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# Solvent Interactions with an Insoluble Liquid-Crystalline Polyester

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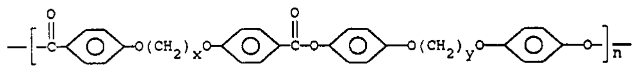
ABSTRACT: Inverse gas chromatography (IGC) was used to study the thermal transitions in an organic liquid-crystalline polyester. A crystal-to-nematic and a nematic-to-isotropic transition were detected, as was a lower temperature transition, presumably a crystal-to-crystal transition. The probe molecules used were *nonsolvents* of the polyester, which was insoluble in normal organic solvents. The IGC retention diagram, or a plot of the apparent weight fraction activity coefficient vs inverse temperature, could be used for the determination of the transition temperature.

## Introduction

Materials research depends on the availability of characterization techniques for the description of new materials. Inverse gas chromatography (IGC) is one flexible, easy to use, and informative tool which is gaining in popularity and whose scope of applications is constantly increasing.[1] The major material class which has been subjected to IGC investigations is that of amorphous and semicrystalline polymers.[2] In the last 10 years, liquid-crystalline polymers (LCPs) have been synthesized in unprecedented variety, and a wide variety of thermotropic mesophase structures are possible. New structural types are frequently introduced. This explosion of synthetic activity demands informative studies of the bulk phase structure of LCPs. Often, thermal stability or high-temperature liquid-crystallinity requirements are satisfied by a molecular structure which produces polymers of limited solubility. This aspect can be a drawback in the characterization and manipulation of LCPs and may be addressed by IGC.

A number of gas chromatographic investigations of polysiloxane-based liquid-crystal polymers have been undertaken from the perspective of their use as chromatographic stationary phases for the separation of isomeric compounds.[3] Price and Shillcock[4] have recently studied a side-chain polysiloxane with an attached cyanobiphenyl mesogen by IGC. Kelker and Hatz[5] and Witkiewicz[6] have reviewed the information obtained in studies of small-molecule liquid crystals by GC.

We have already shown the possibility of determining phase transition temperatures and activity coefficients for the solution of alkanes and benzene derivatives in a thermotropic, main-chain, soluble liquid-crystal polyester.[7,8] Here, for the first time, are presented IGC results for the interaction of alkane probes with a completely organic main-chain liquid-crystal polymer (I) which is insoluble in most organic solvents. The nematic to isotropic transition in this LCP is outlined.



I

$x = 10$
$y = 10$

The synthesis, characterization, and rheological properties of this polymer have been published previously by Griffin and Havens[9,10] and Wissbrun and Griffin.[11]

## Experimental Section

**Materials.** Reagent grade phenol and 1,1,2,2-tetrachloroethane (Aldrich) were used as received. Chromosorb G (60/80 mesh, acid washed and treated with dimethyldichlorosilane) was used as the chromatographic support. The alkane probes were analytical standards from Polysciences. They were checked for impurities by gas chromatography on a DB-5 capillary column and found to be 99.9% pure.

Owing to the limited solubility of the polymer in common organic solvents, no molecular weight data were available. The molecular weight for a polymer of similar structure ($x = 12, y = 10$) and synthesized by an identical method, was measured viscometrically and found to be 19 200.[9]

**Inverse Gas Chromatography.** The polymer was coated onto the Chromosorb G support from a 60:40 (v/v) solution of phenol/tetrachloroethane by the pile coating method[12] to a loading of 2.43 wt%. After coating, the stationary phase was placed under high vacuum at 50 °C for more than 24 h in order to remove residual phenol. A total of 0.0807 g of polymer was packed into a 280-cm copper GC column of 1/8-in diameter. The pile coating method allows quantitative deposition of polymer onto the chromatographic support, an important factor to consider when only small amounts of sample are available. Ground polymer particles were not used, since very little sample (<100 mg) was available and a considerable amount would have been lost in the grinding process.

IGC experiments were performed on a Hewlett-Packard 5890 series II gas chromatograph equipped with a flame ionization detector, using nitrogen carrier gas at a nominal flow rate of 2.5 mL/min, measured using a soap bubble flow meter at room temperature. Injections of probe vapor at infinite dilution (<0.01 μL of liquid) mixed with methane gas as a marker were performed manually using a Hamilton microsyringe. Retention times were confirmed to be independent of the sample size and were

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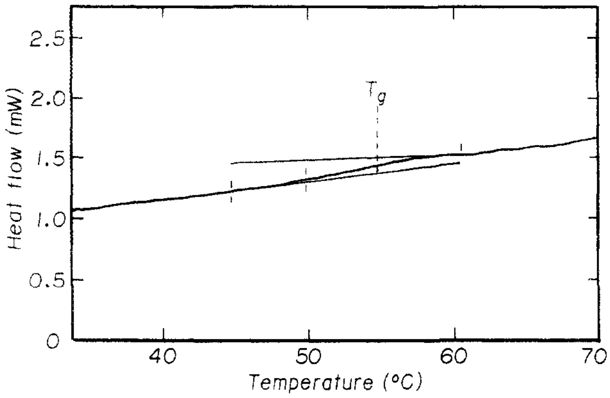

**Figure 1.** DSC heating curve (10 K/min) showing the glass transition.

determined from the positions of the peak maxima. Specific retention volumes $V_g$ (mL/g) were computed in the usual manner[13]

$$V_g = \frac{273F(t_r - t_m)760}{TwP_{\text{out}}} \tag{1}$$

where $w$ is the weight of polymer in the column, $t_r$ is the retention time of the probe, $t_m$ is the retention time of the marker gas (methane), $F$ is the flow rate of the carrier gas at column temperature $T$ adjusted for gas compressibility,[13] and $P_{\text{out}}$ is the carrier pressure at the column outlet.

The column inlet and outlet pressures were monitored using a mercury manometer. Data were collected and recorded using a Hewlett-Packard Vectra ES-12 personal computer with the associated GC software package HP3365 Chemstation. The oven temperature was continuously measured to 0.1 °C using a thermocouple interfaced to the GC. The column was equilibrated for several minutes after each temperature increment of 1 or 2 deg. Equilibration is not necessary for transition temperature determinations but is important when obtaining activity coefficient data. The weight fraction activity coefficient at infinite dilution, $(a_1/w_1)^\infty$, can be calculated according to eq 2,[14] where $M_1$

$$\ln(a_1/w_1)^\infty = \ln(273R/M_1P_1^0V_g) - (B_{11} - V_1)P_1^0/RT + P_1^0J_3^4(2B_{13} - V_1)/RT \tag{2}$$

is the molecular weight of the probe molecule, $P_1^0$ is the saturated vapor pressure at temperature $T$,[15] $B_{11}$ is the probe virial coefficient,[16] $B_{13}$ is the probe-carrier gas virial coefficient, $R$ is the gas constant, and $J_3^4$ is a carrier gas compressibility correction factor. These parameters may be calculated by methods previously summarized.[13] $V_1$ is the probe molar volume calculated from the liquid molar densities at each temperature, using data from Orwoll and Flory.[17]

**Differential Scanning Calorimetry.** The liquid crystalline transition temperatures and enthalpies were measured under $N_2$ using a Perkin-Elmer Series 7 DSC. Heating rates were 10 °C/min, and 10.5 mg of sample was used. The instrument was calibrated with indium.

## Results

The effect of thermal history on the polymer was examined using DSC, by running the sample three times at identical heating and cooling rates of 10 °C/min. The polyester showed a glass transition $T_g$ at 54.8 °C (Figure 1) and three initial endotherms with peak maxima at 123.6, 187.5, and 214.7 °C (Figure 2). The last two endotherms have also been reported by Griffin and Havens.[9] The glass transition had not been previously observed. Irreproducible low-temperature endotherms, often due to the crystal-to-crystal transformation of solvent-precipitated crystal forms, are occasionally observed for semicrystalline polymers. On the first cooling scan, no exotherm attributable to the low-temperature transition was observed (Figure 2). On the second and third heating scans (Figure 3), the low-temperature endotherm was not observed, reinforcing the assignment of the transition as a solvent-formed crystal transformation. Postannealing transitions on heating, observed at 185 and 212 °C, were assigned by Griffin and Havens[9] as crystal-to-nematic (K→N) and nematic-to-isotropic (N→I) on the basis of binary phase diagrams and X-ray diffraction data. The transition temperatures and enthalpies of transition obtained by DSC are listed in Table 1.

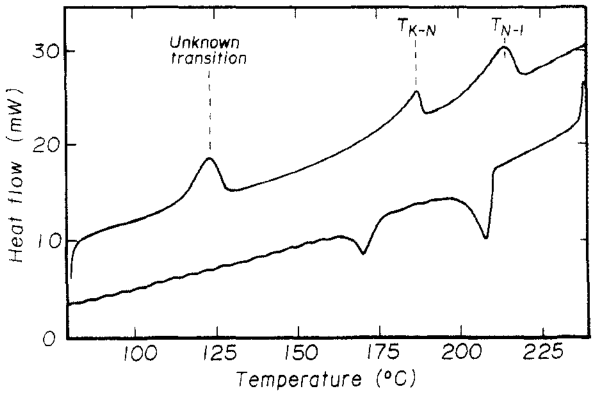

**Figure 2.** DSC first heating (top) and cooling (bottom) curves (10 K/min), showing the low-temperature endotherm, K→N and N→I transitions.

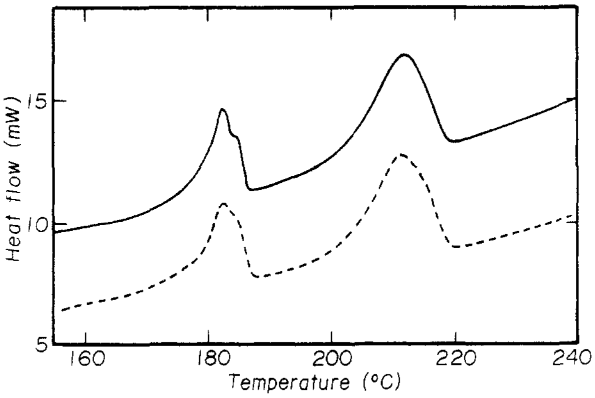

**Figure 3.** DSC curves obtained on (—) second and (- - -) third sample heatings (10 K/min) showing the K→N and N→I transitions.

**Table 1. Transition Temperatures and Enthalpies for Solid–Nematic (K→N) and Nematic–Isotropic (N→I) Transitions for the Liquid-Crystalline Polyester**

| heating run no. (exptl) | transition temp (°C) $T_{K\to N}$ | enthalpy of transition $\Delta H_{K\to N}$ (J/g) | transition temp (°C) $T_{N\to I}$ | enthalpy of transition $\Delta H_{N\to I}$ (J/g) |
|---|---|---|---|---|
| | | DSC | | |
| 1 | 187.5 | 15.0 | 214.7 | 25.2 |
| 2 | 182.7 | 13.0 | 211.9 | 26.5 |
| 3 | 182.4 | 13.1 | 211.2 | 26.6 |
| lit.[a] | 185 | 9.7 | 212 | 19.3 |
| | | IGC | | |
| | 192 | | 220 | |

[a] Reference 9.

IGC retention diagrams are plotted as ln $V_g$ vs $1/T$ according to eq 3, where $-\Delta H_s^\infty$ is the heat of solution of the probe molecule in the polymer.

$$\delta \ln V_g/\delta(1/T) = -\Delta H_s^\infty/R \tag{3}$$

The low-temperature transition on the first heating of the column is illustrated in the retention diagrams for

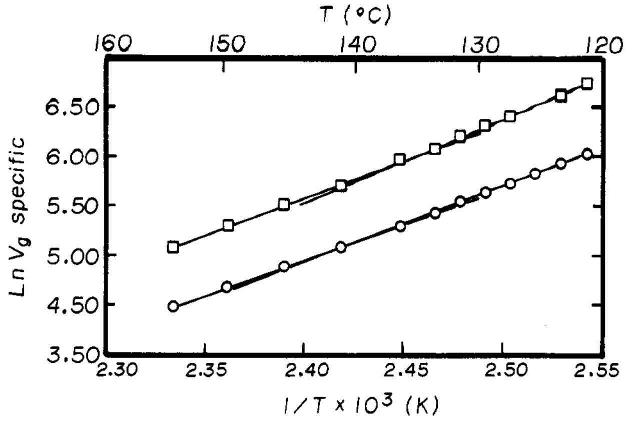

**Figure 4.** Retention diagram obtained using hexadecane (○) and heptadecane (□) as probes. First heating of column showing the low-temperature transition.

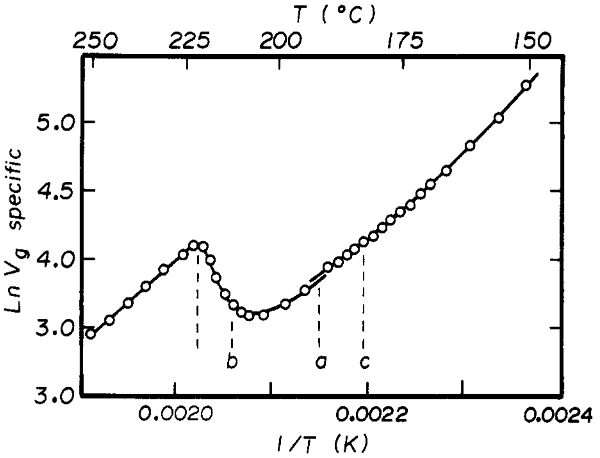

**Figure 5.** Retention diagram obtained using octadecane as a probe. Third run showing the K→N and N→I transitions. (a) Corresponds to $T_{K\rightarrow N}$ in Figure 2. (b) Corresponds to $T_{N\rightarrow I}$ in Figure 2. (c) Is the beginning of the nonlinear portion of the diagram.

heptadecane and hexadecane in Figure 4. The transition is manifested in a change in the slope of the retention and activity coefficient plots for the probe. It occurs in the vicinity of 135 °C, whereas DSC experiments showed a peak maximum at 124 °C. This transition may be a crystal–crystal transformation or, as was also suggested, a loss of water or other solvent bound to the polymer. However, the latter seems highly unlikely in view of the fact that (a) the coated packing for IGC experiments was dried in vacuo for several days and (b) the GC experiment, involving thermal equilibration under $N_2$ flow, should have driven off residual volatiles.

The K→N transition is illustrated using octadecane as a probe. The retention diagram shown in Figure 5 is for the annealed sample on the third heating. Similar data were collected on the second column heating. Extrapolation of the straight-line portions of the diagram in the vicinity of the change in slope (c) produces an intersection point of 182 °C, the same temperature at which the K→N transition was observed by DSC. Another change in slope (a), quite visible on the retention diagram, is estimated to occur between 190 and 195 °C.

The interpretation of IGC retention diagrams with respect to liquid-crystalline transitions must be clarified. In the case of an amorphous polymer, probe molecules are assumed to adsorb on the polymer surface below $T_g$ and to penetrate into the bulk of the polymer above $T_g$. An IGC retention diagram reflects this transition in a deviation from linearity as segmental motion begins. For a semicrystalline polymer below its melting point but above $T_g$, an assumption is made that the probe molecule penetrates only the amorphous regions and that crystalline regions are impervious to the probe.[2,18] As the crystallites melt, probe molecules can penetrate into the bulk, and a maximum is observed in a retention diagram when the amount of amorphous phase available is maximized. The retention diagram then reverts to linearity and a slope governed by the rise in partial pressure of the probe[14] with increased temperature. In IGC studies of small-molecule liquid crystals, the assumption that a homogeneous phase is being investigated is implicit.[3,5] Some recent studies[20,21] suggest a two-phase model of liquid-crystalline and amorphous zones in a main-chain polymer which is presumably in a mesophasic state. Therefore, the observed changes in retention diagrams may be due to solubilization of the probe in a biphasic analogy to a semicrystalline polymer below $T_m$ or to a manifestation of the change in activity coefficient of the probe dissolved in a homogeneous liquid-crystalline phase.

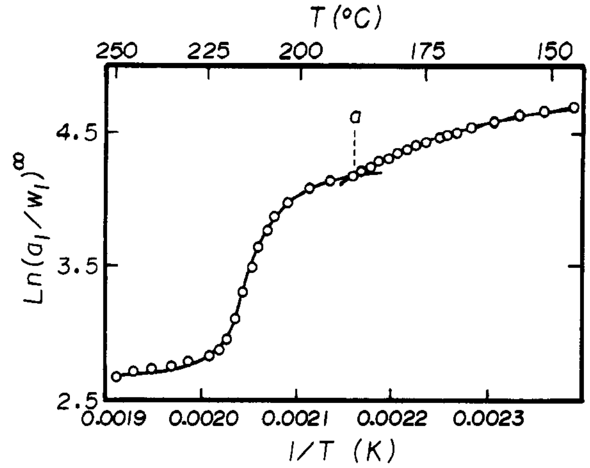

**Figure 6.** Apparent weight fraction activity coefficient diagram using octadecane as a probe. Third run showing the K→N and N→I transitions: (a) corresponds to $T_{K\rightarrow N}$ in Figure 2.

When the local maximum in the retention diagram (Figure 5) is used as an indicator of the completion of a phase transition, as is the case for the melting point determination in semicrystalline polymers,[13,18] a transition temperature of 220 °C is found for the N→I transition using the octadecane probe on the second and third runs. This is compared to point (b), the value of 212 °C found by DSC. However, the DSC peak at a 10 °C/min heating rate from onset to end spans from 200 to 215 °C. Therefore, different aspects of the transition may be observed; the choice of the transition temperature depends on how the transition point is defined. For this type of polymer, that is, with a presumably high polydispersity, such a broad melting range is normal. Due to the low percent loading of polymer on the chromatographic support used, some stabilizing effects of the support on the LC phase may have been introduced. It is also known that some residual nematic order may persist in polymer melts above an observed transition temperature. The above factors are possible causes for the difference in melting points found by DSC and IGC.

A significant change in the apparent weight fraction activity coefficient (calculated using eq 2) for a solution of octadecane in the LCP is found at the K→N and N→I transition temperatures determined by DSC (see Figure 6). The terminology "apparent weight fraction" in the vicinity of the crystalline and nematic phases is used. The utility of treating the data in terms of activity coefficients rather than retention volume is obvious when Figures 5

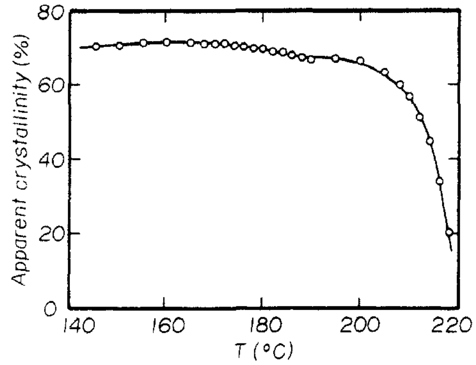

**Figure 7.** Apparent percent crystallinity of the polymer using octadecane as a probe, as in Figure 5.

and 6 are compared. The improved visualization of the transition temperatures has also been previously observed.[4,7,8] As discussed above, for a crystalline polymer the assumption is that the probe molecule dissolves solely in the amorphous part of the bulk phase. Hence, the activity coefficients must be corrected for this change in the weight of polymer available for solution formation. In the nematic phase, there is insufficient information on the phase structure to make any assumptions about local probe solubilization. Also, without sufficient sample to perform surface-to-volume corrections for possible adsorption of probe molecules on the bulk surface, only the first approximation values for the percent crystallinity are quoted. These factors will be further investigated when more samples of these types of polymers are available. Polymers containing polar groups are known to require these corrections to IGC experimental data.[18,19]

The percent crystallinity of a polymer sample may be calculated from

$$\% \text{ crystallinity} = 100[1 - (V_{g_e}/V_{g_a})] \qquad (4)$$

where $V_{g_e}$ is the experimentally determined specific retention volume at a temperature $T$ and $V_{g_a}$ is the theoretical retention volume (assuming the polymer is completely amorphous at the same temperature), found by extrapolating specific retention volumes in the isotropic phase to temperatures below the melt transition, using eq 3 and the procedure described by Braun and Guillet.[13] As discussed above, we are quoting the values for % crystallinity in the nematic phase as "apparent" crystallinity. The apparent crystallinity change with respect to temperature is shown in Figure 7. This plot also illustrates the K→N and N→I transitions clearly.

## Conclusions

IGC has been shown to be useful in the determination of thermal transitions to a nematic phase from a crystalline phase, and to the isotropic phase from a nematic one in a liquid-crystal polymer which is insoluble in common organic solvents at room temperature. This is the first time, to our knowledge, that inverse gas chromatography has been used to follow these types of transitions in a main-chain intractable LC polymer. The results are significant in that probe molecules which are nonsolvents of the liquid-crystal polymer investigated at low temperatures may be used to discover thermal transitions at high temperatures. As we have shown, a crystal–crystal transition that was previously not found using other methods has been located using IGC.

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