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P–V–T relations in a series of longitudinal polymer liquid crystals with varying mesogen concentration

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Pressure–volume–temperature (P–V–T) relationships were determined for polymer liquid crystal (PLC) solids and melts up to 400°C and 240 J cm^{-3}. We have studied a series of longitudinal PLC copolymers with the formula PET/xPHB, where PET = poly(ethylene terephthalate), PHB = p-hydroxyben-zoic acid (the LC component), with the mole fractions of the LC component $0 \geq x > 0.8$. The P–V–T results are represented by the Hartmann equation of state and its characteristic parameters v^*, T^* and P^* evaluated. In both solid and liquid phases the $v^*(x)$ and $T^*(x)$ curves show minima near the concentration $\theta_{\mathrm{LC\ limit}}$ above which islands of the LC-rich phase are formed. Surface tensions of melts are calculated as a function of x from the P–V–T data for the liquid state using the theory of Prigogine and Patterson. Increasing x first causes lowering of the cohesion of the single-phase structure dominated by the flexible PET. Above $\theta_{\mathrm{LC\ limit}}$ the islands appear to impart their orientation to both phases; this is the channeling effect predicted earlier from the Flory statistical-mechanical theory of PLCs (Blonski *et al.*, *Macromolecules*, 1993, **26**, 84) © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION: APPLICATIONS OF P–V–T DATA

Pressure–volume–temperature (P–V–T) relationships in polymer solids and melts constitute an *underappreciated* kind of knowledge. As a consequence, the amount of information available in this area is far from sufficient. P–V–T data can be used in at least five major areas:

(A) prediction of polymer + polymer miscibility;
(B) prediction of service performance and service life of polymeric materials and components on the basis of free volume concepts;
(C) evaluation of start and progress of chemical reactions in polymer melts in the cases when volume effects accompany the reaction;
(D) optimization of processing parameters, instead of establishing such parameters by trial and error;
(E) calculation of the surface tension of polymer melts.

The dearth of P–V–T data is particularly acute for polymer liquid crystals (PLCs). Exceptions include: V–T results (not full P–V–T) by Achard *et al.* for several combs[1], for some short-chain smectics by Kiefer and Baur[2] and by Engberg *et al.*[3] for some blends of PLCs with amorphous polymers; full P–V–T data by Walsh and coworkers[4] based on the technique of Zoller[5] for several azomethine-ether PLCs, all of them longitudinal, that is with the LC sequences in the main chain along the backbone[6–8].

BASIC RELATIONS

We will now briefly characterize the five areas defined above and at the same time list pertinent equations. In all cases one works with two key (and twin) quantities: the isobaric expansivity (also called the coefficient of thermal expansion, CTE)

$$\alpha = V^{-1}(\partial V/\partial T)_P \tag{1}$$

and the isothermal compressibility

$$\kappa_T = -V^{-1}(\partial V/\partial P)_T \tag{2}$$

As for area *A*, polymer + polymer miscibility is related to the differences between α values of the components. This subject has been well reviewed by Olabisi *et al.*[9], largely on the basis of free volume statistical mechanical theory of Flory *et al.*[10–12]. It should be noted, however, that one can also go from the interfacial tension γ_{ij} towards miscibility prediction. Thus, Sammler *et al.*[13] predict the miscibility from γ_{ij} measured during imbedded fibre retraction. Enders *et al.*[14] connected γ_{ij} to the Gibbs function of mixing. Measuring γ_{ij} by a pendant drop technique, Hu *et al.*[15] have found a reduction in the tension in a binary system caused by the addition of a third component.

Turning now to area *B*, Ferry[16] did pioneering work demonstrating the importance of free volume v^f for mechanical properties of polymer solids. v^f can be defined

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as

$$v^f = v - v* \qquad (3)$$

Here v is the specific volume, for instance in cm^{-3} g; the other quantities are expressed in the same units. $v*$ has been called by Flory *et al.* the net volume[10], and in later publications the hard-core volume[17,12,18]. Both names—as well as equation (3) itself—imply that $v*$ remains when the free volume is 'squeezed out'. While numerical values of v^f depend on the procedure used to compute $v*$, the usefulness of the v^f concept has been amply demonstrated.

Since Ferry's book, further progress in prediction of mechanical performance in terms of free volume has been made. The Williams–Landel–Ferry equation for the temperature dependence of the temperature shift factor a_T turned out to be a special case of a more general formula[19,20]

$$\ln a_T = A + B/(\tilde{v} - 1) \qquad (4)$$

The reduced volume v is used in equation (4), so let us define the pertinent reduced parameters:

$$\tilde{P} = P/P*\,,\ \tilde{v} = v/v*\,,\ \tilde{T} = T/T*\,,\ \tilde{\gamma} = \gamma/\gamma* \qquad (5)$$

where the reducing parameters $P*$, $T*$ and $v*$ are obtainable from experimental P–V–T results via an equation of state (EOS) while γ will be discussed below.

For pre-drawn materials with the draw ratio $\lambda = \varepsilon + 1$, where ε is the engineering strain, equation (4) was generalized further[21,22] to

$$\ln a_T = 1/(a + c\lambda) + B/(\tilde{v} - 1) \qquad (6)$$

where v depends on $T*$ via an EOS, while in turn $T*$ depends also on λ.

Area *B* will be the subject of future papers, in which we shall use the P–V–T results from this work. Area *C* is outside the scope of the present paper, but we would like to note the work of Kressler *et al.*[23] who followed the intramolecular cyclization reaction of poly(acrylonitrile) with poly(styrene-*co*-acrylonitrile) in which a contraction accompanies the reaction. P–V–T data enabled them to determine the onset temperature of the reaction.

Areas C and E involve polymer melts. As for D, unless we know α and κ_T, the establishment of processing parameters is a long and tedious process. Even more importantly, the trial-and-error 'optimization' of processing typically produces acceptable but not the best parameters.

We shall now concentrate on E, for which we also need an EOS. Hartmann[24–26] has developed for both polymer solids and melts the following equation:

$$\tilde{P}\tilde{v} = \tilde{T}^{3/2} - \ln \tilde{v} \qquad (7)$$

Earlier work[27,21] has shown that the Hartmann EOS provide good results in the prediction of long term mechanical performance of polymers on the basis of short-term tests. Moreover, the use of the $\tilde{T}^{3/2}$ term has been justified by Bueche[28] and more convincingly by Litt[29] on the basis of consideration of hole creation. Therefore, we shall also use equation (7) for the present purposes.

The electronics industry and also all industries using adhesives and/or fibre-reinforced heterogeneous composites (HCs) are increasingly interested in the surface tension γ of polymer melts (with respect to air) and also in the interfacial tension γ_{ij} between two condensed phases, such as between two polymers or between a fibre and a polymer matrix. In turn, γ_{ij} depends on γ. It should be noted that for monomer liquid crystals (MLCs) as well as for some comb PLCs there is an *increase* in γ when approaching the clearing (isotropization) temperature from below[30]. While methods of experimental determinations of both γ_{ij} and γ exist, some of these methods are time consuming, while a good method of dynamic imbedded fibre retraction (IFR) developed by Kirjava *et al.*[31] requires fairly elaborate equipment. However, there are theoretical approaches which enable the computation of γ from P–V–T data.

The γ-EOS connection is based on the theory of corresponding states already formulated by Johannes D. van der Waals in 1881. The theory was extended to chain molecules by Prigogine *et al.* in 1950[32,33]. Patterson and Rastogi[34] developed an equation for the computation of γ. This was followed by the work of Siow and Patterson (S-P)[35] and later on by Dee and Sauer[36]. Thus, there are several versions of the theory. We have checked by calculations (which are not included here, for non-PLC polymers) that the best agreement with experimental γ values is provided by the S-P version. According to them, the characteristic surface tension $\gamma*$ may be calculated from the other characteristic parameters, namely

$$\gamma* = (kc)^{1/3} P^{*2/3} T^{*1/3} \qquad (8)$$

where k is the Boltzmann constant. The parameter $c \leq 1$ takes into account the fact that a segment in a polymer chain has $3c$ (rather than 3) degrees of freedom due to the connectedness. However, since this would result in an extra parameter, and such its independent evaluation is difficult, following Patterson *et al.*[34,35] we assume c to be equal to unity. The reduced surface tension is[34,35]

$$\tilde{\gamma}\tilde{v}^{5/3} = m - (1 - \tilde{v}^{-1/3}) \ln [(\tilde{v}^{1/3} - b)/(\tilde{v}^{1/3} - 1)] \qquad (9)$$

Here m is a parameter for which the lowest value recommended by Patterson and Rastogi is 0.29, while the same authors also used succesfully 0.53; clearly large variations are possible. Dee and Sauer[36] recommend $m = 0.52$, but they have also used other values. To minimize the degree of arbitrariness, out of three parameters featured in the theory, b, c and m, we have fixed the first two, so that m is the only one which can be adjusted for a given polymer or class of polymers. We have taken $b = 0.5$ as recommended by previous investigators[34,35]. Equations (8) and (9) were applied with success to several polymers by S-P and also by Kano *et al.*[37] to one more, but *only to flexible* non-PLC polymers. Since the original theory was developed by Prigogine, but the adaptation to polymers—used by us—was by Patterson *et al.*[34,35], in the following we shall refer to it as the Prigogine–Patterson theory. We shall see whether it will give us the capability to obtain the melt surface tension from P–V–T results *also* for PLCs.

EXPERIMENTAL PROCEDURE

The principle of the Gnomix apparatus that we use has been already described in 1976 by Zoller *et al.*[5]. Results for several polymers have been reported since, including those quoted above[4], largely by Zoller *et al.*[38–40]. The sample to be studied can have any shape; its usual weight is between 1.5 and 2.5 g. It is first dried under vacuum for several hours (overnight). Then the sample is placed in a rigid cell with flexible bellows at the bottom and degassed again. The volume which is not taken by the sample is filled with mercury, all the time under vacuum. The cell is installed inside a pressure vessel in which pressures up to 240 J cm^{-3} (=240 MPa) and temperatures up to 400°C can be maintained. The deflection of the bellows resulting from changes in temperature and/or pressure is measured with a linear variable differential transducer (LVDT). These deflections are converted into volume changes of the sample proper on the basis of well-established P–V–T properties of mercury. The accuracy of the Gnomix apparatus as established by Fakhreddine and Zoller[39] is ± $0.002\ \mathrm{cm}^3\ \mathrm{g}^{-1}$ up to 250°C and ± $0.004\ \mathrm{cm}^3\ \mathrm{g}^{-1}$ at higher temperatures, with a sensitivity better than ± $0.0005\ \mathrm{cm}^3\ \mathrm{g}^{-1}$.

Experiments were performed isothermally, with stepwise increases in pressure, starting at 30°C. The results for $P = 0$ were obtained by extrapolation. Three to five samples of each composition were studied, so that several days were needed to obtain results for a given composition; the results presented below constitute averages.

MATERIALS

The PLCs we have studied are all longitudinal, with the same general structure PET/xPHB, where PET is poly(ethylene terephthalate) and PHB is p-hydroxybenzoic acid. We have varied the mole fraction x of the LC (in this case PHB) component in a series of copolymers. The polymers were the same as used and characterized in earlier studies[41–44]. Pure PET and copolymer samples with $0.5 \le x \le 0.8$ were provided by Eastman Kodak Co., Kingsport, TN; samples with $0.24 \le x \le 0.8$ were synthesized by us in Duisburg following the method of Jackson and Kuhfuss[45]; PET/0.6 PHB was also obtained from Unitika Ltd., Kyoto, under their trade name LC-3000; samples with $x = 0.8$ were provided by Prof. Lew Faitelson of the Institute of Polymer Mechanics of the Latvian Academy of Sciences in Riga and synthesized by Prof. Vladilen Budtov and collaborators in St. Petersburg[46]. There were no discernible differences in the P–V–T behaviour of samples with the same x from different sources.

DEPENDENCE OF THE P–V–T PROPERTIES ON THE LC CONCENTRATION

We have studied a series of PET/xPHB copolymers varying x. In other words, we have varied the numbers of liquid crystalline sequences in the chains, with the chemical structure of the building blocks constant throughout the series. $x = 0$ was also included, so as to have a direct measure of the effects of the presence and concentration of LC sequences on P–V–T properties. To our knowledge, no such study was made before.

On the basis of the experimental data we have calculated the characteristic parameters v^*, T^* and P^* in the Hartmann equation of state (7).

The physical significance of v^* was discussed in conjunction with definition (3). T^* is high when the interparticle (intermolecular, intersegmental) interactions are strong; see also the discussion of equation (11) in the following section. The physical significance of P^* has been elucidated by one of us and Szymanski[47]; the result is:

$$P* = [2\pi N/9\mu V]R[\mathrm{d}u(R)/\mathrm{d}R]g(R) \qquad (10)$$

where N/V is the number density (here in segments per unit volume), μ is a geometric factor which depends on the coordination number z (for $z = 6$, one has $\mu = 1$ exactly), $u(R)$ is the interaction potential, $g(R)$ the binary radial distribution function while R is the *average* distance between particles, here between the polymer chain segments.

We have performed computations separately for the solid and separately for the liquid phases. The Hartmann equation (7) reproduces our experimental specific volume values within $0.0026\ \mathrm{cm}^3\ \mathrm{g}^{-1}$, which is comparable to the experimental accuracy; we recall that for each composition we perform three to five runs and the total set of results is used to evaluate the characteristic parameters. Consider now the dependence of v^* on x for the PLC solids shown in *Figure 1*. Starting with pure PET, we see that initially the inclusion of PHB sequences causes a lowering of v^*. We infer that the LC sequences of PHB somehow fit into the structure of PET—a manifestation of the channeling effect discussed more in detail at the end of Section Section 7. Thus, when relatively rigid PHB sequences impart their orientation to PET, the hard-core volume v^* of the material decreases.

However, at around $x = 0.3$ we have the $\theta_{\mathrm{LC\ limit}}$ above which a second predominantly LC phase (*islands*[48]) is formed from the LC-poor (matrix, PET-rich) phase; see the phase diagram of PET/xPHB copolymers in reference [41]. The islands have relatively well-oriented LC sequences, as studied by wide-angle X-ray scattering (WAXS)[49]. Given the connectedness between the LC and flexible sequences in the chains, an overall increase in x also produces an increase in the concentration of LC sequences outside of the islands

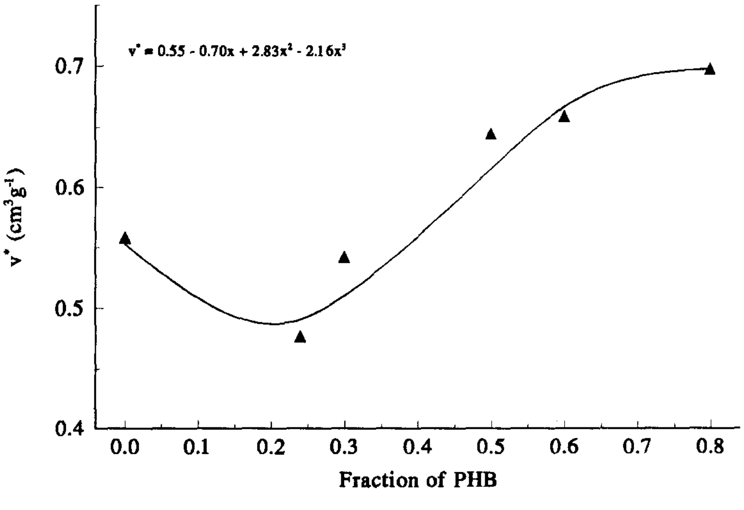

Figure 1 Dependence of the characteristic parameter v^* of the Hartmann equation of state on the concentration x of liquid crystalline (PHB) sequences in PET/xPHB copolymers for the solid phases

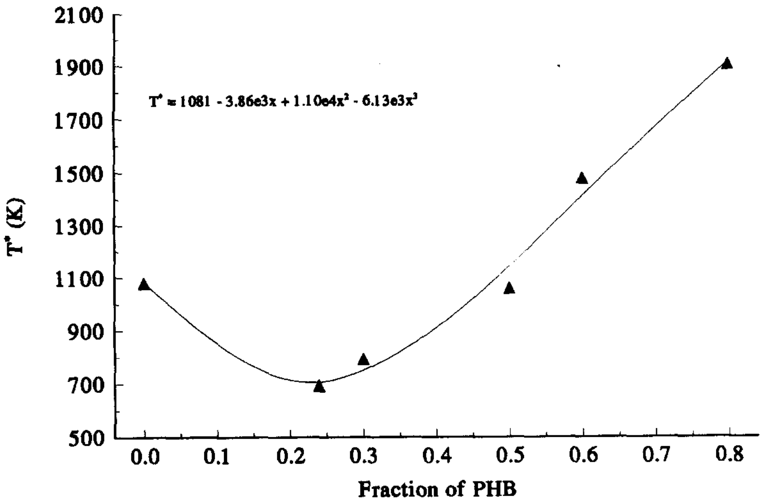

Figure 2 Dependence of the characteristic parameter T^* of the Hartmann equation of state on the concentration x of liquid crystalline (PHB) sequences in PET/xPHB copolymers for the solid phases

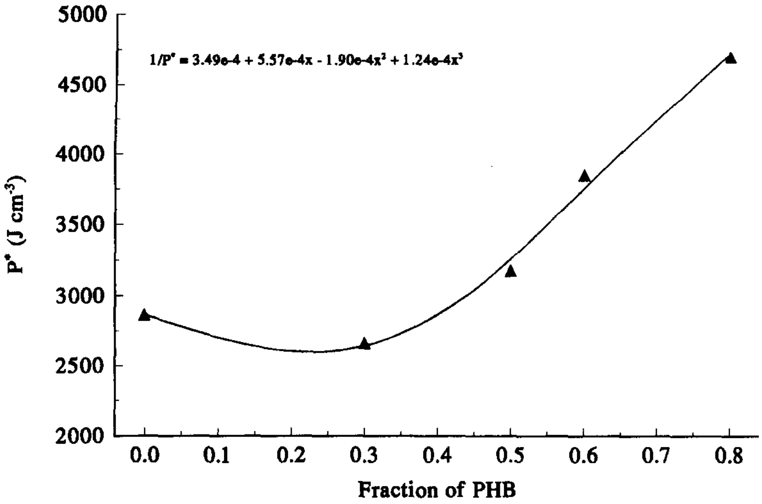

Figure 3 Dependence of the characteristic parameter P^* of the Hartmann equation of state on the concentration x of liquid crystalline (PHB) sequences in PET/xPHB copolymers for the solid phases

in the LC-poor phase. Below $\theta_{\mathrm{LC\ limit}}$, the PHB sequences caused an orientation in the PET-rich phase; above that limit *disruption* of that phase by the appearance of the PHB-rich phase apparently dominates the situation. Since v^* pertains to the entire two-phase PLC, we see that it goes symbatically with x after passing through the $\theta_{\mathrm{LC\ limit}}$. The values of v^* at $x \geq 0.5$ are higher than those for pure PET, showing that the LC sequences in the solid cannot be compressed as easily as flexible PET sequences.

Figure 2 shows the behavior of T^* as a function of x in the solid state. The diagram can be explained in terms of $\theta_{\mathrm{LC\ limit}}$ similarly as $v^*(x)$. Above $\theta_{\mathrm{LC\ limit}}$ we see an increase in T^*, clearly due to the increased orientation of the LC sequences. Since T^* is related to α, more aspects of *Figure 2* are discussed in Section 6.

Figure 3 presents the $P^*(x)$ curve for the solid state. At first variations of P^* with x are not large, but a clear increase is visible above $\theta_{\mathrm{LC\ limit}}$, similarly for v^* and T^*. As equation (10) informs us, P^* is a relatively complex function, but it is proportional to the radial distribution function $g(r)$. An analytical formula for $g(r)$ is available[50]. Concentrating on the first maximum of $g(r)$, it should become higher in a system with a higher degree of orientation. Since the extent of orientation is proportional to x, the increase of P^* at high x values is explained.

Figure 4 shows the $v^*(x)$ diagram for the liquid PLC phases. The shape is similar to that of the $v^*(x)$ curve for solids—and for the same reasons. Moreover, note that at $x = 0$ the absolute value of v^* for the liquid is higher than that for the solid. Clearly the hard-core (incompressible) volume in a polymer liquid is higher than in the respective solid, a consequence of higher thermal energy in the molten state. However, along with the x increase, the difference $\Delta v^* = v^*_{\mathrm{liq}} - v^*_{\mathrm{solid}}$ becomes insignificant. The values of v^*_{liq} have been obtained on the basis of P–V–T results above the melting point but *below* the clearing points of the copolymers. Once again the extent of ordering imparted by LC sequences dominates the structure at high x values. Apparently that ordering is similar in the solid and in the LC phases.

Figure 5 presents the $T^*(x)$ diagram for the PLCs in the molten states, again below the clearing temperatures. The shape of the curve is similar to the $T^*(x)$ curve for the solids, and arguments in terms of $\theta_{\mathrm{LC\ limit}}$ similar to those above for v^* apply here too—as does the discussion of T^* in the following section. At the same time, there is

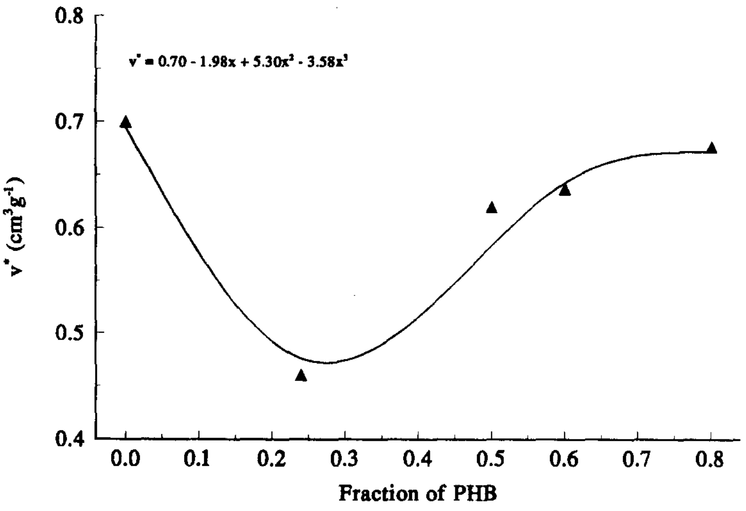

Figure 4 Dependence of the characteristic parameter v^* of the Hartmann equation of state on the concentration x of liquid crystalline (PHB) sequences in PET/xPHB copolymers for the melt phases below the clearing temperatures

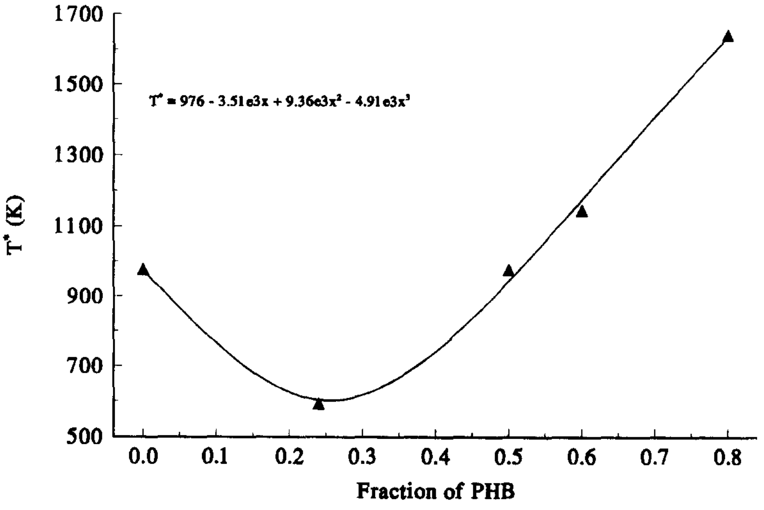

Figure 5 Dependence of the characteristic parameter T^* of the Hartmann equation of state on the concentration x of liquid crystalline (PHB) sequences in PET/xPHB copolymers for the melt phases below the clearing temperatures

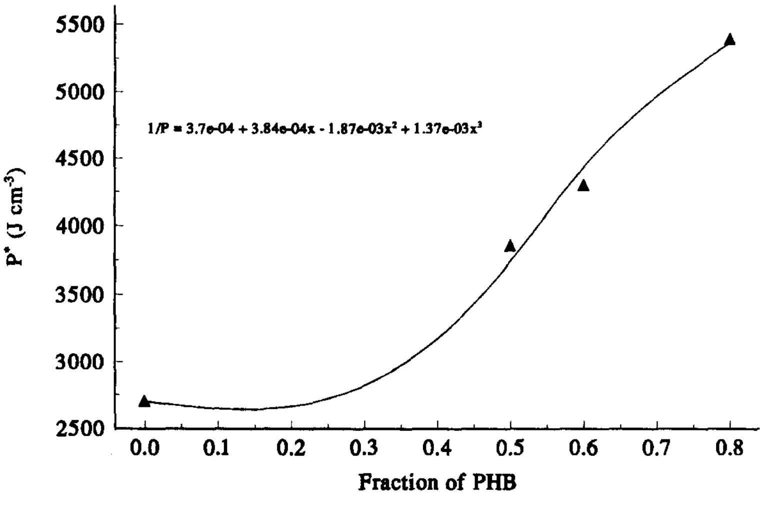

Figure 6 Dependence of the characteristic parameter v^* of the Hartmann equation of state on the concentration x of liquid crystalline (PHB) sequences in PET/xPHB copolymers for the melt phases below the clearing temperatures

a clear difference between the two phases: for any x, we have $T^*_{\mathrm{solid}} > T^*_{\mathrm{liq}}$. This is expected: we have shorter intersegmental distances (thus stronger interactions) in the solid phases than in the melts. Thus, the experiments also testify to the physical significance of the Hartmann EOS parameters.

Figure 6 shows the $P^*(x)$ diagram for the PLC melts in their LC states. As in the solids, the highest value of P^*

corresponds to the highest $x = 0.8$; the explanation for this is also analogous to that for the solids. We also have $P^*_{\mathrm{solid}} < P^*_{\mathrm{liq}}$ for all x. This is in spite of the fact that the number density N/V is higher in the solids. Equation (10) also tells us that P^* is proportional to $[\mathrm{d}u(r)/\mathrm{d}r]g(R)$. Consider the most popular interaction potential developed by Mie in 1903 and discussed for instance in reference [51]. Using the Mie potential, one of us and Szymanski[47] analysed the dependence of $[\mathrm{d}u(r)/\mathrm{d}r]g(R)$ on R. It was found that beyond the minimum R_m of the Mie potential a rapid increase of $P^*(R)$ takes place. Since R is the average value for the material, in the solid we have $R \approx R_m$. Going from the solid to the liquid, we have an increase in R beyond R_m, therefore an increase in P^*—as indeed observed experimentally.

COMPARISON OF ISOBARIC EXPANSIVITY OF FLEXIBLE POLYMERS AND PLCS IN THE SOLID STATE

Industry is increasingly interested in materials with low thermal expansivity. Since liquid crystallinity is often connected to rigidity, one expects that PLCs have values lower than engineering polymers (EPs), since the latter are typically flexible. Before analysing our actual data, however, let us find out what the Hartmann equation of state (7) tells us about the isobaric expansivity. For pressure $P = 0$, definition (1) in conjunction with equation (7) gives

$$\alpha = 3\tilde{T}^{1/2}/2T* \qquad (11)$$

This result enhances our understanding of the physical significance of the characteristic parameters v^* and T^*. Perhaps contrary to some expectations, v^* does not appear in equation (11) at all. v^* is known to reflect the molecular structure, including degree of branching, length of branches, etc.—as argued before in references [19–22]; this interpretation can be based on equation (3). As mentioned in the preceding section, T^* is known to represent energetics in the material, specifically the internal cohesion or the strength of intermolecular (in polymers intersegmental) interactions. Equation (11) confirms these interpretations for both v^* and T^*. With a temperature change the molecular structure does not change, hence, v^* does *not* appear in the equation. Moreover, higher T^* means stronger interactions, that is lower α—as predicted by equation (11). At the same time, the isobaric expansivity increases with increasing T since this also lowers the cohesion in the material. Thus, T^* deals with intrinsic energy density of the material while T reflects the energy input from the surroundings.

The increase in T^* with x above $\theta_{\mathrm{LC\ limit}}$, shown for solids in *Figure 2*, now confirms that indeed more liquid crystallinity (more rigidity) lowers the isobaric expansivity of the material. From equation (11) and the polynomial fit displayed as an insert in *Figure 2*, we find for $T = 298$ K that $\alpha = 9.57\times10^{-4}\ \mathrm{K}^{-1}$ for $x = 0$. For $x = 0.8$ the calculation gives less than the half of that value, namely $\alpha = 4.10\times10^{-4}\ \mathrm{K}^{-1}$; the purely experimental values are comparable, for this concentration we have $\alpha = 3.42\times10^{-4}\ \mathrm{K}^{-1}$.

It is instructive to extrapolate the connection we have found between the degree of orientation, T^* and α to non-PLC polymers. If our connection is valid there too, then an increase in orientation should decrease α. Changes in the expansivity of polyethylene caused by drawing have been analysed by Choy[52]. It turns out that indeed orientation caused by drawing results in decreases in α in the direction perpendicular to drawing, and even negative α-values along the draw direction.

CALCULATION OF SURFACE TENSION OF POLYMER MELTS FROM P-V-T RESULTS

As noted in Section 2, experimental determination of the polymer melt surface tension requires fairly elaborate equipment, and reliable such data are scarce. There are, however, γ results of Kiryava *et al.*[31] for polypropylene (PP) and for our PET/0.6 PHB at 523 K. Given the three adjustable parameters in the Prigogine–Patterson theory, b, c and m, already discussed in Section 2, we have decided to fix the first two. Using equations (8) and (9) and the last of equation (5) *a rebours*, as well as the Hartmann EOS parameters for PP[25], we have obtained $m = 0.705$ at 523 K. A similar calculation has been made for PET/0.6 PHB, using the EOS parameters determined in Section Section 5. This leads to $m = 0.860$, and we have assumed that this value does not change with x. Now equations (5), (8) and (9) have been solved for γ for $x \neq 0.6$ and the melt temperature $T = 523$ K.

The invariance of the Prigogine–Patterson parameter m with x is a plausible assumption, except perhaps for $x = 0$, that is for pure PET with no liquid crystallinity. However,

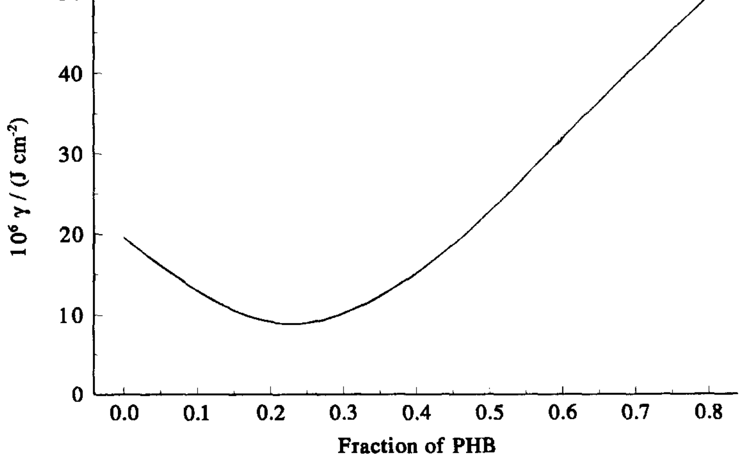

Figure 7 Dependence of the surface tension γ on the concentration x of liquid crystalline (PHB) sequences in PET/xPHB copolymers in the melt phase calculated from equation (5), equation (8) and equation (9) for $T = 523$ K

our predicted value γ (PET, 523 K) = $19.6\times10^{-6}\,\mathrm{J\,cm^{-2}}$ can be compared with γ (PET, 563 K) = $(27 \pm 3) \times 10^{-6}\,\mathrm{J\,cm^{-2}}$ quoted in a table by Wu[53]. Given problems with the experimental determination of γ as noted above, and the assumption we have made, the agreement is satisfactory.

The results of the calculation of the surface tension are shown in *Figure 7*. The phase diagram of the PET/xPHB copolymers[41] shows that at 523 K we have smectic E and smectic B phases coexisting with the isotropic liquid. Starting with $x = 0$ in *Figure 7*, it can be seen that the increase in x first causes lowering of γ. We infer that the cohesion of the single-phase structure dominated by the flexible PET is diminished by the addition of LC sequences of PHB. As already noted in Section 5, the same phase diagram[41] shows that at $x \approx 0.3$ we have $\theta_{\mathrm{LC\ limit}}$ at which the formation of the LC-rich islands begins. If we were dealing with blends, we would have the concentration θ of the LC sequences different from the mole fraction x of the same sequences in the PLC component; for our copolymers of course $\theta = x$, hence also $\theta_{\mathrm{LC\ limit}} = x_{\mathrm{LC\ limit}}$. Above the limit it can be seen that γ goes symbatically with x, similarly in fact as did the characteristic parameters in the earlier figures.

To explain the increase in γ with x above $\theta_{\mathrm{LC\ limit}}$, we recall the statistical-mechanical theory of LC systems developed by Flory[54,55] and extended by us[56–59]. Calculations from the theory have shown that LC sequences cause *channeling* of flexible sequences (and of solvent molecules[57]). The channeling should results in the alignment in the melt. This is indeed observed experimentally, as demonstrated in *Figure 5* above $\theta_{\mathrm{LC\ limit}}$ by the increase in T^* along with an increase in x. Above $\theta_{\mathrm{LC\ limit}}$, for the same reason γ should increase as well—and we see this in *Figure 7*. The LC phases (such as smectic E, smetic B, or both) impart their orientation to the LC-poor phase via channeling and thus enhance the overall orientation.

SOME CONCLUDING REMARKS

We have been concerned primarily with the P–V–T behaviour of our series of PLC copolymers. However, the γ values obtainable via the EOS and the Prigogine–Patterson theory can be used for several purposes. To give an example, creation of synthetic polymer+wood composites involves the knowledge of the capillary rise of the molten polymer in wood pores, a problem analysed theoretically by Kostiukov[60,61].

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