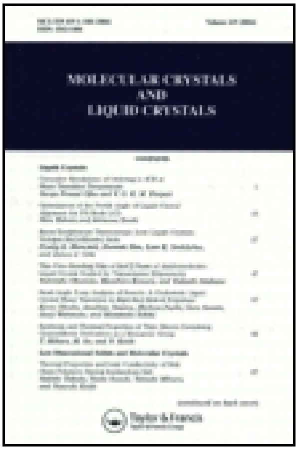


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Study of Molecular Dynamics of a Nematic Main Chain Liquid Crystalline Polyester by Dielectric Spectroscopy

Maria Mucha [a] & Alexandre Blumstein [b]

[a] Faculty of Process and Environmental Engineering Technical, University of Lodz, Wólczańska 175, 90-924, łódź, Poland

[b] University of Massachusetts Lowell, Chemistry Department, One University Avenue, Lowell, MA, 01854, USA

Version of record first published: 24 Sep 2006.

Mol. Cryst. Liq. Cryst. 1994, Vol. 249, pp. 61–74
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

STUDY OF MOLECULAR DYNAMICS OF A NEMATIC MAIN CHAIN LIQUID CRYSTALLINE POLYESTER BY DIELECTRIC SPECTROSCOPY

MARIA MUCHA
Faculty of Process and Environmental Engineering Technical University of Łódź, Wólczańska 175 ,90-924 Łódź, Poland

ALEXANDRE BLUMSTEIN
University of Massachusetts Lowell, Chemistry Department, One University Avenue, Lowell, MA 01854, USA

Abstract Dielectric spectroscopy was applied to study the molecular dynamics of a nematic main-chain liquid crystalline polyester using a Du Pont Dielectric Analyser. The dielectric measurements covered a frequency range from 0.03 to 100000Hz and a temperature range from -100 to 160°C leading from the transition region up to the isotropic fluid region. Dielectricrelaxation processes α,β,γ and δ were observed and analysed. Apparent activation energies of the processes were calculated.

INTRODUCTION

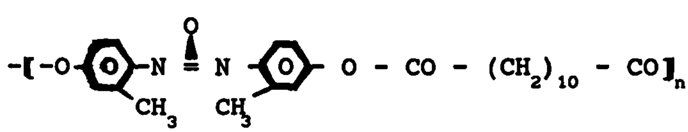
Dielectric relaxation spectroscopy is a useful and widely applied method for estimating the nature and extend of cooperative motion of dipoles, their relaxation frequencies at different temperatures[1-8]. The dipoles associated with sites on the polymer chain are of three kinds: dipoles parallel, perpendicular to the main chain and side chain (if they are) dipoles. Major location for permanent electric dipoles in LCP's are mesogenic groups having effective dipole moment. The length of spacer is influential in determining the mesophase behaviour. The dielectric activity of the spacer arises from its flexibility allowing reorientations of mesogenes.

The polymer backbone frequently carries polar groups and may be dielectrically active. Liquid crystalline polymers show dielectric phenomena familiar from low molecular liquid crystals but the polymer chains present a considerable impediment to molecular motions with radically changed dynamics. The molecular dynamics are determined by transition between different conformations of the polymer backbone. In case of LCP's α,β,γ and δ relaxations are recognized. The α and β processes are assumed to be associated with the motion of the transverse component of the dipole moment (β-oscillating local motions, α-segment rotation around backbone), δ process is affected by the nematic longitudinal component of dipole moment, the γ process is connected with motion within the spacer.

EXPERIMENTAL

In order to carry out a detailed analysis of the molecular dynamics response in the main chain liquid crystalline polyester, the dielectric measurements were made and analyzed over a frequency from 0.03 to 100000Hz and from -100 to 160°C, temperature interval ranging from γ relaxation region to the isotropisation. Dielectric measurements were performed with a Du Pont 2970 Dielectric Analyser. The circular samples of the polymer film of diameter 0.025m and thickness 60μm ware prepared from solution in chloroform and vacum dried. They were kept between two parallel gold plate sensors. The measurements were fully computer controlled.

The nematic liquid crystalline polyester (called DDA-9) poly(2,2'dimethyloazoxy benzene dodecane dioyl):



was prepared and characterized as previously described[9-10]. A systematic investigation of the influence of chain length on the level of order for DDA-9 was investigated in the previous work. In the oligomeric range aliphatic chain ends destabilize the liquid crystalline (LC) order.

The order parameter of the mesogen increases strongly with increasing chain length and levels off at DP 10 displaying values larger then low molecular liquid crystal (LMLC). Molecular mass dependence of the isotropization temperature has been established for the unfractionated polymer samples and for fractions[10]. The polymer DDA-9 (M_n=18000) is characterized by a crystalline-nematic transition at 118°C and a nematic-isotropic transition at 163°C (as measured by DSC[11]).

RESULTS AND DISCUSSION

The interaction between the applied electric field and the dipole moment of molecules changes the distribution of their reorientation. Dielectric properties of material depend on both frequency ω and temperature T. Four major properties are reported in dielectric analysis: permittivity ε' and loss factor ε'' both provide valuable information about the molecular motion (ε' measures the alignment of dipoles, ε'' represents the energy required to align dipoles and move ions), dissipation factor $tg\delta = \varepsilon''/\varepsilon'$ and ionic conductivity, which becomes significant in the liquid state $\sigma=\varepsilon''\omega\varepsilon_o$. A survey of the dielectric absorption ε', ε'' and $tg\delta$ as a function of frequency and temperature was made.

The temperature dependence of lg(tgδ) obtained for different frequencies is given in Fig.1.

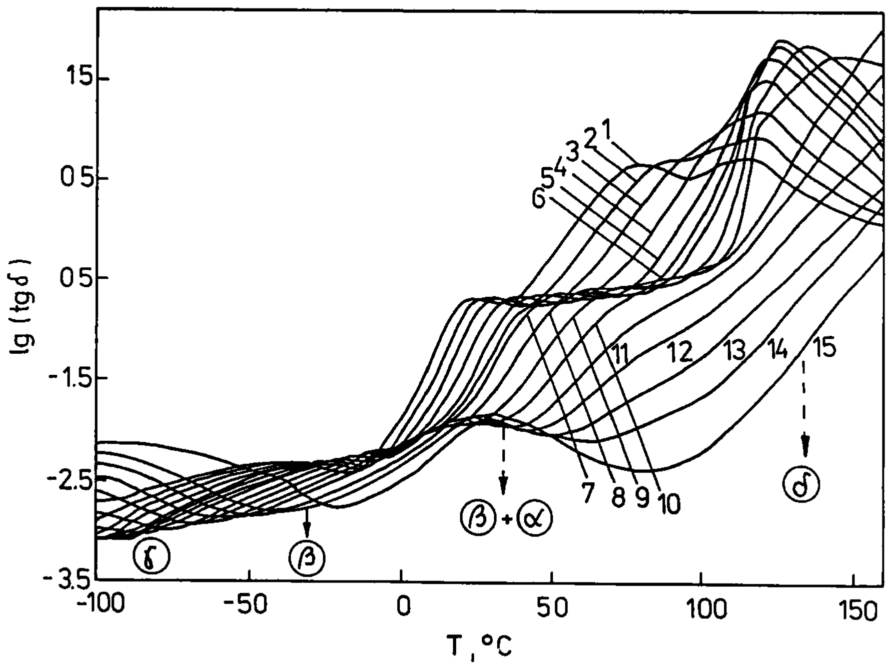


FIGURE 1 Lg(tgδ) versus temperature T measured for 15 frequencies(0.03 - 100000Hz, curves 1-15) γ,β,α and δ relaxation processes are visible.

The following four dielectric dispersions (dominated by motions involving the ester-group of the polymer) are observed in the temperature range -100 to 160^{o}C : the γ relaxation process occurs at high frequency and at temperatures close to -90°C, the β relaxation process in at low frequency and at temperature of -40°C and the secondary β relaxation at higher frequency and the temperature in the vicinity of the polymer glass transition temperature Tg=10^{1}C, finally α relaxation process at Tg associated with reorientation of the mesogenic groups and involving polar ester groups linked to the alkyl spacer in a rotational motion of segments around the polymer backbone. The α process is hundreds times slower (low frequency) than the β secondary process of the oscillating motion of the same dipoles.

Figure 2 shows the curves of ε'' and ε' plotted adjust temperature for the lowest and the highest applied frequencies (0.03 and 30000 Hz.) in order to illustrate the presence of primary β' and secondary β'' relaxation peaks at regions of low (-40°C) and high (20°C) temperatures respectively (curves 2 and 3 on figure 3).

Figure 3 gives the relaxation temperature T at the maximum (taken from ε'' and tgδ spectra) of γ,β,α and δ processes respectively versus lg ω. The relaxation temperatures of all processes increase with rising frequency. Two peaks observed for the δ transition are associated with the dipole motion in the crystalline and nematic states. These peaks merge into one peak at the temperature of isotropization. The γ relaxation process is better visible at frequencies higher then 10^4 Hz.

The dielectric loss factor ε'' for β and part of α absorption process versus lg frequency is presented in Figure 4. The curves at low temperatures are broad, this suggests a wide variety of constrains on the dipole motion. As the temperature increases the whole system moves faster narrowing the loss peak of the β process. Simultaneously an α process starts to appear at low frequency. The observed increase of ε'' at low frequencies starts at a temperature near 0°C. In this region in the vicinity of T_g the ionic conductivity σ is very low (see figure 5). A fast increase of ionic conductivity in the vicinity of the δ relaxation process in the low frequences range is visible (as illustrated by a lack of σ dependence on frequency),but does not affect yet the behaviour of the β and α relaxation processes.

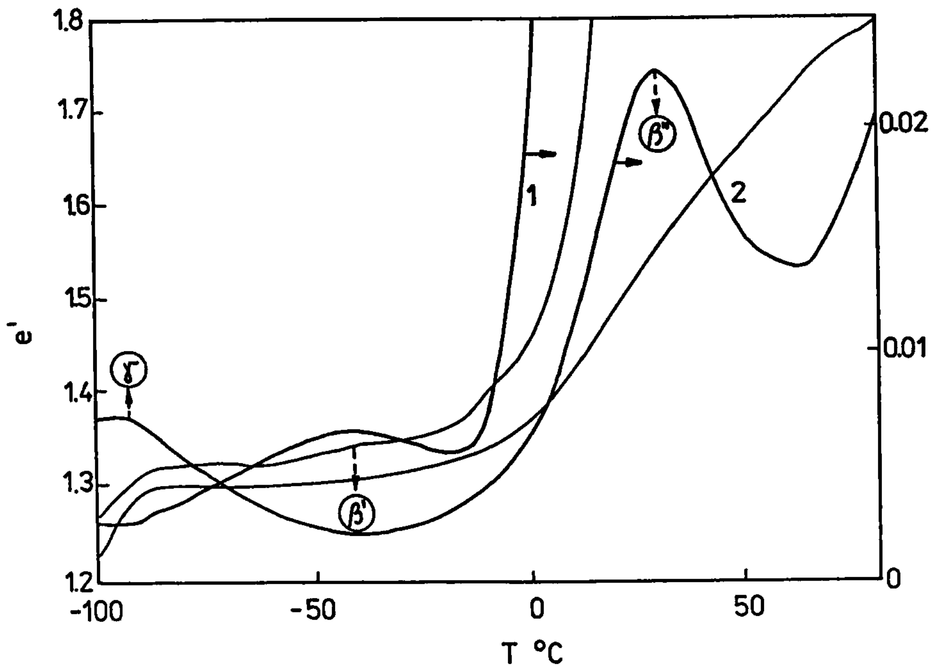


FIGURE 2 ε'' and ε' spectra for two different frequencies: curve 1-0.03 Hz and curve 2-30000 Hz. Primary β' and secondary β'' relaxations are shown.

Cole-Cole semi-circle curves representing the loss factor ε'' versus ε' are drawn in Figure 6 for the β process. In lower frequency range and at higher temperature the α relaxation begins to merge with the β relaxation process and the Cole-Cole equation does not fit well the experimental data. The relaxation strength $\Delta\varepsilon' = \varepsilon'_0 - \varepsilon'$ associated with reorientation of the dipole moment in the β process is relatively small and its increase in the vicinity of Tg is clearly visible. The relaxation amplitude ε''_{max} rises with increasing temperature. In the vicinity of Tg it's jump is observed (see insert Figure 6).

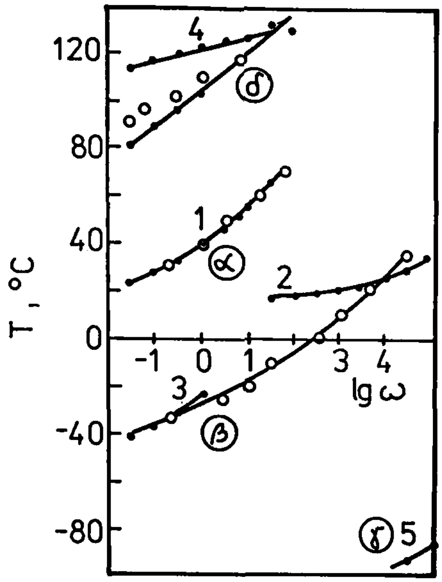


FIGURE 3 The relaxation temperature T versus lgω for γ,β,α and δ processes (open points are taken from tgδ versus temperature).

In Fig 7 two examples of fitting of the experimental data obtained at -10°C (curve 1)and 0°C (curve 2) with the common distribution functions of Fuoss-Kirkwood (equation (1)) and of Cole-Cole (equation (2)) are given

$$\cosh^{-1}(\varepsilon''_{max}/\varepsilon'')=\beta\ln\omega\tau \qquad (1)$$

$$\varepsilon'_{o}-\varepsilon'_{\infty} = 2\varepsilon''_{max}\ /\beta$$

$$\varepsilon'' =\frac{\frac{1}{2}(\varepsilon'_{o}-\varepsilon'\ )\cos\alpha\pi/2}{\cosh(1-\alpha)S+\sin\alpha\pi/2}\gamma \qquad (2)$$

$$\varepsilon'' = (\varepsilon'_{o}-\varepsilon_{\infty})\quad 1-\alpha$$

where: β - Fuoss-Kirkwood width parameter

α - Cole-Cole width parameter

γ - additional skewing parameter

S - $\lg(\omega/\omega_{max})$

Curve 5 fits well the experimental results with one fitting parameter β=0.47 or two fitting parameters α=0.4 and γ=0.415 Curves 3 and 4 are fitted with parameters β=0.52 and β=1 (description of the experimental results obtained in low frequency measurements).

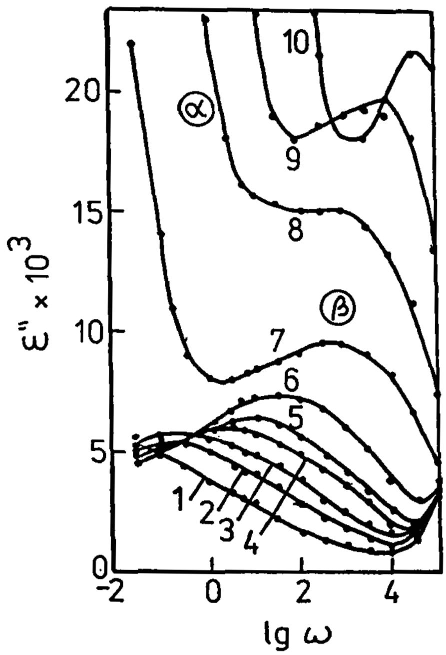


FIGURE 4 The dielectric loss ε'' as a function of lgω drawn for different temperature from-50 to 35°C in the region of β and α relaxation processes. Cu r ves 1-10 represents temperatures -50°, -40°, -33°,-25°,-20°,-10°,0°,10°,20° and 35°C.

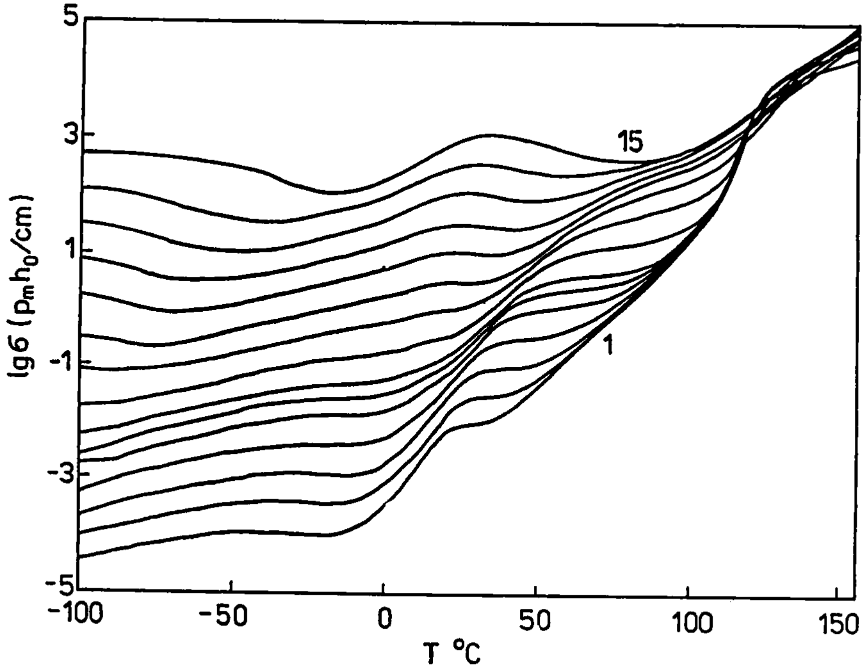


FIGURE 5 lg ionic conductivity σ versus temperature. Curves 1-15 are taken for different frequencies and cover the range from 0.03 Hz (curve 1) to 100000 Hz (curve 15).

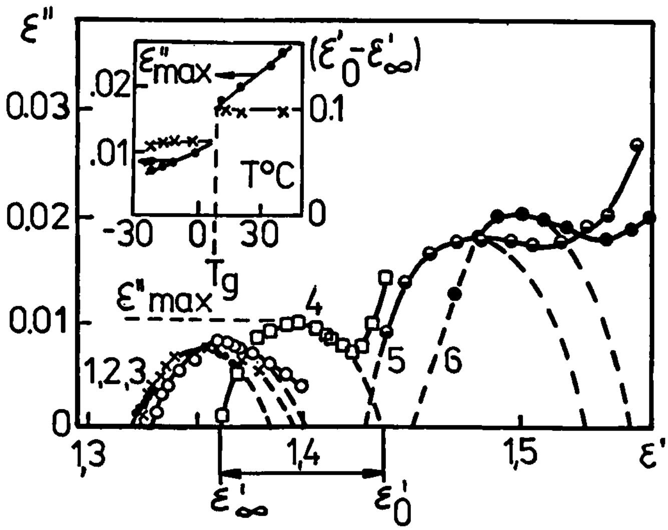


FIGURE 6 Cole-Cole plots for temperature range from -21 to 20°C. Inside: ε''_{max} and $\varepsilon'_o-\varepsilon'_\infty$ versus T.

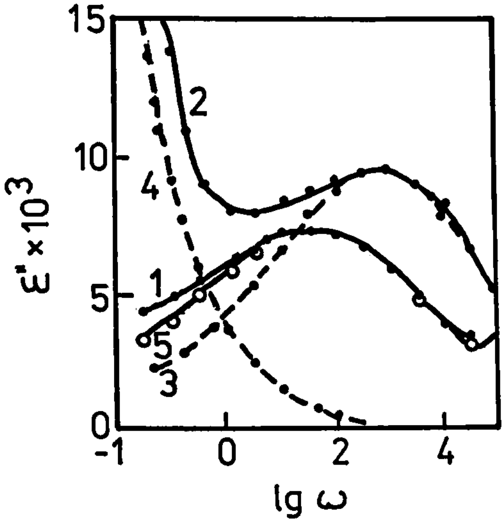


FIGURE 7 ε''versus lgω. Curves 1- and 2-experimental; curves 3- and 4- Fuoss-Kirkwood distribution curves with β=1 and β=0.52; curve 5- Fuoss-Kirkwood and Cole-Cole distribution curves with β=0.47, α=0.415.

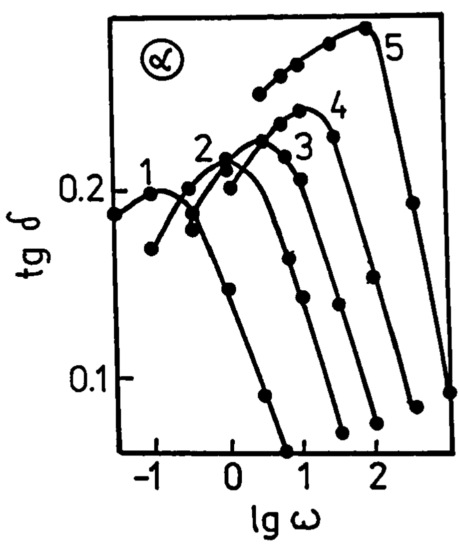


FIGURE 8 tgδ versus lgω in α process region. Curves 1-5 represent temperatures 30°,40°,50°,60 and 70°C.

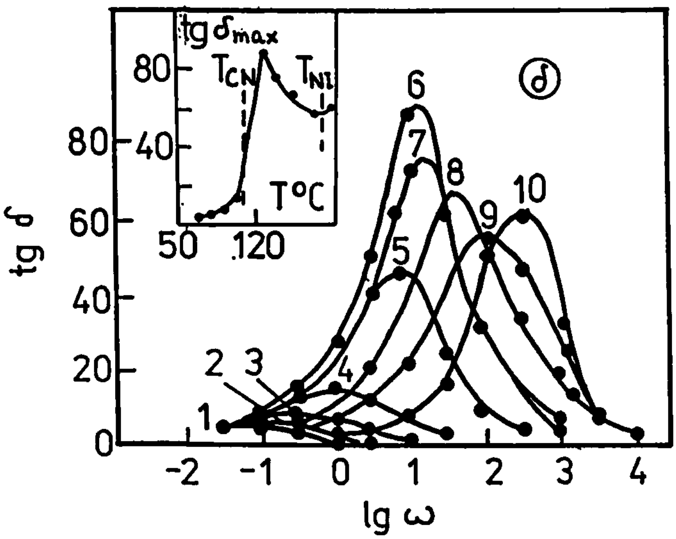


FIGURE 9 tgδ versus lgω in the δ process region. Curves 1-10 represent temperatures 92°,97°,102°,110°, 115°,125°,130°,140°,150°,160°C.Iside:$tg\delta_{max}$ vs. T

Figures 8 and 9 represent the dielectric loss tgδ versus lgω for the α relaxation process (temperature range 30°-70°C -curves 1-5) and the δ relaxation process (temperature range 92-160°curves 1-10) respectively. The shift of $tg\delta_{max}$ higher values in the region of the crystalline-nematic transition is due to the increase in dipole alignment. The subsequent drop of Tgδ is associated with an increase in thermal motion of the whole system on izotropisation and presence of ionic conductivity (see insert Figure 9).

Plots of the lg of the relaxation frequencies versus reciprocal temperature fitted to an Arrhenius relation are presented in Figures 10 and 11. In the case of the α relaxation process a strong devation from Arrhenius behaviour was expected[1,3].Also, the activation energy value of the α process was expected to be higher than that of the β process. However at hight enough frequencies the spectra of both processes (associated with the motion of the same dipoles) could merge together at higher temperatures, leading to similar values of their activation energies. The values of the apparent activation energies associated with these processes are: $E(\beta)$=50kJ/mol, $E(\alpha)$=48kJ/mol, $E(\delta)$=75kJ/mol (in the solid state) and $E(\delta)$=43kJ/mol (in the nematic state).

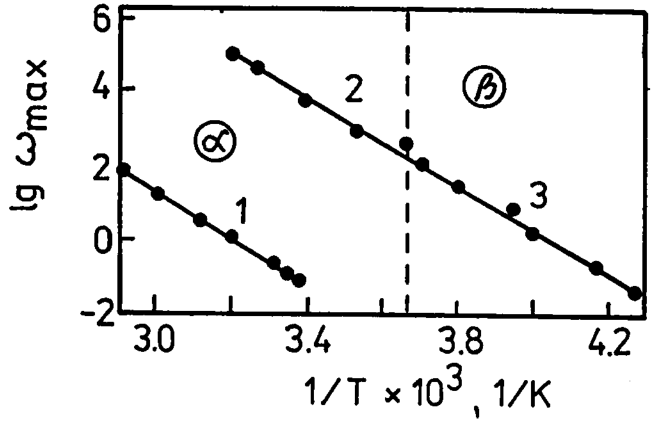


FIGURE 10 lg ω versus reciprocal temperature. Plot 1-α relaxation process, plots 2- and 3- β relaxation processes (primary and secondary).

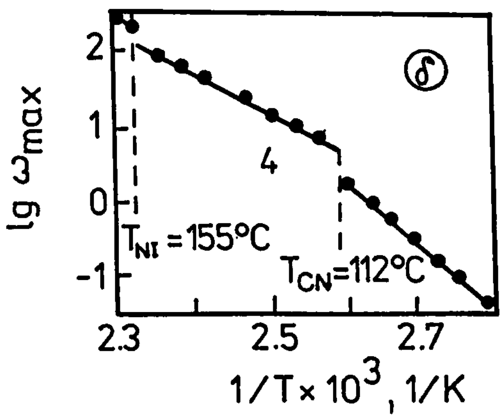


FIGURE 11 lgω_{max} versus reciprocal temperature. Plot 4- the δ relaxation process.

CONCLUSIONS

Dielectric measurements are a powerfull tool in the study of molecular dynamics of liquid-crystalline polymers. Dielectric relaxation processes γ,β,α and δ can be clearly observed. Cooperative motion in the vicinity of Tg leads to a combined $\alpha+\beta$ relaxation process. Discontinuous change of dielectric strength $\Delta\varepsilon'$ at Tg is observed. The δ process is visible in the vicinity of phase transitions of the polymer. Activation energies of the β,α and δ processes were calculated. The drop in the value of E for the δ process from 75 to 43 kJ/mol at the solid - nematic transition is connected with the difference in the dynamics of the longitudinal component of the dipole moment in these phases.

ACKNOWLEDGEMENT

This study was supported by the IREX Foundation (USA) and the Government Foundation Grant Nr 30089 9101 (Poland). One of us acknowledges the support of the NSF Polymer Science Program under DMR-8823084. Thanks are expressed to Mr. Jong Geon Jegal for preparation of DDA-9 samples.

REFERENCES

1. L.Monnerie, Pure and Appl.Chem., 57, 1563 (1985)
2. G.S.Attard, G.Williams,G.W.Gray, D.Lacey and P.A.Gemmel ,Polymer 27, 185 (186)
3. F.J.Bormuth and W.Hasse, Liquid Crystals 3, 881 (1988)
4. C.M.Haws,M.G.Clark and G.S.Attard, Dielectric Relaxation Spectroscopy, (Academic Press London, 1989),chap.3,p.186
5. H.Kresse, H.Stetin, E.Tennstedt and S. Kostromin, Molecular Cryst.Liq.Cryst. 191, 135 (1990)
6. G.Williams, A.Nazemi, F.E.Karasz, J.S.Hill, D.Lacey and G.W.Gray, Macromolecules, 24, 5134 (1991)

7. R.Diaz-Calleja, E.Riande and J.San Roman, Macromolecules 24, 264 (1991)
8. H.Kresse, S.Ernst, B.Krucke, F Kremer and S.U.Vallerien, Liquid Crystals, 11, 439 (1992)
9. A.Blumstein and S.Vilasagar, Molecular.Cryst.Liq.Cryst. 72 (Letters), 1 (1981)
10. R.B.Blumstein, E.M.Stickles, M.M.Guathier, A.Blumstein and F.Volino, Macromolecules, 17 177 (1984)
11. R.B.Blumstein, D.Y.Kim and C.B.McGowan, ACS Symp.Series 435, Liquid Crystalline Polymers Ed's R.A.Weiss and C.B.Ober, (American Chem. Soc.,Washington DC 1990), chap.22,p.294.