PVT properties of main-chain liquid-crystalline polymers

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The densities, as a function of temperature and pressure, of several main-chain liquid-crystalline polymers were measured. The polymers were a copolyester and a series of azomethine ether polymers containing flexible spacer groups along the chain. An equation-of-state theory was developed, which was based on a cell model where expansion of the lattice occurred only in two dimensions. The ability of the theory to describe the *PVT* properties was investigated and compared to a simple cell model that has been used for flexible polymers. It was found that the liquid-crystal cell model described the *PVT* properties of the liquid-crystalline polymers better than the simple cell model. The fit became worse for polymers with flexible spacing groups, and the equation did not describe flexible polymers such as polyethylene. It is inferred that the liquid-crystal model gives a better physical description of the structure of rigid polymers.

(Keywords: liquid crystals; equation of state; spacer group)

INTRODUCTION

The *PVT* properties of substances can be described by equations of state. One class of equations are based on cell models where N molecules, or parts of molecules, are considered to be located within distinct cells. The partition function can be written as[1,2]:

$$Z_n = g[\lambda^{-3} v_f \exp(-E_0/kT)]^N \tag{1}$$

where $\lambda = (h^2/mkT)^{1/2}$; m is the mass of a molecule or molecule segment; E_0 is the potential energy of interaction of a molecule at its origin within its cell with all other molecules, at their cell centres; v_f is the free volume; and g is the communal entropy, which reflects the ability of a molecule to move to other cells, and is taken to be a constant.

The equation of state can then be derived from:

$$P = kT[\mathrm{d}(\ln Z_n)/\mathrm{d}V]_T \tag{2}$$

Within this formalism, the equation of state can be calculated for various cell geometries and for various potential forms for the interaction. Equations have also been developed that include the possibility of vacant cells[3,4], which might hope to work over a wide range of densities where the assumption of a constant value for g may not be a good approximation.

The equations of state that were developed for small molecules have been applied with some success to polymers by assuming that a polymer segment now occupies a lattice site. The problem of connectivity is not properly addressed but, nevertheless, the models perform reasonably well[5,6]. It is found that those equations which assume that the interaction scales as $1/V$, such as that developed by Flory and coworkers, do not describe the *PVT* properties of polymer melts as well as those which are based on a Lennard-Jones 6–12 potential.

In a main-chain liquid-crystalline polymer the orientation and the connectivity would appear to be even more serious problems. In this paper we examine the *PVT* properties of such polymers and the performance of cell models in describing them. We also compare a model that takes into account the orientation and connectivity.

THEORY

In modelling the properties of the liquid-crystalline polymers, we will use a cell model approach. In the cell model, the polymer is assumed to be made up of n mers, which are laid down on a lattice. Each mer is allowed to wander about its cell, and all cells are assumed to be occupied. A clear distinction is made between the internal and external degrees of freedom of each mer. Only the external degrees of freedom are manifested in the *PVT* properties of the liquid. Each mer has $3c$ degrees of freedom and c is a constant independent of the state variables. The mers interact with each other through a Lennard-Jones 6–12 potential. In the case of polymers with a flexible backbone, the connectivity of the polymer chains is taken into account by the choice of the value of c. The partition function for this system is of the form:

$$Z_n = Z_{\mathrm{int}}(T)[v_f^c \exp(-E_0/2kT)]^{nN} \tag{3}$$

where v_f is the so-called free-volume contribution; E_0 is the energy of interaction of a mer at its origin within its cell with all other mers at the origins of their respective cells; and Z_{int} is the contribution from the translational degrees of freedom of each mer and is only a function of the temperature. The equation of state is then derived using equation (2). The equation of state derived in this fashion has contributions from the functions $v_f(V)$ and $E_0(V)$.

In what follows, we will outline the derivation of an equation of state for (a) polymers with flexible backbones and (b) those with 'stiff' backbones. In the case of flexible polymers, we will assume that the mers occupy a hexagonal close-packed (h.c.p.) lattice structure. In the case of liquid-crystalline polymers, we will assume that

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the local structure is such that domains of aligned rigid rods exist and that the rods are arranged with hexagonal symmetry. Using this picture, we can define the cell volume per mer for each of these cases as follows:

$$v=0.707r^3 \tag{4}$$

$$v=0.866lr^2 \tag{5}$$

where r is the intermolecular separation; l is the mer–mer separation along the rigid backbone; and the numerical factors reflect the geometry of the systems. In the case of rigid rods, we are assuming that the molecules are not compressible in the direction along the chains, and in this fashion, explicitly include in the model the connectivity of the molecules. Clearly, these are very crude assumptions but they allow us to derive analytically simple equations to describe the properties of these two different systems. We assume that the mers interact with each other via a Lennard-Jones 6–12 potential of the form:

$$\phi=e[-(r^*/r)^6+(r^*/r)^{12}]] \tag{6}$$

where r is the inter-mer separation; e is a characteristic energy; and r^* is the value of r for which ϕ is zero. In the case of the flexible polymer, we can sum this interaction over all the other mers, and using (4) to express r as a function of v we obtain:

$$E_0=4ez[-A(v^*/v)^2+B(v^*/v)^4] \tag{7}$$

where z is the number of nearest neighbours ($z=12$ for h.c.p. lattice), $A=2.4091$, $B=1.011$ and $v^*=r^{*3}$. In the case of the rigid polymer chains, we first compute the effective interaction of a mer with a neighbouring rigid rod a distance r away. If we then sum the contributions from all the neighbouring rods on a two-dimensional lattice and use the relation (5), we obtain the following expression:

$$E_0=ezr^*[-A(v^*/v)^{5/2}+B(v^*/v)^{11/2}]/l \tag{8}$$

where z is the number of neighbouring rods ($z=6$), $A=1.327$, $B=0.775$ and $v^*=0.866lr^{*2}$.

The function v_f is given by the expression:

$$v_f=\int \mathrm{d}\boldsymbol{a}\,\exp\{-[E(\boldsymbol{a})-E_0]/kT\} \tag{9}$$

where $E(\boldsymbol{a})$ is the interaction energy of a mer at position $\boldsymbol{a}$ within its cell, with all other mers placed at the origins of their respective cells. The integration is performed over the cell volume. In order to evaluate (9), we replace the exact cell potential with a square-well approximation. The function $E(\boldsymbol{a})-E_0$, even with the square-well approximation, is quite complex. To facilitate the calculation, the exact free volume is sphericalized so that it is only a function of the magnitude of $\boldsymbol{a}$. This reduces the problem in our case to computing the volume of the largest sphere that can fit inside the volume defined by the square-well potential. For the case of the flexible polymer, we obtain the following expression:

$$v_f=\text{const.}(v^{1/3}-0.8909v^{*1/3})^3 \tag{10}$$

where we have again expressed r and the hard-core radius in terms of the cell volume and v^*. In the case of the rigid rod, we obtain:

$$v_f=\text{const.}(v^{1/2}-0.9322v^{*1/2})^2 \tag{11}$$

In defining the hard-core radius, we have used the value of r for which the potentials vanish.

Using these expressions for v_f, and those previously derived for E_0 in the partition function (3), we can use equation (2) to derive the equation of state for the two different cases. For the case of the polymer with a flexible backbone, we obtain the following equation:

$$\tilde{P}\tilde{V}/\tilde{T}=\tilde{V}^{1/3}/(\tilde{V}^{1/3}-0.8909) \\ -(2/\tilde{T})(1.2045/\tilde{V}^2-1.011/\tilde{V}^4) \tag{12}$$

where $\tilde{P}=P/P^*$, $\tilde{V}=v/v^*$ and $\tilde{T}=T/T^*$; P^*, T^* and v^* are the reduction parameters, with $T^*=ze/ck$ and $P^*=ckT^*/v^*$. In the case of the rigid-rod polymer, we obtain the following equation of state:

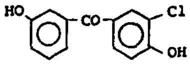
$$\tilde{P}\tilde{V}/\tilde{T}=\tilde{V}^{1/2}/(\tilde{V}^{1/2}-0.9322) \\ -(1/\tilde{T})(3.3175/\tilde{V}^{5/2}-4.263/\tilde{V}^{11/2}) \tag{13}$$

where again $\tilde{P}=P/P^*$, $\tilde{V}=v/v^*$ and $\tilde{T}=T/T^*$, but now $T^*=zer^*/2lck$ and $P^*=ckT^*/v^*$. Equation (12) is the usual cell model that has been shown to be a good description of polymer liquids[5]. Equation (13) is similar to that derived by Ishinabe and Ishikawa for the description of polymer glasses[7]. However, we will consider it here as a model for the polymer liquid-crystal state.

EXPERIMENTAL

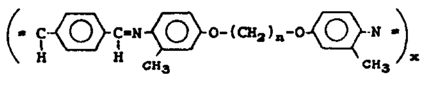
In order to study *PVT* properties it is essential that the polymers studied exist as a nematic liquid-crystal phase over a wide range of temperature and pressure so that the performance of the various theories can be differentiated.

One polymer chosen was a terpolymer composed of the following monomers:



at a mole ratio of 3:1:1. It was prepared by melt polymerization of acetates at 300°C. The inherent viscosity in pentafluorophenol at 60°C was 0.8 g dl^{-1}, and, based on our experience of similar polymers, this infers a weight-average molecular weight between 20 000 and 40 000. It is henceforth designated LCP1. Samples were dried and then pressed at 275°C and broken to form pieces with dimensions of the order 2–5 mm suitable for testing.

The other polymers were a series of azomethine ether polymers with structure:



where the value of n in the flexible spacer group can vary. They are henceforth designated LCPn. These polymers have been described in detail in the literature[8,9]. We used data for those available polymers which existed in the nematic state over a reasonable range of temperature, and these had values of $n=4$, 7, 8 and 9. In order to obtain a moderate melt viscosity and stabilize the polymer for the cases where $n=4$ and 8, it was necessary to use polymers that had been end-capped by the addition of 1/15th mole of p-aminoacetanilide. This was not necessary for the odd-numbered of the series.

The densities of the polymers were measured at room temperature and atmospheric pressure using an autopycnometer (Micromeritics) using approximately 8 g samples. The changes in density as a function of temperature and pressure were measured using a *PVT* apparatus, which has been described fully elsewhere[10]. It consists of a sample cell containing about 1–2 g of sample and mercury as a containing fluid. A flexible bellows closes off one end of the sample cell. The expansion and contraction of this bellows under temperature and pressure changes is used to calculate the volume change of the sample, making allowance for the well known volume change of the mercury. In the isothermal mode, volume readings are obtained at fixed pressure intervals (100 kg cm^{-2} or about 10 MPa apart) at a constant temperature. The temperature is then changed by 8–15°C and the process repeated. The absolute accuracy of the device is $1-2\times10^{-3}$ cm^3 g^{-1}, but volume changes much smaller than this can be resolved. A version of this *PVT* apparatus is available from Gnomix Research, Boulder, CO.

RESULTS

The *PVT* data for the polyester LCP1 are shown in *Figure 1*. It shows a T_g at about 80°C, increasing to about 140°C at 2000 kg cm^{-2}. Above the T_g, there are uniform data associated with the liquid-crystal phase. A few per cent crystallinity is not expected to be observed. Thus, we have up to 250 K of usable data to test the theories.

The *PVT* data for the poly(azomethine ethers) are shown in *Figures 2–5* for structures with flexible segments having $n=4$, 7, 8, 9. The principal transitions and the range of data in the liquid-crystalline phase used for testing the theories are shown in *Table 1*. They all show weak signs of a glass transition in the amorphous fraction a little above room temperature, and this is also evidenced in the polymers' physical handling properties. The polymers also show evidence of increased crystallization (densification) in a region above the T_g. The melting transitions then occur (volume expansion), followed by a period in the nematic phase. The final transition from nematic to isotropic (further volume expansion) occurs at higher temperatures and tends to run into what is probably the limit of thermal stability shown by a falling off in the volume. In each case the range of data available in the nematic phase was about 100 K. It should be noted that all the transitions can be pressure-dependent. The T_g, melting and nematic–isotropic transition are reversed by pressure, depending on thermodynamic and kinetic considerations, and this factor is taken into account when choosing a data set.

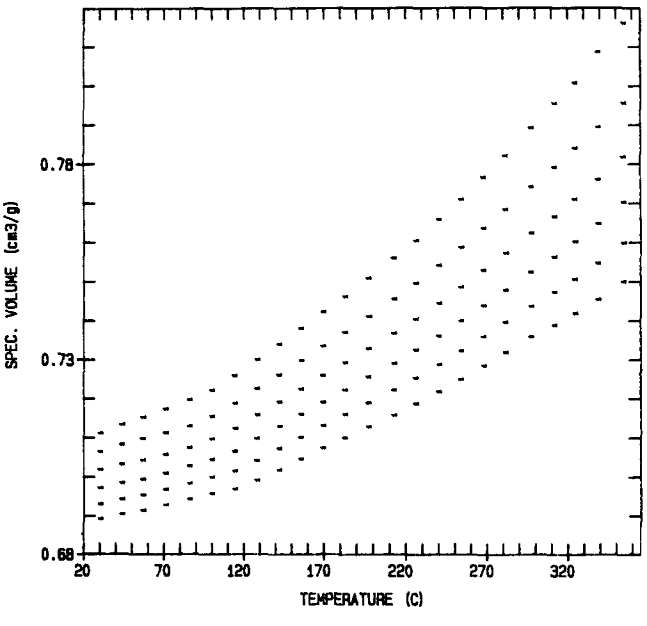


Figure 1 *PVT* data for the liquid-crystalline polyester LCP1, showing plots of volume against temperature at a series of pressures. Only part of the data is shown for clarity

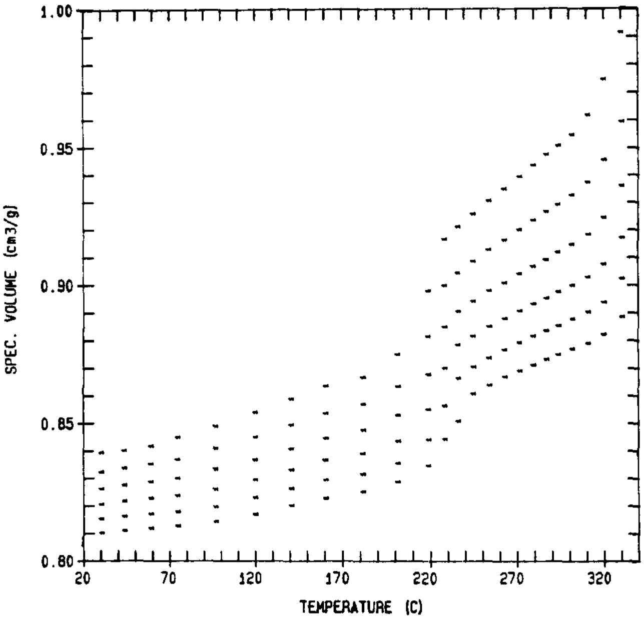


Figure 2 *PVT* data for the liquid-crystalline azomethine ether polymer LCP4, having four CH$_2$ groups in the flexible spacer

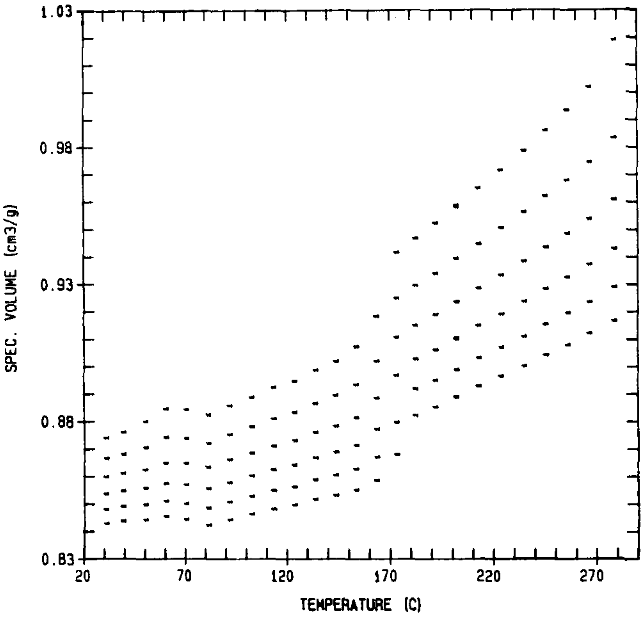


Figure 3 *PVT* data for the liquid-crystalline azomethine ether polymer LCP7, having seven CH$_2$ groups in the flexible spacer

We compared the equations of state described in the 'Theory' section with the same sets of *PVT* data. We performed a nonlinear least-squares fit of each equation by minimizing the quantity:

$$S^2=\sum_i\,[P_i(\text{data})-P_i(\text{fit})]^2/(N-3) \qquad (14)$$

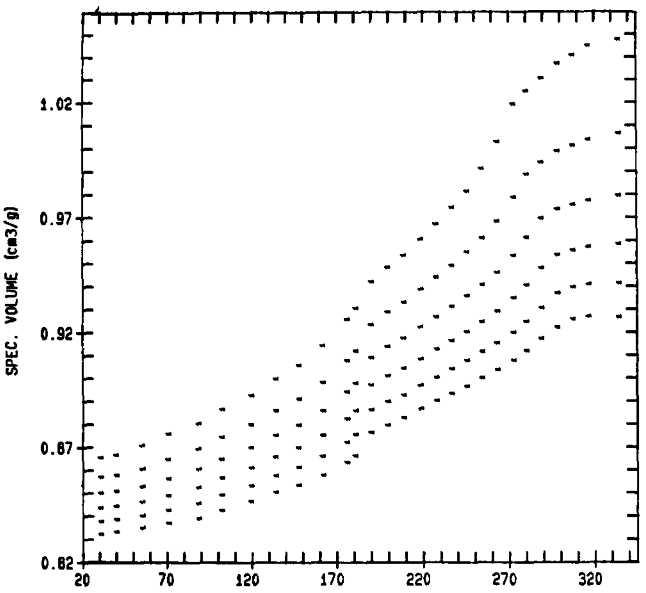


Figure 4 *PVT* data for the liquid-crystalline azomethine ether polymer LCP8, having eight CH_2 groups in the flexible spacer

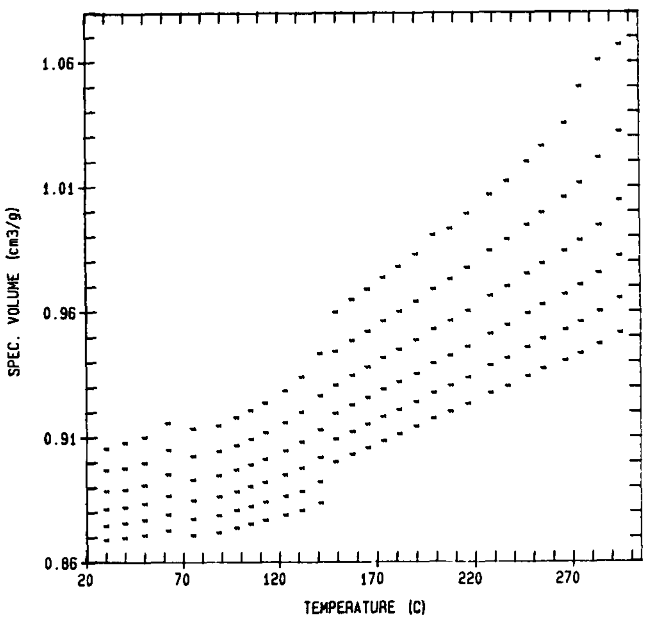


Figure 5 *PVT* data for the liquid-crystalline azomethine ether polymer LCP9, having nine CH_2 groups in the flexible spacer

Table 1 Properties of liquid-crystalline polymers (zero pressure)

	LCP1	LCP4	LCP7	LCP8	LCP9
T_g (°C)	80	<50	<40	<50	<40
M.p. (°C)	–	220	170	180	145
Nem.-iso. (°C)	–	>320	>280	>270	>265
Minimum data used (°C)	105	235	173	189	148
Maximum data used (°C)	356	310	282	272	254

Table 2 The reduction parameters and goodness-of-fit parameters (S^2) for the polymers using the cell model (CM) and liquid-crystal model (LC) theories

Polymer	Model	P^* (MPa)	V^* (cm^3)	T^* (K)	S^2 (MPa^2)	r
LCP1	LC	1021	0.5912	4015	1.41	0.11
	CM	1004	0.6926	6023	12.6	
LCP4	LC	826	0.7114	3930	0.76	0.50
	CM	815	0.8295	5792	1.53	
LCP7	LC	945	0.7135	3300	1.98	1.29
	CM	912	0.8289	4765	1.54	
LCP8	LC	1002	0.7084	3279	0.93	0.30
	CM	959	0.8226	4721	3.06	
LCP9	LC	907	0.7450	3353	1.79	1.08
	CM	887	0.8689	4934	1.66	
Polyethylene	LC	603	0.9694	3006	6.0	3.09
	CM	588	1.1265	4341	1.94	

where N is the number of data points; P(data) is the measured pressure at a given value of (V, T) for the system; and P(fit) is the value of the pressure predicted by the relevant equation of state. In performing nonlinear least-squares regression, the quantity of most statistical significance is the regression sum of squares, S^2. For small data sets (a single isotherm, for example), the value of S^2 as computed for the different equations is of the order of 0.2. This value corresponds to errors in the volume, which is consistent with the precision of the present apparatus. For such small data sets, the various equations are indistinguishable and they all provide adequate fits to the data. Therefore, to use the regression sum of squares as a means to discriminate between these theories, we performed the fitting procedure to liquid data sets which encompassed the largest thermodynamic range available. Under these circumstances, the value of S^2 becomes large. Since much effort has been expended to eliminate systematic errors from the experimental procedure, these values of S^2 reflect the inability of the various equations to fit the data. Under these circumstances, it becomes a trivial matter to compare the equations of state by using the regression sum of squares.

The fits of the data to the three equations are shown in *Table 2*. Also shown is the ratio, r, of the values of S^2 from the LC and CM models. The LC model works better (gives a lower S^2) for the polymers that most closely approximate to a rigid rod, that is the polyester LCP1, which has no flexible spacers, and the poly(azomethine ethers) with the even numbers of CH_2 groups which might be expected to fit most easily into a liquid-crystal structure. The simple cell model fits better with the more flexible polymers. For comparison we have also included fits for a very flexible polymer, polyethylene. It can be seen that the LC theory works poorly in this case.

CONCLUSIONS

It can be seen that the liquid-crystal model equation of state works best for those polymers which are more rigid and worse for those polymers which are more flexible. It is reasonable to infer that this is because the liquid-crystal model gives a better physical description of the structure of rigid polymers.

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