Dielectric Relaxation of Polyacrylonitrile in Its Pristine and Cyclized Stage

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ABSTRACT: The dielectric behavior of polyacrylonitrile (PAN) in its pristine and cyclized stages was investigated. A PAN homopolymer displays a strong secondary relaxation at an activation energy of $E_a = 111$ kJ/mol in the pristine stage and a weak relaxation at $E_a = 48$ kJ/mol in the cyclized stage. By contrast, a PAN copolymer with itaconic acid, which is used in carbon fiber production, displays a strong secondary relaxation at $E_a = 134$ kJ/mol in the pristine stage and two relaxations with activation energies of $E_a = 24$ kJ/mol for the lower frequency relaxation and $E_a = 9$ kJ/mol for the higher frequency relaxation. No relaxations were found for either polymer in the aromatized stage. The relaxation spectra were interpretated in terms of the Havriliak−Negami (HN) function.

1. Introduction

PAN fibers are widely used for textiles and as precursors in carbon fiber production. It is known that the cyclized structure of PAN is an important intermediate step in the formation of carbon fibers, and therefore, there are a large number of publications concerning these reaction and the corresponding changes of the physical and structural properties during carbon fiber production. Some reviews on this subject have been written by Wöhrle,[1] Olive,[2] Abhiraman,[3,4] and Bashir.[5]

The present work deals with the investigation of their dielectic properties at the pristine, cyclized, and aromatized stages of their transformation. The dielectric method used was broadband ac dielectric relaxation spectroscopy in the frequency range of 10^1-10^6 Hz and within a temperature range of 100−370 K.

2. Experimental Section

Dielectric relation measurements were performed with a Hewlett-Packard impedance analyzer (4284A) in the frequency range of 10^1-10^6 Hz. The temperature of the samples, which were in a nitrogen atmosphere, was controlled by a QUATRO temperature controler produced by Novocontrol. Film samples were prepared from PAN fibers which were dissolved in dimethyl formamide (HPLC grade, Aldrich), and then the solution was cast onto a glass plate. The solvent was removed within 4 h at room temperature and for a further 24 h at 50−70 °C in an air stream. To remove traces of solvent, the films were stored for 1 week in a vacuum chamber (10^{-3} mbar) at 100 °C. By using this procedure, films were obtained with thicknesses in the range of 50−100 μm. The films could be removed from the supporting glass sheets easily. For film preparation two types of PAN fibers were used. The first type was a PAN homopolymer (<0.7% methyl acrylate) produced by Hoechst (Dolanit). The homopolymer fibers have initial tensile moduli of about 17 GPa, extensions at a break of about 8%, and diameters of about 16 μm. The second type was a PAN copolymer fiber produced by Sigri, which contains 2−6% methyl acrylate as well as itaconic acid. The copolymer fibers have an initial tensil modulus of about 11 GPa, extensions at a break of 17%, and diameters of about 14 μm. The cyclized PAN films were prepared at 230 °C for 10 h in nitrogen. Aromatized filmes were prepared from cyclized films by heating them in nitrogen to 450 °C, with a heating rate of 5 K/min.

3. Results and Discussion

PAN homo- and copolymer films were investiated by frequency and temperature-dependent dielectric relaxation spectroscopy at different stages of transformation. These stages were the pristine and cyclized. Brief surveys of the dielectric behavior of the materials were given by three-dimensional representations of the imaginary part of the permittivity, which is the loss DK $\epsilon''(\omega,T)$. Films of the pristine homo- and copolymer show one relaxation within the temperature range of 300 and 450 K. In both cases the relaxation strength was high and the contribution of the electric conductivity increases with increasing temperature and decreasing frequency. The strength of this relaxation reduces for partially cyclized PAN and a new relaxation process near 280 K appeared, which was due to cyclized regions. For the fully cyclized homopolymer a broad region of a relaxation was observed in a temperature range of 320−450 K (see Figure 1a). By contrast, two relaxations were found for the copolymer (see Figure 1b). We used the Havriliak−Negami function[7] for a quantitative interpretation of the spectra. In the lower frequency region of 10−1000 Hz, and at higher temperatures, the electric conductivity made a significant contribution to the $\epsilon''(\omega)$ spectra. This was described by an additive conductivity term:[13]

$$\epsilon_1''(\omega) = \frac{\sigma_0}{\epsilon_0\, \omega^{1-s}} \tag{1}$$

The conductivity contribution σ_0 describes the direct current conductivity. The exponent s is related to the charater of the charge transport. A scaling exponent $s > 0$ is typical for nonohmic charge transport and the influence of polarization close to the electrode and on inner surfaces. A question of interest was whether the relaxation processes were cooperative or thermally activated. Usually a cooperative relaxation process of polymers (α-relaxation, glass transition) can be described by the WLF equation[8]

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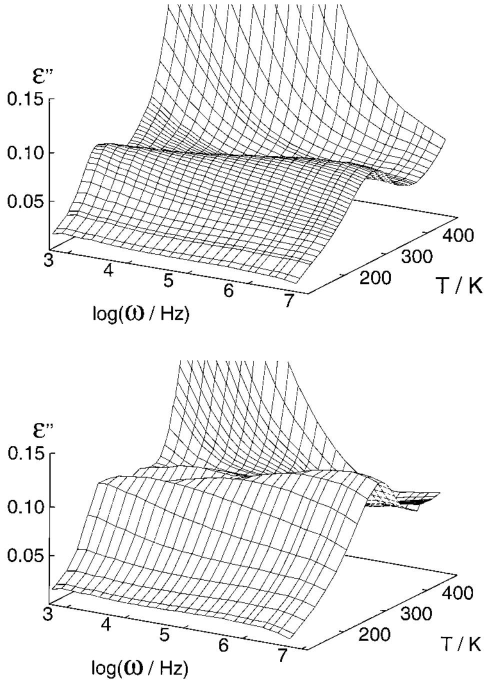

Figure 1. The temperature and frequency dependence of the loss permittivity of cyclized PAN homopolymer films (a) and cyclized copolymer films (b). The homopolymer shows one and the copolymer two relaxation processes.

$$\log a = -\frac{c_1(T - T_g)}{c_2 + (T - T_g)} \tag{2}$$

and thermally activated processes obey Arrhenius's law

$$\tau_{HN} = c \exp(-E_a/RT) \tag{3}$$

The type of relaxation can be determined from the temperature dependency of the HN relaxation times.

3.1. PAN Homopolymer. In the dielectric spectra of the homopolymer a relaxation process was identified with an unusually high relaxation strength. The storage permittivity of this relaxation was evaluated by the real part of the Havriliak–Negami equation:

$$\epsilon'(\omega) = \epsilon_{\infty,1} + \mathrm{Re}\left[\frac{\epsilon_{s,1} - \epsilon_{\infty,1}}{(1 + (i\omega\tau_{HN,1})^{\alpha_1})^{\gamma_1}}\right] \quad \text{for} \quad T \leq 398\ \mathrm{K} \tag{4}$$

Above 398 K a second relaxation process exists at lower frequencies which was taken into consideration additively and is expressed by

$$\epsilon'(\omega) = \epsilon_{\infty,1} + \mathrm{Re}\left[\frac{\epsilon_{s,1} - \epsilon_{\infty,1}}{(1 + (i\omega\tau_{HN,1})^{\alpha_1})^{\gamma_1}}\right] + \mathrm{Re}\left[\frac{\epsilon_{s,2} - \epsilon_{\infty,2}}{(1 + (i\omega\tau_{HN,2})^{\alpha_2})^{\gamma_2}}\right] \quad \text{for} \quad T > 398\ \mathrm{K} \tag{5}$$

The loss permittivity within the range from 298–393 K was described by the imaginary part of the Havriliak–Negami equation which is defined as

$$\epsilon''(\epsilon) = -\mathrm{Im}\left[\frac{\epsilon_{s,1} - \epsilon_{\infty,1}}{(1 + (i\omega\tau_{HN,1})^{\alpha_1})^{\gamma_1}}\right] \quad \text{for} \quad T \leq 393\ \mathrm{K} \tag{6}$$

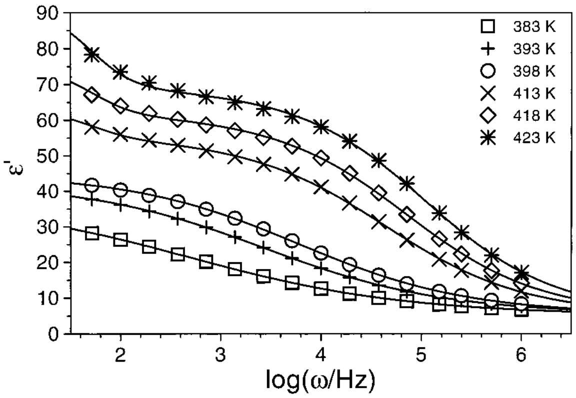

Figure 2. Experimental values of the storage permittivity of the PAN homopolymer at different temperatures (squares, crosses, etc.) and fits of the Havriliak–Negami equation (solid lines).

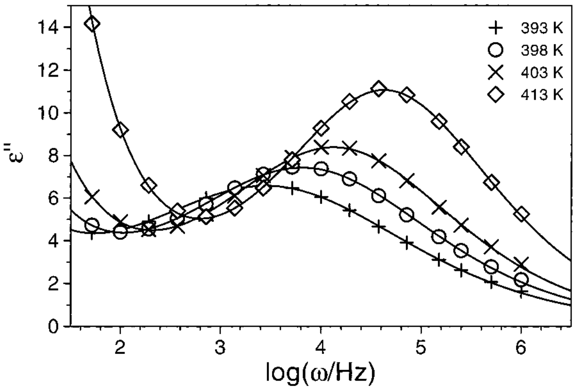

Figure 3. Experimental values of the loss permittivity of the PAN homopolymer at different temperatures (squares, crosses, etc.) and fits of the Havriliak–Negami equation (solid lines). For the higher temperatures (413 and 403 K) the increase of the curves are the result of conductivity (see eq 1).

A conductivity term (1) was used in the temperature range of 393–458 K such that

$$\epsilon''(\omega) = \frac{\sigma_0}{\epsilon_0\, \omega^{1-s}} - \mathrm{Im}\left[\frac{\epsilon_{s,1} - \epsilon_{\infty,1}}{(1 + (i\omega\tau_{HN,1})^{\alpha_1})^{\gamma_1}}\right] \quad \text{for} \quad T > 393\ \mathrm{K} \tag{7}$$

Some typical experimental relaxation curves and corresponding fits of $\epsilon''(\omega)$ and $\epsilon'(\omega)$ at different temperatures are shown in Figures 2 and 3. It can be seen there that only one relaxation process is present at lower temperatures and two relaxations at high temperatures. The logarithm of the reciprocal relaxation times, $\ln(1/\tau_{HN})$, which result from fits of the Havriliak–Negami equation, were plotted against the reciprocal temperature $1/T$ to determine the activation energy of the relaxation at higher frequencies. These Arrhenius plots result in an activation energy of $E_a = 111 \pm 8$ kJ/mol for τ_{HN} from $\epsilon'(\omega)$ and $E_a = 112 \pm 4$ kJ/mol for τ_{HN} from $\epsilon''(\omega)$ (see Figure 4). Both values are in good aggreement. From the absence of a WLF-like behavior according to eq 2, we conclude that this transition is purely thermally activated and is not a glass transition. This conclusion was supported by differential calorimetric measurements, in which no glass transition was detectable. Earlier dielectric investigations of a PAN homopolymer ($M_w = 99800$ g/mol), which were reported by Ishida et al.,[14] confirmed the presence of a thermally activated relaxation. The quality of the fits using γ as

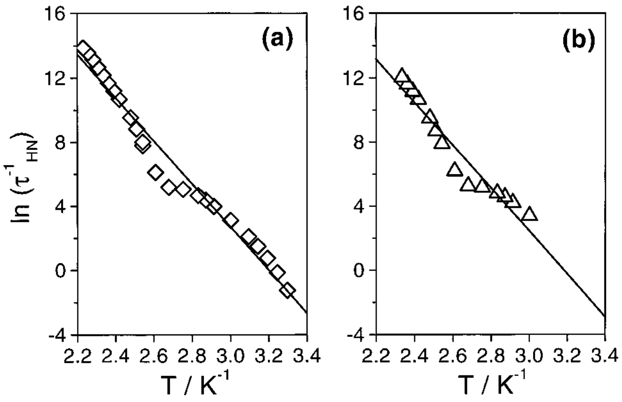

Figure 4. Arrhenius plots for the determination of the activation energy of the dielectric relaxation process. Fits of the Havriliak−Negami relaxation times of the loss modulus gave an activation energy of 112 ± 4 kJ/mol (a), and times of the storage permittivity gave 111 ± 8 kJ/mol (b).

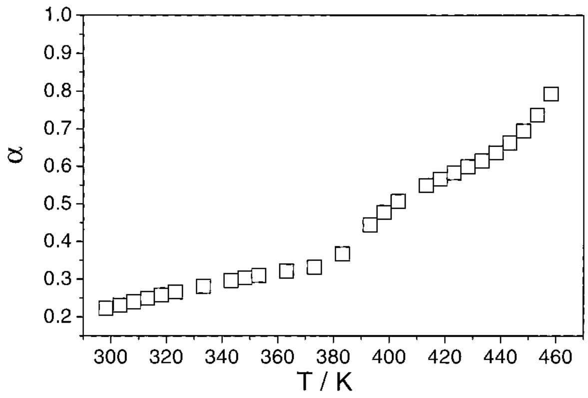

Figure 5. Temperature dependency of the HN parameter α for the PAN homopolymer.

Table 1. Havriliak−Negami Parameters of the PAN Homopolymer Calculated from the Storage Permittivity

T/K	τ_{HN}/s	α	$\epsilon_s - \epsilon_\infty$	ϵ_∞
333.26	$3.417 \cdot 10^{-2}$	0.303	7.15	5.05
343.24	$1.509 \cdot 10^{-2}$	0.303	8.63	5.08
348.18	$1.055 \cdot 10^{-2}$	0.310	9.43	5.10
353.16	$8.227 \cdot 10^{-3}$	0.315	10.63	5.11
363.20	$5.694 \cdot 10^{-3}$	0.325	14.46	5.11
373.21	$5.239 \cdot 10^{-3}$	0.333	22.86	5.06
383.19	$2.065 \cdot 10^{-3}$	0.369	32.55	5.141
393.18	$3.740 \cdot 10^{-4}$	0.431	37.25	5.43
398.16	$1.700 \cdot 10^{-4}$	0.451	39.81	5.31
403.18	$7.522 \cdot 10^{-5}$	0.478	41.95	5.11
413.20	$2.354 \cdot 10^{-5}$	0.522	50.54	5.11
418.17	$1.436 \cdot 10^{-5}$	0.538	56.95	5.11
423.18	$9.159 \cdot 10^{-6}$	0.552	64.20	5.11
428.17	$5.887 \cdot 10^{-6}$	0.559	69.44	5.11

Table 2. Havriliak−Negami Parameters of the PAN Homopolymer Calculated from the Loss Permittivity

T/K	τ_{HN}/s	α	$\epsilon_s - \epsilon_\infty$	σ_0/A(V m)$^{-1}$	s
298.18	$1.140 \cdot 10^{1}$	0.223	7.56		
303.29	3.480	0.231	7.12		
308.19	1.170	0.240	6.83		
313.17	$4.743 \cdot 10^{-1}$	0.249	6.74		
318.18	$2.259 \cdot 10^{-1}$	0.258	6.83		
323.18	$1.232 \cdot 10^{-1}$	0.266	7.08		
333.26	$4.458 \cdot 10^{-2}$	0.281	7.83		
343.24	$1.862 \cdot 10^{-2}$	0.296	8.97		
348.18	$1.263 \cdot 10^{-2}$	0.304	9.76		
353.16	$9.362 \cdot 10^{-3}$	0.310	10.89		
363.16	$6.406 \cdot 10^{-3}$	0.321	14.78		
373.21	$5.643 \cdot 10^{-3}$	0.332	23.10		
383.19	$2.216 \cdot 10^{-3}$	0.367	32.93		
393.18	$3.310 \cdot 10^{-4}$	0.444	35.80	$2.45 \cdot 10^{-10}$	0.24
398.16	$1.460 \cdot 10^{-4}$	0.478	37.36	$4.13 \cdot 10^{-10}$	0.27
403.18	$7.200 \cdot 10^{-5}$	0.507	39.52	$7.31 \cdot 10^{-10}$	0.27
413.20	$2.294 \cdot 10^{-5}$	0.549	47.79	$2.57 \cdot 10^{-9}$	0.22
418.17	$1.359 \cdot 10^{-5}$	0.566	53.95	$4.62 \cdot 10^{-9}$	0.20
423.18	$8.370 \cdot 10^{-6}$	0.583	60.91	$7.87 \cdot 10^{-9}$	0.19
428.17	$5.138 \cdot 10^{-6}$	0.599	65.93	$1.23 \cdot 10^{-8}$	0.19
433.19	$3.138 \cdot 10^{-6}$	0.614	68.31	$1.80 \cdot 10^{-8}$	0.19
438.18	$1.949 \cdot 10^{-6}$	0.636	68.93	$2.44 \cdot 10^{-8}$	0.20
443.17	$1.245 \cdot 10^{-6}$	0.663	68.93	$3.10 \cdot 10^{-8}$	0.22
448.18	$8.164 \cdot 10^{-7}$	0.694	68.93	$3.69 \cdot 10^{-8}$	0.24
453.16	$5.586 \cdot 10^{-7}$	0.737	68.93	$4.15 \cdot 10^{-8}$	0.26
458.14	$4.063 \cdot 10^{-7}$	0.793	68.93	$4.43 \cdot 10^{-8}$	0.28

[a] Below 393 K no significant conductivity contribution was observed.

a fit parameter, or with a fixed $\gamma = 1$, did not differ significantly. Therefore, it was concluded that the relaxation time distribution of the relaxation is symmetric on a logarithmic time scale. The deviation from a Debye type of relaxation is given by the parameter α, which broadens the relaxation time distribution. α was found to change with temperature. Starting with a broad relaxation time distribution (α = 0.223 at 298 K), the distribution becomes smaller with temperature (α = 0.793 at 458 K, see Figure 5). An extrapolation of the curves hypothetically gave a single relaxation time (α = 1) at about 490 K. Such Debye behavior can be observed in only two cases. First, when the inter- and intramolecular interactions for all dipoles are identical. Second, when the movements within the surroundings of the relaxing object are much faster than the relaxation itself. In the second case, which is called motional averaging,[15] every relaxing object experiences the same average interaction during the process of relaxation. Wendorff et al. observed such behavior in NLO polymers.[16] We conclude from the temperature dependence of the α that the reason for the reduction of the width of the relaxation time distributions with increasing temperature is due to the reduction of inter- and intramolecular interaction and not due to motional averaging. A temperature of 490 K is high enough in the PAN homopolymer to induce the cyclization reaction (24 h for a complete cyclization[17]). Therefore, from the dielectric behavior, it may be suggested that an almost uncorrelated movement of the nitrile groups is nescessary to induce the cyclization reaction. The HN parameters are summarized in Tables 1 and 2. It is certain that the orientation of the nitrile groups causes this strong relaxation. Because the nitrile groups are bounded directly to the polymer backbone, the movement of nitrile groups is very likely correlated to the movement of the polymeric backbone. It is known from wide-angle X-ray investigations that kinking is an essential structure element of PAN fibers.[18] Therefore, we assume that the relaxation of kinks is involved in the dielectric relaxation process. The influence of kinks on the mechanical properties of PAN is evident, but the movement of kinks alone cannot explain such a strong dielectric relaxation. Further it was found that the strength of the relaxation, $\epsilon_s - \epsilon_\infty$ depends on the temperature (see Figure 6). It increases from $\epsilon_s - \epsilon_\infty = 7$ at 298 K to $\epsilon_s - \epsilon_\infty = 69$ at 458 K. Such behavior was reported earlier by Ishida.[14] This is unusual because, due to thermal motion, the relaxation strength typically decreases with temperature. An increase of the relaxation strength results from an increase in the average square value of the dipole moment per monomer unit. The high value of the dipole moment of the nitrile group in aliphatic compounds[20] of $13.4 \cdot 10^{-30}$ Cm explains the high maxi-

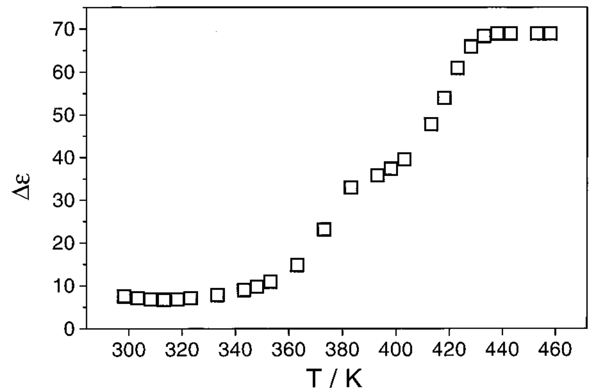

Figure 6. Temperature dependency ot the relaxation strength of the PAN homopolymer.

mum value of their relaxation strength (69). The temperature dependence of the relaxation strength seems to be a measure of how the local surroundings of the nitrile groups, and the conformation of the polymeric chains, change. At the relatively low relaxation strength of 7, only a limited relaxation is possible and only a few nitrile groups participate in the relaxation. Since the dipole moment of the nitrile group is so large, dipole–dipole cancellations may be very important at low temperatures. Many of the chain segments are frozen and chain conformations dominate that minimize the dipole moment. It is also possible that chain segments move from one situation where dipoles cancel with dipoles to another situtation where again dipole cancels with dipole, only the partners have changed. At low temperatures the nitrile groups near to and in the kinks are the main contributing factor to the relaxation. By contrast, at high temperatures the limit value of the relaxation strength of 69 results from the high moblity of all nitrile groups which orient to the external electric field. The static conductivity increases with temperatures more than 2 decades from $\sigma_0 = 2.45 \cdot 10^{-10}$ A/(V m) at 393 K to $\sigma_0 = 4.43 \cdot 10^{-8}$ A/(V m) at 458 K. Whereas, the parameter s has a constant value of about 0.22. Therefore, the conductivity behaves according to a constant power law, which is indicative of a constant mechanism of conductivity within the temperature range investigated. This will be discussed in the next section. For the relaxation process, which was observed at lower frequencies and temperatures higher than 403 K, it was possible to estimate the τ_{HN}. For fixed $\alpha = \gamma = 1$ the relaxation time was determined to be about $2 \cdot 10^{-2}$ s. This process is very slow and can be observed within the experimental window only at high temperatures. It is probable that the lower frequency relaxation found at high temperatures is the glass transition of PAN.

Table 3. Havriliak–Negami Parameters Calculated for the PAN Copolymer Calculated from the Storage Permittivity

T/K	τ_{HN}/s	α	$\epsilon_s - \epsilon_\infty$	ϵ_∞
388.14	$5.610 \cdot 10^{-4}$	0.359	55.69	5.11
398.15	$1.140 \cdot 10^{-4}$	0.390	55.35	5.11
403.14	$5.547 \cdot 10^{-5}$	0.405	55.08	5.11
408.17	$2.815 \cdot 10^{-5}$	0.422	54.71	5.11
413.14	$1.589 \cdot 10^{-5}$	0.434	55.04	5.11
418.18	$9.657 \cdot 10^{-6}$	0.443	55.76	5.11
423.19	$6.326 \cdot 10^{-6}$	0.444	57.05	5.11
428.16	$4.261 \cdot 10^{-6}$	0.441	58.35	5.11
433.19	$2.946 \cdot 10^{-6}$	0.432	59.85	5.11
438.21	$2.049 \cdot 10^{-6}$	0.415	61.38	5.11
443.14	$1.408 \cdot 10^{-6}$	0.392	62.81	5.11
448.19	$9.366 \cdot 10^{-7}$	0.360	63.88	5.11
453.17	$6.252 \cdot 10^{-7}$	0.314	65.22	5.11
458.14	$4.744 \cdot 10^{-7}$	0.251	68.05	5.11

Table 4. Havriliak–Negami Parameters of the PAN Copolymer Calculated from the Loss Permittivity

T/K	τ_{HN}/s	α	$\epsilon_s - \epsilon_\infty$	σ_0/A(V m)$^{-1}$	s
383.18	$2.140 \cdot 10^{-4}$	0.363	31.50	$1.02 \cdot 10^{-8}$	0.35
388.14	$1.130 \cdot 10^{-4}$	0.383	33.78	$1.66 \cdot 10^{-8}$	0.33
393.19	$6.419 \cdot 10^{-5}$	0.401	36.17	$2.70 \cdot 10^{-8}$	0.30
398.15	$3.416 \cdot 10^{-5}$	0.425	37.30	$4.21 \cdot 10^{-8}$	0.28
403.14	$1.950 \cdot 10^{-5}$	0.447	38.69	$6.28 \cdot 10^{-8}$	0.27
408.17	$1.179 \cdot 10^{-5}$	0.467	40.34	$9.26 \cdot 10^{-8}$	0.25
413.14	$7.493 \cdot 10^{-6}$	0.477	42.68	$1.33 \cdot 10^{-7}$	0.23
418.18	$4.937 \cdot 10^{-6}$	0.472	46.48	$1.88 \cdot 10^{-7}$	0.21
423.19	$2.718 \cdot 10^{-6}$	0.546	41.06	$1.54 \cdot 10^{-7}$	0.26
428.16	$1.851 \cdot 10^{-6}$	0.552	43.44	$1.89 \cdot 10^{-7}$	0.25
433.19	$1.218 \cdot 10^{-6}$	0.546	47.20	$2.33 \cdot 10^{-7}$	0.24
438.21	$8.220 \cdot 10^{-7}$	0.570	47.84	$2.17 \cdot 10^{-7}$	0.25
443.14	$5.479 \cdot 10^{-7}$	0.587	49.37	$1.85 \cdot 10^{-7}$	0.27
448.19	$3.535 \cdot 10^{-7}$	0.593	52.85	$1.96 \cdot 10^{-7}$	0.27
453.17	$2.240 \cdot 10^{-7}$	0.598	57.18	$2.62 \cdot 10^{-7}$	0.25
458.14	$1.470 \cdot 10^{-7}$	0.613	60.69	$3.34 \cdot 10^{-7}$	0.23

3.2. PAN Copolymer. A strong relaxation process was found in the spectra of the copolymer that is similar to that of the homopolymer. The storage permittivity was fitted into the temperature range of 388–458 K by the real part of the HN function (4) with ϵ_∞ fixed at 5.11 and γ fixed at 1. These are the same values as found for the homopolymer. The loss permittivity was fitted in the temerature range of 383–458 K by eq 7. The conductivity of the copolymer was found to be significantly higher than that of the homopolymer. For comparison, the fitting parameters are listed in Tables 3 and 4. In the case of the homopolymer, the activation energy of the relaxation was determined by using Arrhenius plots (not shown). By calculation we determined that $E_a = 134 \pm 3$ kJ/mol from the ϵ' fit values and that $E_a = 139 \pm 1$ kJ/mol from the ϵ'' fit values. Both values agree well and are about 25 kJ/mol higher than those calculated for the homopolymer. Probably the molecular process of the relaxation is a movement of kinks along the polymer chains. Assuming this, the movement may be hindered by monomers of itaconic acid. This is a possible reason for the higher activation energy of the relaxation of the copolymer. As found for the homopolymer, the relaxation strength of the copolymer increases with increasing temperature. The explanation for this atypical behavior is probably the same as that for the homopolymer. As found for the homopolymer, the deviation of the relaxation from a Debye process is given by α alone. The temperature dependency of the α of both polymers is nearly identical. A single relaxation time ($\alpha = 1$) should be present at about 522 K, a temperature at which the time of the cyclization of the copolymer is about 45 min. As stated for the homopolymer, we assume a correlation between the relaxation and the start of the cyclization. We assume further that the cyclization begins when the movement of the nitrile groups is not hindered, which means that the dipole–dipole interaction energy is much smaller than the thermal energy. It is of interest to compare the temperature dependence of σ_0 of homo- and copolymers. This is shown in Figure 7. It can be seen that σ_0 for the copolymer is much higher than it is for the homopolymer. When interpreting this, it has to be taken into account that a conductivity of about 10^{-9} A/V m can be caused by even a small amount of impurities.[20] The observed conductivity of $2.45 \cdot 10^{-10}$ A/V m at 393 K for the homopolymer may be caused by impurites

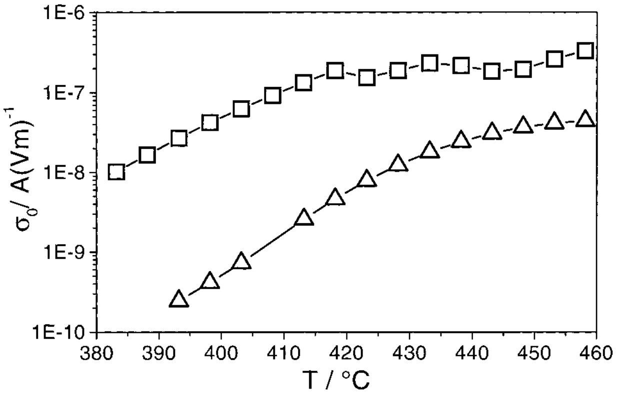

Figure 7. Temperature dependency of the conductivity parameter σ_0 for the homopolymer (triangles) and the copolymer (squares).

introduced during the production process. However, if we asume that the amount of impurities within the homo- and copolymer are roughly similar, then the difference in conductivity of both polymers must be explained by the contribution of itaconic acid. Even a small degree of dissociation of the acid causes a considerable increase in conductivity. For both polymers it was found that the conductivity increases with increasing temperature. This behavior is similar to that of many polymers, such as nylon-6,6.[20] The difference in conductivity between homo- and copolymers becomes smaller with increasing temperature. At 398 K, the difference is about 2 decades and at 458 K the difference is about 1 decade. For the evaluation of the temperature dependency of the conductivity caused by ionic impurities simple formulas exist,[20] such as $\sigma_0 = (K_0 n_0)^{1/2}(\mu_+ + \mu_-) \exp(-\Delta W/2\epsilon_s kT))$. K_0 is a constant, n_0 is the concentration of the ionic pairs, μ_+ and μ_- are the movabilities of the ions, ϵ_s is the dielectric consant and ΔW is the energy which is nescesarry to separate the ion pairs in a medium with $\epsilon_s = 1$. In this case the conductivity should be proportional to the square root of the concentration of the ion pairs. Given the supposition that the homo- and copolymer contain approximately the same ionic impurities, then it must be possilbe to shift the conductivity of the homopolymer to that of the copolymer by using a factor of $\sigma^2(T)$. But this is not the case. It seems to be realistic to assume that the difference in the conductivity of the polymers is caused by the difference in the content of itaconic acid. The exponent of the conductiviy term for both polymers is temperature independent and s is about 0.22, a value which is typical for hopping conduction. Because this value is constant, it is probable that the mechanism of conductivity is the same within the investigated temperature range.

Table 5. Havriliak−Negami Parameters of the Cyclized PAN Homopolymer Calculated from the Storage Permittivity

T/K	τ_{HN}/s	α	γ	$\epsilon_s - \epsilon_\infty$	ϵ_∞
248.17	$1.932\cdot10^{-5}$	0.187	1.000	1.17	4.08
253.15	$1.338\cdot10^{-5}$	0.202	1.000	1.11	4.12
258.16	$9.558\cdot10^{-6}$	0.216	1.000	1.06	4.14
263.15	$5.665\cdot10^{-6}$	0.216	1.000	1.09	4.12
268.15	$3.387\cdot10^{-6}$	0.215	1.000	1.12	4.09

Table 6. Havriliak−Negami Parameters of Cyclized PAN Homopolymer Calculated from the Loss Permittivity

T/K	τ_{HN}/s	α	γ	$\epsilon_s - \epsilon_\infty$	σ_0/A(V m)$^{-1}$	s
248.17	$1.440\cdot10^{-4}$	0.190	1.000	1.13	$5.74\cdot10^{-11}$	0.24
253.15	$4.879\cdot10^{-5}$	0.240	1.000	0.91	$2.38\cdot10^{-11}$	0.07
258.16	$4.810\cdot10^{-5}$	0.207	1.000	1.06	$7.82\cdot10^{-11}$	0.29
263.15	$2.876\cdot10^{-5}$	0.227	1.000	0.98	$5.70\cdot10^{-11}$	0.17
268.15	$1.642\cdot10^{-5}$	0.263	1.000	0.85	$1.77\cdot10^{-11}$	0.19
278.16	$9.416\cdot10^{-6}$	0.255	1.000	0.88	$2.02\cdot10^{-11}$	0.17
283.16	$6.900\cdot10^{-6}$	0.276	1.000	0.81	$1.39\cdot10^{-11}$	0.30
288.16	$5.298\cdot10^{-6}$	0.264	1.000	0.85	$1.51\cdot10^{-11}$	0.28
293.20	$4.326\cdot10^{-6}$	0.298	1.000	0.74	$1.13\cdot10^{-11}$	0.40
298.16	$3.422\cdot10^{-6}$	0.290	1.000	0.76	$1.14\cdot10^{-11}$	0.40
303.16	$2.918\cdot10^{-6}$	0.292	1.000	0.74	$1.23\cdot10^{-11}$	0.41
308.17	$1.417\cdot10^{-6}$	0.223	1.000	0.97	$1.68\cdot10^{-11}$	0.30
313.24	$6.173\cdot10^{-7}$	0.193	1.000	1.12	$1.90\cdot10^{-11}$	0.28

Table 7. Havriliak−Negami Parameters of the Lower Frequency Relaxation of the Cyclized PAN Copolymer Calculated from the Loss Permittivity

T/K	$\tau_{HN,1}$/s	α_1	γ_1	$\epsilon_{s,1} - \epsilon_{\infty,1}$	σ_0/A(V m)$^{-1}$	s
323.22	$8.140\cdot10^{-4}$	0.746	1.000	0.143	$1.96\cdot10^{-11}$	0.27
333.26	$6.220\cdot10^{-4}$	0.663	1.000	0.194	$2.12\cdot10^{-11}$	0.27
343.24	$5.070\cdot10^{-4}$	0.611	1.000	0.237	$2.37\cdot10^{-11}$	0.26
353.27	$3.870\cdot10^{-4}$	0.600	1.000	0.236	$1.79\cdot10^{-11}$	0.33
363.24	$2.930\cdot10^{-4}$	0.612	1.000	0.211	$1.33\cdot10^{-11}$	0.42
373.27	$2.490\cdot10^{-4}$	0.576	1.000	0.244	$1.77\cdot10^{-11}$	0.38
383.21	$1.980\cdot10^{-4}$	0.619	1.000	0.201	$1.46\cdot10^{-11}$	0.46
393.18	$1.760\cdot10^{-4}$	0.616	1.000	0.195	$1.52\cdot10^{-11}$	0.49
403.21	$1.480\cdot10^{-4}$	0.748	1.000	0.101	$1.31\cdot10^{-11}$	0.56
408.16	$1.330\cdot10^{-4}$	0.794	1.000	0.080	$1.30\cdot10^{-11}$	0.58
413.15	$1.230\cdot10^{-4}$	0.897	1.000	0.053	$1.24\cdot10^{-11}$	0.60
418.17	$1.120\cdot10^{-4}$	0.967	1.000	0.039	$1.21\cdot10^{-11}$	0.62
423.14	$9.423\cdot10^{-5}$	1.000	1.000	0.032	$1.19\cdot10^{-11}$	0.64
428.16	$7.855\cdot10^{-5}$	1.000	1.000	0.029	$1.16\cdot10^{-11}$	0.66
433.17	$6.125\cdot10^{-5}$	1.000	1.000	0.025	$1.16\cdot10^{-11}$	0.68

3.3. Cyclized PAN Homopolymer. In the dielectric spectra of a cyclized PAN homopolmyer a relaxation process was found within the temperature range of 248−313 K (see Figure 1a). Equation 4 was used for a fit of its storage permittivity and eq 7 for its loss permittivity. The resultant parameters are summarized in Tables 5 and 6. Arrhenius plots of τ_{HN} resulted in activation energy values for the relaxation of 48 ± 3 kJ/mol from ϵ' fits and 45 ± 2 kJ/mol from ϵ'' fits (not shown). Again, the HN parameter γ was 1, which indicates a symmetric relaxation time distribution. The strength of the relaxation is essentially constant with an average of $\epsilon_s - \epsilon_\infty = 1$ and ϵ_∞ is 4.1. The molecular process behind this relaxation is probably the movement of nitrile groups, which do not react during cyclization. They include about 20% of all nitrile groups.[17] The local movement of these nonreacted groups within a stiff matrix of cyclized material may be responsible for the observed relaxation. The conductivity parameters are also independent of the temperature. σ_0 is about $1.47\cdot10^{-11}$ A/V m and s is about 0.28. The latter is indicative of a hopping conduction.

3.4. Cyclized PAN Copolymer. Two relaxations were found in the dielectric spectrum of the cyclized PAN copolymer (see Figure 1b). Both processes have a relatively small relaxation strength and overlap. The contribution of conductivity is significant. For a quantitative description of the spectra we used the equation

$$\epsilon''(\omega) = \frac{\sigma_0}{\epsilon_0 \omega^{1-s}} - \mathrm{Im}\left[\frac{\epsilon_{s,1} - \epsilon_{\infty,1}}{(1 + (i\omega\tau_{HN,1})^{\alpha_1})^{\gamma_1}}\right] - \mathrm{Im}\left[\frac{\epsilon_{s,2} - \epsilon_{\infty,2}}{(1 + (i\omega\tau_{HN,2})^{\alpha_2})^{\gamma_2}}\right] \quad (8)$$

The parameter γ_1 and γ_2 were fixed at 1 and the resulting fit parameters are listed in Tables 7 and 8. From Arrhenius plots of the relaxation times the activation energies were calculated to be 24 ± 1 kJ/mol for

Table 8. Havriliak−Negami Parameters of the Higher Frequency Relaxation of the Cyclized PAN Copolymer Calculated from the Loss Permittivity

T/K	$\tau_{HN,2}$/s	α_2	γ_2	$\epsilon_{s,2} - \epsilon_{\infty,2}$
323.22	$2.562 \cdot 10^{-6}$	0.366	1.000	0.845
333.26	$1.911 \cdot 10^{-6}$	0.400	1.000	0.740
343.24	$1.555 \cdot 10^{-6}$	0.433	1.000	0.641
353.27	$1.405 \cdot 10^{-6}$	0.452	1.000	0.566
363.24	$1.340 \cdot 10^{-6}$	0.460	1.000	0.510
373.27	$1.194 \cdot 10^{-6}$	0.486	1.000	0.427
383.21	$1.132 \cdot 10^{-6}$	0.487	1.000	0.401
393.18	$1.031 \cdot 10^{-6}$	0.513	1.000	0.356
403.21	$9.948 \cdot 10^{-7}$	0.460	1.000	0.401
408.16	$9.442 \cdot 10^{-7}$	0.454	1.000	0.397
413.15	$8.531 \cdot 10^{-7}$	0.430	1.000	0.412
418.17	$7.840 \cdot 10^{-7}$	0.430	1.000	0.399
423.14	$4.965 \cdot 10^{-7}$	0.447	1.000	0.404
428.16	$5.560 \cdot 10^{-7}$	0.509	1.000	0.335
433.17	$6.442 \cdot 10^{-7}$	0.588	1.000	0.268

relaxation 1, present at lower frequencies, and 9 ± 1 kJ/mol for relaxation 2, present at higher frequencies. The α increases greatly with increasing temperature and is nearly 1 at temperatures higher than 423 K, which means that the relaxation has a single relaxation time. By contrast, relaxation 2 showed only a small dependence on the temperature. The strength of both relaxations is different. $\epsilon_{s,1} - \epsilon_{\infty,1}$ decreases from 0.20 at 333 K to about 0.03 at 433 K and relaxation 2, $\epsilon_{s,2} - \epsilon_{\infty,2}$, has a constant value of about 0.50. The conductivity is very similar to that of the cyclized homopolymer ($\sigma_0 = 1.65 \cdot 10^{-11}$ A/(V m)).

4. Summary

The results given above show that the dielectric behavior of polyacrylonitrile in the pristine and in the cyclized state is very sensitive to the presence of comonomers within the polymer. It was shown that the strong relaxation, which is present in pristine PAN homo- and copolymer, is a thermally activated process. A weak relaxation is present in the cyclized homopolymer and two weak relaxations are present in the cyclized copolymer. By contrast, no relaxation phenomena were found for aromatized PAN.

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References and Notes

(1) Wöhrle, D. *Advances in Polymer Science*; Springer: New York, 1977; Vol. 10.
(2) Olive, G. H.; Olive, S. *Advances in Polymer Science*; Springer: New York, 1983; Vol. 51.
(3) Jain, M. K.; Abhiraman, A. S. *J. Mater. Sci.* **1987**, *22*, 278.
(4) Jain, M. K.; Abhiraman, A. S. *J. Mater. Sci.* **1987**, *22*, 278.
(5) Jain, M. K.; Abhiraman, A. S. *J. Mater. Sci.* **1987**, *22*, 278.
(6) Burger, C. Dissertation thesis, Philipps-University Marburg, 1994.
(7) Havriliak, S.; Negami, S. *Polymer* **1967**, *8*, 161.
(8) Williams, M. L.; Landel, R. F.; Ferry, J. D. *J. Am. Chem. Soc.* **1955**, *77*, 3701.
(9) Kohlrausch, F. *Pogg. Ann. Phys.* **1847**, *12*, 393.
(10) Kohlrausch, F. *Pogg. Ann. Phys.* **1863**, *29*, 337.
(11) Williams, G.; Watts, D. C. *Pogg. Ann. Phys.* **1970**, *73*, 3348.
(12) Alvarez, F.; Alegria, A.; Colmenero, *J. Phys. Rev. B* **1993**, *47*, 125.
(13) Kremer, F.; Vallerien, S. U.; Zentel, R.; Kapitza, H. *Macromolecules* **1989**, *22*, 4040.
(14) Ishida, Y.; Amano, O.; Takayanagi, M. *Kolloid Z.* **1960**, *172*, 129.
(15) Spiess, H. W. *Adv. Polym. Sci.* **1985**, *66*, 23.
(16) Baehr, C.; Glüsen, B.; Wendorff, J. H. *Colloid Polym. Sci.* **1997**, *275*, 234.
(17) Thünemann A. F. *Thesis*, 1991.
(18) Liu, X. D.; Ruland, W. *Macromolecules* **1993**, *26*, 3030.
(19) Read, B. E. *Trans. Faraday Soc.* **1965**, *61*, 2140.
(20) Blythe, A. R. In *Electrical Properties of Polymers*; Cambridge University Press: Cambridge, 1980.
(21) Ferry, J. D.; Williams, M. L.; Fitzgerald, E. R. *J. Phys. Chem.* **1955**, *59*, 403.

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