Study of polymer liquid crystals by gas chromatography

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The technique of inverse gas chromatography (i.g.c.) has been used to investigate the transitions between liquid-crystalline phase in a polysiloxane bearing cyanobiphenyl mesogens and in a low-molar-mass analogue. The transition temperatures were found by considering the variation of retention volume with temperature and also the activity coefficients of the probes used, the latter giving clearer results. The possibility of using the method to study the thermodynamics of the transitions is also discussed. Although not the most convenient method for measuring solely the phase transitions, it allows the simultaneous determination of a number of other properties, so that our results extend the already wide range of applicability of i.g.c. in polymer science.

(Keywords: liquid-crystal polymer; mesophases; inverse gas chromatography; activity coefficients; thermodynamics; phase behaviour)

INTRODUCTION

Perhaps one of the most studied types of polymer in recent years has been those with liquid-crystalline properties[1]. Polymers with the mesogenic group as part of the backbone have been used as high-strength, high-modulus materials, while side-chain liquid-crystalline polymers (LCPs) have been studied since they often combine the interesting optical and electronic properties of mesogenic materials with the stability and processability of polymers.

Over the past two decades, gas chromatography (g.c.) has become an important tool in polymer chemistry[2], not only as an analytical technique but also as a method for measuring physicochemical properties, termed by some workers 'inverse gas chromatography' (i.g.c.). By studying the retention of small-molecule solvents or 'probes' by polymer stationary phases, and the temperature dependence, a wide range of properties can be measured, including glass and melting transition temperatures, degrees of crystallinity and a number of thermodynamic parameters of the polymer and its solutions. A range of low-molar-mass liquid-crystalline materials have been used as stationary phases for analytical g.c. where they allow the separation of closely related isomers[3] on the basis of their molecular shapes. A small number of these materials have been studied using i.g.c.[4–6], and activity coefficients and other parameters have been calculated in the various phases. Romansky and Guillet have also studied main-chain liquid-crystal polymers, but their results were not as clear-cut as in non-mesogenic systems[7]. Although Laub and coworkers[8] have investigated some of the thermodynamic properties of side-chain LCPs from the point of view of their use as analytical stationary phases, there has not been, to our knowledge, a systematic study of a range of side-chain liquid-crystalline polymers where the behaviour of the mesogen might be expected to follow more closely that of the low-molar-mass analogues. The aim of this work, therefore, was to determine the usefulness of i.g.c. for studying these, in measuring both transition temperatures and their thermodynamic properties.

EXPERIMENTAL

The essence of the i.g.c. technique is the measurement, under accurately known conditions, of the chromatographic retention times for various components over the polymer of interest, which is usually coated onto a support and packed into a column. In this case, the chromatograph was a 'Pye Unicam 204' equipped with a flame ionization detector (f.i.d.) and modified by the addition of fittings that allowed the pressure at the inlet to the column to be measured using a mercury manometer. The apparatus conformed in terms of temperature and flow-rate stability to the accepted requirements for this type of work[9] and was checked by measuring the glass transition temperature of poly(methyl methacrylate) and thermodynamic properties of a range of solvents in poly(isobutylene) at 60°C, both of which gave satisfactory agreement with literature results. Nitrogen gas was used as the carrier at flow rates between 20 and 80 $cm^3 min^{-1}$, measured using a soap-bubble flow meter. The column temperature was measured to $\pm 0.1°C$ using a thermocouple attached to the column, which had been calibrated against a Tinsley type 5840 platinum resistance thermometer. The temperature variation through the oven was less than 0.2°C. To avoid supercooling effects, measurements were made only on ascending temperature experiments.

The retention times of solvents detailed below were determined by injecting approximately 0.01 μl from a syringe and recording to ± 0.01 min with a Spectra-Physics SP4270 integrator. The mean of at least three

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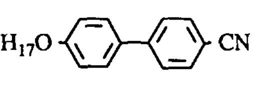
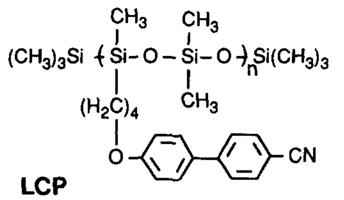
readings agreeing to within 1.0% was taken. No dependence on the amount of probe injected was noted for any system reported here.

Column preparation

For this initial study, we chose a side-chain liquid-crystal polymer having a cyanobiphenyl mesogen attached to a siloxane polymer backbone and also a low-molar-mass analogue, 4-cyano-4′-n-octyloxybiphenyl. They will be denoted here by LCP and OCB respectively. These were generously donated by Merck Ltd (UK). Their structures are shown below:



OCB



LCP

The liquid-crystalline material was dissolved in the minimum amount of chloroform required to completely cover the weight of solid support needed to give the required percentage loading. The support (Chromosorb 'P' of 100–120 mesh size) was added and the chloroform removed slowly using a rotary evaporator to give constant agitation. The resulting stationary phase was dried under vacuum to constant weight and a known amount packed into 1/4 inch (~6.5 mm) copper tubing. The exact amount of liquid crystal on the column was determined by calcination for OCB and by exhaustive Soxhlet extraction with chloroform for LCP, with corrections for the uncoated support applied in both cases. A loading of approximately 8% by weight was used.

Differential scanning calorimetry

To give a comparison with our g.c. results, the transition temperatures for the LC phases were also measured using a Perkin Elmer DSC employing an indium control and heating rate of 5°C min^{-1}. To determine whether the chromatographic support influenced the phase transitions, supported materials were used in addition to the pure LCs.

RESULTS AND DISCUSSION

The primary datum in this type of experiment is the specific retention volume[10] of a component, V_g°, corresponding to the volume of carrier gas at standard temperature and pressure (s.t.p.) per gram of polymer required to elute the component from the column:

$$V_g^\circ = F(t_r - t_m)/W \qquad (1)$$

where t_r and t_m are the retention times of the solvent and an inert marker respectively, W is the weight of polymer on the column and F is the flow rate of carrier gas, corrected to s.t.p. given by:

$$F = F'\left(\frac{273.2}{T_f}\right)\left(\frac{760}{P_0}\right)\left(\frac{P_0 - P_w}{P_0}\right)\left(\frac{3[(P_i/P_0)^2 - 1]}{2[(P_i/P_0)^3 - 1]}\right) \qquad (2)$$

where F' is the flow rate measured at a flow meter temperature T_f and atmospheric pressure P_0. Thus, the first three terms of equation (2) represent F corrected to s.t.p., while the last two account respectively for the vapour pressure of water in the flow meter, P_w, and the compressibility of the gas as it passes through the column, P_i being the pressure at the column inlet.

LC phase transition temperatures

The basis of measurement of T_g and T_m values by i.g.c. has been to detect deviations from the smooth temperature dependence of V_g° on passing from glassy to rubbery or from crystalline to amorphous regions of the polymer[11]. Thus, we were interested to determine whether similar effects were seen on moving between the various liquid-crystalline phases.

OCB displays two LC phases between the solid (K) phase and the isotropic liquid (I), the nematic (N) and smectic-A (S_A) phases. *Figure 1* shows an Arrhenius-type plot of the results for OCB on a column loaded at 8% by weight. As can be seen, there is a distinct break in the plot corresponding to N → I transition. Although not as clear, the slope of the plot also changes at temperatures corresponding to the other phase transitions. To eliminate as far as possible any subjective errors, 'best-fit' lines were drawn through the results in the mid-range of each phase using a linear regression program, and the intersection of these lines taken as the transition temperature. This is shown in more detail in *Figure 2*.

The same type of retention plot for LCP is shown in *Figure 3*. The T_g of the polymer is approximately −9°C[12] and is too low to be detected by our current apparatus. However, the transition from smectic LC to isotropic behaviour is again clearly shown. The shape of the plot is similar to those found at the T_m of other synthetic polymers[13] but the magnitude of the change in V_g° and the temperature range over which it occurs is considerably lower, indicating the narrower range of melting in these materials. However, the change in V_g° for LCP takes place over a range of 5–7°C, which is rather wider than seen by conventional methods such as polarized microscopy. In common with previous work[13], the melting temperature has been taken as the point

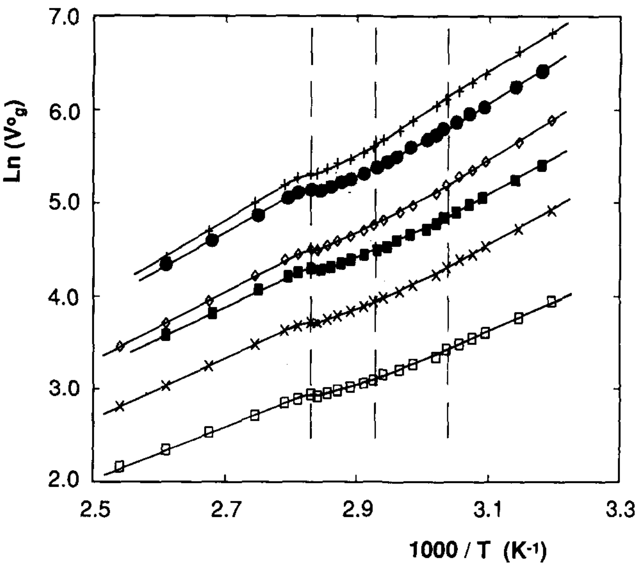


Figure 1 Retention diagram, i.e. logarithm of specific retention volume *versus* reciprocal temperature, for liquid-crystal OCB, using various probes: (+) n-nonane; (●) toluene; (◇) n-octane; (■) benzene; (×) n-heptane; (□) n-hexane

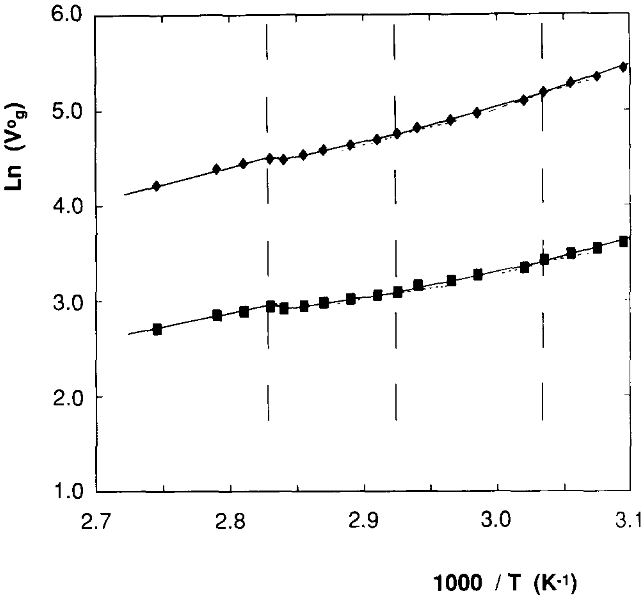


Figure 2 Detail from *Figure 1* showing determination of phase transition temperatures, using various probes: (◆) n-octane; (■) n-hexane

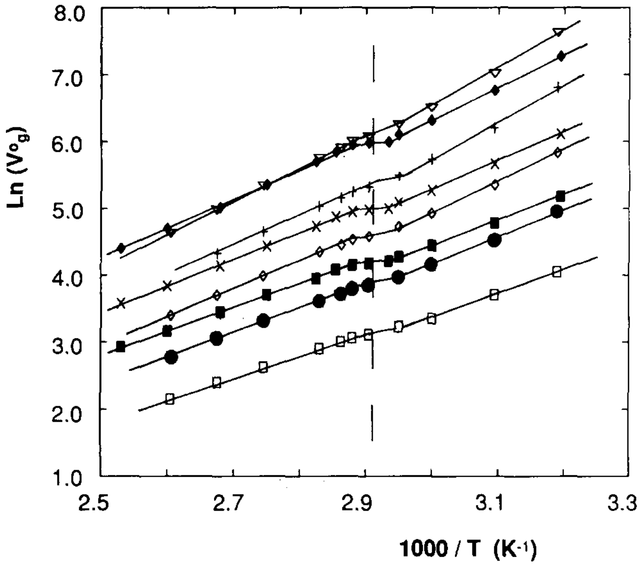


Figure 3 Retention diagram for liquid-crystal polymer LCP, using various probes: (▽) n-decane; (◆) *o*-xylene; (+) n-nonane; (×) toluene; (◇) n-octane; (■) benzene; (●) n-heptane; (□) n-hexane

where the trace returns to linearity, i.e. the maximum temperature at which any LC phase exists. The reasons for this relatively wide transition region is not clear. In the polymeric materials, polydispersity effects could provide some explanation. Alternatives are that the stationary phase support is interacting with the compounds to modify the LC structures slightly, broadening the transition, or that (as suggested by one of the referees) interaction with the probe is affecting the transition. Under the conditions used for our work, the probe is usually considered to be at infinite dilution and to have no influence on the stationary phase. The lack of probe sample size effects would appear to confirm this, but it is not possible to calculate the concentration of the probe at any instant along the column. Further study of these effects will feature in our future work.

When measuring the T_g of polymers, it was noticed that the results varied somewhat depending on the probe[14], in general non-solvents giving higher values since these required a higher temperature to penetrate the polymer. *Table 1* shows the phase transition temperature for LCP and OCB for each probe used. There is clearly no systematic variation and the values are independent of the probe used (for the admittedly narrow range used here).

To give an independent value for the transition temperatures with which to compare our results, they were also recorded using d.s.c. Also, to ensure that a comparison of the results from the two methods is valid, and that being coated on the support does not influence the transition temperatures, d.s.c. thermograms were recorded on the pure LC materials and on the coated supports. The average transition temperature for each system from *Table 1* is compared with that from d.s.c. results in *Table 2*. Also included are the values supplied by the manufacturers of the compounds[12].

The precision of this technique is comparable with that of, for example, d.s.c. and could possibly be improved by measuring more points over a small temperature range near the transition. Clearly, the chromatographic method is not as convenient as d.s.c. to measure merely the transition temperatures, but it could be valuable since a number of other parameters can be measured in the same experiment.

Thermodynamics of LC phases and transitions

One of the major applications of i.g.c. has been to measure activity coefficients for a wide range of solvents at infinite dilution in the polymer. These are usually calculated on a weight-fraction basis in macromolecular

Table 1 Transition temperatures for liquid crystals measured using different probes

	OCB			LCP[a]
Probe	$K \rightarrow S_A$	$S_A \rightarrow N$	$N \rightarrow I$	$S_A \rightarrow I$
n-Hexane	56.7 ± 0.5	67.2 ± 0.8	79.5 ± 0.5	74 ± 1.5
n-Heptane	56.3 ± 1.0	66.7 ± 1.0	79.3 ± 1.0	71 ± 1.0
n-Octane	56.4 ± 0.8	68.0 ± 1.0	79.7 ± 0.5	73 ± 1.0
n-Nonane	54.6 ± 0.9	67.8 ± 0.9	79.0 ± 0.6	72 ± 1.0
n-Decane				73 ± 1.0
Benzene	56.5 ± 1.0	68.2 ± 0.6	79.0 ± 0.6	73 ± 1.5
Toluene	55.1 ± 0.9	67.8 ± 0.9	78.8 ± 0.8	74 ± 1.0
o-Xylene				74 ± 1.5
Average	55.9 ± 1.1	67.6 ± 0.9	79.2 ± 0.5	73 ± 1.5

[a] The results for LCP were more difficult to ascertain and so are only quoted to ±1°C

Table 2 Comparison of liquid-crystal transition temperatures measured using different methods

	OCB			LCP
Method	$K \rightarrow S_A$	$S_A \rightarrow N$	$N \rightarrow I$	$S_A \rightarrow I$
Chromatography	55.9	67.6	79.2	73
D.s.c. (pure)	53.4	–[a]	78.1	71
D.s.c. (coated)	53.1	–	79.1	71
Manufacturers	54.5	67	80	74

[a] Transition not seen in d.s.c.

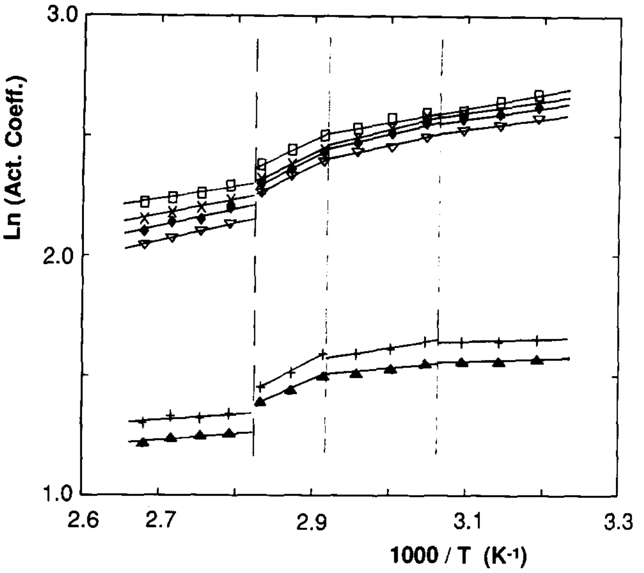


Figure 4 Weight-fraction infinite-dilution activity coefficients for OCB, using various probes: (□) n-hexane; (×) n-heptane; (◆) n-octane; (▽) n-nonane; (+) benzene; (▲) toluene

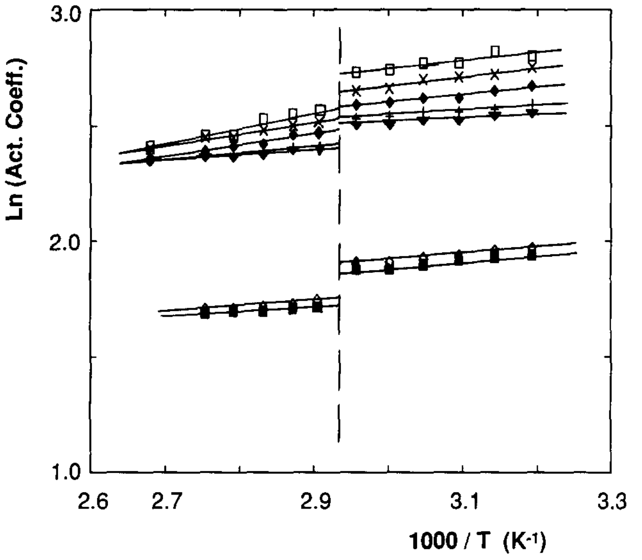


Figure 5 Weight-fraction infinite-dilution activity coefficients for LCP, using various probes: (□) n-decane; (×) n-nonane; (◆) n-octane; (+) n-heptane; (▼) n-hexane; (◇) toluene; (■) benzene

systems because of difficulties in defining mole fractions[15]. Infinite-dilution activity coefficients, Ω_1^∞, calculated on this basis are given by:

$$\ln \Omega_1^\infty = \ln\left(\frac{273.2R}{P_1^\circ M_1 V_g^\circ}\right) - \left(\frac{P_1^\circ}{RT}\right)(B_{11} - V_1^\circ) \quad (3)$$

where M_1 is the molecular weight of the solvent and P_1°, B_{11} and V_1° are its saturated vapour pressure, second virial coefficient and molar volume at the column temperature T. The more usual Raoult's law activity coefficients on a mole-fraction basis were calculated for OCB but only the Ω_1^∞ are quoted here.

The values of Ω_1^∞ calculated over the temperature range studied are displayed in *Figure 4* for OCB and *Figure 5* for LCP. A note of caution should be introduced here: to be certain that the activity coefficients are true thermodynamic properties, there should be no dependence of the results on the amount of probe solvent injected or on the loading of polymer on the stationary phase. In this work, there was a small, but significant, change on moving from 4% to 8% loadings, so that even higher loadings may be necessary for valid results. This could not be checked during this work and, for this reason, no detailed discussion on the Ω_1^∞ values will be presented. However, all of the values should be affected similarly, so that the trends and conclusions drawn here will be valid.

Clearly, there are significant differences in the values of Ω_1^∞ for a particular probe in the various mesophases, the transition temperatures as determined above being indicated by the vertical lines in the figures. This has been demonstrated for low-molar-mass materials previously[4–6] but not, to our knowledge, for polymeric LCs. The values are generally lower in the less ordered phases, indicating a lesser degree of interaction. For LCP, the values of Ω_1^∞ increase with increasing alkane chain length, showing decreasing compatibility along the series. Those for the aromatic probes are lower, indicating greater compatibility, as would be expected considering the structure of the LCP. The Ω_1^∞ values are similar in both the polymer and low-molar-mass compounds, indicating that the primary interactions are with the mesogenic groups.

An additional point worthy of note is that the form of the plots shown in *Figures 4* and *5* also represents a more sensitive method for detecting the temperatures of the phase transitions than consideration of the specific retention volumes.

CONCLUSIONS

We have shown that inverse gas chromatography can be used to investigate the phase transitions and thermodynamics of mesophases in side-chain liquid-crystal polymers. The temperatures at which the phase changes take place can be detected, particularly by considering activity coefficients, with an accuracy and precision equal to that of calorimetric methods. Although not presented here, the results can also be used to calculate the enthalpy and entropy of mixing or solution for the probes in each of the phases and also for the phase transitions. A thorough study of these properties, and differences in behaviour of the different phases, will be the basis of our future work in this area. Thus, while i.g.c. would never be the method of choice for determining solely the phase transition temperatures, it has the advantage that a range of other measurements can be made during the same experiment.

Our results extend the usefulness of inverse gas chromatography as a means of studying structure and interactions in a wide range of polymer materials.

ACKNOWLEDGEMENT

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