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

Dielectric Relaxation of Side-Chain Liquid Crystalline Polyethers

G. Day [a], G. Simon [b], E. Akiyama [c], Y. Nagase [c] & N. Koide [d]

[a] Chemistry, Monash University, Clayton, Victoria, Australia

[b] Materials Engineering, Monash University, Clayton, Victoria, Australia

[c] Sagami Chemical Research Center, Nishi-Ohnuma, Sagamihara, Kanagawa, 229, Japan

[d] Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo, 162, Japan

Version of record first published: 04 Oct 2006

To cite this article: G. Day, G. Simon, E. Akiyama, Y. Nagase & N. Koide (1997): Dielectric Relaxation of Side-Chain Liquid Crystalline Polyethers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 299:1, 187-192

To link to this article: http://dx.doi.org/10.1080/10587259708041993

Mol. Cryst. Liq. Cryst., 1997, Vol. 299, pp. 187–192
Reprints available directly from the publisher
Photocopying permitted by license only

DIELECTRIC RELAXATION OF SIDE-CHAIN LIQUID CRYSTALLINE POLYETHERS

GARY DAY [1] and GEORGE SIMON[2]*
[1] Chemistry [2] Materials Engineering, Monash University, Clayton, Victoria, Australia
EIICHI AKIYAMA and YU NAGASE
Sagami Chemical Research Center, Nishi-Ohnuma, Sagamihara, Kanagawa 229, Japan
NAOYUKI KOIDE
Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, Japan

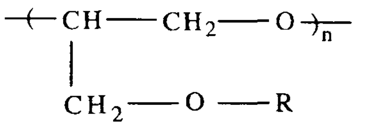
Abstract It is demonstrated in this work that dielectric relaxation spectroscopy is a potent means for characterising the changes in smectic-to-smectic transitions observed in two polyether backbone side-chain liquid crystalline polymers with very short spacers. The enthalpy of the transitions are themselves suprisingly high and this has previously been assigned to conformational changes in the polyether backbone. The relaxation spectra of these materials show a low frequency d.c. conductivity tail and a relaxation due to a combination of backbone and side-chain motion. The conductivity is found to be a strong indicator of phase change and associated order, whilst the position of the relaxation peak is found to be less dependent on such a change in environment. The broadness and strength of the dipolar relaxation is also found to reflect changes in the molecular environment in the different smectic states.

INTRODUCTION

Dielectric relaxation spectroscopy (DRS) has proven to be a powerful technique in the characterisation of side-chain liquid crystalline polymers (SCLCP) [1-3]. In this work we demonstrate the ability of DRS to contribute to an understanding of transitional behaviour in some novel SCLCPs - those produced by ring-opening polymerisation of glycidyl ether derivatives with attached mesogens - leading to SCLCPs with polyether backbones. These materials have been recently reported by us [4, 5] and are interesting for a number of reasons. It is found that they can form the liquid crystalline (LC) state even though the spacers used are very short (mesogens almost directly attached) and even side-groups consisting of a simple phenylene ring show mesogenic properties. In addition, a number of these materials show multiple smectic phases with suprisingly large transition enthalpies between the smectic phases. This is surprising since there would be expected to be little energetic (and entropic) change between two relatively highly ordered smectic phases. Since these changes clearly rely on some motion of the main-chain and/or side-chain during the structural rearrangement, it is of interest to see whether this can be observed by DRS.

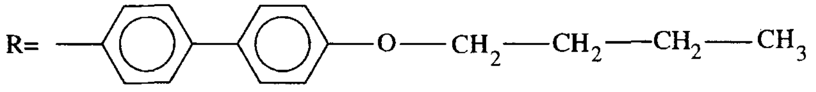
EXPERIMENTAL

The three samples forming the basis of this study were synthesised and characterised as previously reported [4, 5]. The temperatures and enthalpies of transitions were determined from DSC cooling scans at 10°C/minute and, along with the assignments of the phases, are shown in Figure 2.



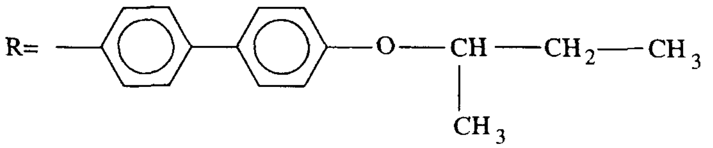
$$-\!\left(\underset{\displaystyle \mathrm{CH_2{-}O{-}R}}{\mathrm{CH}}-\mathrm{CH_2}-\mathrm{O}\right)_n\!-$$

FIGURE 1 Basic structure of polymers



PE-1

g 0 S_E 118 S_B 165 S_A 198 I
(0) (-17.8) (-8.2)



PE-2

g 2 S_C 117 S_A 182 I
(-14.8) (-6.1)

FIGURE 2 Mesogen unit R, with phase temperatures in C and phase enthalpies (ΔH) in J/g from DSC cooling scan shown in brackets for each transition.

The dielectric measurements were performed as described previously 6 with a GenRad 1689 Digibridge and a three-terminal guarded cell, covering the frequency range 10 to 10^5 Hz. The loss peaks were primarily measured, shown in terms of G/ω (pF) where G is conductance and ω is the angular frequency (=2.π. f where f is in Hz). $(G/\omega)/C_0 = \varepsilon''$ where ε" is the imaginary component of dielectric permittivity and C_0 the empty capacitance. All measurements were done of samples in the unaligned state.

RESULTS AND DISCUSSION

PE-1 - Dielectric spectra were obtained for PE-1 from 18°C (just above its Tg) to 200°C (above its clearing point). At temperatures below approx. 119°C the loss spectra were flat and relatively featureless, clearly any mobility of the side chains at these temperatures was not in the frequency range being measured. At temperatures greater than 119°C, the spectra increased due to an apparent low frequency d.c. conductivity tail (as shown for data at 150°C in Figure 3). It was found, however, that if the loss due to d.c. conductivity $(G/\omega)_{cond}$ was mathematically described as $(G/\omega)_{cond} = A/f$ where A is a parameter related to d.c. conductivity and f is frequency [6] and this contribution to the spectrum was subtracted away, a clear relaxation peak was found concealed beneath (also shown in Figure 3). Indeed, this relaxation peak was seen in all subtracted PE-1 relaxation spectra above 119°C and moved to higher frequencies as temperature was increased. Since there are no strong dipoles in the side group as is often the case with CN or NO_2 terminated SCLCP mesogens [1-3], the dipole must arise from the ethylene-oxide moieties, either on the main-chain or the side-chain. It is expected that the motions of both will be closely correlated anyway, due to lack of a long, decoupling spacer unit.

It is interesting to note that the relaxation peaks only became apparent at approximately the same temperature that the material went from a S_E to S_B phase, and this may indicate increased mobility in the less ordered S_B phase. The next transition occurs at about 165°C where the material becomes S_A and we looked at a range of dielectric relaxation parameters to determine whether DRS measurements are sensitive to such a change. Two of these parameters are the position of the relaxation peak (ln f_{max}) and the log of the parameter A, mentioned above as a measure

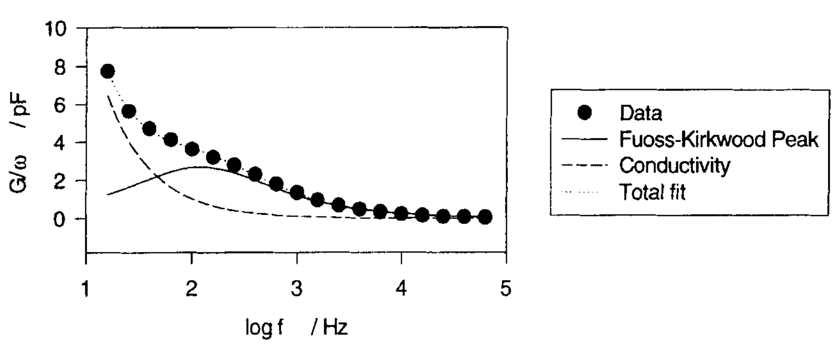


FIGURE 3 PE-1 relaxation loss peak at 150°C, with both conductivity and Fuoss-Kirkwood peak fitted

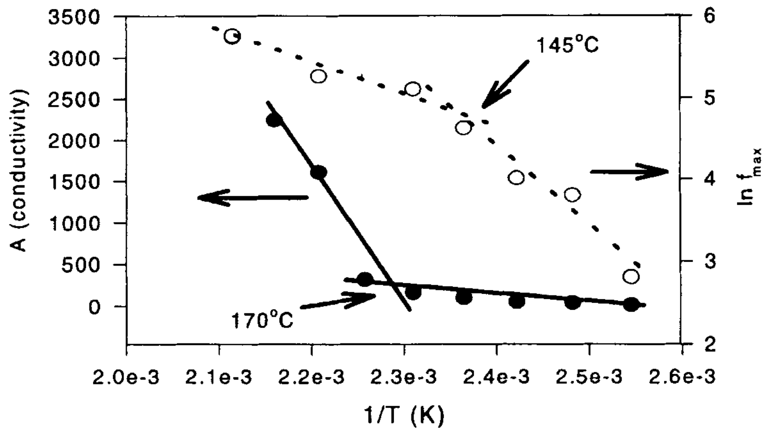


FIGURE 4 Conductivity (A) and relaxation time (ln f_{max}) parameters vs. 1/T for PE-1

of conductivity. In order to determine the conductivity parameter A, it is necessary to fit simultaneously the data to the $(G/w)_{cond}$ function mentioned above and a loss function, the Fuoss-Kirkwood relaxation function [6] being used here and of the form

$$G / \omega(\omega) = \frac{C_0 . \Delta\varepsilon . \beta}{2} . \sec h[\beta . \ell n(\omega\tau)] \tag{1}$$

where $\Delta\varepsilon$ is the relaxation strength, β is a parameter related to the breadth of the relaxation curve and τ is the relaxation time. All other symbols are as previously defined. Both conductivity, A and ln f_{max} are shown in Figure 4. In most SCLCP systems, the logarithm of these parameters would be linear as a function of reciprocal temperature, however this is not found to be the case in PE-1. It appears there are two regions of linearity which dog-leg at slightly different temperatures. Interestingly, if one looks at the effects of *increasing* temperature, the rate of motion (as seen from the ln f_{max} curve) deviates to a longer relaxation time (slower motion) at above 145°C. On the other hand, the conductivity is found to deviate to greater conductivity, as the 170°C point is reached from below. Since the transition from the more ordered S_B to less ordered S_E transition occurs at this temperature, it appears such a phase change effects motion of d.c. charges and indicates the effect of LC structure and anisotropy on conductivity, as has been noted elsewhere [1]. The reason for the seeming decrease in the rate of increase of the speed of relaxation in Figure 4 is not clear, but it should be noted that in any event the change in ln f_{max} is less dramatic than for A.

PE-2 - By contrast, the relaxation spectrum of PE-2 with its bulkier, chiral substituent showed much stronger dielectric relaxation peaks from temperatures quite close to the glass transition temperature, without any need for subtracting the conductivity, and is shown for a number of temperatures in Figure 5. Clearly, given the strong relaxation peaks, the S_C state has a higher degree of mobility at the same low temperatures than that of the S_E state in PE-1, above. As for PE-1, it is of interest to see whether the smectic-to-smectic transitions with their large enthalpies will cause a change in dielectric parameter. By looking at Figure 5 it can be seen that there is a change a significant low frequency d.c. conductivity tail at higher temperatures, complicating the spectra and requiring it to be subtracted. If this is done and ln f_{max} vs. 1/T is plotted (not shown here) it is found that the line is linear over the whole temperature range (quite Arrhenius in nature). It appears (as for PE-1) relaxation time is not a sensitive indicator of smectic phase change.

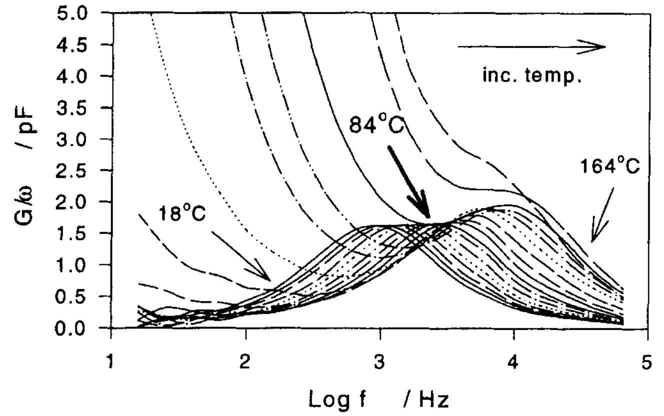


FIGURE 5 Loss peaks for PE-2 as a function of isothermal temperature (18 to 164°C)

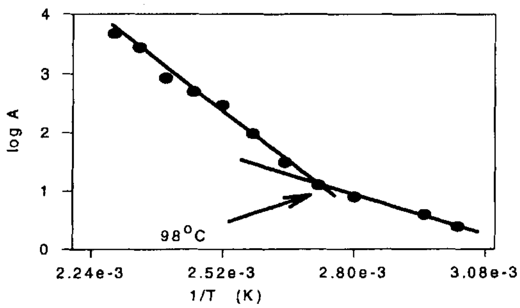


FIGURE 6 Conductivity (A) parameter vs. 1/T for PE-2

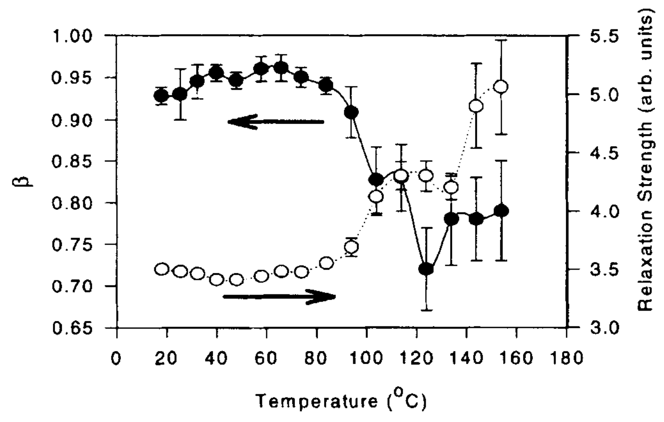


FIGURE 7 Fuoss-Kirkwood parameters (Equation 1) for PE-2 vs. temperature

However, as shown in Figure 6, the parameter A, a measure of conductivity found by simultaneous fitting of conductivity and the Fuoss-Kirkwood relaxation function to data does show a dog-leg increase at about 100°C as the less ordered S_A phase is reached (close to the 117°C transition observed by DSC). Because of the greater number of relaxation peaks measured for PE-2, compared to PE-1, the parameters from the Fuoss-Kirkwood Equation 1 can also be plotted as a function of temperature in Figure 7. The broadness (β) is found to increase dramatically at approximately 100°C (decrease in β) whilst the strength of the relaxation increases. Decreasing β (increasing broadness) is indicative of greater intermolecular coupling and range of environments in the less ordered smectic states. This - along with the increasing relaxation strength - indicates that it may well be the changes in conformation of the backbone - whose motion is strongly coupled to the mesogen - that is responsible for the large changes in enthalpy at the transition temperatures.

REFERENCES

1. C. M. Haws, M. G. Clark, G. S. Attard, in Side Chain Liquid Crystal Polymers; edited by C.B. McArdle (Blackie, Glasgow, 1989), Chap. 7
2. G.P.Simon, in Dielectric Spectroscopy of Polymeric Materials, edited by J.P.Runt and J.J.Fitzgerald (ACS Publications, Washington), in press
3. J.K. Moscicki, In Liquid Crystal Polymers: From Structures to Applications;edited by A. A. Collyer (Elsvier Applied Science, London, 1992), Chap. 4
4. E. Akiyama, Y. Nagase, N. Koide, Makromol. Chem., Rapid Commun., 14, 251(1993)
5. E. Akiyama, M. Ohtomoto, Y. Nagase and N. Koide, Macromol. Chem. Phys., 196, 3391 (1995)
6. McCrum, N. G., Read, B. E., Williams, G.; Anelastic and Dielectric Effects in Polymeric Solids (Wiley, New York, 1967)