polymer papers

An extended analysis of the dielectric properties of poly[(2-cyanoethyl vinyl ether)-*co*-(vinyl alcohol)]

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Poly[(2-cyanoethyl vinyl ether)-*co*-(vinyl alcohol)] is a polymer with a high dielectric constant ($\varepsilon = 15$ at 1 kHz) at room temperature and is therefore used as a binder in electroluminescent lamps. Two different dipole relaxations are observed: a β relaxation, associated with the rotation of the cyanomethyl moiety, at temperatures below 273 K; and an α relaxation at the glass–rubber transition temperature (291 K). The high- and low-frequency limits of the dielectric constant for the β relaxation are observed to be 3.4 and 9.5, respectively. There is good agreement between the observed molecular dipole moment (12.1×10^{-30} C m) derived from the temperature dependence of the static dielectric constant at high temperatures and the literature values for the dipoles present in the polymer. Finally, it is shown that an accurate determination of the characteristic relaxation time for the β relaxation demands fitting to a proper model because using merely the maximum of the imaginary part of the dielectric constant might lead to erroneous results.

(Keywords: impedance spectroscopy; cyanoethylated PVA; dielectric properties)

INTRODUCTION

As a consequence of the general trend to smaller electronic circuits and devices, the passive components have to be reduced in volume. In particular, a reduction of capacitor size is of great importance for the electronics industry. Polymeric materials with a high dielectric constant can be helpful for this purpose[1]. Another, already widespread, use of polymeric materials with a high dielectric constant is as a binder for the phosphor grains in so-called thick-film electroluminescent lamps (see e.g. ref. 2). Using a binder with a high dielectric constant allows operation at low voltage. Commercially available polymeric materials with a high dielectric constant are, for example, cellulose, pullulan, poly(vinylidene fluoride) and the random copolymer of 2-cyanoethyl vinyl ether and vinyl alcohol (see *Figure 1*) discussed in this paper. Also promising for the applications mentioned before are poly[(2-cyanoethyl vinyl ether)-*co*-(cyanoethyl acrylate)[3] and cyanoethylated *O*-(2,3-dihydroxypropyl)-cellulose[4].

This paper is not the first on the dielectric properties of poly[(2-cyanoethyl vinyl ether)-*co*-(vinyl alcohol)]. The real and imaginary parts of the dielectric constant of the copolymer at six frequencies between 60 and 300 Hz for six temperatures between 223 and 348 K were already published in 1964[5]. Another study, over a much wider temperature and frequency range, and with a more extended discussion on the polarization mechanism, was published in 1970[6]. The present paper is an extension of these studies with respect both to the conditions (temperature, frequency) at which the dielectric properties are measured and to the interpretation of the experimental data. This extension, among other things, is possible because of the availability of computer models for analysing the data. Even more important is the availability of the copolymer in a rather pure form at present. This makes it possible, in contrast to the studies in the past, to measure the dielectric properties at high temperatures and low frequencies.

SAMPLE PREPARATION AND CHARACTERIZATION

The poly[(2-cyanoethyl vinyl ether)-*co*-(vinyl alcohol)], better known as cyanoethylated poly(vinyl alcohol) (CEPVA), was synthesized by Shin-Etsu Chemical via

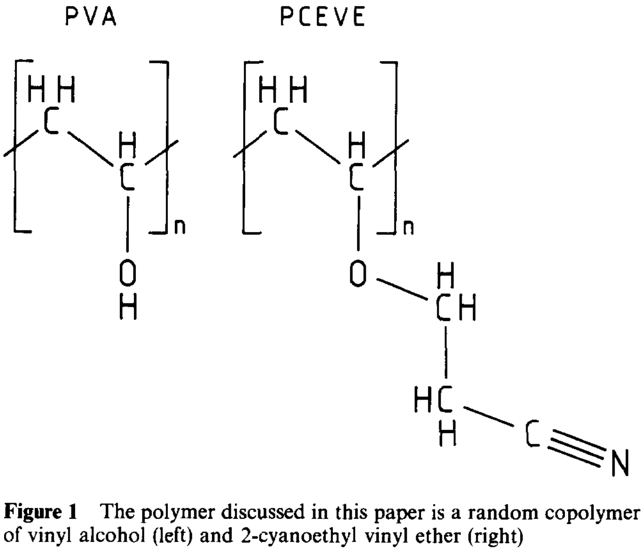

Figure 1 The polymer discussed in this paper is a random copolymer of vinyl alcohol (left) and 2-cyanoethyl vinyl ether (right)

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a substitution reaction of acrylonitrile on poly(vinyl alcohol) (PVA) and is commercially available[7].

The degree of substitution of the alcohol groups by cyanoethyl ether has been determined by measuring the nitrogen content, being 12.41 wt%, by elemental analysis. This corresponds to a substitution of 73.7%.

The refractive index n_D of the copolymer, being 1.4953, has been measured with an Abbe refractometer at a temperature of 300 K.

The molecular-weight distribution (*Table 1*) has been measured by gel permeation chromatography (g.p.c.) using an acetone/tetrahydrofuran 5/40 mixture. A number-average molecular weight $M_n = 2 \times 10^4$ and a dispersion ratio $M_w/M_n = 2$ have been obtained with columns calibrated using polystyrene (PS) standards.

There are several techniques that allow the determination of the glass–rubber transition temperature T_g. Besides the dielectric technique, which will be discussed in detail in this paper, differential scanning calorimetry (d.s.c.) can be used. To determine T_g by d.s.c. the following experiments have been performed in a dry nitrogen atmosphere. The polymer was heated at a rate of $10\,\mathrm{K\,min^{-1}}$ from 173 to 373 K and kept at the latter temperature for half an hour. Subsequently, the sample was cooled to 173 K at a rate of approximately $30\,\mathrm{K\,min^{-1}}$ and a second run to 573 K was performed. The T_g (extrapolated 'onset' temperature) of the polymer was observed to be 282 and 291 K in the first and second runs, respectively (see *Figure 2*). In both runs the heat capacity of the sample increases by $0.7\,\mathrm{J\,g^{-1}\,K^{-1}}$ at the glass–rubber transition. No melting peak has been observed up to the decomposition temperature of approximately 510 K. The lower T_g in the first run is assumed to originate from a higher water content, since the sample was stored in an ambient atmosphere preceding the d.s.c. experiment. It is well established that the T_g of poly(vinyl alcohol) is strongly affected by moisture content; it increases from approximately 300 K to 340 K if the moisture content decreases from 5 to 0%[8]. At a temperature of approximately 200 K there is a change of the heat flow, which might be an indication of another second-order (T_g-like) phase transition.

Table 1 Molecular-weight distribution

Sample no.	M_z	M_w	M_n	M_w/M_n
1	46 600	38 100	20 600	1.9
2	49 700	39 400	19 100	2.1

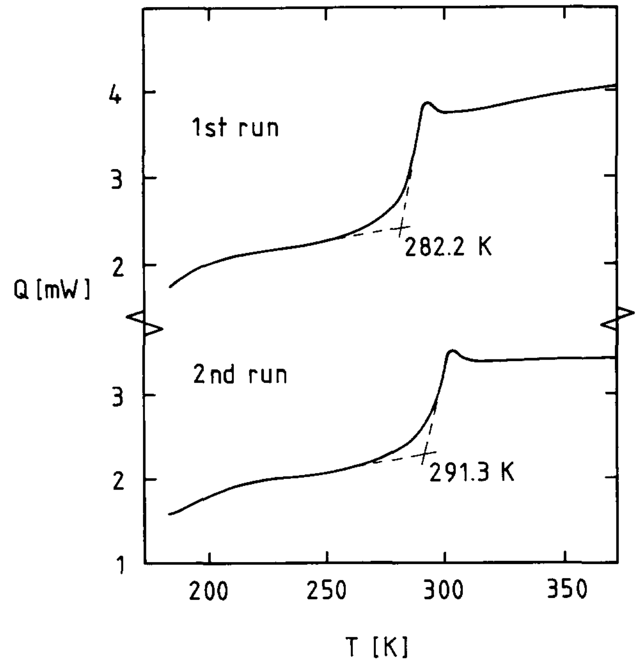

Figure 2 The d.s.c. thermogram of the copolymer in the first and second heating runs

The polymer was dissolved in acetone (pro analyse quality, Merck) to allow casting (at room temperature) on a glass substrate with a circular gold electrode. After casting and drying under atmospheric conditions, the film was heated to 373 K in a dry nitrogen atmosphere for more than 12 h to allow the evaporation of the solvent. Subsequently, the film has been placed in a vacuum chamber (pressure 10^{-5} Pa) for half an hour and a second gold electrode was vacuum deposited on top of the film.

EXPERIMENTAL DETAILS

The dielectric characterization of the polymer was performed at temperatures between 113 and 393 K at intervals of 2.5 K in a dry nitrogen atmosphere during both heating and cooling at a rate of approximately $20\,\mathrm{K\,h^{-1}}$. A harmonic voltage of 1 V was applied across the 32 μm (measured at room temperature) thick sample. The impedance of the sample with an electrode area of $200\,\mathrm{mm^2}$ was measured at three frequencies per decade between 10 mHz and 1 MHz. For frequencies up to 1 kHz a Solartron 1250 Frequency Response Analyzer in combination with a home-made amplifier was used. The measurements at high frequencies (from 1 kHz up to 1 MHz) were performed with a Hewlett-Packard 4284A LCR Meter.

It is well established that the dielectric response of common polymers must satisfy the Kramers–Kronig relations (see e.g. ref. 9), provided the experiments are performed with sufficient experimental accuracy. For the polymer discussed in this paper, this has been checked with positive results by performing a simplified Kramers–Kronig transformation[10] at a few temperatures.

THEORY

The molar polarization P_M and the molar refraction R_M of a dielectric are defined by the Clausius–Mossotti and Lorentz–Lorenz relations:

$$P_M = \frac{\varepsilon - 1}{\varepsilon + 2}\frac{M}{\rho}$$
$$R_M = \frac{n^2 - 1}{n^2 + 2}\frac{M}{\rho} = \frac{N_A \alpha_p}{3\varepsilon_0} \tag{1}$$

with n the refractive index, ε the (real part of the) relative dielectric constant, M the molecular weight, ρ the density, ε_0 the permittivity of vacuum, N_A Avogadro's number and α_p the polarizability of the dielectric. Both the molar refraction and the molar polarization are temperature-independent if there is no orientation of permanent dipoles in the applied field. They are obtained by addition of the molar refraction or polarization of the structural units in the molecule. Although equations (1) are, strictly speaking, only valid if the Lorentz local-field

Table 2 Physical properties of the polymers

	PVA	PCEVE	CEPVA	Units
R_M(calc.)	10.73	24.69	21.01	$10^{-6}\,m^3$
R_M(exp.)	11.05	-	19.26	$10^{-6}\,m^3$
M	44.05	97.12	83.15	g
n(calc.)	1.531	1.559	1.555	
n(exp.)	1.55[24]	-	1.50	
P_M(calc.)	14.27	33.77	28.63	$10^{-6}\,m^3$
P_M(exp.)	14.40	-	29.23	$10^{-6}\,m^3$
ε_∞(calc.)	3.10	3.37	3.33	
ε_∞(exp.)	3.20	-	3.42	
μ(eq. (2))	1.38	2.21	2.02	10^{-30} C m
$\mu\sqrt{g}$(eq. (3))	1.43	2.31	2.11	10^{-30} C m

approximation can be used (e.g. in dilute systems and cubic crystals), they are used to estimate the refractive index and the dielectric constant of a polymer by using the tabulated values (see e.g. ref. 11) of the contribution of several structural units, such as the C≡N bond. In this case M is chosen to be the molecular weight of the repeat unit.

In *Table 2* several of the relevant physical properties of poly(vinyl alcohol) (PVA), poly(2-cyanoethyl vinyl ether) (PCEVE) and the copolymer discussed in this paper (CEPVA) are given. The calculated values are obtained by using the parameters for the structural units of the polymers given by Van Krevelen[11].

The properties of PVA and PCEVE are tabulated for comparison with the copolymer. Unfortunately, the experimental data of PCEVE found in the literature[12] are limited, and no experimental value for the high-frequency limit of the dielectric constant ε_∞ is reported.

The dipole moment μ of the permanent dipoles can be obtained via the Debye equation:

$$P_M - R_M = \left(\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right)\frac{M}{\rho} = \frac{N_A\mu^2}{9\varepsilon_0 kT} \tag{2}$$

Here it is assumed that the permanent dipoles are free to rotate. For non-polar dielectrics ($\mu = 0$) the dielectric constant is equal to the square of the refractive index: $\varepsilon = n^2$. A more rigorous theoretical approach results in the Kirkwood–Fröhlich equation (see e.g. ref. 13) for the relation between the static dielectric constant ε_s, the high-frequency limit of the macroscopic dielectric constant ε_∞, and the molecular dipole moment μ:

$$\frac{(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{\varepsilon_s(\varepsilon_\infty + 2)^2} = \frac{\rho}{M}\frac{N_A g\mu^2}{9\varepsilon_0 kT} \tag{3}$$

with g the dipole correlation factor. Values both below and above 1 are theoretically predicted and experimentally observed for g (ref. 13) depending on whether the dipoles hinder each other or have a strong interaction. Often ε_∞ is chosen to be equal to n^2. The calculated values for μ, using equation (2), and for $\mu\sqrt{g}$, using equation (3), are given in *Table 2*. If there are two possible configurations of the dipoles with an energy difference ΔU, then the correlation factor is given by[14]:

$$g = 2(1-\cos\gamma)\frac{\exp(-\Delta U/k_B T)}{[1+\exp(-\Delta U/k_B T)]^2} \tag{4}$$

with γ the angle of rotation of the dipole in the applied field.

The frequency- and temperature-dependent complex dielectric constant is given by:

$$\varepsilon^*(\omega, T) = \varepsilon'(\omega, T) - i\varepsilon''(\omega, T) \tag{5}$$

with ω the angular frequency, T the temperature and $i = \sqrt{(-1)}$. It is common practice to characterize a dielectric by the real part of the dielectric constant and the dielectric loss factor $\tan\delta$, which is defined by $\tan\delta = \varepsilon''/\varepsilon'$. In general, the dielectric constant as a function of the frequency can be described mathematically at a given temperature by the empirical Havriliak–Negami[15] equation:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{[1+(i\omega\tau)^{1-\alpha}]^\beta} \tag{6}$$

Here, τ is a characteristic relaxation time, and both α and β are fitting parameters characterizing the functional form of the dispersion relation. The parameter β (having a numerical value between 0 and 1) is related to the skewness of the dispersion; if $\beta = 1$ equation (6) reduces to the Cole–Cole[16] relation. In a plot of ε'' *versus* ε' such a dispersion gives a semi-circle with its centre below the ε' axis. The parameter α $(0 \leqslant \alpha \leqslant 1)$ is related to the width of the dispersion; equation (6) reduces to the Debye relation (single relaxation time) if, in addition to $\beta = 1$, $\alpha = 0$. The relaxation of side chains, functional groups and chain segments in polymers is usually described very well by the Havriliak–Negami equation.

The relaxation time τ is temperature-dependent, often according to the Arrhenius relation:

$$\tau = \tau_0 \exp\left(\frac{E_{act}}{k_B T}\right) \tag{7}$$

with E_{act} the activation energy and k_B the Boltzmann constant, or according to the relation:

$$\tau = \frac{h}{k_B T}\exp\left(-\frac{\Delta S}{k_B}\right)\exp\left(\frac{\Delta H}{k_B T}\right) \tag{8}$$

with h the Planck constant, ΔS the activation entropy and ΔH the activation enthalpy. Often the temperature dependence of the prefactor $h/k_B T$ can be neglected and equation (7) is used to determine the activation energy. A few years ago, the relation between equations (7) and (8) was discussed[17]. For the Debye and the Cole–Cole model the characteristic time τ can easily be obtained from the measured imaginary part (ε'') of the dielectric constant (as a function of temperature or frequency); ε'' has a maximum value at $2\pi f\tau = 1$, with f the measuring frequency at the peak maximum. It is common practice to use the criterion of the maximum in ε'' to determine the value of τ even if the experimental data do not fit the Debye or the Cole–Cole relations, probably because the maximum of ε'' can easily be obtained. To determine τ in the more general Havriliak–Negami model ($\beta < 1$) requires fitting of the experimental data to that model. It will be shown in this paper that using the criterion of the maximum in ε'' might lead to erroneous results.

It is well established that the mechanical properties of polymers at different temperatures above the glass–rubber transition can be correlated with the properties at a characteristic temperature (e.g. T_g) via the WLF

(Williams–Landel–Ferry)[23] equation:

$$\log_{10} a_T = -\frac{C_1(T-T_g)}{C_2+T-T_g} \tag{9}$$

Here a_T is the shift along the temperature axis to obtain a master curve at all temperatures and both C_1 and C_2 are 'universal' constants equal to 17.44 and 51.6 K, respectively. If one assumes that the dielectric relaxation is correlated to the free volume of the polymer, then the WLF equation is satisfied for the quotient $a_T = \tau(T)/\tau(T_g)$ of the characteristic relaxation times at a temperature T and at T_g (ref. 18). The relaxation of chain segments at the glass–rubber transition is called the α relaxation.

If the characteristic time $\tau(T)$ of the WLF process is presented in an Arrhenius type of plot ($\log_{10}\tau(T)$ vs. $1000/T$) then an apparent activation energy can be defined by the slope of the curve. According to equation (6) the activation energy is defined by:

$$E_{\mathrm{act}} = k_B \frac{\mathrm{d}\ln\tau}{\mathrm{d}(1/T)} = k_B \ln(10)\frac{\mathrm{d}\log_{10}\tau}{\mathrm{d}(1/T)} \tag{10}$$

Substitution of the WLF relation for τ gives:

$$E^{\mathrm{a}}_{\mathrm{act}} = k_B \ln(10)\frac{C_1 C_2 T^2}{(C_2+T-T_g)^2} \tag{11}$$

for the apparent activation energy $E^{\mathrm{a}}_{\mathrm{act}}$. This energy varies with temperature and has a value of $k_B T_g^2 \ln(10) C_1/C_2 = 6.71\times10^{-5} T_g^2$ eV ($6.47\times10^{-3} T_g^2$ kJ mol^{-1}) at T_g.

Most polymers are insulators and the conductivity of these polymers finds its origin in the transport of ions (in most cases impurities) that are present in the material. Such a conductivity is a thermally activated process, viz.:

$$\sigma = \sigma_0 \exp\left(\frac{-E_{\mathrm{act}}}{k_B T}\right) \tag{12}$$

The conductivity might be determined by two mechanisms: the generation of free charge carriers and their mobility. In this case the conductivity is given by:

$$\sigma = \sigma_0(T)\exp\left(\frac{-\Delta W}{2\varepsilon_s k_B T}\right) \tag{13}$$

with ΔW the energy to separate the ions in a medium of unit dielectric constant[18] (dissociation energy). The prefactor $\sigma_0(T)$ is determined by, among other things, the mobility of the ions. If it is assumed that the mobility near T_g is correlated to the free volume, then the temperature dependence of σ_0 is given by the WLF equation, viz.:

$$\log_{10}\sigma_0(T) = +\frac{C_1(T-T_g)}{C_2+T-T_g} + \log_{10}\sigma_0(T_g) \tag{14}$$

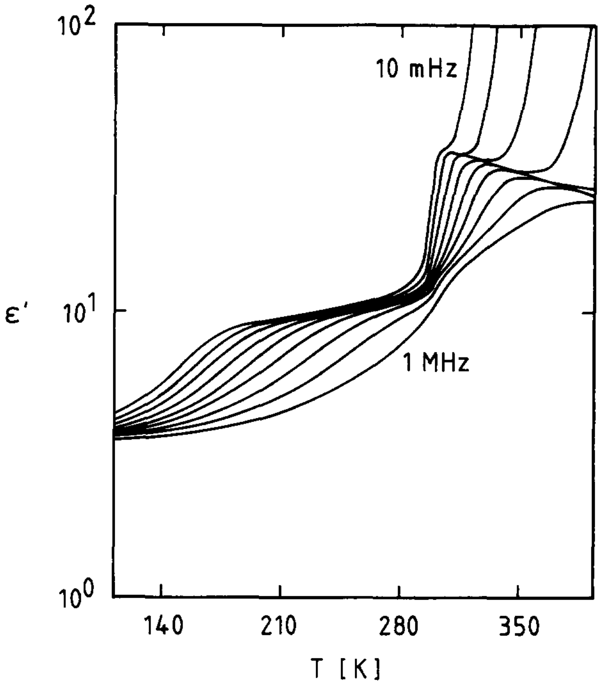

Figure 3 The real part of the dielectric constant ε' as a function of temperature for one frequency per decade between 10 mHz and 1 MHz

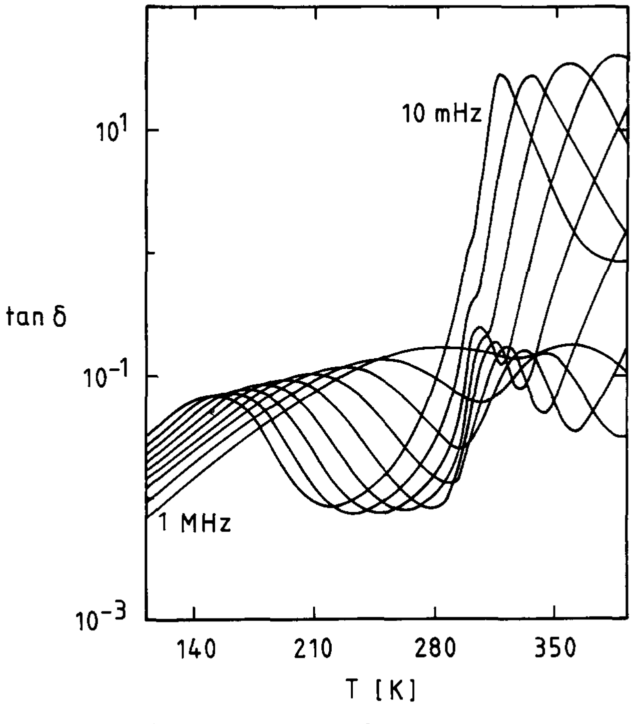

Figure 4 The dielectric loss factor tan δ as a function of temperature for one frequency per decade between 10 mHz and 1 MHz

EXPERIMENTAL RESULTS

Overview of the dielectric relaxations

In *Figures 3* and *4* the real part of the dielectric constant and the dielectric loss factor are given as a function of the temperature. For clarity only one frequency per decade is plotted in these figures. Two relaxation mechanisms are observable: the β relaxation at temperatures below 280 K and the α relaxation at temperatures between 280 and 350 K. The β relaxation in polymers is attributed to the rotation of side groups, whereas the α relaxation corresponds to rotations of chain fragments in the applied field. These two relaxations will be discussed in more detail in the next sections of this paper. At high temperatures the so-called electrode polarization is observable in the plot by a peak in tan δ and a strong increase of the macroscopic (i.e. measured) dielectric constant.

Low-temperature (β) relaxation

Fitting the β relaxation for temperatures lower than 220 K to the Havriliak–Negami equation (equation (6)) gives values of 3.42 and 9.5 for the high- and low-frequency limits of the dielectric constant, respectively. It has been observed that a good fit at these temperatures can be obtained with a constant value of $\beta = 0.50$. In *Figure 5* a so-called Cole–Cole plot is given for the dielectric data at 183 K.

For temperatures below 220 K, the dipole strength $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ is observed to be constant. Whereas ε_∞ is constant in the whole temperature range where the relaxation is experimentally observable, viz. up to 280 K, $\Delta\varepsilon$ increases with temperature for temperatures higher than 220 K, as can be seen in *Figure 6*.

The parameter α is temperature-dependent, as can be seen in *Figure 7*, and seems to be linear with temperature below and above 200 K. The best linear fits are:

$$\alpha = 1.194 - 2.691 \times 10^{-3} T \quad \text{for } T > 200\,\text{K} \quad (15)$$

$$\alpha = 1.036 - 1.894 \times 10^{-3} T \quad \text{for } T < 200\,\text{K} \quad (16)$$

Equation (16) shows that $\alpha = 1$ at $T = 0$ K. This means that the dielectric constant is independent of the frequency at this temperature. Extrapolation of equation (15) gives $\alpha = 0$ at 443 K.

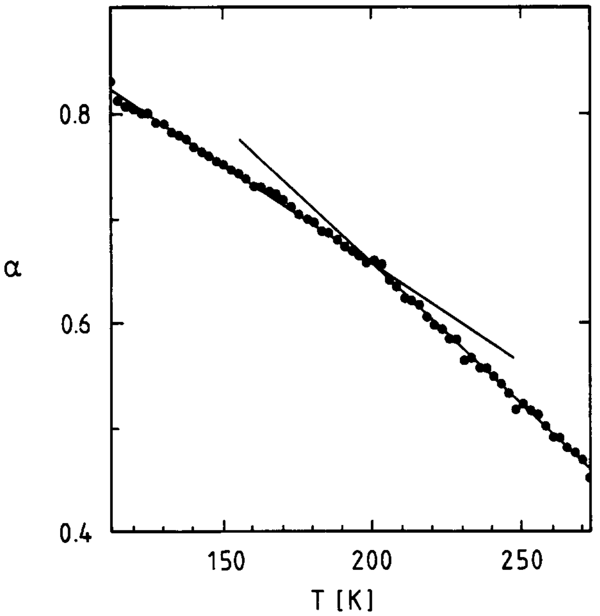

Figure 7 The fitting parameter α of the Havriliak–Negami equation as a function of temperature. The best linear fits for temperature below and above 200 K are shown

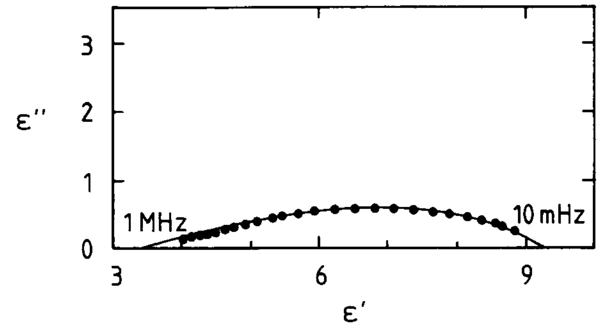

Figure 5 The relation between the real (ε') and the imaginary (ε'') parts of the dielectric constant at 183 K for frequencies between 10 mHz and 1 MHz

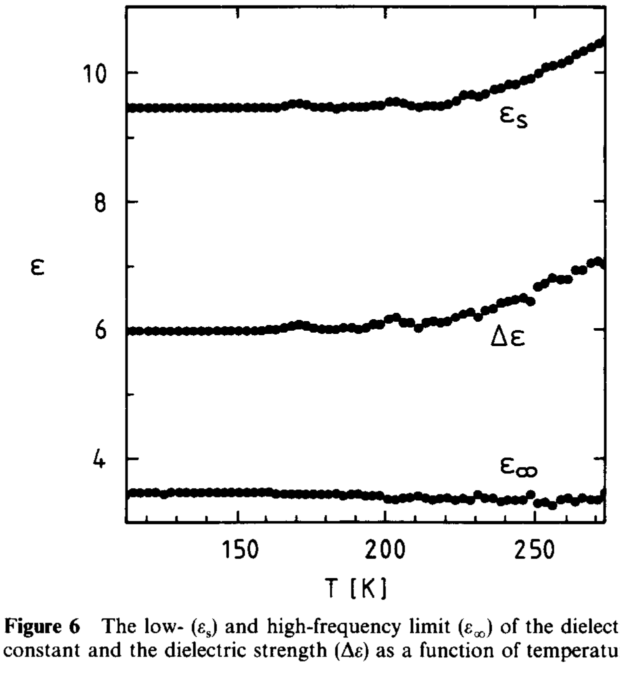

Figure 6 The low- (ε_s) and high-frequency limit (ε_∞) of the dielectric constant and the dielectric strength (Δε) as a function of temperature

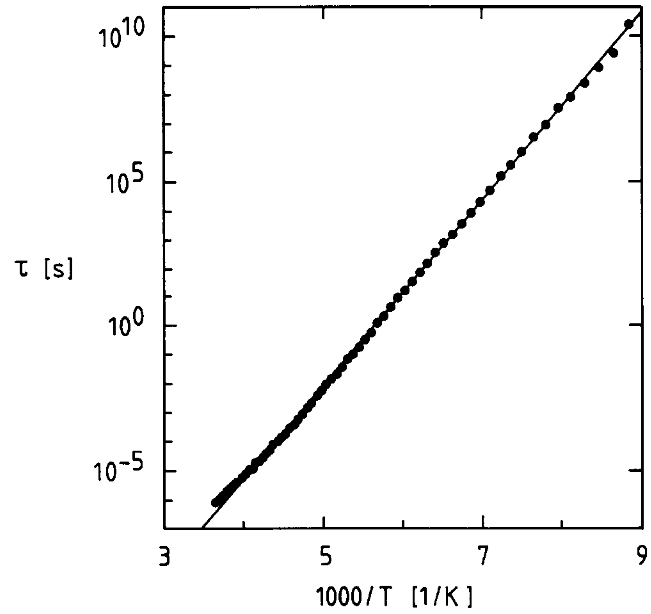

Figure 8 The relaxation time τ, obtained via fitting of the experimental data to the Havriliak–Negami equation, as a function of reciprocal temperature

The relaxation time τ obtained from the fitting procedure is given in *Figure 8*. This figure reveals that the β relaxation is thermally activated with an activation energy of 0.65 eV (62 kJ mol^{-1}). The prefactor τ_0 (see equation (7)) is equal to 4×10^{-19} s. The correlation factor of the data is 0.996.

Often the characteristic relaxation time and its activation energy are determined from the peak position of $\varepsilon''(f, T)$. The result of this method will be given here to show that this procedure might lead to erroneous results. It is common practice to plot the frequency at which $\varepsilon''(f, T)$ has a maximum as a function of the reciprocal temperature, as shown in *Figure 9*. Fitting this curve to equation (7) (with $\tau = 1/2\pi f$) gives an activation energy $E_{act} = 0.57\,\mathrm{eV}$ ($55\,\mathrm{kJ\,mol^{-1}}$) and $\tau_0 = 1 \times 10^{-17}\,\mathrm{s}$. The correlation factor for the data is 0.998. Taking a closer look at *Figure 9* reveals a slight deviation from the Arrhenius behaviour. This deviation becomes more clear if the activation energy E_{act} obtained from the slope of this curve is plotted as a function of the reciprocal temperature, as shown in *Figure 10*; the activation energy for the low-temperature relaxation decreases with increasing temperature.

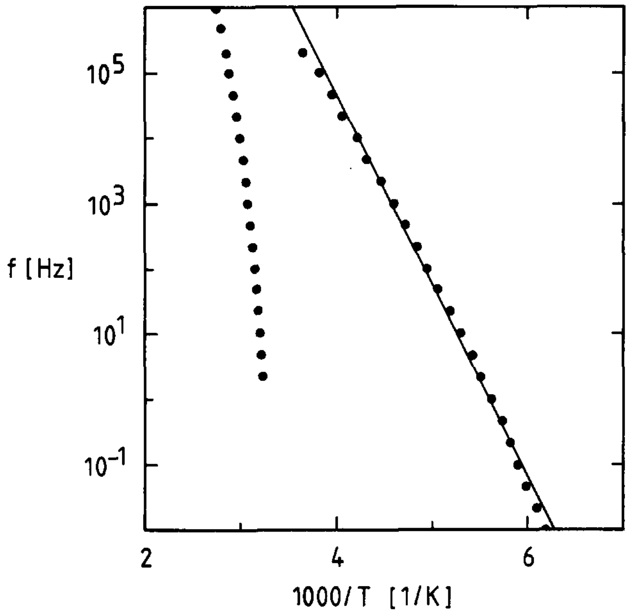

Figure 9 The relation between the frequency f, viz. $\omega/2\pi$, and the temperature T where $\varepsilon''(f, T)$ has a maximum. The line is the best fit to equation (7) for $\tau = 1/\omega$

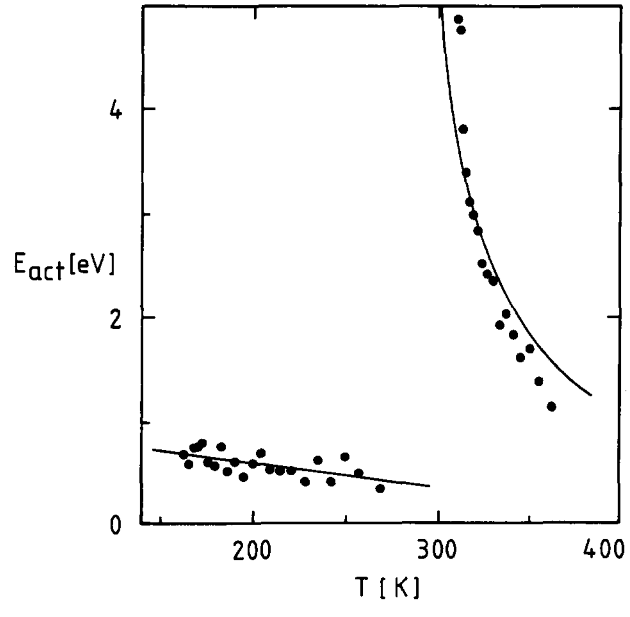

Figure 10 The activation energy for the β relaxation and the apparent activation energy for the α relaxation obtained from the derivative of the curves in *Figure 9*. Also shown is the best linear fit (β relaxation) and the best fit to equation (11) using the 'universal' constants

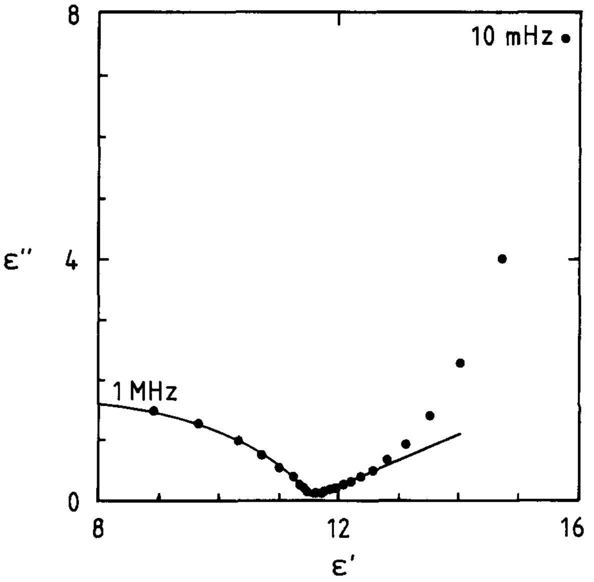

Figure 11 The relation between the real (ε') and the imaginary (ε'') parts of the dielectric constant at 293 K for frequencies between 10 mHz and 1 MHz

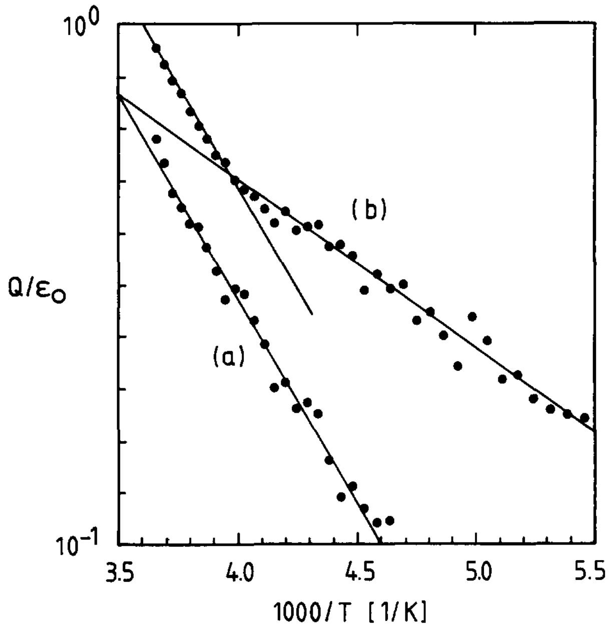

Figure 12 The factor Q/ε_0 as a function of reciprocal temperature for the slowly cooled sample (a) and the quenched one (b)

A second low-temperature relaxation

In addition to the relaxation described above, there is an indication of a second dielectric loss mechanism in the plot of the dielectric constant at temperatures between 210 and 300 K. This loss is characterized by a constant phase relation between ε' and ε'', viz. $\varepsilon''/\varepsilon' = \tan(\phi\pi/2)$ for all frequencies and $\varepsilon' = (Q/\varepsilon_0)\omega^{\Phi}\cos(\phi\pi/2)$. The phase factor $\phi\pi/2 = 1/3$ for all temperatures.

In *Figure 11* a Cole–Cole plot at 293 K is shown. In this figure the β relaxation at high frequencies (semicircle), the α relaxation at low frequencies, and the constant phase relation (straight line) at intermediate frequencies can be seen.

In contrast to all other dielectric properties discussed in this paper, the prefactor Q is observed to be influenced by the (thermal) history of the sample. This is best illustrated by the experiment in which the polymer was cooled down from 393 K to 113 K at a rate of 20 K h^{-1} preceding the dielectric measurements and the experiment in which the polymer was quenched. In the latter case, the polymer was cooled down from 393 to 113 K by purging nitrogen gas (100 K) in the measuring cell. The polymer reached the temperature of 113 K within approximately 15 min. In *Figure 12*, Q/ε_0 is given as a function of the reciprocal temperature. Experiments with the slowly cooled sample strongly suggest that the relaxation (of unknown origin) is thermally activated with an activation energy of 0.15 eV (14 kJ mol^{-1}). For the quenched sample the same activation energy is observed for temperatures above approximately 250 K. However, for lower temperatures, the activation energy is 0.07 eV.

High-temperature (α) relaxation

At temperatures above T_g, chain fragments can move like in a viscous fluid. This α relaxation allows a high polarization for polymers with strong polar groups. However, because of the thermal motion, the static dielectric constant decreases with increasing temperature above T_g.

The characteristic parameters for this α relaxation have been obtained by using the computer program of Boukamp[19]. The data have been fitted to an equivalent circuit, being a model for a Cole–Cole relaxation in parallel with a conductivity element. For a more detailed discussion, see e.g. ref. 20. At temperatures higher than 320 K a capacitor and resistor in parallel have been placed in series with the equivalent circuit to take into account the electrode polarization.

To estimate the dipole moment of the moiety that causes the α relaxation, it is assumed that the density ρ of the polymer, the dipole correlation factor g and the dipole moment μ are independent of temperature. With these assumptions there is a linear relation between the left-hand side of equation (3) and the reciprocal temperature. In *Figure 13* it can be seen that such a relation holds in a good approximation for the polymer under discussion. This allows the calculation of the dipole moment $\mu\sqrt{g}$ from the slope of the curve. With $M = 83.15$ g and $\rho = 1.27 \times 10^3$ kg m^{-3}, the dipole moment $\mu\sqrt{g} = 12.1 \times 10^{-30}$ C m.

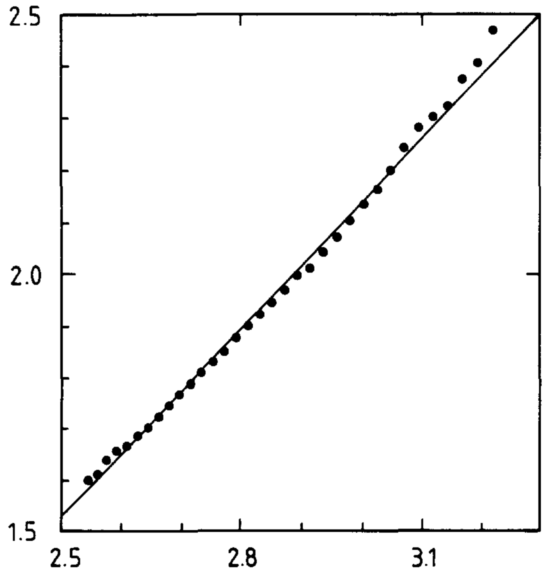

Figure 13 The left-hand side of equation (3), viz. $\psi = [(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)]/[\varepsilon_s(\varepsilon_\infty + 2)^2]$, as a function of reciprocal temperature

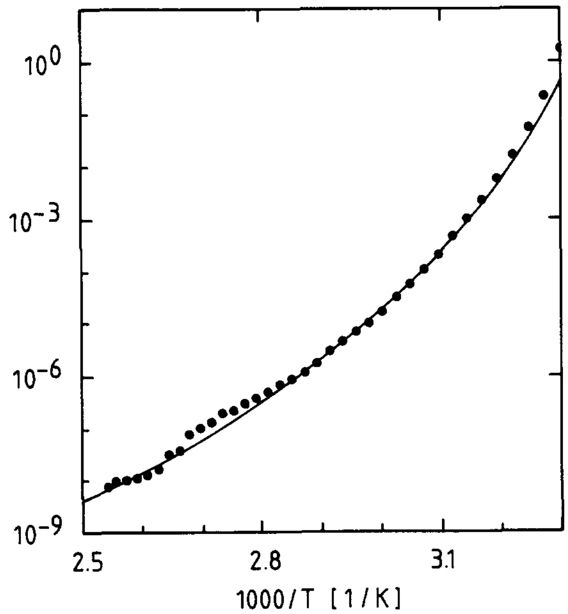

Figure 14 The relaxation time τ from the Cole–Cole relation, as a function of reciprocal temperature. The full curve is the best fit to the WLF equation

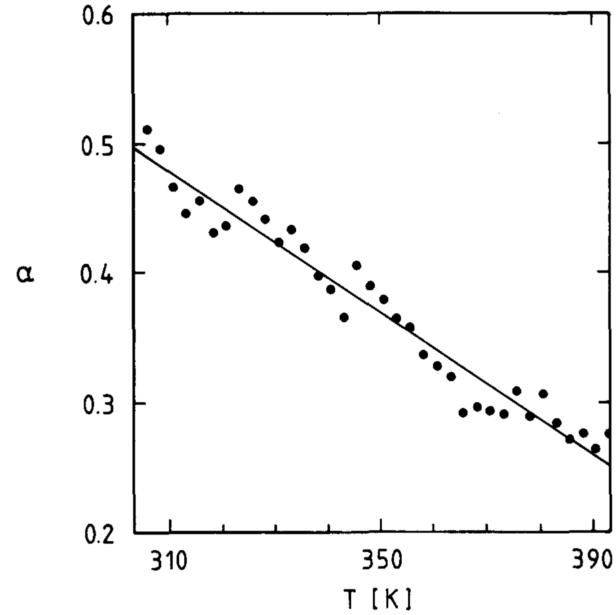

Figure 15 The parameter α in the Cole–Cole relation as a function of the temperature. The line is the best linear fit to the data

The relaxation times τ that have been obtained by fitting the experimental data to the Cole–Cole relation ($\beta = 1$ in equation (6)) are given in *Figure 14*. Fitting these relaxation times to the WLF relation gives $T_g = 288$ K and a characteristic time constant $\tau(T_g) = 3 \times 10^3$ s if the 'universal' values $C_1 = 17.44$ and $C_2 = 51.6$ K are used. If these constants are also considered as fitting parameters, then $T_g = 295$ K, $\tau(T_g) = 2 \times 10^3$ s, $C_1 = 14.1$ and $C_2 = 29.4$ K.

Another way to determine T_g is by fitting the apparent activation energy E^a_{act}, defined in equation (10), to equation (11). This leads to $T_g = 294$ K and $E^a_{act}(T_g) = 5.8$ eV with the 'universal' constants, or $T_g = 290$ K and $E^a_{act}(T_g) = 14.3$ eV with $C_1 = 17.3$ and $C_2 = 20.3$ K.

The parameter α is observed to decrease with increasing temperature, as can be seen in *Figure 15*. There seems to be a linear relation between the temperature and α, which is a measure for the width of the distribution of relaxation times; this width decreases with increasing temperature. The best linear fit is given by $\alpha = 1.322 - 2.721 \times 10^{-3} T$. Extrapolation to low and high temperatures of this relation gives $\alpha = 1$ at 118 K and $\alpha = 0$ at 485 K.

In the preceding paragraphs the dielectric properties of the polymer were discussed on the basis of data obtained from fitting to the Cole–Cole relation. For completeness the same procedures were applied to the data obtained from the maximum in ε''. This led to identical fitting results for the glass–rubber transition temperature T_g, the characteristic time $\tau(T_g)$ and the apparent activation energy E^a_{act}. Of course, this method does not give the parameter α.

Conductivity

The conductivity of the polymer as obtained by applying the fitting procedure described before is given in *Figure 16*. It is evident from this figure that the conductivity is not thermally activated. If the conductivity is completely determined by the free volume of the polymer, i.e. equation (13) can be applied for σ, then $T_g = 261$ K and $\sigma(T_g) = 8 \times 10^{-19}$ S m^{-1} are obtained if the 'universal' values for C_1 and C_2 are used. If these constants are also used as fitting parameters, then $T_g = 268$ K, $\sigma(T_g) = 3 \times 10^{-18}$ S m^{-1}, $C_1 = 16.0$ and $C_2 = 42.6$ K.

As is the case for the relaxation time, also for the conductivity an apparent activation energy E^a_{act} can be calculated. If this E^a_{act} is fitted to equation (11), then $T_g = 262$ K and $E^a_{act}(T_g) = 4.6$ eV, using the 'universal' values for C_1 and C_2. If these parameters are also used as fitting parameters, then $T_g = 279$ K, $C_1 = 12.7$, $C_2 = 54.0$ K and $E^a_{act}(T_g) = 3.6$ eV.

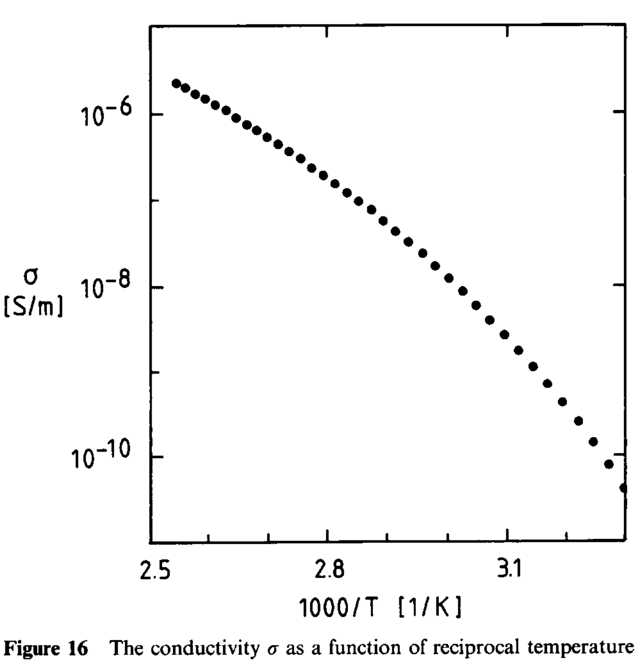

Figure 16 The conductivity σ as a function of reciprocal temperature

In a more rigorous approach, also the thermally activated generation of charge carriers (dissociation) has to be taken into account. In this case the temperature dependence of ε_s has to be considered (see equation (13)). It is observed that ε_s varies linearly with inverse temperature for the relevant temperatures, viz. $\varepsilon_s(T) = -19.65 + 17.63 \times 10^3/T$. Combining equations (13) and (14) with this relation gives $T_g = 266$ K, $\sigma(T_g) = 3 \times 10^{-16}$ S m^{-1} and $\Delta W = 10.1$ eV (viz. $E_{act}(T_g) = 0.11$ eV) if the 'universal' values for C_1 and C_2 are used. If these constants are also used as fitting parameters, then $T_g = 286$ K, $\sigma(T_g) = 9 \times 10^{-13}$ S m^{-1}, $\Delta W = 3.8$ eV (viz. $E_{act}(T_g) = 0.05$ eV), $C_1 = 11.8$ and $C_2 = 64.5$ K.

DISCUSSION

The measured high-frequency limit of the dielectric constant $\varepsilon_\infty = 3.42$ agrees, within experimental accuracy (thickness, electrode area), with the calculated value of 3.33.

Figure 8 shows that relaxation times far larger than the reciprocal of the lowest measuring frequency can be obtained if the relaxation time τ for the β relaxation is obtained by fitting to the Havriliak-Negami equation. This is a great advantage of this method in comparison with obtaining τ from the peak in ε''. In principle, also much smaller times than the reciprocal of the highest measuring frequency can be obtained. However, for the polymer discussed here, such relaxation times correspond to temperatures close to the glass–rubber transition. At these temperatures the α relaxation dominates the relaxation.

The β relaxation is observed to be thermally activated, as can be seen in *Figure 8*, with an activation energy of 0.65 eV (62 kJ mol^{-1}). However, if the activation energy E_{act} is derived from the maximum in ε'' (*Figure 9*) then $E_{act} = 0.57$ eV, which is exactly the value obtained by others[6] using this technique. A close examination reveals that the activation energy obtained from the maximum in ε'' decreases with increasing temperature, as can be seen in *Figure 10*. This temperature dependence will be even stronger if the relaxation time satisfies equation (8) instead of equation (7). A similar systematic deviation from a straight line is also observed for the data obtained from the Havriliak–Negami equation in the same temperature range. However, *Figure 8* shows that this deviation does not occur at lower temperatures. A possible explanation for the observed deviation in *Figure 9* from an Arrhenius relation with a constant activation energy is the fact that the relaxation time is actually not defined by the peak in ε'' but by $\omega\tau = 1$ in the Havriliak–Negami equation. Or, stated otherwise: the dispersion relation is not symmetric. It has been shown by others[21] that in a first approximation the relation between the relaxation time τ_{CC} obtained from the maximum in ε'' and τ_{HN} in the Havriliak–Negami model is given by $\tau_{HN} = \beta^{1/(1-\alpha)} \tau_{CC}$.

The dipole moment $\mu\sqrt{g}$ for the β relaxation has been obtained by fitting the experimental data to the Kirkwood–Frölich equation (equation (3)) in combination with equation (4). This gives $\Delta U = 0.03$ eV and $\mu\sqrt{2(1-\cos\gamma)} = 9.63 \times 10^{-30}$ C m. The contribution of the cyanomethyl group to the dipole moment of each monomer is almost equal to this latter value, viz. 9.6×10^{-30} C m. Consequently, the rotation angle $\gamma = 60°$ if the β relaxation originates from the orientation of all cyanomethyl groups in the polymer. Such an angle, however, is not expected for this molecular group. A more likely explanation for the observed polarization is that not all cyanomethyl groups orientate in the applied field due to hindrance by other groups. The increase of $\Delta\varepsilon$ (and ε_s) with temperature is an indication that an increasing number of cyanomethyl groups rotate in the applied field.

The parameter $\beta = 0.50$ in the Havriliak–Negami equation is observed to be independent of temperature. This means that the shape of the distribution function does not vary with temperature, apart from the broadening given by the variation of the parameter α. The width of the distribution function is observed to be extremely wide: more than two orders of magnitude at 273 K and more than five orders of magnitude at 113 K[21].

For most polymers, the distribution of relaxation times is smaller for an α relaxation than for a β relaxation. This is also the case for the polymer discussed in this paper. However, it is interesting to note that the parameter α, which is a measure of the width of the distribution function, is given by an almost identical function of temperature for both relaxations, viz. $\alpha \approx 1.2 - 2.7 \times 10^{-3} T$. The α-relaxation peak is only smaller because the temperature is higher.

From previous experiments on the copolymer, it was not clear whether the high polarization at room temperature is (mainly) caused by a rotation of the cyanomethyl ($-CH_2-C\equiv N$) around the central C–C bond in the cyanoethyl ether (ϕ_3 in *Figure 17*). This rotation is the only one that is possible without any significant steric hindrance and has been assumed to be responsible for the β relaxation. Rotation at ϕ_1 is more difficult, whereas rotation at ϕ_2 is only possible for some specific angles of ϕ_3. When the cyanomethyl rotates at ϕ_3, the total dipole moment of the cyanoethyl ether varies between 17.2×10^{-30} and 11.1×10^{-30} C m in the *cis* (see *Figure 17*) and the *trans* (see *Figure 1*) configurations, respectively. The α relaxation is attributed to orientation of the molecular chains. In a first approximation the three dipoles, i.e. $=CH-OH$, $=CH-O-CH_2$ and $-CH_2-C\equiv N$, are assumed to orient independently in the applied field. The sum of the three dipole moments (see *Table 3*) is 14.5×10^{-30} C m if the degree of substitution is taken into account. Comparison with the measured value 12.1×10^{-30} C m for $\mu\sqrt{g}$ gives a correlation factor $g = 0.84$. If only the cyanomethyl group is responsible for the high polarization, then g is calculated to be equal to 1.26. Such a value is rather unrealistic because values higher than 1 occur only if there is a strong correlation between (interacting) dipoles. In the case where the orientation of dipoles is hindered, g values lower than 1 are expected. Therefore it is likely that the high polarization of the polymer discussed in this paper is caused by the orientation of all dipoles.

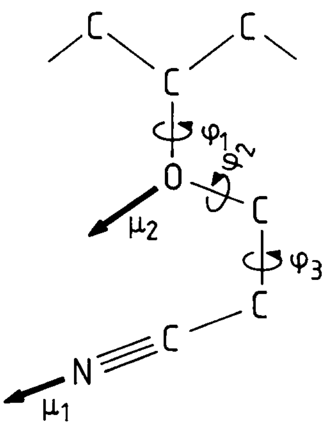

Figure 17 The strong polar character of the cyanoethyl ether side chains originates from the strong dipole moments of the cyano (μ_1) and the ether (μ_2) groups

Table 3 Dipole moments and bond angles[22]

		μ(10^{-30} C m)	Angle (deg)
Cyanomethane	$H_3C-C\equiv N$	13.0	180
Cyanoethane	$H_3C-CH_2-C\equiv N$	13.3	109.5
Dimethyl ether	$H_3C-O-CH_3$	4.3	110
Methanol	H_3C-OH	5.7	–

The glass–rubber transition temperature of the polymer obtained from the characteristic relaxation time in the Cole–Cole model lies between 288 and 295 K, which is in agreement with the d.s.c. experiments ($T_g = 291$ K). The relaxation time at T_g is approximately 3×10^3 s. In contrast to the β relaxation, there is no difference between the parameters obtained via fitting to the Havriliak–Negami (actually the Cole–Cole) model and those obtained via the peak maximum in ε''. This is as expected because the relaxation time in the Cole–Cole model, defined by $\omega\tau = 1$, is actually the maximum in $\varepsilon''(\omega)$. The apparent activation energy at T_g is approximately 6 eV (560 kJ mol^{-1}). For temperatures between 303 and 373 K, $E_{\mathrm{act}}^{\mathrm{a}}$ varies between 5 and 1 eV, which is in agreement with the data reported by others[6].

The T_g obtained from the conductivity data is about 20 K lower than the value obtained from the relaxation times. Such behaviour is common in polymers, but nevertheless not completely understood. However, if, instead of the 'universal' values for C_1 and C_2 in the WLF equation, these parameters are also used as fitting parameters, then $T_g = 286$ K. At this temperature the activation energy $E_{\mathrm{act}} = 0.05$ eV and the energy ΔW to separate the ions in a medium with the permittivity of vacuum is 3.8 eV. This latter energy corresponds rather well to the electron affinity of a CN radical, being 3.2 eV[22]. The conductivity $\sigma(T_g = 286\ \mathrm{K}) = 1 \times 10^{-12}$ S m^{-1}.

Finally, we present a purely speculative discussion on the observed additional dielectric loss at temperatures between 210 and 300 K, viz. at temperatures between the β and the α relaxation. In many dielectrics, such a constant phase relation is observed. The origin of this phenomenon is often attributed to a non-ideal dielectric relaxation or, in the case where the phase factor is equal to 0.5, to a diffusion process. For the polymer discussed in this paper, the activation energy for this loss (0.1 eV) is almost equal to the activation energy for conduction. It is well established that, for temperatures between the β and the α relaxation, physical ageing of polymers occurs. This ageing process corresponds to a reduction of the free volume in time and is affected by the rate at which the polymer is cooled down from the rubbery state to lower temperatures. The observation that the loss is affected by the cooling rate suggests that ageing of the amorphous polymer plays a role. The consideration mentioned here suggests that diffusion of ions might be the origin of the observed additional loss. In a quenched polymer, the free volume is larger than in a slowly cooled polymer, which leads to a faster diffusion. This is in agreement with the observation that the loss is higher in the quenched polymer (see *Figure 12*).

CONCLUSIONS

It is shown that the activation energy for a β relaxation determined by fitting the complex dielectric constant to the Havriliak–Negami equation is higher than that obtained by taking the maximum of ε'' to determine the characteristic relaxation time. Both methods will only give identical results if the relaxation can be described by the Cole–Cole model, viz. $\beta = 1$ in the Havriliak–Negami equation. This is the case for the α relaxation. Using the Havriliak–Negami equation has the advantage that the relaxation time can be obtained in a wider temperature range.

The high polarization (effective dipole moment 12.1×10^{-30} C m) of cyanoethylated poly(vinyl alcohol) at room temperature originates from the orientation (α relaxation) of the three types of polar groups in the copolymer. The temperature dependence of the characteristic time constant and the conductivity of the polymer can be described by the WLF equation, using the 'universal' constants, for temperatures above the glass–rubber transition.

In addition, the dielectric measurements suggest that the β relaxation, with an activation energy of 0.65 eV (62 kJ mol^{-1}), originates from the orientation of only a part of the cyanomethyl groups in the polymer. This relaxation corresponds to a dipole strength $\Delta\varepsilon = 6.1$ at temperatures below 220 K.

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