

# Dielectric Spectroscopy on the Dynamics of Amorphous Polymeric Systems

**A. Schönhals**

**Bundesanstalt für Materialforschung und -prüfung, Fachgruppe VI 3.2,  
Unter den Eichen 87, 12205 Berlin, Germany**

## 1. Introduction

Compared to low molecular weight compounds synthetic polymeric materials are very complex systems. Even for an isolated macromolecule a very large number of atoms (typically hundreds to millions of atoms) are covalently bonded. Related to this large number of linked atoms macromolecular chains can have an even larger (almost unlimited) number of conformations in space and time. Most of the polymer properties are due to this large number of conformations. As some examples for the most important conformation-dependent properties the chain flexibility, the mean-square end-to-end vector of the chain or the mean-square dipole moment should be stated here. Using statistical mechanical methods the theory (**R**otational **I**someric **S**tate model, RIS-model) to predict equilibrium conformational properties of macromolecular chains was mainly developed by Flory /1-2/, awarded with the Nobel Prize in Chemistry in 1974.

Related to this huge number of conformations the behavior and the properties of macromolecules in solutions or/and in the dense state are very complex. For instance in the bulk state a polymeric system in dependence on temperature can behave as a solid, as a rubbery material which is highly deformable or as a more or less ordinary melt or liquid. Furthermore the morphology of dense macromolecular materials can be amorphous (no long range order), liquid crystalline or crystalline where due to thermodynamic reasons for polymers the crystalline state is always a semicrystalline one. Of course the kind of observed morphology depends on the chemistry of the chain.

In addition to linear chains macromolecular systems can be synthesized in wide variety of molecular architectures like comb-like and branched structures, stars (also with chemically different arms), cycles, copolymers (statistical-, di- or multiblock copolymers), physically or chemically bonded networks, hyperbranched polymers or dendrimers. Clearly, these molecular architectures can cause new morphologies in the dense state of these molecules like phase or microphase separated structures.

Since Debye /3/ developed the theory of dipolar relaxation, dielectric spectroscopy has proven very useful for studying the conformation, the structure and the dynamics of polymeric systems. The classical studies in that field were done by Fuoss, Kirkwood and their collaborators /4/ followed by the important contributions of McCrum et al. /5/, Ishida /6/, Hedvig /7/, Karasz /8/, Blythe /9/, Adachi et al. /10/ and Riande et al. /11/. It should be noted that this list can be easily extended. In particular Williams and coworkers published many original papers as well as reviews (see for instance /12, 13/). A very modern collection of review articles can be found in /14/. There is an increasing interest in studying the dielectric properties of polymeric materials recently. This is partly due to the fact that a very broad frequency range from milihertz to gigahertz can be covered by dielectric spectroscopy in its modern form routinely /15,16/ by a tuned combination of different measurement instrumentation. This includes also a computer aided temperature control of the sample /16/. For a recent review about the experimental methods see for instance /15/. In addition to the advances in instrumentation also progress in theory as well as in modeling has been made.

Due to the above mentioned developments in both experimental techniques and evaluation methods there is a wealth of contributions which (i) document the dielectric behavior of traditional and new polymer systems over a large range of frequency and temperature so that a reference dielectric data base could be developed, (ii) interrelate the dielectric method to other spectroscopy tools like dynamic-mechanical, NMR- or

IR- spectroscopy and (iii) compare the experimental results with the results of theories to obtain insights into the molecular factors which are responsible for the observed dielectric behavior.

Besides from this fundamental investigations of the dielectric behavior of polymers dielectric spectroscopy provides direct practical relevant information concerned with :

(i) electric insulation properties of amorphous polymers which are used traditionally for cable insulation as well as for passivation layers in modern electronic devices like microchips. On the one hand side for cable applications a frequency range from mHz to MHz is relevant. On the other side for the development of high speed computers materials with a low dielectric permittivity and low dielectric losses at high frequencies (GHz) are required.

(ii) Microwave adsorption characteristics of polymers that are necessary in relation to microwave transmission and reflection through or from materials used in telecommunication techniques or in radar applications. This is also directly related to the microwave heating characteristic of a polymer used in a microwave cooker. In conclusion also for these technical applications of dielectric spectroscopy measurements in a broad frequency range are necessary.

## 2. Theoretical Considerations

The complex dielectric function  $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$  ( $\epsilon'$ -real part,  $\epsilon''$ -imaginary or loss part,  $i = \sqrt{-1}$ ) is defined as factor between an outer alternating electric field  $\vec{E}(\omega)$  ( $\omega$  angular frequency,  $f$  - frequency,  $f = 2\pi\omega$ ) and the resulting polarization  $\vec{P}$  of the medium where for small electric field strengths /17,18/

$$\vec{P}(\omega) = (\epsilon^*(\omega) - 1) \epsilon_{vac} \vec{E}(\omega) \quad (1)$$

holds.  $\epsilon_{vac} = 8.85 \cdot 10^{-12} \text{ AsV}^{-1} \text{ m}^{-1}$  denotes the permittivity in vacuum. The complex dielectric function or permittivity is a materials property depending on frequency, temperature, pressure and structure. For anisotropic compounds  $\epsilon^*$  is a tensor. This has to be considered for systems with anisotropic properties like liquid-crystalline and semicrystalline polymers or oriented amorphous systems.

According to statistical mechanics both  $\epsilon'$  and  $\epsilon''$  have a direct physical interpretation.  $\epsilon'$  is related to the energy stored reversible in the material whereas  $\epsilon''$  is proportional to the energy which is dissipated per cycle. In technical applications of dielectric relaxation spectroscopy the dissipation factor  $\tan \delta = \epsilon'' / \epsilon'$  is often discussed and evaluated where  $\delta$  is the phase angle between applied voltage and resulting current. So this quantity is quite important for the electro-technical characterization of a material. In scientific applications  $\tan \delta$  should not be used because two quantities with a definite physical meaning are mixed up.

The complex dielectric function is related to the complex conductivity of the system by /17/

$$\sigma^*(\omega) = i \omega \epsilon_{vac} \epsilon^*(\omega) \quad (2)$$

Equation (2) provides the basis to measure the conductivity for polyionomers /19/, for solid state electrolytes based on macromolecules /20/ or for intrinsic conductive polymers /21/. For materials with permanent molecular dipoles  $\epsilon^*(\omega)$  is related to the correlation function  $\Phi(t)$  of the polarization fluctuations by the phenomenological theory of dielectric relaxation /17/

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_{Sta} - \epsilon_\infty} = \int_0^\infty \left[ \frac{d\Phi(t)}{dt} \right] \exp(-i\omega t) dt \quad \text{with} \quad \Phi(t) = \frac{\langle \Delta P(t) \Delta P(0) \rangle}{\langle \Delta P(0)^2 \rangle}. \quad (3)$$

In equation (3) the quantities  $\epsilon_\infty$  and  $\epsilon_{Sta}$  are the permittivities at very high (relaxed permittivity) and at quasistatic (unrelaxed permittivity) frequencies, respectively.  $\Delta P = P - \langle P \rangle$  means the fluctuation of the polarization  $P$  around its equilibrium value  $\langle P \rangle$ . The brackets symbolize the averaging over an ensemble or time  $t$ .

Basically there are two different possibilities to achieve a dielectric experiment. Experiments working with sinusoidal alternating fields are called measurements in the frequency domain and  $\epsilon^*(\omega)$  is measured. Moreover the experiments can also be carried out in the so called time domain where a step like change of  $E$  is supplied to the sample. In that case the dielectric behavior is discussed in terms of the time dependent dielectric function  $\epsilon(t)$  which is direct proportional to the dipole correlation function. Therefore

$$\frac{d\epsilon(t)}{dt} = \dot{\epsilon}(t) = \frac{1}{\pi} \int_0^{\infty} [\epsilon^*(\omega) - \epsilon_{\infty}] \exp[i\omega t] d\omega \quad (4)$$

holds. A very crude approximation of equation (4) is the so called Hamon-relation /22/. A plot of  $\frac{\pi}{2} t \dot{\epsilon}(t)$  versus  $(-\log t - 1)$  corresponds to  $\epsilon''$  versus  $\log f$ .

The macroscopic observable polarization  $P$  is related to the dipole density of  $N$  permanent molecular dipoles  $\mu_i$ <sup>1</sup> in a volume  $V$ . For low molecular weight molecules the molecular dipole moment can be well represented by a single rigid vector /3/. The situation is different for long chain molecules. According to Stockmayer /24,25/ there are three different possibilities for the orientation of molecular dipole vectors with respect to the polymer backbone. A classification gives Fig. 1.

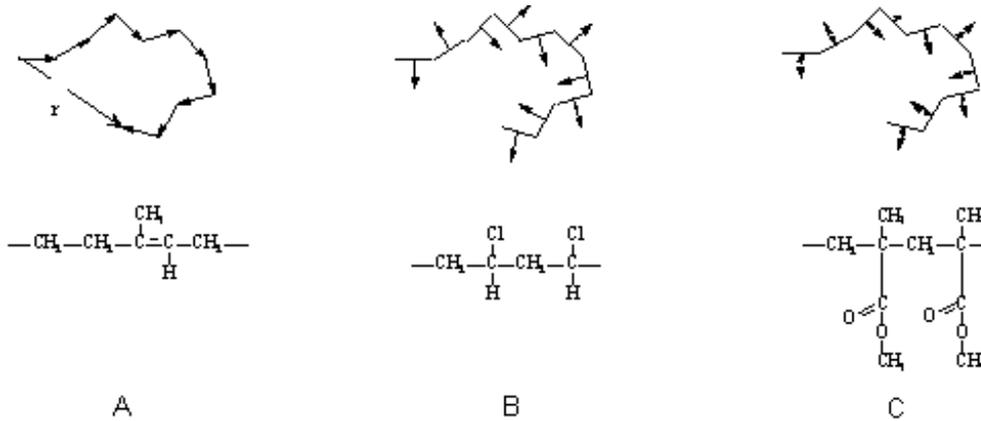


Fig. 1 Representation of chains with a dipole component oriented parallel (Type A, Example: cis-1,4-polyisoprene) and rigid perpendicular to the chain (Type B, Example: poly(vinyl chloride)). For type C polymers the dipole is located in a more or less flexible side group (Example : poly(methyl methacrylate))

Macromolecules with molecular dipole vectors oriented parallel to the main chain are called type A polymers. The opposite case are type B polymers where the dipole moment is rigidly attached perpendicular to the chain skeleton. Most of the synthetic macromolecules like polystyrene or polybutadiene are of type B. But there are few examples for polymers having a dipole component both parallel and perpendicular to the chain. These molecules are also called type A polymers. Cis-1,4-polyisoprene or poly(propylene glycol) are typical flexible type A-polymers where poly( $\epsilon$ -caprolactone), polypeptides and poly(n-alkyl-isocyanate)s are some examples for semi-rigid and stiff polymers having a dipole component parallel to the chain backbone /10/. Type C macromolecules have the main dipole component in a more or less flexible side chain. Examples for that type of macromolecules are for instance the poly(n-alkyl methacrylate)s. It should be noted that a dipole in a side chain usually implies both a dipole component that contributes to the polarization by main chain reorientation and a component whose reorientation is due to local side chain motions /25/. A more complete and detailed discussion for each type of polymer chain can be found in reference /10/.

To obtain the dipole moment per unit volume (polarization) one has to summarize over all molecular dipole types in the repeating unit, the polymer chain, and over all chains in the system. This means

$$\vec{P} = \frac{1}{V} \sum_{\text{all chains}} \sum_{\text{chain}} \sum_{\text{repeating unit}} \vec{\mu}_i \quad (5)$$

Using equation (3) the correlation function  $\Phi(t)$  of the polarization fluctuations can be calculated in principle using statistical mechanical methods /26,27/. As it was pointed out polymers are complicated many-body systems and so the calculation of  $\Phi(t)$  is already for an isolated chain with a simple structure very difficult and

<sup>1</sup>Also space-charges which normally are responsible for conductivity contribution can contribute to  $P$  as Waxwell-Wagner-Sillars-polarization /23/ if they are partially trapped.

impossible in the general case. To overcome this problem different modes of polymer dynamics well separated in their relaxation times or relaxation rates are discussed. This is possible because the fluctuation of the net dipole moment given by equation (5) can be driven by different motional processes. An overview is given in Fig.2.

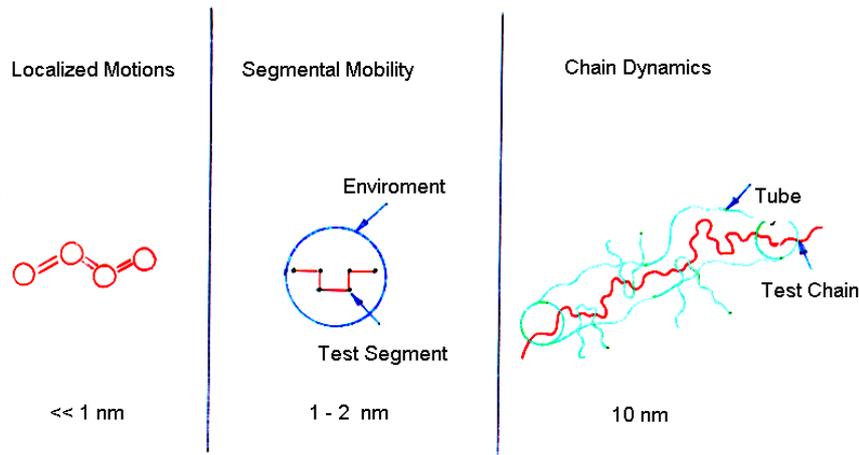


Fig. 2 Length scales and motional processes in polymeric systems.

Such motional processes can be fluctuations within a monomeric unit or rotational fluctuations of a short side chain. On a larger spatial scale or at equivalently at longer times the so called segmental motion which is responsible for the glass transition becomes relevant. At a much greater length scale than a segment the molecular motion of the whole molecule characterized by the entanglement spacing or by the end-to-end vector of the chain takes place. This motional process is directly related to the viscoelastic properties of a solution or a melt [28]. Provided that the motional process under consideration is related with a dipole orientation, a dielectric relaxation process can be observed which is characterized by a peak in  $\epsilon''$  and a step-like decrease of  $\epsilon'$  versus frequency at isothermal conditions (frequency domain, see Fig. 3).

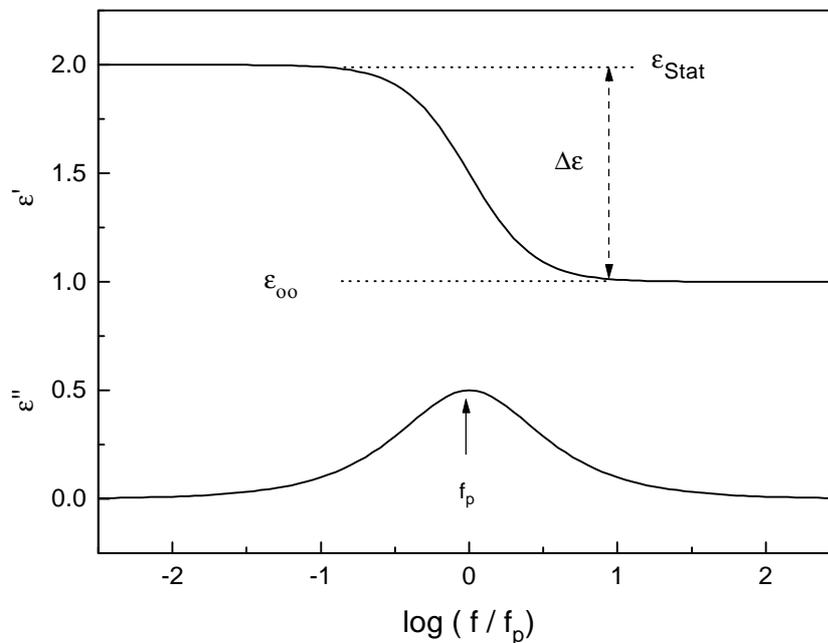


Fig. 3 Principal behavior of the complex dielectric function in the frequency domain.

For relaxation processes  $\epsilon'$  and  $\epsilon''$  are connected by the Kramers-Kronig relations /17,27/

$$\epsilon'(\omega) = \epsilon_{\infty} + \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\epsilon''(\omega_1)}{\omega_1 - \omega} d\omega_1 ; \epsilon''(\omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\epsilon'(\omega_1)}{\omega_1 - \omega} d\omega_1 \quad (6)$$

and so  $\epsilon'$  and  $\epsilon''$  deliver the same information about the relaxation process in principle. Therefore the  $\epsilon''$  behavior will be discussed mainly. As an example Fig. 4 shows the dielectric loss for poly (propylene glycol) with a molecular weight of 2000 g/mol over a frequency range of 14 decades.

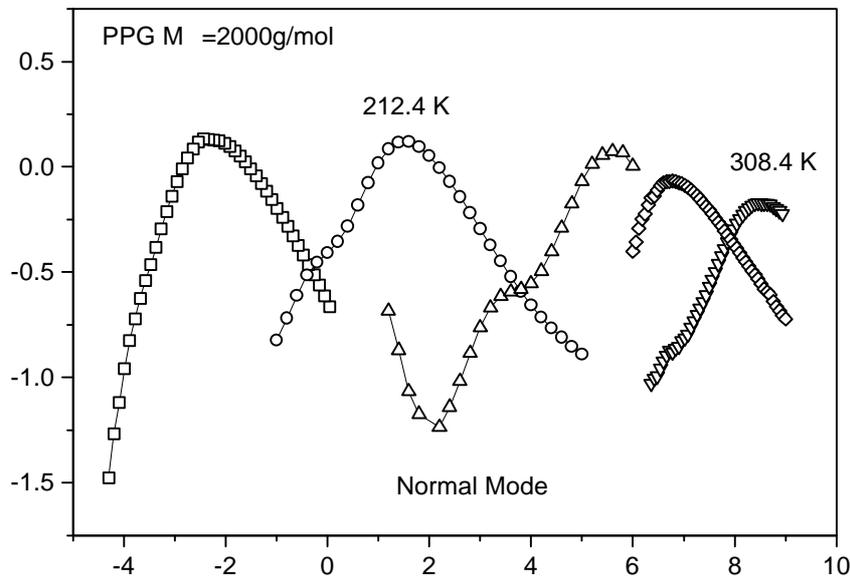


Fig. 4 Dielectric loss  $\log \epsilon''$  for bulk poly(propylene glycol) versus logarithm of frequency at the labeled temperatures. Lines are guides for the eyes.

Two relaxation processes indicated by peaks in  $\epsilon''$  are visible. The relaxation process at higher frequencies is due to the segmental relaxation which corresponds to the dynamic glass transition. The relaxation process at lower frequencies corresponds to the overall chain dynamics because poly(propylene glycol) is a typical type A polymer. A more detailed discussion will be given later in this contribution.

To be complete a dielectric experiment can also be carried out keeping the frequency fixed but sweeping the temperature.  $\epsilon''$  also exhibits a loss peak, at a temperature depending on the selected frequency and  $\epsilon'$  displays a step-like increase with increasing temperature. It should be noted that in such a representation low temperatures correspond to high frequencies whereas high temperatures are related to lower motional frequencies. An example for such a measurement is presented in Fig. 5 where the dielectric loss is given of polycarbonate blended with a main chain polymeric liquid crystal.

At low temperatures a local  $\beta$ -relaxation can be detected. At higher temperatures the dynamic glass transitions of both components can be studied in dependence on blend composition. For a detailed discussion of that system see /29/.

In the frequency domain an  $\epsilon''$  peak can be fully characterized by (i) its frequency position determined by the frequency of maximal loss  $f_p$  from which a characteristic relaxation time  $\tau=1/(2\pi f_p)$  can be obtained, (ii) its shape properties such as width and symmetry and (iii) its relaxation strength  $\Delta\epsilon$ . According to /17/  $\Delta\epsilon$  is given by

$$\Delta\epsilon = \int_{\text{Peak}} \epsilon''(\omega) d \ln \omega \quad (7)$$

The relationship of  $\Delta\epsilon$  with the dipole moment under investigation can be calculated in the framework of the Debye-theory of dielectric relaxation. This theory improved by Onsager, Fröhlich and Kirkwood (see ref. /17/ and references quoted there) gives

$$\Delta\epsilon = \epsilon_{\text{Stat},i} - \epsilon_{\infty,i} = F_{\text{Onsager}} g \frac{N\mu^2}{3k_B T} \quad \text{with} \quad F_{\text{Onsager}} = \frac{1}{3} \frac{\epsilon_{\text{Stat},i} (\epsilon_{\infty,i} + 2)^2}{2\epsilon_{\text{Stat},i} + \epsilon_{\infty,i}} \quad (8)$$

( $T$  the temperature,  $k_B$  the Boltzmanns constant).  $\epsilon_{\infty,i}$  and  $\epsilon_{\text{Stat},i}$  denote here the permittivities at high and at low frequencies with respect to  $f_{pi}$  of the relaxation region  $i$  under investigation. Using experimental values it was found that for the correction factor for internal field effects  $F_{\text{Onsager}} \approx 1$  holds.

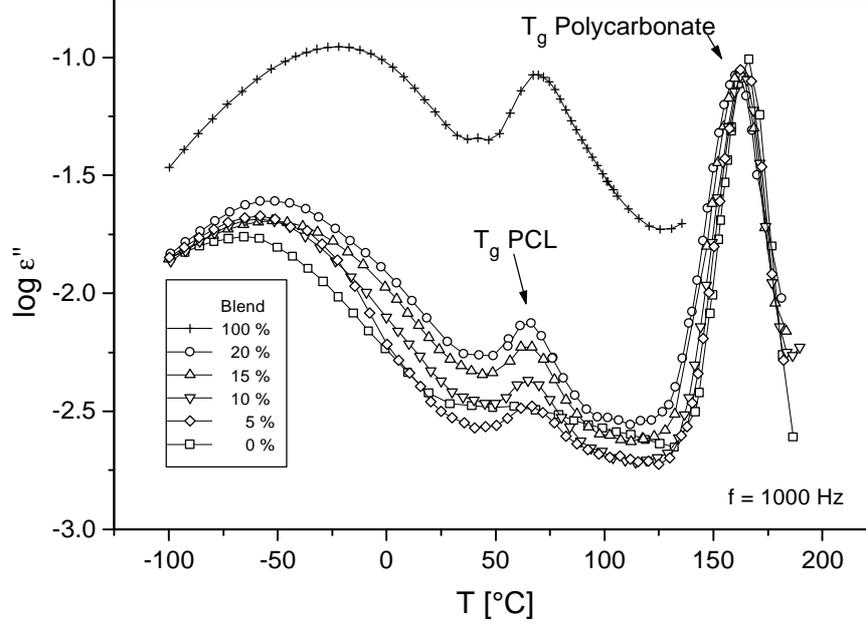


Fig. 5 Dielectric loss  $\log \epsilon''$  versus temperature at a frequency of 1000 Hz for a blend of polycarbonate with the statistical copolymer poly((1-x) ethylene terephthalate-co- x-p-hydroxybenzoic acid) (PCL) where  $x=0.6$  is the mol fraction of p-hydroxybenzoic acid. For details see /29/.

In equ. (8)  $g$  is the correlation factor introduced by Kirkwood. The  $g$ -factor describes local static correlation of dipoles caused by hydrogen bonding or steric hindrance. The Kirkwood correlation factor is defined by

$$g = 1 + \langle \cos \theta_{i,j} \rangle \quad (9)$$

where  $\theta_{i,j}$  is the angle of  $i^{\text{th}}$ -dipole moment averaged with respect to its  $j$  nearest neighbor. The comparison of measured  $\Delta\epsilon$  values with molecular dipole moments delivers so information about the correlation of dipole moments and so of the correlation of molecules. For several types of isolated polymer chains the Kirkwood correlation factor can be calculated using the statistical mechanics of polymers and the RIS-model /11,30/.

### 3. Evaluation of dielectric measurements

To characterize the position, the shape and the dielectric intensity of a loss peak in more detail evaluation methods have been developed which are based on model functions. Using this methods the measured information can be condensed in a set of few parameters which can be compared with the predictions of theories. Moreover a separation of overlapping relaxation regions or conductivity contributions is possible. There are several model functions used in literature to describe the data like the Cole-Cole - /31/, the Cole-Davidson- /32,33/ or the Fuoss-Kirkwood-function /34/. The most flexible one is the model function of Havriliak and Negami /35,36/ (HN-function) which is defined by

$$\epsilon_{\text{HN}}^* (\omega) - \epsilon_{\infty} = \frac{\Delta\epsilon}{(1 + (i\omega\tau_{\text{HN}})^{\beta_{\text{HN}}})^{\gamma_{\text{HN}}}} \quad (10)$$

$\beta_{\text{HN}}$  and  $\gamma_{\text{HN}}$  are fractional shape parameters with  $0 < \beta_{\text{HN}}; \beta_{\text{HN}} \gamma_{\text{HN}} \leq 1$  due to the symmetric and asymmetric broadening of the loss peak. It should be noted that the shape parameters are related to the slopes of  $\log \epsilon''$

versus  $\log \omega$ . This means  $\epsilon'' \propto \omega^{\beta_{HN}}$  for  $\omega \ll 1/\tau_{HN}$  and  $\epsilon'' \propto \omega^{-\beta_{HN} \gamma_{HN}}$  for  $\omega \gg 1/\tau_{HN}$ .  $\tau_{HN}$  is a relaxation time related to the peak frequency  $f_p$  where the relationship between  $\tau_{HN}$  and  $f_p$  depends on  $\beta_{HN}$  and  $\gamma_{HN}$  /37,38/.

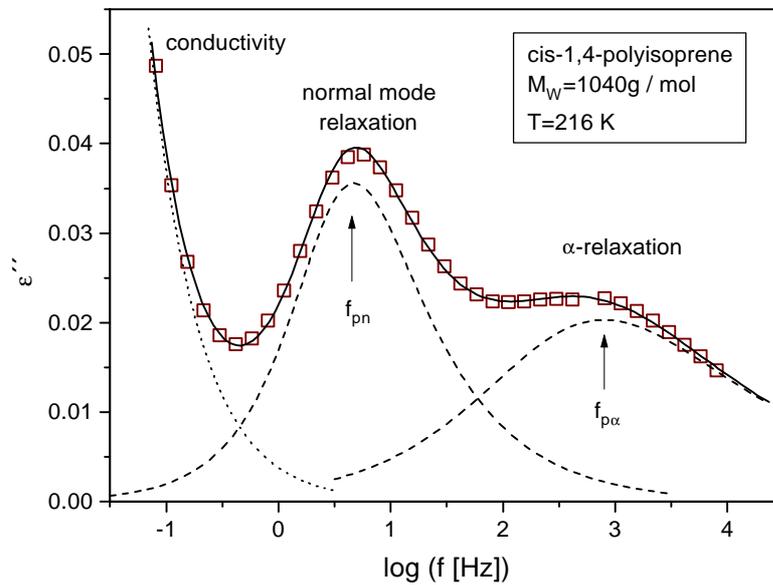


Fig. 6 Separation of the measured dielectric loss  $\epsilon''$  versus frequency into the  $\alpha$ -relaxation (dashed line), the normal mode relaxation (dashed-dotted line) and the conductivity contribution (dotted line) in the frequency domain.

The parameter can be estimated by fitting equ. (10) to the data

$$\sum_i [\epsilon''_i - \sum_k \epsilon''_{HN,k}(\omega_i)]^2 \rightarrow \text{minimum} \quad (11)$$

where  $i$  counts the number of data points and  $k$  denotes the number of relaxation regions. So a separation of different relaxation regions is possible assuming that the measured behavior is a superposition of individual contributions. For more details see /38,39/. Very often the dielectric relaxation behavior is influenced by low frequency conductivity contribution. This can be modeled by

$$\epsilon''(\omega) = \epsilon_{\text{Relaxation, HN}}(\omega) + \frac{\sigma}{\omega^s}, \quad (12)$$

where  $\sigma$  is directly related to the DC-conductivity and  $s$  is a fitting parameter. For ohmic contacts and no Maxwell-Wagner-polarization  $s=1$  holds. In the most practical cases  $0.5 < s \leq 1$  is obtained. Nevertheless equ. (12) can be used to estimate the DC-conductivity from frequency dependent measurements. One example of the fitting of two HN-equations to the dynamic glass transition and to the chain dynamics of cis-1,4-polyisoprene is given in Fig. 6.

The dielectric behavior in the time domain is often modeled by a stretched exponential function which also named Kohlrausch-Williams-Watts- (KWW-) function /40/

$$\Phi(t) = \exp[-(t/\tau_{KWW})^{\beta_{KWW}}] \text{ with } 0 < \beta_{KWW} \leq 1, \quad (13)$$

where  $\beta_{KWW}$  is the stretching parameter. There is no simple four-parameter model function for the time domain as the HN-function for the frequency domain. But there are several attempts to relate  $\beta_{KWW}$  to  $\beta_{HN}$  and  $\gamma_{HN}$  /41,42/. But however because in the time domain there is one shape parameter less than in frequency domain information must be lost during the transformations. Another way is outlined in /37,43/. Using equations (4) and (10) one gets

$$\dot{\epsilon}_{HN}(t) = \frac{1}{\pi} \int_0^{\infty} \left[ \frac{\Delta\epsilon}{(1 + (i\omega\tau_{HN})^{\beta_{HN}})^{\gamma_{HN}}} \right] \exp[i\omega t] d\omega. \quad (14)$$

Equ. (14) defines a model function with four parameters in the time domain which can be evaluated and fitted to the data in the same way than in the frequency domain using /43/. Moreover a consistent evaluation of measurements carried out partly in the frequency and partly in the time domain is possible by minimizing

$$\left[ \sum_i [\varepsilon''_i - \sum_k \varepsilon''_{\text{HN},k}(\omega)]^2 + \sum_j [t_j \dot{\varepsilon} - \sum_k t_j \dot{\varepsilon}(t_j)]^2 \right] \rightarrow \text{minimum} \quad (15)$$

with the same parameter set /37/. An example for such joint evaluation is given in Fig. 7 for poly(propylene glycol).

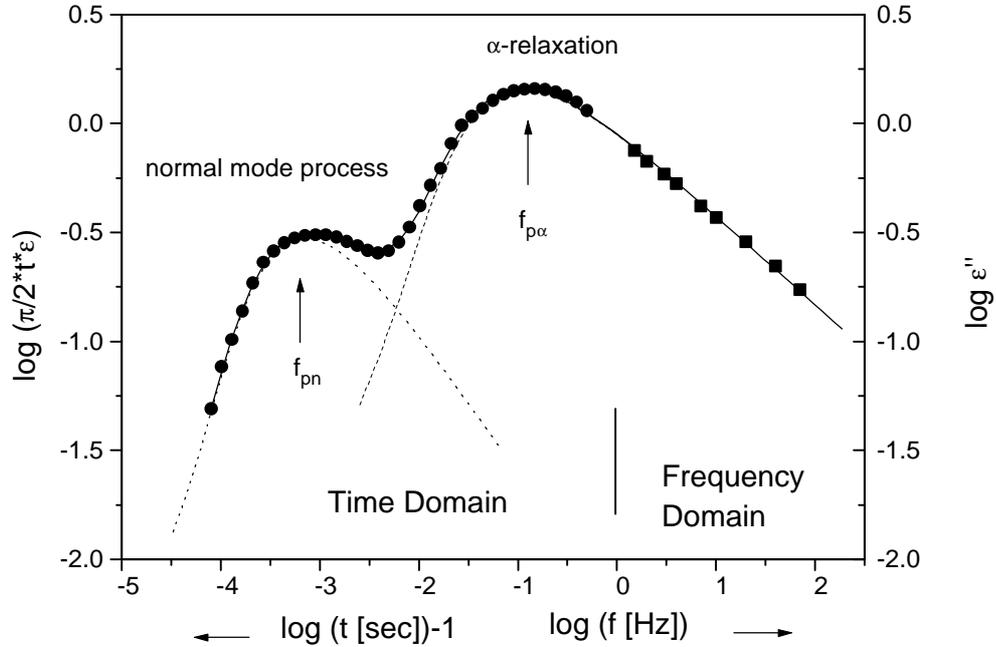


Fig. 7 Evaluation of data measured partly in the time domain and partly in the frequency domain for poly(propylene glycol) at 202.15 K by fitting two HN- functions

Another way to analyze the measurements is to calculate the relaxation time spectra  $g(\tau)$  from the data according to /17/

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_{\text{Sta}} - \varepsilon_\infty} = \int_0^\infty \frac{g(\tau)}{1 + i\omega\tau} d\tau. \quad (16)$$

To estimate  $g(\tau)$  from the experimental data is mathematically an ill-conditioned problem. However with the aid of modern regularization procedures it is possible to obtain the spectra with high accuracy /44/. Because  $g(\tau)$  is calculated from the experimental data it delivers with regard to the experimental data no new information. The relaxation spectra displays a peak for each relaxation process like  $\varepsilon''$  but because  $g(\tau)$  for the Debye-function is the Dirac-function the spectra is essentially narrower than  $\varepsilon''$ . This may be important for the separation of different relaxation regions.

To analyze dielectric data in the temperature domain is quite more difficult than for isothermal measurements because the shape, the dielectric strength as well as the relaxation rate depend more or less on temperature. One way to analyze temperature dependent relaxation data is to use model functions like the HN-function and to treat the HN-parameter as a function of temperature. Clearly the most strongest temperature dependence of these quantities exhibits the relaxation rate or  $\tau_{\text{HN}}$  and  $\Delta\varepsilon$ . Compared to that the temperature dependence of the shape parameters can be omitted for seek of simplicity. So we have

$$\varepsilon_{\text{HN}}^*(T) - \varepsilon_\infty = \frac{\Delta\varepsilon(T)}{(1 + (i\omega_{\text{Meas}} \tau_{\text{HN}}(T))^{\beta_{\text{HN}}})^{\gamma_{\text{HN}}}}. \quad (17)$$

where  $\omega_{\text{Meas}}$  is the frequency of the measuring field. Some examples for the temperature dependence of  $\tau_{\text{HN}}(T)$  and  $\Delta\varepsilon(T)$  are discussed in /45/. Fig. 8. gives an example for such an analysis for poly(propylene glycol) confined to nanoporous glasses /46/.

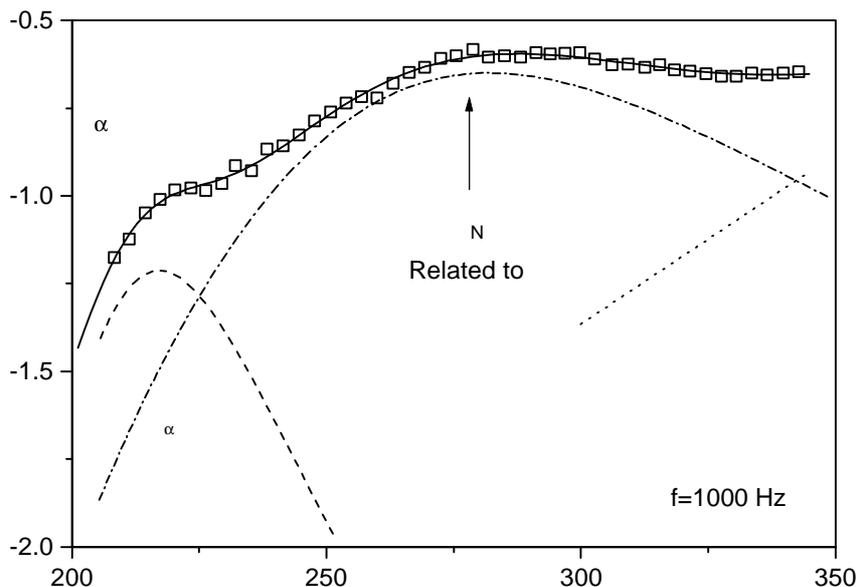


Fig. 8 Decomposition of temperature dependent dielectric loss of poly(propylene glycol) confined to nanoporous glasses with a pore size of 2.5nm into the  $\alpha$ -relaxation (dashed), the chain dynamics (dotted-dashed) and into the Maxwell-Wagner-contribution (dotted) at 1000 Hz. The solid line represents the whole fit-function. For details see /46/.

#### 4. Dielectric relaxation behavior of dense amorphous polymers

It is well known that most of the amorphous polymers exhibit a secondary- or  $\beta$ - process and a principal- or  $\alpha$ -relaxation located at lower frequencies or higher temperatures than the  $\beta$ -relaxation. For type A polymers at frequencies below the  $\alpha$ -relaxation a further process called  $\alpha'$ - or normal mode relaxation can be observed which corresponds to the overall chain dynamics.

In this chapter the characteristic and fundamental peculiarities of the  $\beta$ -,  $\alpha$ - and the normal mode relaxation of bulk amorphous polymers are discussed. Apart from these processes amorphous polymers can also exhibit further dielectric active relaxation processes provided that a fluctuation of the dipole moment is involved.

##### 4.1 $\beta$ -Relaxation of amorphous polymers

The most authors agree that the dielectric  $\beta$ -relaxation of amorphous polymers arises from localized rotational fluctuations of the dipole vector. For the first time Heijboer /47/ developed a nomenclature for the molecular mechanisms which can be responsible for that process. According to that approach fluctuations of localized parts of the main chain, or the rotational fluctuations of side groups or parts of them, are discussed. This picture is mainly supported by investigations on model systems (see for instance /48-50/). Also investigations on poly(n-alkyl methacrylate)s in dependence on the length of the alkyl side chain seems to support this picture /51-55/. But however it has to be noted that the relaxation behavior of the poly(n-alkyl-methacrylate) is quite unusual compared to other polymers. Normally for the dielectric relaxation strength of the  $\beta$ -relaxation  $\Delta\epsilon_{\beta} \ll \Delta\epsilon_{\alpha}$  or  $\Delta\epsilon_{\beta} \ll \Delta\epsilon_{\alpha}$  (see for instance /56-61/) holds where  $\Delta\epsilon_{\alpha}$  is the dielectric relaxation strength of the  $\alpha$ -relaxation. For poly(n-alkyl-methacrylate)  $\Delta\epsilon_{\beta} \gg \Delta\epsilon_{\alpha}$  is measured. The reason for this behavior is unclear up to now. There is some evidence from NMR-measurements that this might be due to coupled motion of the main and the side chain /60/. Furthermore a degeneration of the thermal glass transition with increasing length of side chain is observed /61/.

Another approach to the  $\beta$ -relaxation was outlined by Goldstein and Johari /62/ many years ago. They argued that the  $\beta$ -relaxation is a generic feature of the amorphous state moderated by that intrinsic structure to

a great extent. Therefore such  $\beta$ -relaxation processes could be observed apart from polymeric systems for great variety of glass-forming materials like low molecular weight glass forming liquids and rigid molecular glasses /63/. Recently there is a strong discussion in the literature about the relationship of the  $\beta$ -relaxation and the dynamic glass transition. For an overview see for instance /64/. This includes also the bifurcation or splitting behavior of both relaxation processes /64,54,55/. It is expected that by such investigations the physical nature of the dynamic glass transition which is an unsolved problem of condensed matter physics /65,66/ can be clarified. For such investigations also combinations of dielectric experiments with other methods like frequency dependent heat capacity measurements /67/ or neutron scattering /68/ are used.

The temperature dependence of the relaxation rate of the  $\beta$ -relaxation  $f_{p\beta}$  can be well described by an Arrhenius-equation

$$f_{p\beta} = f_{\infty,\beta} \exp\left[-\frac{E_A}{k_B T}\right], \quad (18)$$

where  $f_{\infty,\beta}$  is a preexponential factor.  $f_{\infty,\beta}$  should be of the order of magnitude of  $10^{12}$  to  $10^{13}$  Hz. For greater values than these other factors like activation entropies have to be considered. The activation energy  $E_A$  depends on the internal rotation barriers as well as on the environment of a moving molecular unit. Typical values for  $E_A$  are in the range from 20 to 50 kJ/mol.

The loss peaks of the  $\beta$ -relaxation are symmetric but very broad (with half widths of 4-6 decades). Because the  $\beta$ -relaxation is assigned to local motional processes these broad loss peaks are interpreted by a distribution of relaxation times in the sense of equation (16). This distribution of relaxation times can be, according to equation (18), due to both a distribution of activation energies or/and a distribution of the preexponential factor caused by a distribution of the molecular environments of the moving moiety.

#### 4.2 Dynamic glass transition or $\alpha$ -relaxation of amorphous polymers

As it was mentioned above the understanding of the  $\alpha$ -process or dynamic glass transition which is related to the thermal glass transition of the system is an unsolved problem of condensed matter physics /65,66/. If a glass forming system is supercooled a dramatic increase of its viscosity  $\eta$  from values of  $10^2$  -  $10^1$  poise up to values of  $10^{12}$  poise near the calorimetric glass transition temperature  $T_g$  is observed (see Fig. 9). The time scale of the relevant relaxation process, the  $\alpha$ -relaxation, increases by more than twelve decades.  $T_g$  can be defined by the step in the specific heat capacity (see Fig 9).

For polymers it seems to be clear that the glass transition corresponds to the microbrownian segmental motions of chains. Most workers agree that these motions are related to conformational changes like gauche-trans transitions which lead to rotational fluctuations of a molecular dipole around the chain which is perpendicular (rigidly) attached to it. This picture is supported by a correlation of the local dielectric segmental relaxation time in dilute solution with the glass transition temperature  $T_g$  /69/. Even for an isolated macromolecule this elementary motional process - called local chain motion - involves many degrees of freedom. The first models developed for this process are the Shatzki crankshaft /70/ or the three-bond motion /71-73/. Helfand /74/ and Skolnick /75/ described this process as a damped diffusion of conformational changes along the chain. This model is in agreement with most experimental results as well as with computer simulations (see for instance /76-79/).

It seems further clear that the  $\alpha$ -relaxation is a cooperative phenomenon and so a selected segment moves together with its environment. The cooperative character of the molecular motion should set in at temperatures well above  $T_g$  at a temperature  $T_{\text{Onset}}$  and the extent of cooperativity should increase with decreasing temperature. The extent of the cooperativity which can be described by a length scale is a topic of a controversial discussion. The fluctuation approach to the glass transition predicts a length scale of around 2 nm at  $T_g$  /80-81/. There are several experimental approaches to estimate the extent of the length scale which is relevant for the  $\alpha$ -relaxation. One approach is to investigate the dielectric behavior of low molecular weight glass forming molecules /82-84/ and polymers /46,85,86/ in confining geometry's. These investigations seem to support that a length scale which increases with decreasing temperature is responsible for the glass transition. Another approach is based on sophisticated multi-dimensional NMR-measurements /87/.

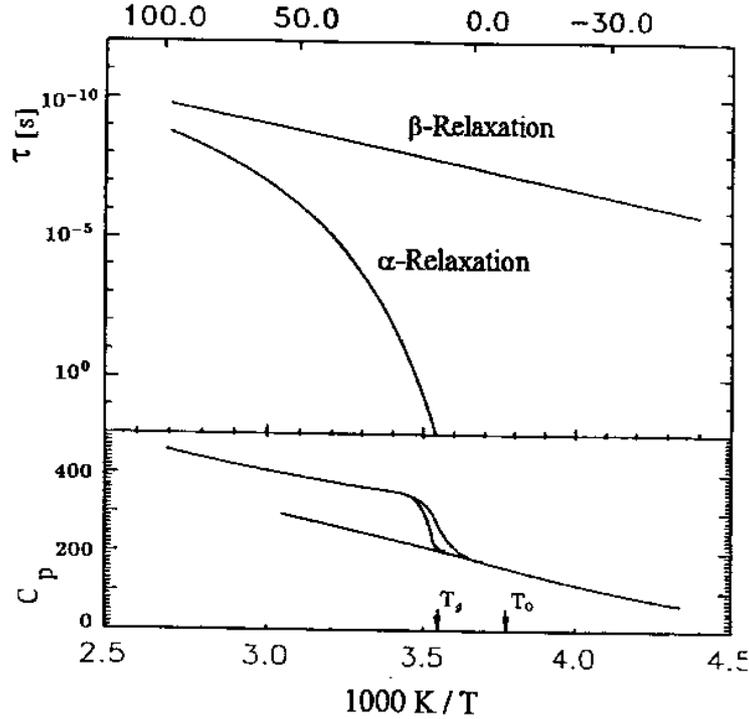


Fig. 9 Temperature dependence of the specific heat  $c_p$  (arbitrarily units) and of the relaxation times for the  $\beta$ - and  $\alpha$ -relaxation in the glass transition region.

The temperature dependence of the relaxation rate of the  $\alpha$ -relaxation  $f_{p\alpha}$  is curved in a plot of  $\log f_{p\alpha}$  versus  $T^{-1}$ . This dependence can be described by the Vogel-Fulcher-Tammann-Hesse (VFT) /89-91/ equation

$$\log f_{p\alpha} = \log f_{\alpha\infty} - \frac{A}{T - T_0} \quad (19)$$

where  $\log f_{\alpha\infty}$  ( $f_{\alpha\infty} \cdot 10^{10} - 10^{13}$  Hz) and  $A$  are constants.  $T_0$  is the so called ideal glass transition or Vogel temperature which is found to be 30-70 K below  $T_g$ . An example for a fit of the VFT equation to relaxation of poly(propylene glycol) is given in Fig. 9.

An analog representation for the temperature dependence of the relaxation rate of the  $\alpha$ -relaxation is the Williams/Landel/Ferry (WLF) relation /28/

$$\log \frac{f_{p\alpha}(T)}{f_{p\alpha}(T_r)} = - \frac{C_1 (T - T_r)}{C_2 + T - T_r} \quad (20)$$

$T_r$  is a reference temperature and  $f_{p\alpha}(T_r)$  is the relaxation rate at this temperature.  $C_1$  and  $C_2 = T_r - T_0$  are so called WLF-parameters. It has been argued that these parameters should have universal values if  $T_r = T_g$  is chosen /28/. But however it was found experimentally that these universal values are only rough approximations. Equations (19) and (20) are mathematically equivalent.

The generality of the VFT equation near  $T_g$  suggests that  $T_0$  is a significant temperature for the dynamics of glass forming materials although the physical meaning of  $T_0$  is not clear up to now. In the free volume approach of Cohen and Turnbull (see for instance /100/) the fractional free volume becomes zero at  $T_0$ . In the approach of Adam and Gibbs /101/ - which treated the  $\alpha$ -relaxation as a cooperative process for the first time- and later in the fluctuation model of Donth /80-81/ the length scale which is supposed to be responsible for the glass transition diverges at  $T = T_0$ . Just to be complete also the thermodynamic lattice theory developed by DiMarzio /102/ should be mentioned here. In that model  $T_0$  is related to a second order phase transition.

Recently the temperature dependence of the relaxation rate of the  $\alpha$ -relaxation was analyzed by a temperature derivation method /103/. This method is very sensitive to differences in the functional form of  $f_p$

(T) where the prefactor plays no role. For a temperature dependence according to the VFT-equation one obtains

$$\left[ \frac{d \log f_{\text{VFT}}}{d T} \right]^{-1/2} = A^{-1/2} ( T - T_0 ) . \quad (21)$$

For many low molecular weight glass forming materials it was found, that the relaxation rate of the  $\alpha$ -relaxation has to be described by two different VFT equations a low temperature and a high temperature /103/ one. This is also true for polymeric materials. As it is shown in the inset of Fig. 9 for relaxation data of poly(propylene glycol). This change in the temperature dependence of  $f_{p\alpha}$  is interpreted by a change in the molecular dynamics of the  $\alpha$ -relaxation and the corresponding temperature is assigned to the onset temperature  $T_{\text{Onset}}$  of the cooperativity of the glass transition /104, 105/.

Besides cooperativity approach the glass transition is treated in the frame of mode-mode coupling theory (MCT) /107/. The MCT describes in the hydrodynamic limit the slowing down of the dynamics of the density fluctuation by a nonlinear feedback mechanism. For the rate of the  $\alpha$ -relaxation

$$f_{p\alpha} \propto \left( \frac{T - T_c}{T_c} \right)^{-\gamma} \quad (22)$$

is predicted where  $T_c$  is a critical temperature well above  $T_g$  with  $T_c \approx T_{\text{Onset}}$  and  $\gamma$  is a fit parameter. By broadband dielectric measurements and by the application of the above introduced deviation technique it could be shown that in general the dielectric data cannot be described by equ. (22) /103/.

The shape of the dielectric relaxation function of the  $\alpha$ -relaxation is quite broad and asymmetric. If this is an intrinsic feature of the glass transition due to the cooperative nature or if this due to a distribution of relaxation times is still a question of actual research. Probably both effects play a role. That a distribution of relaxation times is involved near the glass transition was demonstrated by dielectric hole burning experiments recently /106/.

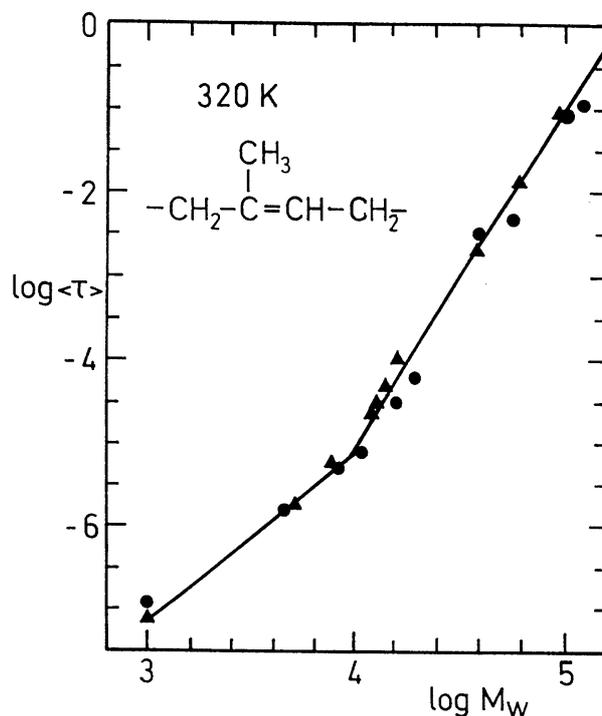


Fig.11 Relaxation time  $\tau_N=1/(2\pi f_{pN})$  versus molecular weight for cis-1,4-polyisoprene (adapted from /114/)

### 4.3 Chain dynamics

For type A polymers having a dipole component parallel to the chain contour the molecular motion of the whole polymeric chain can be observed as a separate relaxation process at frequencies below the  $\alpha$ -relaxation (see Fig. 4) which is called dielectric normal mode relaxation. The theory of this relaxation process outlined in /10/ predicts that the contribution of this relaxation process to the dielectric is proportional to the correlation function of the fluctuations of the end-to-end vector of the polymer chain  $\langle r(0)r(t) \rangle$ ,

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\Delta \epsilon_{\text{Chain}}} = \frac{1}{\langle r^2 \rangle} \int_0^\infty \frac{d \langle r(0)r(t) \rangle}{dt} \exp(-i\omega t) dt. \quad (23)$$

where the relaxation strength of this relaxation process  $\Delta \epsilon_{\text{Chain}}$  is related to mean end-to-end vector  $\langle r^2 \rangle$  by

$$\Delta \epsilon_{\text{Chain}} = \frac{4\pi N_A \mu_{\parallel}^2 F_{\text{Onsager}}}{3 k T M} \langle r^2 \rangle, \quad (24)$$

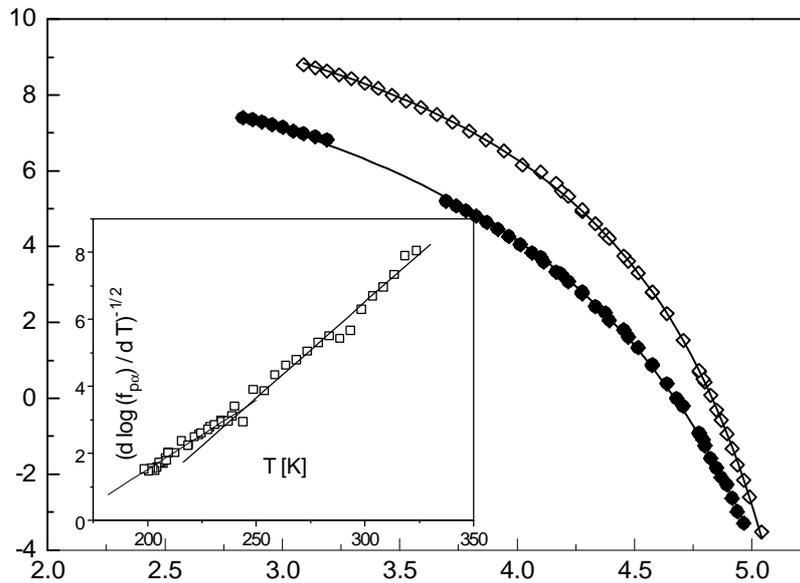
where  $\mu_{\parallel}^2$  is the square of dipole moment per monomer unit which is parallel to the polymer chain.  $M$  is the molar mass of the chain and  $N_A$  is the Avogadro number. For dense polymeric systems  $\langle r(0)r(t) \rangle$ , can be expressed by /10/

$$\langle r(0)r(t) \rangle / \langle r^2 \rangle = (8/\pi^2) \sum_p (1/p^2) \exp(-t/\tau_p) \quad (25)$$

where  $\tau_p$  is a characteristic relaxation time of the mode  $p$ . For undiluted oligomeric melts of flexible chains below the critical molecular weight for the formation of entanglements  $M_c^2$   $\tau_p$  can be calculated in the framework of the Rouse theory /108/. It holds

$$\tau_p = \frac{\zeta N^2 b^2}{3\pi^2 k T p^2}, \quad p = 1, 3, \dots, \quad (26)$$

where  $N$  is the number of statistical chain segments with length  $b$  and  $\zeta$  is the monomeric friction coefficient. It becomes clear from equation (25) that only the modes with  $p=1$  and  $3$  should contribute significantly to the dielectric loss. For that reason an effective normal mode relaxation time  $\tau_N = 1/(2\pi f_{pN})$  can be defined where  $f_{pN}$  is the frequency of maximal loss for the normal mode process. Equ. (26) shows that for  $M < M_c$  the dependence of  $\tau_N$  on molecular weight should be quadratic. This is well confirmed by the experimental results presented for cis-1,4-polyisoprene in Fig. 11 and also for poly(propylene glycol) /38/.



<sup>2</sup>For the most polymers  $M_c$  is in the order of magnitude of  $10^4$  g/mol

Fig.10 Temperature dependence of the relaxation times of the  $\alpha$ - (open symbols) and normal mode relaxation (solid symbols) for poly(propylene glycol) with a molecular weight of 2000 g/mol. Lines are fits according to the VFT-equation. The inset shows data evaluated according to equation (21).

For  $M > M_C$  the polymeric chains are entangled. For that case the functional shape of equation (25) is maintained but the expression for the relaxation times (equ. (26)) is changed to

$$\tau_p = \frac{\zeta N^3 b^4}{\pi^2 kT a^2 p^2}, \quad (27)$$

where  $a$  is a so called tube diameter. Equation (27) is calculated in the frame of the reptation or tube model /109/ and predicts a cubic dependence of  $\tau_p$  on molecular weight whereas the evaluation of mechanical experiments give a value around 3.4. The difference between 3 and 3.4 could be understood within the framework of extended conceptions of chain dynamics like the contour length fluctuation /110/ or the constraint release model /111/. The dielectric experiments on cis-1,4-polyisoprene give an exponent around 4 (see Fig. 10). The reason for the discrepancies of mechanical and dielectric data is not clear in the moment.

The temperature dependence of  $\tau_N$  can be well described by the VFT-equation for both the Rouse regime ( $M < M_C$ ) and the entangled state ( $M > M_C$ ) /10/. It should be also added that the functional shape of the dielectric function for the normal mode process is much broader since predicted by equation (25). This is also true for samples with very narrow distribution of molecular weights /10/ so that the broadening of the loss peak cannot be explained by polydispersity-effects alone. The reason for this broadening of the dielectric normal mode relaxation is still under discussion /10/.

The dielectric behavior of rigid-backbone polymers like poly(n-alkyl isocyanate)s or polypeptides is discussed in references /11/. The theoretical description of these stiff or wormlike chains can be done within the concept of persistence length. For low molecular weights these polymers behave as stiff rods where for higher molecular weights a transition to the Gaussian behavior is observed. Dielectric data for these polymers which can form lyotropic mesophases can be found for instance in /112,113/.

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