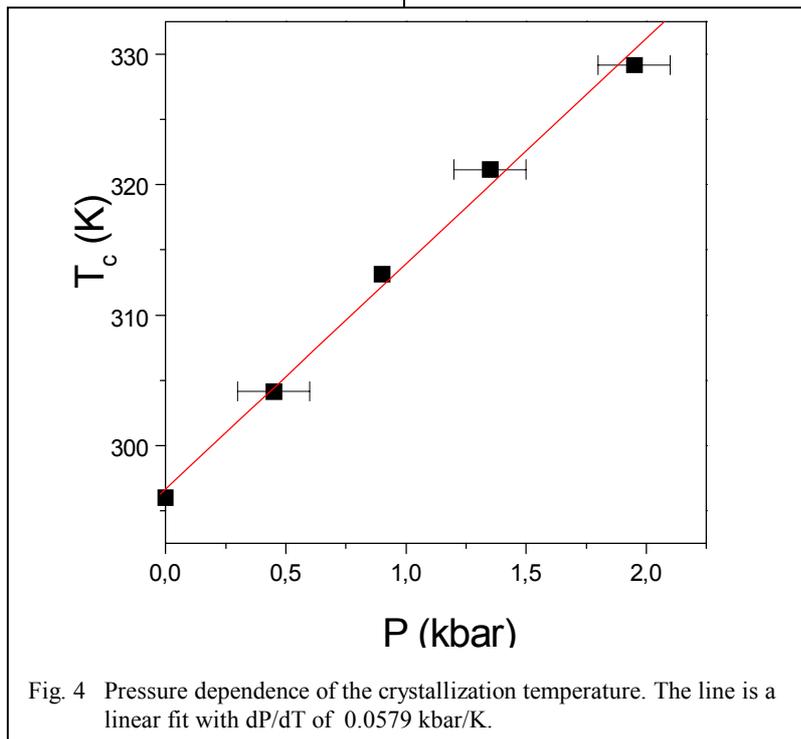


Fig. 4 Pressure dependence of the crystallization temperature. The line is a linear fit with dP/dT of 0.0579 kbar/K.

T=296 K we deduce a latent heat of 98 J/g. The latter is much higher than the latent heat obtained from DSC at atmospheric pressure (45 J/g). The higher latent heat results from the incorporation of additional CH₂ units within the crystal phase. Given that each CH₂ unit of lower alkanes contributes about 10 J/g to the latent heat we deduce that pressure results in the incorporation of 4-5 additional CH₂ units in the side-chain crystal phase.

conclusions

The main results from the T- and P- dependent DS experiments are as follows:

1. Time-temperature-superposition (tTs) and time-pressure-superposition (tPs) works in the melt state and only approximately in the crystal state.
2. Below the melting temperature (T_m^0) or above some critical pressure (P_c), upon crystallization, the spectrum shifts to lower frequencies and broadens considerably towards the lower frequency side.
3. From the T- and P-dependencies of the characteristic relaxation times we found that the (single) relaxation process in the semicrystalline state possess higher activation energy and higher activation volume as compared to the melt.
4. Melts with the same density differ in their relaxation times by 2 decades while crystals of the same density differ by as much as 4 decades, and
5. From the linear increase of the transition temperature on pressure and using the Clausius–Clapeyron equation we found that pressure increases the number of the crystallizing CH₂ units thus increasing the crystal thickness.

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How to Contact Ultra-Thin ($d \leq 50$ nm) Organic Layers Without Evaporation of Metal Electrodes?

introduction

It is a challenge for broadband dielectric spectroscopy to enable measurements of the molecular dynamics in ultrathin organic layers. This is especially true in view of the fact that the dielectric method increases in sensitivity with decreasing thickness of a sample capacitor. But the difficulties to provide an ultrathin organic layer with electrical contacts are manifold:

- (i) ultrathin organic layers are full of defects,
- (ii) they have often a rough surface,
- (iii) evaporation of a metal electrode leads usually to electrical shorts,
- (iv) during the process of evaporation remaining solvent in the sample might be pumped out hence leading to cracks in the molecular layer and
- (v) the UV-exposure of the glowing evaporation source can damage the sample.

new preparation technique

To avoid these drawbacks, a novel sample preparation technique was developed which enables for the first time to study in a broad frequency and temperature range the molecular dynamics in ultrathin grafted polymers (e. g. poly(γ -benzyl-L-glutamate)). [L. Hartmann

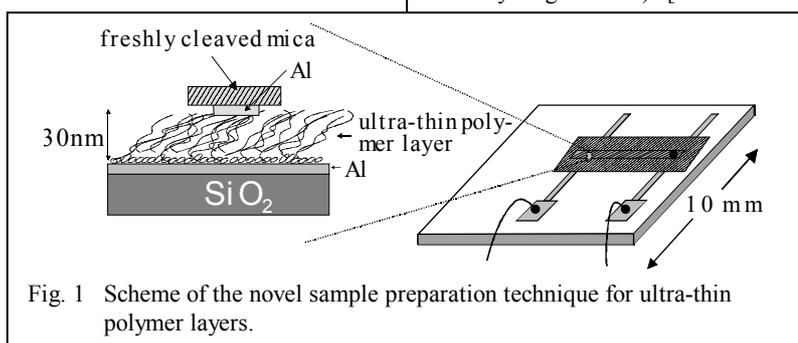


Fig. 1 Scheme of the novel sample preparation technique for ultra-thin polymer layers.

et al.: Macromol. Rapid Commun., in press, 2000].

To prepare the ultrathin polymer in a capacitor arrangement, the organic layer is covered with a freshly cleaved lamella of mica (thickness 5 μm) which was previously evaporated with aluminum stripes heaving a thickness of 70 nm. Thus a sample capacitor with an area of 2 mm² is formed (Fig. 1).

Mica offers the advantage that it shows atomically flat surfaces after the cleaving. To maintain this purity of the surfaces, the mica was cleaved in a flow box and placed immediately afterwards in a small chamber where it could be kept under protection gas (pure nitrogen). Afterwards it was mounted in the evaporation apparatus (Leybold Univex 300) where it could be opened after evacuation of the evaporation chamber by means of a remote control. Thus, contamination of the mica surface and of the electrode surface (after evaporation) was avoided.

In the above mentioned publication the novel preparation technique is described in detail and compared with measurements on samples having evaporated electrodes. It is additionally shown that using the new technique it is possible to measure the dynamics of swollen grafted polymer layers as well.

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Novocontrol News

high voltage extension for Alpha analyzer to +-150V ac and dc up to 1 MHz

Usually, dielectric or conductivity material measurements are done with dielectric or impedance analyzers which apply an ac signal

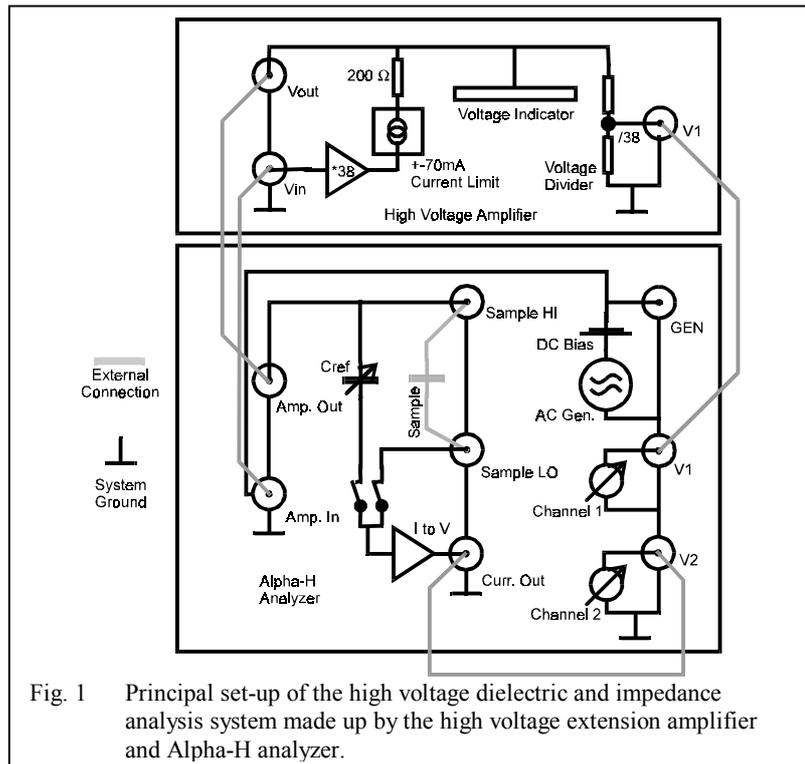


Fig. 1 Principal set-up of the high voltage dielectric and impedance analysis system made up by the high voltage extension amplifier and Alpha-H analyzer.

up to some volts to the sample. The sample impedance Z_s^* is derived by measuring the amplitude and phase of the sample voltage U_s^* and the resulting current I_s^* .

$$Z_s^* = \frac{U_s^*}{I_s^*}$$

For material measurements, highest demands apply to the quality of the impedance analyzer. This is because the impedance of materials may vary from metals to isolators by more than 23 orders of magnitude. In addition to the high impedance, for low loss dielectrics the phase angle between U_s^* and I_s^* has to be measured with highest precision down to 10^{-3}° .

These demands are matched by the new Novocontrol Alpha analyzer which was especially developed for precision material analysis. Compared to other broadband dielectric and impedance analyzers for the frequency range below 10MHz, the Alpha offers world best impedance range from 0.01 Ω .. 10¹⁴ Ω combined with a loss factor resolution < 10⁻⁵ (or <10⁻³°) in a single instrument.

For many applications it is advantageous to increase the voltage applied to the sample. These are

- **Non linear effects.** For electric material measurements, one generally presumes a linear response in the permittivity $\epsilon^*(\omega)$ and conductivity $\sigma^*(\omega)$. This means that $\epsilon^*(\omega)$ and $\sigma^*(\omega)$ do not depend on the magnitude of the applied voltage. For non linear materials, this does not apply anymore. E.g. doped semi- or ion conductors may show significant non linearity even at low electrical field strengths E . In contrast dielectric isolators generally require higher E fields in the order of 10⁸ V/m to cause non linear behaviour.
- **High impedance or low capacity samples.** In this case, the sample current may decrease below the noise limit of the impedance analyzer. If the sample voltage increases, the sample current will increase by the same amount. This shifts the analyzer upper impedance limit to higher values and reduces noise. Especially low loss dielectrics can be measured with lower noise to lower frequencies.

- **Sample test under similar conditions as application.**

For many industrial applications it is necessary to test the sample under similar conditions as they will be exposed to in a later application. E.g. an isolation material may show low loss at low electrical field strength, but higher losses or even electrical breakdown at high fields.

In order to match these kind of applications, Novocontrol introduces a new turn key solution for dielectric and impedance measurements at ac voltages up to $\pm 150\text{Vp}$ (106Vrms) and frequencies from $3\mu\text{Hz}$ to 1MHz . In addition dc bias voltage up to $\pm 150\text{V}$ may be superimposed to the ac voltage. In contrast to most other systems, all signals remain dc coupled even if dc bias is applied. Therefore dc bias measurements are possible over the whole frequency range down to $3\mu\text{Hz}$. The system is based on the Alpha-H analyzer and a high voltage extension amplifier as shown in fig. 1. The amplifier is connected between the Alpha low voltage generator and the sample or the Alpha internal reference capacitors. In order to measure the voltage U_s^* applied to the sample, U_s^* is reduced by a voltage divider mounted in the high voltage extension unit. This low voltage signal is then measured via the Alpha-H V1 channel.

In contrast to other high voltage dielectric analysis systems, the Novocontrol system is not limited to isolators, but operates at impedance from 0.1Ω .. $10^{15}\Omega$. The absolute accuracy in loss factor $\tan(\delta) < 3 \cdot 10^{-5}$ (10^{-5} resolution). The system is fully protected against permanent short and electrical breakdown of the sample and fully automated operated by the Novocontrol WinDETA software package. WinDETA allows impedance or dielectric material measurements in dependence of frequency, ac voltage, dc bias voltage, temperature, time or any

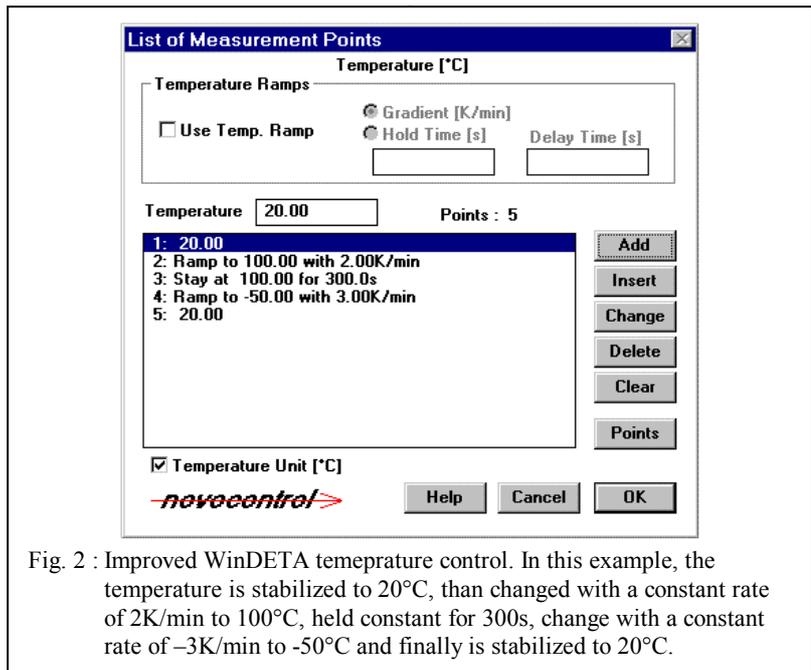


Fig. 2 : Improved WinDETA temperature control. In this example, the temperature is stabilized to 20°C , then changed with a constant rate of 2K/min to 100°C , held constant for 300s , change with a constant rate of -3K/min to -50°C and finally is stabilized to 20°C .

more dimensional combination of these quantities.

For high voltage permittivity or conductivity material measurements, the Novocontrol sample cell BDS 1200 can be used, which fits into the Novocontrol temperature control systems.

In order to not restrict the system to high voltage applications, the Alpha-H analyzer may be operated in a low voltage set-up too, without the amplifier connected. In this case, the performance corresponds to a standard Alpha-N type (ac voltage up to 3Vrms , $\pm 40\text{V}$ dc bias, $3\mu\text{Hz}$.. 10MHz).

latest WinDETA version available

The latest WinDETA version 3.8 has been completed. The following features were added

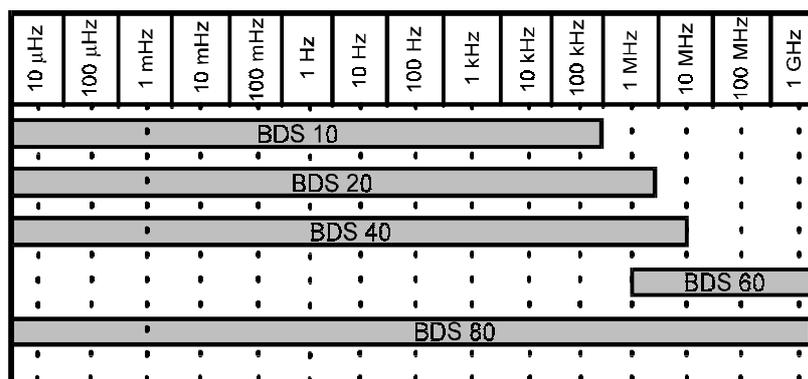
- **Improved temperature list.** In addition to fix temperature set points, intervals with a defined temperature rate or hold time can be defined. In the interval mode, WinDETA does not stabilise to a fix set point, but continuously runs measurements defined by the other independent variables. An example could be continuous repeated frequency sweeps while the temperature is changed at a fixed rate. As an arbitrary series of fixed

set points and continuous temperature and time intervals can be mixed in arbitrary order, any desired temperature – time profile can be programmed in an easy fashion. An example is shown in fig. 2.

- **New impedance analyzers supported.** New drivers for the HP 4294, HP 4194, and HP4285 have been added.
- **Ac voltage as a new independent variable value list.** This allows automatic variation of ac sample voltage in combination with the other independent variables frequency, temperature, dc bias and time, like e.g. frequency sweeps in dependence of ac voltage sweeps.
- **Alpha analyzer load short calibration.** It improves accuracy for low impedance measurements below $1\text{k}\Omega$. As thermal and contact resistance of the cables and the sample cell are eliminated, impedance down to 0.01Ω at the sample can be measured over the entire temperature range.

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