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Lincoln S. Gomes[a]; Nicole R. Demarquette Corresponding author[a]; Renato N. Shimizu[a]; Musa R. Kamal[b]
[a] Metallurgical and Materials Engineering Department, Avenida Prof. Mello Moraes, 2463 - Cidade Universitária, CEP 05508-900, University of São Paulo, São Paulo, Brazil [b] Chemical Engineering Department, McGill University, Montreal, Quebec H3A 2B2 Canada

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Influence of temperature on surface tension of three liquid crystal polymers and polyethylene terephtalate

LINCOLN S. GOMES, NICOLE R. DEMARQUETTE*,
RENATO N. SHIMIZU
Metallurgical and Materials Engineering Department, Avenida Prof. Mello
Moraes, 2463 – Cidade Universitária, CEP 05508-900, University of São Paulo,
São Paulo, Brazil

and MUSA R. KAMAL
Chemical Engineering Department, McGill University, 3610 University Street,
Montreal, Quebec H3A 2B2 Canada

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In this work Pressure Volume Temperature (*PVT*) data for three different liquid crystal polymers (LCPs), namely Vectra A950® and two LCPs based on 4,4′-dihydroxybiphenyl (PB-*n*) (where *n* is the number of methylene units present in the polymer) and polyethylene terephtalate (PET), were obtained for temperatures ranging from 50 to 300°C and pressures ranging from 0.1 to 200 MPa. The experimental data were fitted to the Flory–Orwoll–Vrij equation of state and used to predict the influence of temperature on the surface tension of the four materials studied.

The surface tension of PET was shown to decrease linearly with increasing temperature. The surface tension of both PB-11 ($\gamma_{\text{PB-11}}$) and Vectra A950® (γ_{Vectra}) decreased linearly with increasing temperature for temperatures corresponding to the nematic phases of the materials. Abnormal behaviour was observed for the surface tension of PB-8 ($\gamma_{\text{PB-8}}$): at temperatures just above T_b (the temperature at which the material became birefringent), γ levelled off and then decreased. A clear discontinuity was observed for both $\gamma_{\text{PB-8}}$ and $\gamma_{\text{PB-11}}$ near the mesophase to isotropic transition. For both PB-8 and PB-11, γ decreased linearly with increasing temperature for temperatures corresponding to the isotropic phases of the materials.

1. Introduction

Liquid crystal polymers (LCPs) have been the subject of intense research in the past few decades, due to their various applications such as high strength fibres, processing aids and electro-optical devices [1, 2]; it is thus important to evaluate properties such as surface tension. The knowledge of the surface tension of materials, or interfacial tension between materials, provides important information about adhesion, wetting and the quality of the morphology of a blend involving these materials.

However, few studies have been reported in the literature on the surface tension of LCPs [3, 4]. Research has been limited in this field because there exist few methods that can be used to measure the surface tension of molten polymers, because of shortcomings of the experimental techniques, e.g. inability to ascertain equilibrium accurately and long equilibration times that would exceed the time for a melt to undergo degradation [5]. If studies dealing with the surface tension of low molar mass liquid crystals (LMMLCs) are numerous [6–26], this is not the case for LCPs. The few reported studies indicate that the behaviour of the surface tension as a function temperature of LCPs is very similar to that of LMMLCs, i.e. surface tension, in the nematic phase, decreases with increasing temperature and shows a clear discontinuity close to the nematic to isotropic transition temperature of the LCPs [3, 4].

Several thermodynamic theories have been developed to evaluate the surface tension of molten polymers. These theories can be divided in two groups: (i) those based on the square gradient theory first developed by Cahn–Hilliard (CH) which correlate the surface free energy to the density and square gradient of density profile at the surface, and [27–33] (ii) the cell model

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*Author for correspondence; e-mail: nick@usp.br

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theories that rely on the fact that surface tension follows a principle of corresponding states [27, 32, 34–37]. The latter theories correlate the reduced surface tension, $\tilde{\gamma} = \gamma/\gamma^*$, to reduced parameters for pressure, $\tilde{P} = P/P^*$, volume, $\tilde{V} = V/V^*$, and temperature, $\tilde{T} = T/T^*$, where γ, P, V, T are, respectively, the surface tension, pressure, specific volume and temperature of the system. The starred quantities, reduction parameters, represent the hard core values. The reduced parameters for pressure, volume, and temperature can be obtained from experimental *PVT* data via an equation of state. Several theories have been developed for computing surface tension from *PVT* data [27, 34–36]. The use of the cell theories to evaluate the surface tension of polymers is of great interest because *PVT* data are easily obtained thanks to the development of *PVT* apparatus [38–40], and because they are relatively simple mathematically, when compared with square gradient theories. These theories are explained briefly below; more details can be found in several references [27, 34–36, 41].

Patterson and Rastogi [36] and later Dee and Sauer [27, 34] used a cell formalism to generate an expression to predict the surface tension of a polymer as a function of the thermodynamic properties of that polymer. In both theories, the authors considered a lattice of cells to generate a partition function that was used to calculate the free energy of the inhomogeneous system with a free surface. An expression of surface tension directly related to the free energy was then generated. Equations (1) and (2) present the expressions for reduced surface tension generated for both Patterson and Rastogi [36] and Dee and Sauer's theories [27, 34]:

$$\tilde{\gamma} = \frac{m}{\tilde{V}^{5/3}} - \frac{\left(1 - \tilde{V}^{-1/3}\right)}{\tilde{V}^{5/3}} \ln\left[\frac{\left(\tilde{V}^{1/3} - 0.5 b_{\mathrm{PR}}\right)}{\left(\tilde{V}^{1/3} - b_{\mathrm{PR}}\right)}\right] \tag{1}$$

$$\tilde{\gamma} = \frac{\gamma}{\gamma^*} = \frac{m}{\tilde{V}^{5/3}} - \frac{\tilde{T}}{\tilde{V}^{2/3}} \ln\left[\frac{\left(b_{\mathrm{DS}} \tilde{V}^{1/3}\right)}{\left(\tilde{V}^{1/3} - 1\right)}\right] \tag{2}$$

with

$$\tilde{\gamma} = \frac{\gamma}{\gamma^*} = \frac{\gamma}{P^{*2/3} T^{*1/3} (kc)^{1/3}}. \tag{3}$$

Here $\tilde{V}$, $\tilde{T}$, P^* and T^* are the reduced volume and temperature, and reduction pressure and temperature, respectively; $\tilde{\gamma}$ and γ^* are the reduced and reduction surface tension, m represents the number of nearest neighbours lost when diffusing from bulk to interface, c is a lattice parameter, b_{PR} and b_{DS} correspond to the packing factors of Patterson–Rastogi and Dee and Sauer's theories, respectively, and k is the Boltzman constant.

The packing factors for each theory, b_{PR} and b_{DS}, differ in their definitions. For the Patterson–Rastogi theory, b_{PR} is related to the potential used to model the interaction between the polymer units. Depending on the formalism used for the potential, b could be equal to 0.89 or 1. For Dee and Sauer's theory, b_{DS} is a parameter that correlates the free volume of the polymer units in the surface layer to that of those in the bulk. c is a constant that takes into account the connectivity of the different units of the polymers assuming that each mer has $3c$ (where c is a constant smaller than 1) degrees of freedom. Fitting their theory to surface tension experimental data for various polymers, Patterson and Rastogi [36] recommended the use of $m = 0.25$ and $b_{\mathrm{PR}} = 1$, because other values would lead to lower values of surface energy and entropy. Dee and Sauer [27, 34] fitted their theories to experimental data generated for various polymers to find the best values of m and b_{DS}. In their theoretical prediction they chose a value of c so that the core volume was of the order of the dimension of the chemical unit of polyethylene [28]; the value of c was 0.11. The values of b_{DS} and m producing the best fit to the experimental data were, respectively, of the order of 2 and 0.52.

In order to infer the surface tension using equations (1) and (2) it is necessary to know the reduced and reduction parameters. These parameters can be obtained by differentiation of the Flory–Orwoll–Vrij equation of state which is given by [42]:

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{\tilde{V}^{1/3}}{\tilde{V}^{1/3} - 1} - \frac{1}{\tilde{V}\tilde{T}}. \tag{4}$$

Differentiation of this equation of state with respect to temperature at constant pressure at zero volume, and with respect to temperature at constant volume at zero pressure, yields the reduced volume and pressure as follows:

$$\tilde{V} = \frac{V}{V^*} = \left(\frac{1 + T\alpha}{1 + 4T\alpha/3}\right)^{1/3} \tag{5}$$

$$\tilde{P} = P/P^* = P/\left(\tilde{V}^2 T\alpha/\beta\right) = P/\left(\tilde{V}^2 T\lambda\right) \tag{6}$$

where $\alpha = \frac{\partial \ln V}{\partial T}|_P$ is the thermal expansion coefficient; $\lambda = \frac{\partial P}{\partial T}|_V$ is the thermal pressure coefficient and $\beta = -\frac{\partial \ln V}{\partial P}|_T$ is the isothermal compressibility.

The reduced temperature can then be obtained algebraically using equations (5) and (7):

$$\tilde{T} = T/T^* = \left(\tilde{V}^{1/3} - 1\right)/\tilde{V}^{4/3}. \tag{7}$$

The combination of equations (1) to (7) with the knowledge of experimentally determined $V(T)$, $\alpha(T)$, $\lambda(T)$ or $\beta(T)$ is sufficient for the determination of the reduced and reduction parameters $\tilde{P}$, $\tilde{V}$, $\tilde{T}$, V^*, P^* and T^*, respectively.

In this work *PVT* data for three different liquid crystal polymers and polyethylene terephthalate were obtained and used to predict their surface tensions as a function of temperature.

2. Materials and experimental procedures

Three different liquid crystal polymers (LCPs) represented in figures 1 (*a*) and 1 (*b*) were used in this work: a random co-polyester based on *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA), namely Vectra A950® from Ticona Polymers, figure 1 (*a*); and two LCPs based on 4,4′-dihydroxybiphenyl (PB-*n*), figure 1 (*b*), where *n* is the number of methylene units in the polymer. The two PB-*n* studied in this work were synthesized by the reaction between dicarboxylic acid and 4,4′-dihydroxybiphenyl following the method of Asrar *et al.* [43]. Commercially available polyethylene terephthalate (PET) (S800 from Rhodia Ster do Brazil) was also used, figure 1 (*c*).

The transition temperatures of the LCPs were obtained by differencial scanning calorimetry using a DSC-50 Shimadzu calorimeter. Indium and lead standards were used for temperature calibration. The samples (5 mg) were examined at a scanning rate of 10°C min^{-1} under nitrogen and the transition temperatures were taken during the second run. The transition temperatures were also determined by observing the texture changes using an Olympus polarizing microscope equipped with a Mettler FP82 hot stage. The samples were held between a slide and a cover slip and photographs were taken with a Hitachi CCD KP-M2U camera.

PVT data were obtained using a dilatometer manufactured by Gnomix; the data were measured in the isothermal mode. The measurements consisted of the recording of volumes along isotherms with increasing pressures from 0.1 to 200 MPa by increments of 10 MPa. A typical experiment started at room temperature under 0.1 MPa; the sample was then heated to the desired temperature. After temperature stabilization, the pressure was increased to 200 MPa by increments of 10 MPa. The holding time, which is the time that the program pauses at each of the pressure points requested, was set at a value of 20 s, taking into account a compromise between accuracy and thermal degradation. After reaching 200 MPa, the pressure was released and the sample heated to the next isotherm. Details of the apparatus and the different modes of operation have already been described by Zoller [38–40] and Capt and Kamal [44]. Before the *PVT* measurements, the densities of the samples were determined with a pycnometer at 30°C under atmospheric pressure.

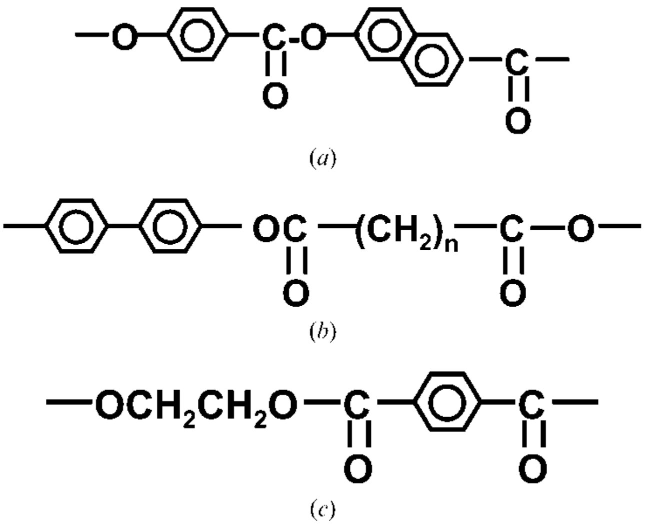


Figure 1. Chemical structure of the compounds used in this work: (*a*) Vectra A950, (*b*) PB-*n*, (*c*) PET.

3. Results and discussion

Figures 2 (*a*) and 2 (*b*) show typical thermograms for PB-8 and PB-11, respectively. Two peak temperatures

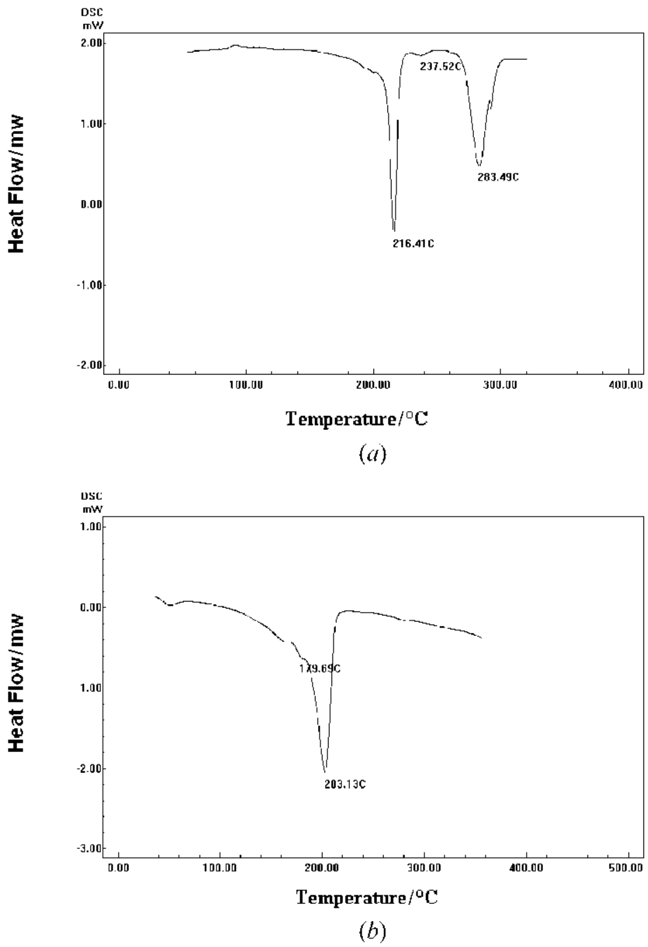


Figure 2. DSC curves for PB-8 and PB-11: (*a*) PB-8, (*b*) PB-11.

(labelled T_b and T_i) were observed during the second cycle at a rate of 10°C min^{-1} for PB-8 and PB-11. The same results were obtained for four different samples. The transition temperatures of the various polymers studied here, measured by DSC are reported in table 1. Table 1 also shows the temperature T_b at which the crystalline phases transformed into birefringent liquid, and the temperature T_i at which the entire system became isotropic, obtained through the observation of mesophases as a function of temperature. For temperatures ranging from 186 to 200°C PB-11 exhibited a schlieren texture characteristic of a nematic phase [47]. The optical observations showed that PB-8 exhibited a smectic phase for temperatures ranging from 215 to 283°C, corroborating the results of Asrar *et al.* [43]. The transition temperatures obtained through the analysis of *PVT* measurements are also reported in table 1, see figures 3 (*a–d*) and 4 (*a*, *b*). These temperatures were taken as those at which the thermal expansion coefficient, $\alpha = -\left(\frac{\partial \ln V}{\partial T}\right)$, suffered a discontinuity.

It can be seen from table 1 that the transition temperatures obtained for the four samples, using the three different experimental methods used in this work, corroborate within experimental error. It can also be seen that, except for PB-11, the values of transition temperature obtained here corroborate the values reported in the literature [43]. The differences observed for PB-11 could be due to a low molar mass of the samples synthesized in this work when compared with the literature reported samples. Figure 2 (*a*) clearly indicates that the temperature at which PB-8 transforms into a birefringent structure, T_b, and the clearing temperature, T_i, are well defined first order transition temperatures. The same cannot be said for the T_b of PB-11, most likely because of the proximity of the two transition temperatures of PB-11. The transition observed at 237°C (T_2) by *PVT* could correspond to the melting of a small proportion of high molecular mass crystallites corroborating the small shoulder observed in the melting point of 283°C.

Figures 3 (*a–d*) show the *PVT* (*V-T*) data for PET and the three LCPs used in this work. The uncertainty of the results was 0.003 g cm^{-3}. The values of specific volume were extrapolated to atmospheric pressure using polynomial expressions, those values are indicated by open squares.

Figures 4 (*a*, *b*) and 5 (*a*, *b*) show the density at atmospheric pressure and the thermal expansion coefficient, $\alpha = -\left(\frac{\partial \ln V}{\partial T}\right)$, for PET and the three different LCPs as a function of temperature. Both quantities were fitted to polynomial functions by least square regressions. The fitting parameters of the regressions are given in table 2.

It can be seen that the specific volumes of the different polymers studied in this work can be ranked in the following order: Vectra A950® < PET < PB-8 < PB-11. This order can be explained by the chemical structure of the molecules: specific volume seems to be a decreasing function of the rigidity of the molecules. Using equation (5) the free volume $f_v = (V - V^*)/V$ at the vicinity of the isotropic to nematic transition was evaluated and found to be around 0.23, for both PB-8 and PB-11, corroborating the results obtained by Abe *et al.* [48] for CBA-9 and CBA-10. It can also be seen from figure 5 (*b*) that the thermal expansion coefficient increase rapidly in the pretransition regions as T approches T_i, and then decreases with increasing temperature when $T > T_i$ for both PB-8 and PB-11. Such behaviour is well known for liquid crystal substances [48].

In order to evaluate the surface tension of these substances using equations (1) to (3) it was necessary to evaluate the isothermal compressibility, $\beta = -\frac{\partial \ln V}{\partial P}\big|_T$, which was found fitting $\ln V = f(P)$ at a constant temperature, for pressures ranging from 0 to 40 MPa, to a straight line. The values of β were also fitted to polynomial functions by least square regression and the fitting parameters of the regression are also given in table 2. Knowing the values of α and β, it was then possible to infer the values of surface tension as a function of temperature. Figures 6, 7 (*a*) and 7 (*b*) show the surface tension as a function of temperature for PET and the three different liquid crystal polymers

Table 1. Transition temperatures (°C). T_b is the temperature at which the crystalline structures transform into birefringent structures, T_i is the temperature at which the mesophase turns into a isotropic structure, T_g is the glass transition temperature, T_m is the melting temperature.

	PB-8			PB-11		Vectra A950	PET	
	T_b	T_2	T_i	T_b	T_i	T_b	T_g	T_m
DSC	216	237	283	180	203	282	75	244
Observation of mesophases	215	Not observed	277	186	200	Not observed	—	—
PVT	210	240	280	185	205	Not observed	75	248
Literature	215 [43]		285 [43]	213 [43]	216 [43]	282 [45]	70–80 [46]	250–265 [46]

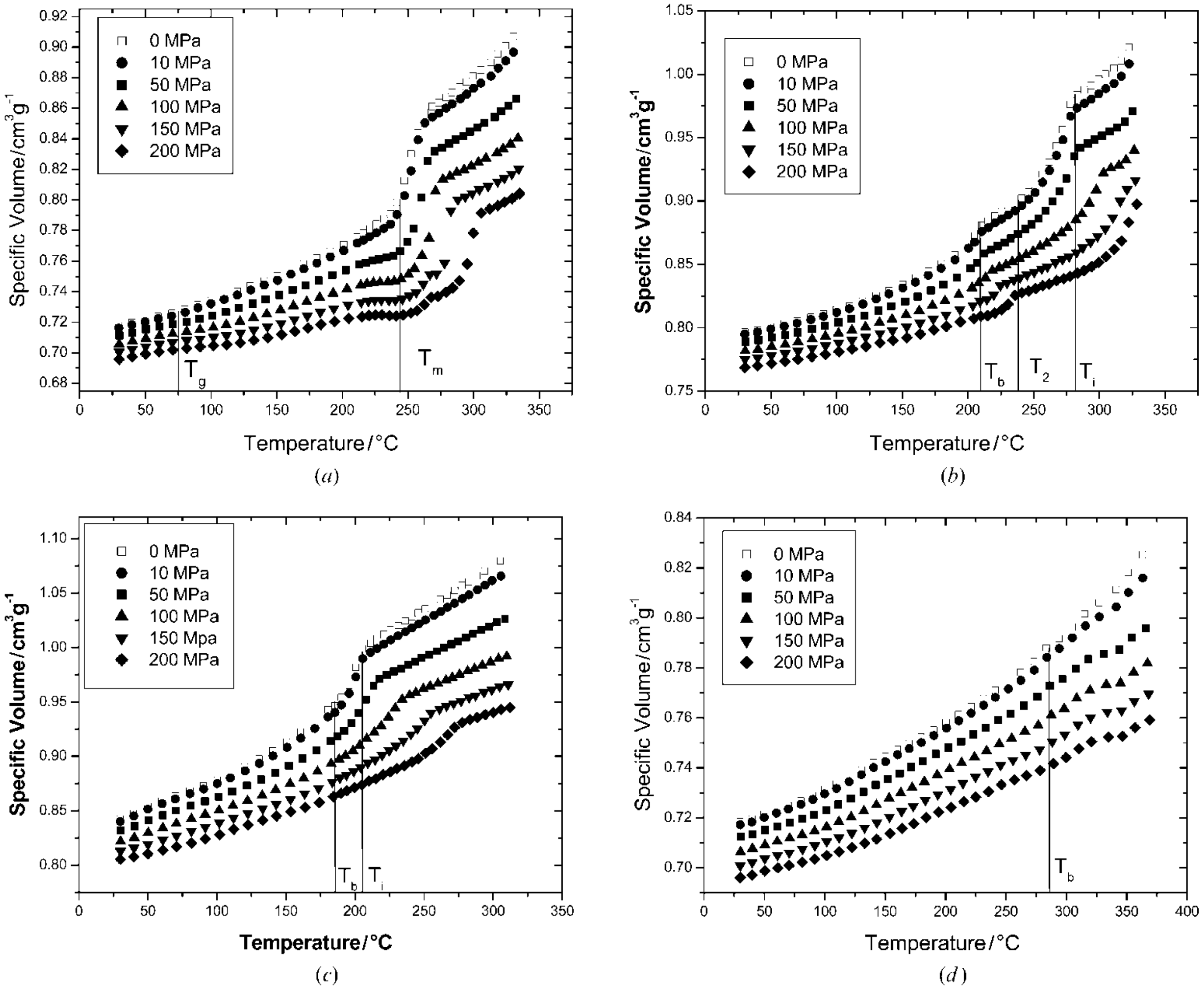


Figure 3. Volume versus temperature for: (*a*) PET, (*b*) PB-8, (*c*) PB-11, (*d*) Vectra A950. Values extrapolated to zero pressure are indicated by open symbols.

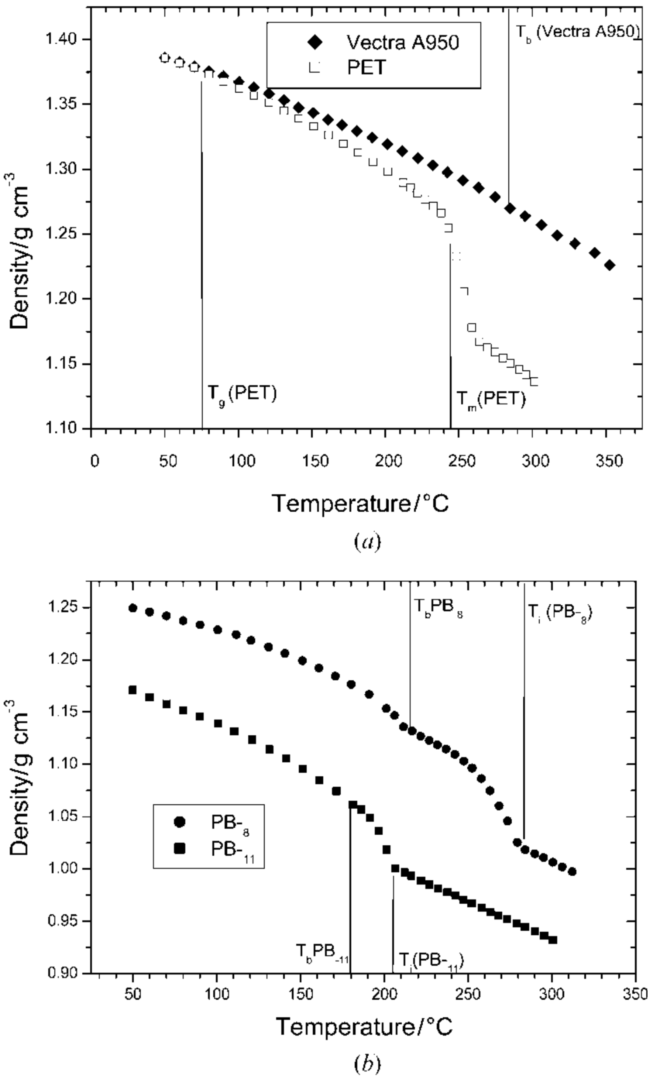
studied here, respectively. Figure 7 (*a*) show the predictions of Patterson and Rastogi, and figure 7 (*b*) the predictions of Dee and Sauer's theories for the three liquid crystals polymers used in this work. The values of *m*, *b*, *c* used in the calculation for the predictions of the Patterson–Rastogi and Dee–Sauer theories were respectively (0.25, 1, 1) and (0.52, 2, 1).

It can be seen from figure 6 that both theories predict a linear decrease of surface tension of PET with temperature, which is expected thermodynamically; however, a large discrepency between the values predicted by the Patterson–Rastogi and Dee–Sauer theories is observed. This discrepency could be because *m*, quantifying the enthalpic contribution of surface tension, is an adjustable parameter [35, 41]. Since no experimental data for the surface tension of PET have been reported to our knowledge, only the dependence of surface tension on temperature and not its absolute values can be discussed here. Equations (8) and (9) are obtained by linear regression for the Patterson–Rastogi and Dee–Sauer theories, respectively.

$$\gamma(T)=46.8-0.09T,\ r^2=0.99 \tag{8}$$

$$\gamma(T)=59.9-0.10T,\ r^2=0.99. \tag{9}$$

It can be seen that, $\Delta S=-\mathrm{d}\gamma/\mathrm{d}T$, the entropy of surface formation, is around 0.1 dyn cm^{-1} °C^{-1} for the predictions of both theories. This value corroborates those obtained for other thermoplastic polymers for which $-\partial\gamma/\partial T$ is of the order of 0.05 to 0.13 dyn cm^{-1} °C^{-1} [28, 49–51].

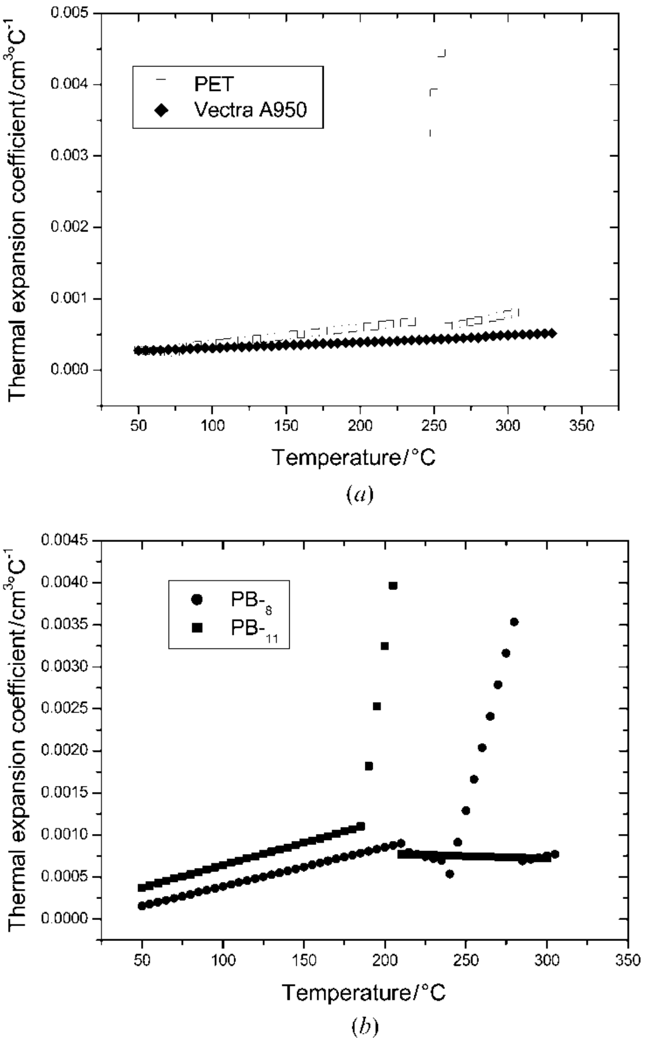


(*a*)

(*b*)

Figure 4. Density versus temperature for: (*a*) PET (□) and Vectra A950 (♦); (*b*) PB-8 (●) PB-11 (■). T_b is the temperature at which the crystalline structures transform into birefringent structures, T_i is the temperature at which the mesophase turns into a isotropic structure, T_g is the glass transition temperature, T_m is the melting temperature.

It can be seen from figures 7 (*a*) and 7 (*b*) that both theories (Patterson–Rastogi and Dee–Sauer) predict the same trends for the influence of temperature on surface tension of the LCPs studied here. However, a large discrepency can be observed between the theories, even if the values of surface tension obtained for the LCPs studied in this work are of the same order of magnitude as those obtained experimentally using the pendant drop method for side group polyacrylates [3]. The difference observed between the absolute values of surface tension can be due to the choice of the values of the parameters *m* and *b* inherent to the theories. To our knowledge, there are no reported data for the surface tension of PB-8, PB-11 and Vectra A950®, therefore only trends and not the absolute values will be discussed here.



(*a*)

(*b*)

Figure 5. Thermal expansion coefficient, $\alpha = -\left(\frac{\partial \ln V}{\partial T}\right)$ for: (*a*) PET (□) and Vectra A950 (♦); (*b*) PB-8 (●) PB-11 (■).

It can be seen from figures 7 (*a*) and 7 (*b*) that for both PB-11 and Vectra A950®, γ decreases linearly with increasing temperature in the nematic phase. Abnormal behaviour can be observed for PB-8: at temperatures just above T_b, γ levels off around 237°C and then decreases. A clear discontinuity can be observed for $\gamma_{\text{PB-8}}$ and $\gamma_{\text{PB-11}}$ near the liquid crystalline to isotropic transition. These transitions are first order, and discontinuities of physical properties such as specific volume, heat capacity, index of refraction and surface tension are expected for these temperatures [52]. Such behaviour has already been observed for several low molar mass liquid crystals [6–26] and liquid crystal

Table 2. Specific volumes V_{sp}, thermal expansion coefficient $\alpha = -\frac{\partial \ln V}{\partial T}|_P$ estimated for atmospheric pressure, and isothermal compressibility $\beta = -\frac{\partial \ln V}{\partial P}|_T$.

PB-8	PB-11
Crystalline phase (50–210°C)	Crystalline phase (50–180°C)
$V_{sp} = 0.8025 + 8.1368.10^{-5}\ (T\text{-}50) + 2.3092 \times 10^{-6}\ (T\text{-}50)^2\ r^2 = 0.99546$	$V_{sp} = 0.8555 + 3.0556 \times 10^{-4}\ (T\text{-}50) + 2.6124 \times 10^{-6}\ (T\text{-}50)^2\ r^2 = 0.99898$
$\alpha = 1.5447 \times 10^{-4} + 4.6578 \times 10^{-6}\ (T\text{-}50)\ r^2 = 1$	$\alpha = 3.7317 \times 10^{-4} + 5.3349 \times 10^{-6}\ (T\text{-}50)\ r^2 = 1$
$\beta = 1.1984 \times 10^{-4} + 2.7441 \times 10^{-6}\ (T\text{-}50)\ r^2 = 0.99537$	$\beta = 5.5046 \times 10^{-6} + 5.3846 \times 10^{-6}\ (T\text{-}50)\ r^2 = 0.99903$
Mesophase (215–235°C)	Mesophase (185–205°C)
$V_{sp} = 0.8829 + 6.5547 \times 10^{-4}\ (T\text{-}215)\ r^2 = 0.99895$	$V_{sp} = 0.9444 + 1.01 \times 10^{-3}\ (T\text{-}185) + 7.2388 \times 10^{-5}\ (T\text{-}185)^2\ r^2 = 0.99846$
$\alpha = 7.9405 \times 10^{-4} - 4.9712 \times 10^{-6}\ (T\text{-}215)\ r^2 = 1$	$\alpha = 1.10 \times 10^{-3} + 1.4336 \times 10^{-4}\ (T\text{-}185)\ r^2 = 1$
$\beta = 5.5793 \times 10^{-4} - 3.2294 \times 10^{-8}\ (T\text{-}215) + 5.2986 \times 10^{-8}\ (T\text{-}215)^2\ r^2 = 0.99633$	$\beta = 6.3577 \times 10^{-4} + 1.1361 \times 10^{-5}\ (T\text{-}185) + 5.4359 \times 10^{-7}\ (T\text{-}185)^2\ r^2 = 0.99999$
Mesophase (240–280°C)	Isotropic phase (210–300°C)
$V_{sp} = 0.9007 + 4.3394 \times 10^{-4}\ (T\text{-}240) + 3.6794 \times 10^{-5}\ (T\text{-}240)^2\ r^2 = 0.99977$	$V_{sp} = 1.0016 + 7.7359 \times 10^{-4}\ (T\text{-}210)\ r^2 = 0.99993$
$\alpha = 5.3664 \times 10^{-4} + 7.5003 \times 10^{-5}\ (T\text{-}240)\ r^2 = 1$	$\alpha = 7.7074 \times 10^{-4} - 5.5747 \times 10^{-7}\ (T\text{-}210)\ r^2 = 1$
$\beta = 5.9962 \times 10^{-4} + 2.0069 \times 10^{-6}\ (T\text{-}240) + 2.6313 \times 10^{-7}\ (T\text{-}240)^2\ r^2 = 0.99915$	$\beta = 8.9293 \times 10^{-4} + 4.7803 \times 10^{-6}\ (T\text{-}210)\ r^2 = 0.99929$
Isotropic phase (285–300°C)	
$V_{sp} = 0.9823 + 7.3711 \times 10^{-4}\ (T\text{-}285)\ r^2 = 0.9991$	
$\alpha = 6.9361 \times 10^{-4} + 3.7341 \times 10^{-6}\ (T\text{-}285)\ r^2 = 1$	
$\beta = 1.1380 \times 10^{-3} + 4.794 \times 10^{-6}\ (T\text{-}285)\ r^2 = 0.99309$	
Vectra A950	PET
Crystaline phase (50–280°C)	Below T_g (50–75°C)
$V_{sp} = 0.7212 + 1.8528 \times 10^{-4}\ (T\text{-}50) + 3.8452 \times 10^{-7}\ (T\text{-}50)^2\ r^2 = 0.99949$	$V_{sp} = 0.7215 + 2.042 \times 10^{-4}\ (T\text{-}50)\ r^2 = 0.99895$
$\alpha = 2.7094 \times 10^{-4} + 7.9498 \times 10^{-7}\ (T\text{-}50)\ r^2 = 1$	$\alpha = 2.8291 \times 10^{-4} + 1.6081 \times 10^{-6}\ (T\text{-}50)\ r^2 = 1$
$\beta = 2.2054 \times 10^{-4} - 1.5292 \times 10^{-6}\ (T\text{-}50) + 1.3820 \times 10^{-8}\ (T\text{-}50)^2\ r^2 = 0.99999$	$\beta = 1.80478 \times 10^{-4} + 3.5135 \times 10^{-7}\ (T\text{-}50)\ r^2 = 0.96165$
Mesophase (285–300°C)	Below T_m (80–250°C)
$V_{sp} = 0.78686 + 4.0935 \times 10^{-4}\ (T\text{-}285)\ r^2 = 0.99286$	$V_{sp} = 0.7288 + 2.2808 \times 10^{-4}\ (T\text{-}80) + 9.6275 \times 10^{-7}\ (T\text{-}80)^2\ r^2 = 0.99959$
$\alpha = 4.7395 \times 10^{-4} + 9.4331 \times 10^{-7}\ (T\text{-}285)\ r^2 = 1$	$\alpha = 3.2144 \times 10^{-4} + 2.2933 \times 10^{-6}\ (T\text{-}80)\ r^2 = 1$
$\beta = 6.1974 \times 10^{-4} + 5.4084 \times 10^{-6}\ (T\text{-}285)\ r^2 = 0.99926$	$\beta = 9.8139 \times 10^{-6} + 5.1854 \times 10^{-6}\ (T\text{-}80)\ r^2 = 0.99422$
	Above T_m (above 260°C)
	$V_{sp} = 0.8540 + 6.135 \times 10^{-4}\ (T\text{-}260)\ r^2 = 0.99815$
	$\alpha = 6.0408 \times 10^{-4} + 4.5105 \times 10^{-6}\ (T\text{-}260)\ r^2 = 1$
	$\beta = 8.1124 \times 10^{-4} + 5.7242 \times 10^{-6}\ (T\text{-}260)\ r^2 = 0.99983$

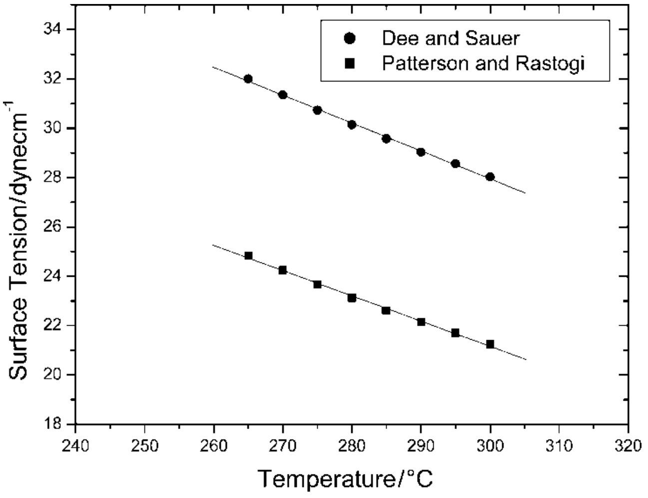
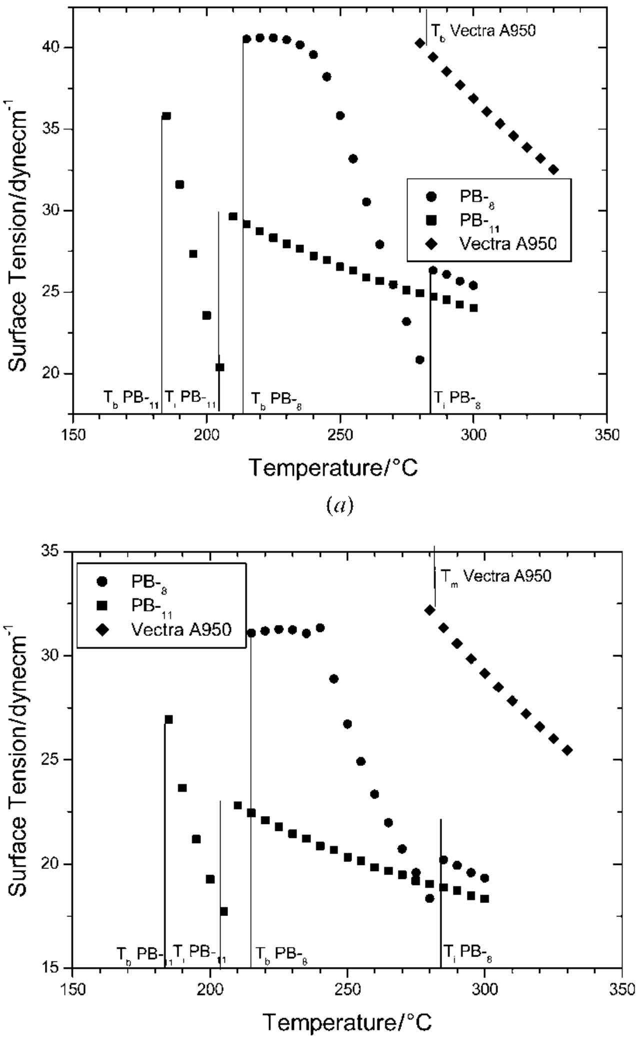


Figure 6. Surface Tension of PET as a function of temperature (●) Dee–Sauer (■) and Patterson–Rastogi.

polymers [3, 4]. For both PB-8 and PB-11, γ decreases linearly with increasing temperature in the isotropic phases. It can also be seen from figures 7 (*a*) and 7 (*b*) that for both PB-8 and PB-11 the influence of temperature is smaller in the isotropic state than in the liquid crystalline state (i.e. $\left|\frac{\partial\gamma}{\partial T}_{\text{lc}}\right| > \left|\frac{\partial\gamma}{\partial T}_{\text{iso}}\right|$). This type of behaviour has already been observed experimentally for LMMLCs [15–18] and LCPs [3–4].

Due to the lack of experimental data for the surface tension of the materials studied here, no direct comparison with the theoretical predictions could be made. Therefore, the results obtained in this work were compared, as far as trend is concerned, to those reported for other LCPs and for LMMLCs. There have been very few experimental studies on the influence of temperature on the surface tension of LCPs; to our knowledge, only two have been reported so far [3, 4]. Uzman *et al.* [3] evaluated the surface tension of two side chain polyacrylates, PAC_5 and PAC_6, for temperatures corresponding to the smectic, nematic and isotropic phases of the materials; Runke *et al.* [4] evaluated the surface tension of two side chain polymethylmethacrylates, $PMAC_4$ and $PMAC_6$, for temperatures corresponding to the nematic and isotropic phases of the materials. Both studies were conducted using the pendant drop method. Both studies showed that at the transition temperatures the surface tensions of the different materials as a function of temperature showed discontinuities. For the four substances studied in [3, 4] the surface tension was shown to decrease with increasing temperature in the nematic phase, present a discontinuity at T_i, increase for temperatures slighly above T_i, reach a maximum and then decrease with increasing temperatures.



(*a*)

(*b*)

Figure 7. Surface tension for PB-8(●), PB-11 (■) and Vectra A950 (◆), as a function of temperature: (*a*) predictions of the Dee–Sauer theory; (*b*) predictions of the Patterson–Rastogi theory.

The influence of temperature on LMMLCs has been studied by many authors [6–26]. A large discrepancy between the different experimental studies reported in the literature can be seen. While some studies report a 'normal behaviour' (i.e. $-\frac{\partial\gamma}{\partial T} > 0$) for both the nematic and isotropic states, other studies report that close to the nematic to isotropic transition $-\frac{\partial\gamma}{\partial T}$ can be negative and that the surface tension may show a discontinuity. More details can be found in Shimizu and Demarquette [26]. $-\frac{\partial\gamma}{\partial T}$ corresponds to the entropy of surface formation, ΔS; for 'normal' liquids or thermoplastic polymers ΔS is positive, suggesting that the molecules at the surface are less ordered than those in the bulk, most likely due to the freedom of the molecules at the surface. The negative value of ΔS observed experimentally for LMMLCs and LCPs for temperatures just above T_i, corresponding to a higher order of the molecules at the surface, has been explained by a nematic wetting of the isotropic vapour surface [53, 54]. Such an anomaly (i.e. $-\frac{\partial \gamma}{\partial T} < 0$) for temperatures just above T_i was not observed in the results presented in this work. This could indicate that the cell theories cannot predict nematic wetting of the isotropic vapour surface or that PB-8 and PB-11 have a behaviour that is closer to that of normal thermoplastics. The LCPs studied here are main chain polymers, in contrast to those studied by Uzman *et al.* [3] and Runke *et al.* [4]. In this case the polymeric and mesogenic properties are more closely coupled and in the isotropic state the polymeric effect could predominate.

4. Conclusions

In this work, *PVT* data were obtained for three main chain liquid crystal polymers: a random co-polyester based on *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) (Vectra A950®) and two LCPs based on 4,4′-dihydroxybiphenyl (PB-8) and (PB-11) and of polyethylene terephtalate (PET). The data were fitted to the Flory–Orwoll–Vrij equation of state and used to predict the effect of temperature on the surface tension of those four substances.

The surface tension of PET was shown to decrease linearly with increasing temperature, corroborating results obtained for other thermoplastics. The surface tension of PB-11 and Vectra A950® decreased linearly with temperature for temperatures corresponding to the nematic phases of both materials. The surface tension of PB-8 seemed to level off just above T_b, up to around 237°C and then decreased linearly with temperature. The surface tensions of both PB-8 and PB-11 showed a discontinuity at T_i (isotropization temperature of the material). The surface tensions of both PB-8 and PB-11 were shown to decrease with increasing temperature for temperatures corresponding to the isotropic state of the materials. Neither substance (PB-8 and PB-11) showed a negative value of the entropy of surface formation, $\Delta S = -\frac{\partial \gamma}{\partial T}$, for temperatures just above T_i, as reported in the literature for many low molar mass liquid crystals and side chain liquid crystal polymers, indicating that the polymeric character of the two main chain liquid crystal polymers studied here could govern the influence of temperature on the surface tension of these materials, or that the cell theories used here to infer surface tension cannot predict the nematic wetting of the isotropic vapour surface at temperatures close to T_i.

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