# MEASUREMENTS OF THE HIGH-TEMPERATURE MICROWAVE (400-3000 MHz) COMPLEX DIELECTRIC CONSTANTS OF MONOMERS ε-CAPROLACTAM AND ε-CAPROLACTONE

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## ABSTRACT

These measurements were part of an ongoing experimental program at the University of Connecticut to study high-temperature microwave-induced polymerization. The complex dielectric constants of monomers, ε-caprolactam (m.p. ~80°C) and ε-caprolactone (liquid at room temperature) were measured to 160°C and 110°C respectively, and a mixture of the two to 160°C. The values suggest that microwave heating of these monomers for polymer formation will be very straightforward. The half-power microwave absorption depths are less than 2.5 cm above 2GHz, suggesting that industrial scale-up to large volumes might benefit from use of a lower frequency, but that application to thin layers will be optimized at higher frequencies. All liquid state data were fitted to a Debye relaxation model to extract dipole moment relaxation times and thermal activation energies for the dielectric parameters.

## INTRODUCTION

Recent studies using microwave induced ring opening polymerization as a technique to generate thermoplastic polymers in a much shorter time period than conventional methods are very promising. In particular, Fang and Scola have shown that the simple polar monomers, ε-caprolactone and ε-caprolactam, can be converted by a solvent free microwave process to their respective thermoplastic polymers, as well as demonstrating copolymerization of the two monomers[1]. One of the steps in the development of this process was to measure the microwave absorption properties and the penetration depths for these monomers and their mixtures, at process temperatures.

The MPN system for measuring high temperature complex dielectric constants[2] is capable of making measurements on a small sample while it is being taken through the simulated steps of any desired industrial process. This means choice of atmosphere and control of the temperature-vs.-time curve. This is particularly useful in characterizing what happens in a microwave applicator during a batch process, and yields the time/temperature dependent microwave penetration depth. In conjunction with RF codes, this also yields the spatial distribution of heating rate and the reflected microwave power.

The frequency dependence of the dielectric response of liquids has often been fitted to the standard Debye relaxation model, where the dipole orienting effect of the microwave field is countered by the randomizing effect of thermal collisions. As the temperature increases, the molecular collision rate increases and the rate of randomization of the dipole direction increases. The expressions for the dielectric constant components use collisional relaxation frequencies which are assumed to have an exponential temperature dependence similar to a thermal activation curve[3]:

$$e'(f,T) := e_{inf} + \left[\frac{e_s - e_{inf}}{1 + \left(\frac{f}{f_r(T)}\right)^2}\right] \qquad e''(f,T) := \left[\frac{\left(e_s - e_{inf}\right)\cdot\left(\frac{f}{f_r(T)}\right)}{1 + \left(\frac{f}{f_r(T)}\right)^2}\right]$$

$$f_r(T) := \frac{2\cdot n_0}{2\cdot p}\cdot e^{\left(\frac{-dH_r}{k_B\cdot T}\right)}$$

$$t(T) := \left(2\cdot p\cdot f_r(T)\right)^{-1}$$

$n_0$= "low temperature" molecular collision frequency

$dH_r$= activation energy for collisional dipole re-orientation

$f_r(T)$= dipole orientation relaxation frequency

$t(T)$ = dipole orientation relaxation time (seconds)

By fitting the complex dielectric constant data, one determines the low frequency (effectively, the static) value of the dielectric constant, which can then be used, together with the Onsager approximation[4] relating the internal electric field, the molecular weight and the density, to extract the value of the permanent electric dipole moment of a liquid molecule.

## COMPLEX DIELECTRIC CONSTANT MEASUREMENT TECHNIQUE

The MPN system for measuring the complex scalar permittivity of materials between 400 MHz and 3 GHz, and up to a temperature of 1400°C, is based on the traditional “cavity perturbation technique”, using a multimode cavity at six frequencies to cover the frequency range[2]. The high temperature measurements are done by moving the hot sample and its holder rapidly from a conventional furnace into the high electric field (central) region of a thick-walled, well-cooled TM$_{0n0}$ cavity. The resonant frequencies and loaded Q`s of the cavity modes are rapidly measured by a Hewlett-Packard 8753 network analyzer and stored for off-line analysis (which includes subtraction of hot empty sample holder effects). During the few seconds the sample and its holder are in the cavity, the temperature drops only a few degrees for temperatures below 500°C. The cooling rate has been calibrated up to 1450°C and is calculated for each measurement. The sample and holder are then quickly returned to the furnace for further processing. The whole measurement sequence is pre-programmed over a desired set of temperatures, with furnace, linear motion actuator (sample movement), and network analyzer all controlled by a PC running Labview software.

The data analysis uses the general formalism of resonant cavity frequency shift theory[5,6]. The real and imaginary parts of the complex electric susceptibility, $\chi = \varepsilon_r - 1$, are related to the change in cavity resonant frequency and Q, through functions dependent on sample shape. The value of $\chi = \chi' - j\,\chi''$ may be determined from resonant-cavity perturbation measurements using the following equation:

$$\frac{\Delta f}{f_E} + j\left(\frac{1}{2Q_{L,S}} - \frac{1}{2Q_{L,E}}\right) = \frac{-\chi}{(1+F_{sh}*\chi)}\frac{V_s}{V_c}A \qquad (1)$$

where $f_E$, $Q_{L,E}$ are the cavity frequency and loaded Q, with the empty holder,
$\Delta f$ is the frequency shift produced by the sample,
$Q_{L,S}$ is the loaded cavity Q, with the holder and sample,
$F_{sh}$ is a real number dependent only on the sample shape,
$V_s$ and $V_c$ are the sample and cavity volumes,
A is a real calibration constant dependent only on the shape of the electric fields in the absence of the sample.

The two calibration constants in the formula, A and $F_{sh}$ can be determined either by comparison with computer simulations or by comparison with known samples. Solid or liquid calibration samples are used, depending upon whether the sample material is liquid (or a tamped-in powder) or solid (carved or cut sample or pressed pellets). The absolute calibration is normally done at room temperatures, and uses measurements on known high purity materials (similar to ASTM Standard Test Method, D2520-86, Method C).

For liquid calibrations, nonpolar materials with very low frequency dependence can be used for the low dielectric constant region (cyclohexane, carbon tetrachloride, benzene ), while polar materials, such as acetone and methanol, may be used for the higher dielectric constant region. In the present case cyclohexane, acetone and methanol were used.

Rapid movement of the sample in and out of a high temperature furnace requires the sample holder to be relatively insensitive to temperature gradients and to high cooling and heating rates. High purity amorphous silica can tolerate these conditions as well as being inert in air up to 1600°C. Thus the sample holders for high temperature work in the high frequency cavity are made from amorphous silica tubes, having 1 mm wall thickness, 4.0 mm inner diameter, and a 1 mm thick sample support base fused into the tube at the required height.

## MEASUREMENTS OF THE MONOMER DIELCTRIC CONSTANT VALUES

### Outline of Physical/Chemical Properties of the Monomers

The gross chemical structures of ε-caprolactam (mol. wt. 113) and ε-caprolactone (mol. wt. 114) appear very similar (Fig. 1), based on a single saturated six-carbon ring, differing only in the inserted functional group ( amide for ε-caprolactam, ester for ε-caprolactone). The amide group has a permanent electric dipole moment of 3 to 4 Debye units, while the ester group has a dipole moment of 1 to 2 Debye units[7]. This implies a higher melting point for ε-caprolactam (mp. 70°C, density 1.02 at 75°C,) than ε-caprolactone ( mp. -1.3°C, density 1.069 at 25°C).

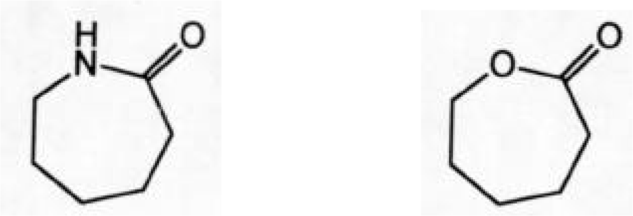

Fig. 1 ε-Caprolactam ε-Caprolactone
Schematic representation of chemical structure

### Measurements of Liquid ε-Caprolactone Monomer

The ε-Caprolactone material is liquid at room temperature, and is a thermally stable and reversible, and is not polymerized by heating. The intent of these runs was to simply study the microwave response up to 105°C, the limit of its practical use (flash point ~ 109°C ). The run was done with fine temperature resolution and long soak times (meaning more uniform temperatures in the sample) (Fig.2). The sample dimensions and mass were unchanged by the heating.

The dielectric response was fitted reasonably (Fig. 3) by a classical Debye relaxation model response for liquids whose molecules have permanent electric dipole moments. Clearly the fit to $\varepsilon'$ was not so good (15% error) at the higher temperatures. The low frequency limit is $\varepsilon' \approx 48 \pm 5$, the high frequency limit $\varepsilon' \approx 4 \pm 2$, with a dipole orientation relaxation frequency, $f_{r,}$ of ~2.4 GHz at 30°C, increasing to ~8.0 GHz at 100°C. The dipole orientation relaxation time, $\tau_{,}$ at 25°C is $76*10^{-12}$ s. Using the Onsager approximation to the internal field (with $n^2$ = the high frequency limit value of $\varepsilon'$), a dipole moment value of $1.2 \pm 0.25*10^{-29}$ Coulomb-Meters ( 3.6± 0.7 Debye units) was determined.

### Measurements on the ε-Caprolactam Monomer

Two samples of ε-Caprolactam were measured. This material is solid at room temperature (m.p.~ 71°C ), and is chemically stable and reversible up to 160°C, the limit of its use, and is not polymerized by heating. The powder samples were melted, returned to room temperature, and then measured.

The ε-Caprolactam has a small dielectric constant below the melting point, but a dramatically larger one after melting, as expected for a molecule with a permanent dipole moment (Fig. 2). The molecules in the solid are fixed in position, and in spite of having a permanent dipole moment, cannot move in the time-varying electric field. However, when melting occurs, the dielectric loss, $\varepsilon''$, increases dramatically and the value of $\varepsilon'$ assumes the frequency dependence, typical of a permanent dipole moment which can move, but which is hindered by collisions with surrounding molecules. The low frequency (static) values of $\varepsilon'$ increase dramatically between the solid state ($\varepsilon' \approx 2.7$ ) and liquid ($\varepsilon' \sim 14$). The $\varepsilon'$ and $\varepsilon''$ values measured in the molten state were fitted to a Debye relaxation model (Fig. 3), and yielded a molecular thermal relaxation frequency of ~3.2 GHz at 100°C, increasing to ~8.6 GHz at 160°C. The dipole relaxation time at 95°C is $57*10^{-12}$ s. A dipole moment of $0.69 \pm 0.20*10^{-29}$ Coulomb-Meters ( 2.1 ±0.6 Debye units) was determined.

## DISCUSSION

The measured values of the complex dielectric constant for both monomers were fitted adequately over the present frequency and temperature range by a simple Debye relaxation dependence. As well, the determined values of the dipole orientation relaxation frequency of the two molecules are almost the same when the temperatures are referred to the melting points of each monomer. This suggests molecular collisions as the prime dipole de-orienting process. However, the values determined for the static (permanent) electric dipole moments of the molecules are inverted from that expected on the basis of the known values of the dipole moments of the amide and ester functional groups.

Microwave heating of these monomers for polymer formation will be very straightforward. The half-power microwave absorption depths are less than 2.5 cm above 2GHz, suggesting that industrial scale-up to large volumes might benefit from use of a lower frequency, but that application to thin layers will be optimized at higher frequencies.

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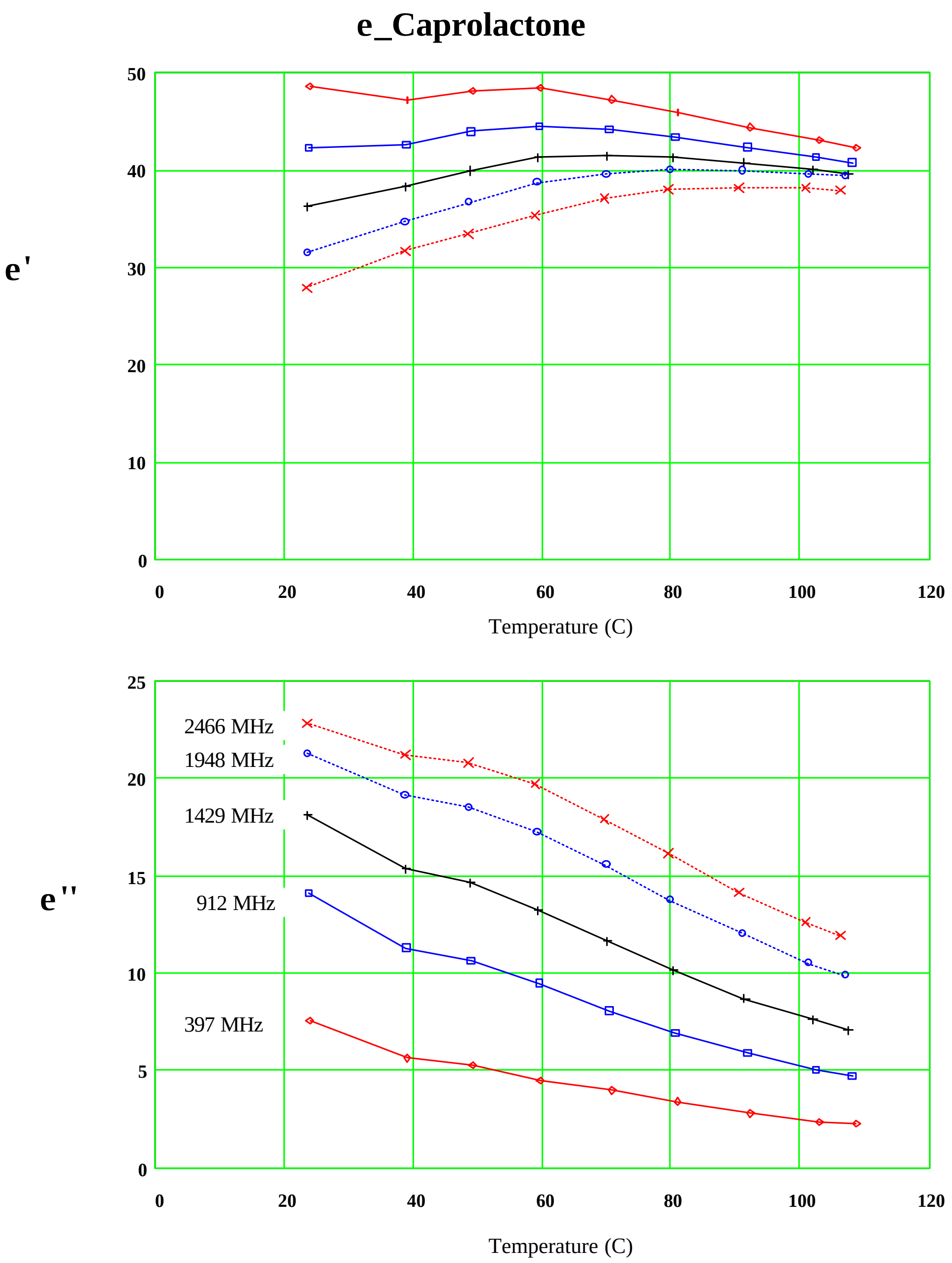


Fig 2 Measured values of real (ε′) and “imaginary” (ε″) parts of the complex dielectric constant of liquid ε-Caprolactone (density ~ 1.34 gm/cc at RT ) .

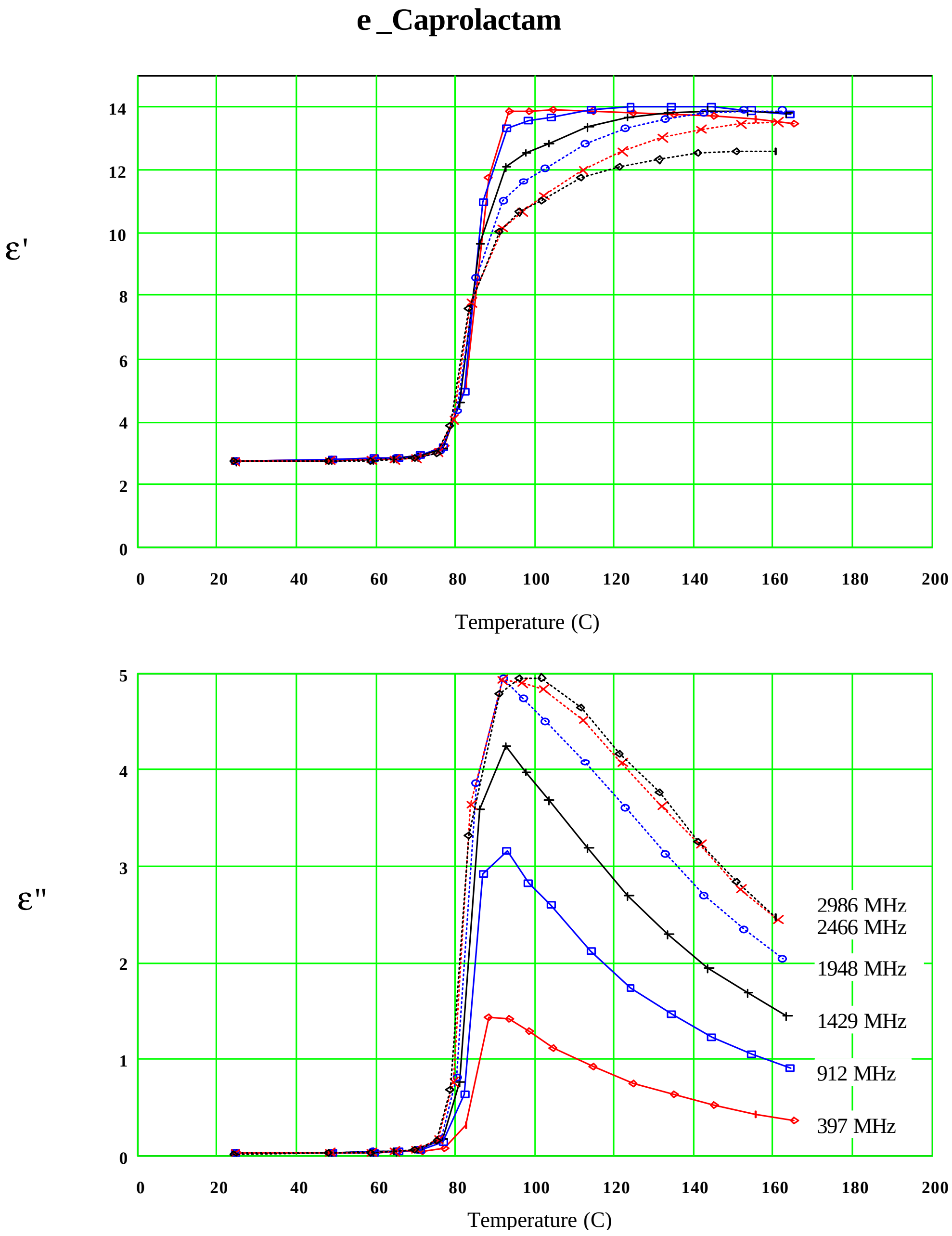
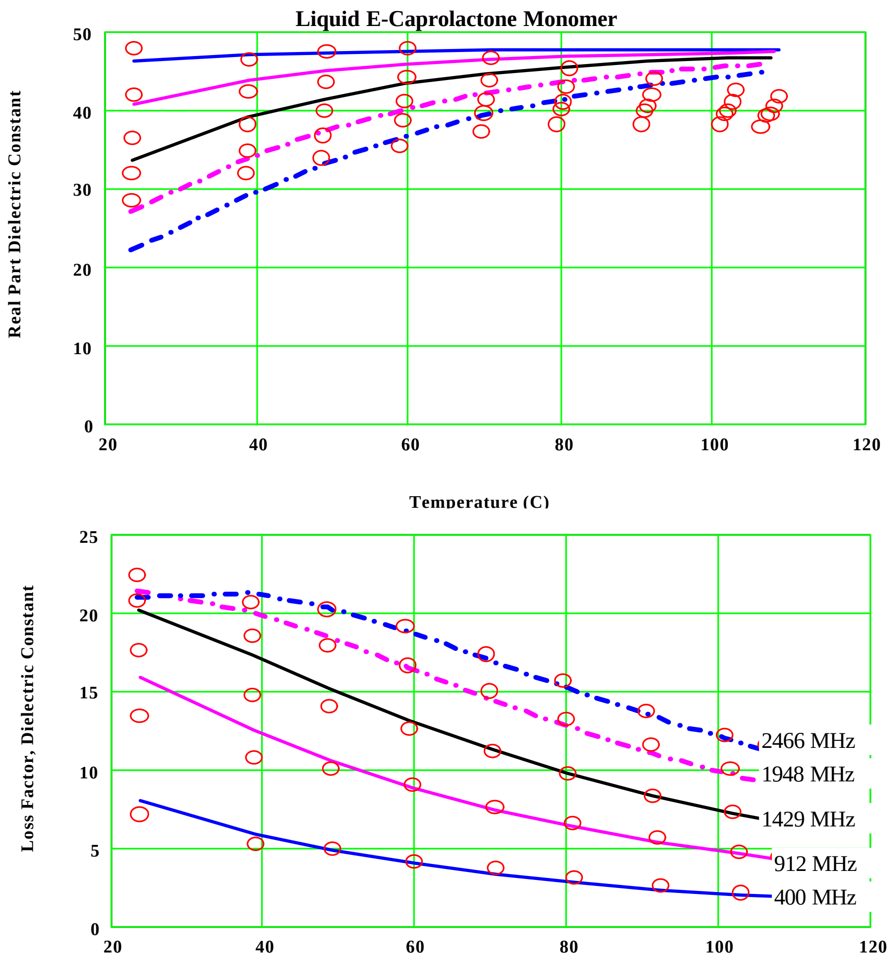


Fig. 3 Measured values of real (ε′) and “imaginary” (ε″) parts of the complex dielectric constant of initially solid (powder plus air, density ~ 0.99 gm/cc ) and then liquid ( density ~ 0.98 gm/cc at 160°C ) ε-Caprolactam.



Debye Relaxation Fit Parameters

ε static = 48 ε high freq. = 5 δH = 0.181 eV ν = 0.5 * 10(13) Hz

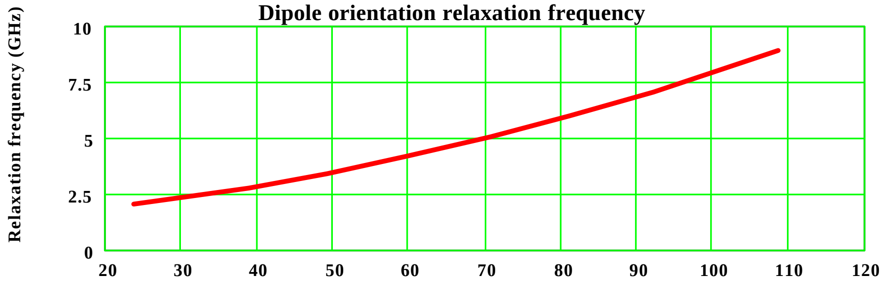
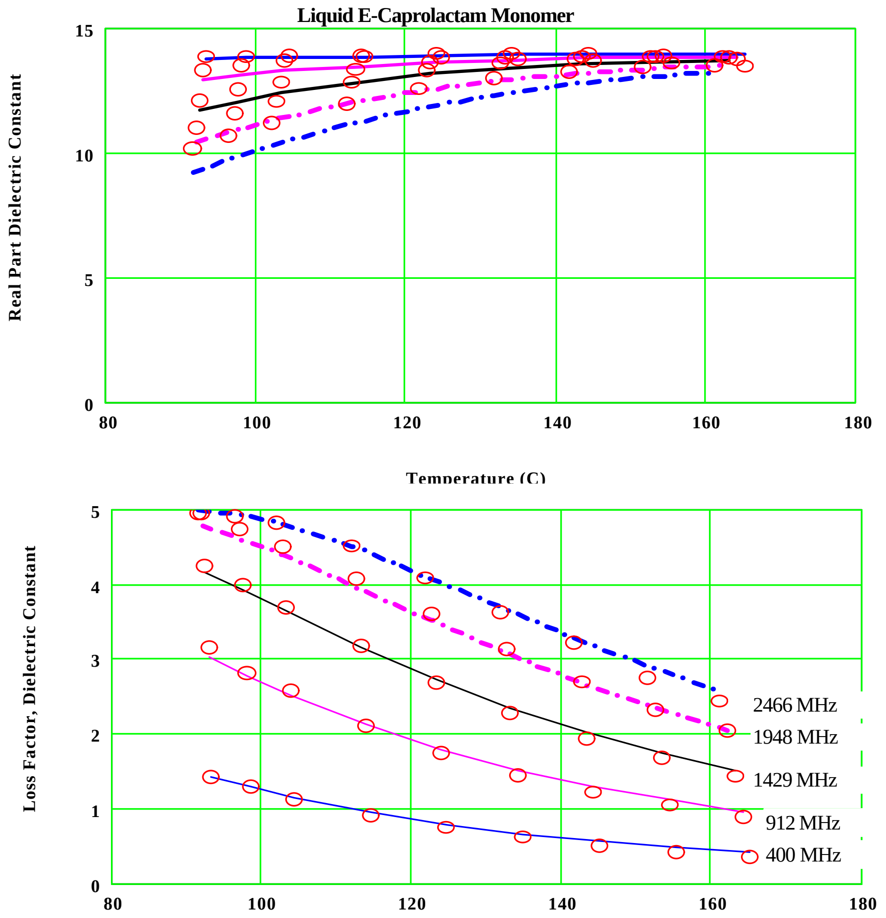


Fig.4 Debye relaxation dependence fit to the measured (circles) real (dielectric constant and imaginary (loss factor) parts of the complex dielectric constant of liquid ε-Caprolactone.



Debye Relaxation Fit Parameters

ε static = 14 ε high freq. = 4 δH = 0.255 eV ν = 1.7 * 10(13) H z

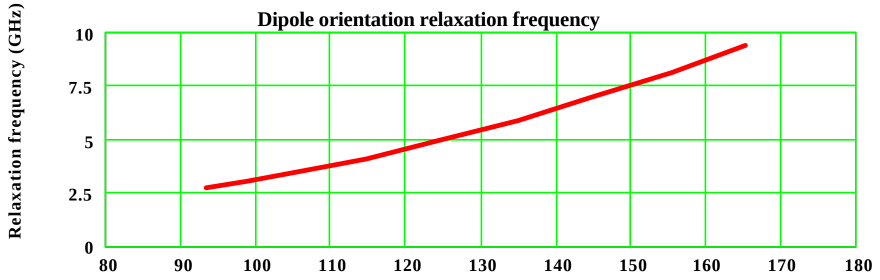


Fig. 5 Debye relaxation dependence fit (solid lines) to the measured values (circles) of the real part (dielectric constant) and imaginary part (loss factor) of the complex dielectric constant of liquid ε-Caprolactam.