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In this study the temperature dependence of the surface properties of a side-chain liquid crystalline polyacrylate is investigated through contact angle measurements. In particular, the effect of the glass transition ($T_g = 46.7$°C) on the surface tension of the liquid crystalline polymer is analysed. The total surface tension as well as its dispersive and polar components are determined as a function of temperature, between 24°C and 73°C, from contact angle values of water, diiodomethane and glycerol. For water and diiodomethane the proximity of the glass transition temperature induces an abrupt change in the temperature dependence of the contact angle; the same is not observed for glycerol. The calculations were performed using the most common techniques: the Neumann equation of state for interfacial tensions, the Owens-Wendt approach (also known as the geometric mean approach) and Lifshitz-van der Waals donor-acceptor approach (also known as the acid-base approach). The results obtained for the total surface tension of the polymer surface were compared and discussed. The temperature dependence of the surface tension exibits the behaviour characteristic of a second-order transition: the surface tension is continuous in the vicinity of the glass transition temperature but its first derivative is discontinuous. Furthermore, the decomposition of the surface tension into its components shows that the polar component, γ_s^p, has a small contribution throughout the entire temperature range, while the dispersive component, γ_s^d, largely predominates. The temperature dependence of both components γ_s^d and γ_s^p is clearly different in the two phases (glassy and liquid crystalline), despite the fact that the total surface tension does not present any appreciable discontinuity across the glass transition.

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Keywords: Contact angle; surface tension; interfacial tension; wettability; glass transition; liquid crystalline polymer

INTRODUCTION

Liquid crystals are orientationally ordered fluids which present a variety of surface phenomena [1]. The idea behind the current interest in surface phenomena occuring in liquid crystals is the use of these complex fluids as examples of systems that can exhibit many surface transitions associated with surface induced order or disorder, molecular anchoring and orientational wetting. In addition to the basic importance of the knowledge of surface phenomena in liquid crystals, understanding the ordering mechanisms at the surfaces of liquid crystals is crucial for the practical applications of these materials, namely in the production of liquid crystal displays. Liquid crystalline polymers (LCPs) are high molecular mass compounds which exhibit mesomorphism. They are hybrid materials since they exhibit simultaneously the electro-optical properties of low molar mass liquid crystals (LCs) and many physical properties of the conventional polymers. This combination of properties confers upon these materials a versatility which makes them useful for different applications, namely in optical information storage, non-linear optics and chromatography [2]. Moreover, LCPs, like LCs, are stimulating materials from an academic point of view since they provide examples of structurally ordered fluid phases. However, the studies of the surface phenomena in LCPs are very scarce when compared with those published on low molar mass LCs and the aim of this work is precisely to give a contribution to the understanding of the surface behaviour of liquid crystalline polymers.

Two important aspects in the context of the surface phenomena in films of ordered fluids are the structures of the two interfaces which separate the LC film from the air and from the solid substrate. In the case of thin films, a correlation may exist between the structures of those two interfaces. Many studies have been published on the LC/solid-substrate interface [3–5] which indicate that the molecular alignement of LCs on solid surfaces depends on: (a) the intermolecular interactions between the LC and the solid surface; (b) the mechanical interactions related to the surface topology and the anisotropic elasticity of LC molecules. The surface tension of the solid, γ_s, seems to have a significant influence on the orientation of the adjacent LC molecules (with surface tension γ_{LC}) [3,4]. This relationship between molecular alignement and surface tension was first explained by

Creagh [6] as follows: (a) If the solid surface energy is low, the intermolecular force between LC molecules is stronger than the force across the interface. Then, the longer axis of the LC molecules are aligned perpendicular to the surface in order to maximise their interactions. (b) When the solid surface tension, γ_s, is higher than γ_{LC} the force across the interface dominates and the interface free energy is minimised if the LC molecules are packed parallel to the surface. Kahn [7] defined the difference $\Delta\gamma = \gamma_{LC} - \gamma_s$ as a measure of the free energy responsible for the LC alignement. Moreover, it was observed [8,9] that the relative magnitude of the components (dispersive and polar) of the surface tension of the solid influences the type of alignements of the LC molecules in such a way that the tilt angle of the LC molecules increases with increasing contribution of $\gamma_s{}^p$ (the polar component).

The structure of the LC/air interface has been extensively studied, mostly in the temperature region of the liquid-crystal/isotropic-liquid transition (i.e. in the vicinity of the clearing temperature, T_c), using different experimental techniques namely X-ray reflectivity [10, 11], reflection ellipsometry [12, 13] and surface tension measurements [14–16]. Theoretical studies on the surface properties of liquid crystals near the LC/isotropic transition were also performed based either on a Landau-de Gennes expansion of the free energy [17, 18] or on a mean-field treatment [19] and they predict a great variety of behaviours. In particular, theory predicts the formation of a boundary ordered layer (called wetting film) at the free surface of the isotropic phase of a liquid crystal. The thickness of the wetting layer, which increases as T_c is approached on cooling, is expected either to diverge (complete wetting) or to remain finite (partial wetting) depending on the nature of the interaction forces introduced by the interface.

The first experimental indication in favour of surface order in the isotropic phase came from measurements of the surface tension (a positive temperature coefficient, $d\gamma/dT$, was observed which indicates an excess surface order) and was confirmed by other techniques [10–13]. These experiments also demonstrated that the surface order has an homeotropic orientation [10–13]. Experimental studies on the temperature dependence of the surface tension in low molar mass liquid crystals showed that the curve $\gamma(T)$ presents special features (changes in slope, discontinuities) near the clearing temperature which are predicted by the statistical thermodynamics analysis of the free surface [20–22]. The slope $d\gamma/dT$ was found to be determined by the competition between orientational order and spatial disorder which develops near the surface. If the orientational states are highly ordered, $\gamma(T)$ has a positive slope. With increasing temperature, the spatial delocalisation of the liquid surface may lead to a regain of the usual monotonic decreasing trend of the surface tension. Furthermore, discontinuities in the slope and the absolute value of $\gamma(T)$ near T_c, associated with the discontinuous variation of the bulk order parameter, are expected. The theory also predicts that the weak surface field may cause a residuum of orientational order at the isotropic liquid surface over a short temperature range above T_c resulting in a positive slope for the curve $\gamma(T)$, even for the isotropic phase.

Among the few reports on the surface properties of liquid crystalline polymers we distinguish the ellipsometric [23] and X-ray reflectivity [24] studies which indicate the presence of smectic boundary layers in the isotropic phase whose thickness decreases with increasing temperature. These specific surface structures show a smaller degree of order and a quite larger thickness when compared to LCs, and were found to be present in a temperature range above T_c which is much larger than that observed in low molar mass liquid crystals. Interfacial phenomena in side-chain LCPs thus present different features when compared with LCs which should certainly be due to the particularities of the chemical structure of side-chain LCPs. In fact, these LCP molecules are composed of three different constitutive units: the main chain, the mesogenic moiety and the spacer (a methylene chain linking the mesogenic moiety to the main-chain). The spacer group partially decouples (or totally decouples if it is sufficiently long) the motions of the mesogenic moiety from those of the main chain. This means that the motions of the mesogenic side groups in side-chain LCPs are more hindered and have probably different mechanisms when compared with those present in low molar mass LCs.

To our knowledge only two works have been published [25, 26] reporting experimental values of the surface tension of side-chain LCPs as a function of temperature. Besides the high value exhibited by the surface tension of these materials, it is interesting to notice that the behaviour of the $\gamma(T)$ curve for side-chain LCPs resembles more that of low molar mass LCs than the one found for the conventional amorphous polymers, showing discontinuities at the phase transitions and temperature regions where the slope $d\gamma/dT$ is positive. This was interpreted [26] considering that the surface properties of side-chain LCPs are essentially determined by the mesogenic side groups. However, none of the cited studies focused on the surface behaviour across the transition from the glassy state of the polymer to the liquid crystalline phase. The study of the effect of phase transitions, in particular the glass transition, on the surface tension of a solid is an interesting subject by itself since it constitutes a potential source of information about the nature of these transitions. In fact, it is known that the molecular rearrangements associated with phase transitions lead to discontinuities in the surface properties [27–30]. Assuming that the surface tension may be decomposed in several contributions arising from different types of intermolecular forces [31–33], we may study the behaviour of each component which allows a deeper understanding of the characteristics of the glass transition.

In the present work we study the temperature dependence of the surface tension and its components for a side-chain liquid crystalline polyacrylate in a temperature range which includes the glass transition temperature, through contact angle measurements.

The surface tension of a solid in equilibrium with the vapour of a liquid, γ_{SV}, may be obtained combining the Young equation:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta \tag{1}$$

where γ_{LV} and θ are experimental values of the surface tension and the contact angle of testing liquids, with one of the thermodynamic approaches used to calculate the solid/liquid interfacial tension, γ_{SL}. The surface tension, γ_{SV}, is related with the surface tension of the solid in contact with its own vapour, γ_S, through the spreading pressure π_e:

$$\gamma_S = \gamma_{SV} + \pi_e \tag{2}$$

which may be appreciable for hydrogen bonding liquids on solids containing electron donor or acceptor groups. However, the measurement of π_e is not trivial and the error caused by its neglect lies within the experimental error when the scatter of the experimental results is relatively large.

Among the various possible methods to determine the solid/liquid interfacial tension, the most frequently used are the Neumann equation of state, the Owens-Wendt approach (also known as the geometric mean approach) and the Lifshitz-van der Waals donor-acceptor approach (also known as the acid-base approach). Since we analysed recently in great detail all these approaches comparing their merits and disadvantages [34], a short description of the main ideas involved in each approach is given here. Neumann *et al.* [35–37] derived the so-called equation of state for interfacial tensions from the equation of Girifalco and Good:

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2\phi(\gamma_{SV}\gamma_{LV})^{1/2} \tag{3}$$

considering that the interaction parameter ϕ was given by the function:

$$\phi = e^{-\beta(\gamma_{LV} - \gamma_{SV})^2} \tag{4}$$

where β is an empirical constant with an average value of $0.0001247\,\mathrm{m}^4\,\mathrm{mJ}^{-2}$. Combining with the Young equation gives the following expression:

$$\cos\theta = -1 + 2\sqrt{\frac{\gamma_{SV}}{\gamma_{LV}}}\,e^{-\beta(\gamma_{LV}-\gamma_{SV})^2} \tag{5}$$

which enables the evaluation of the surface tension of a solid, γ_{SV}, from a single measurement of the contact angle of a liquid with known surface tension γ_{LV}.

The approach of Owens and Wendt [32], is based on the following equation for the interfacial tension, γ_{SL}:

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2(\gamma_S^d\gamma_L^d)^{1/2} - 2(\gamma_S^p\gamma_L^p)^{1/2} \tag{6}$$

where γ^d and γ^p are the dispersion and the polar components of the surface tension (for the liquid or the solid) such that $\gamma = \gamma^d + \gamma^p$. Combining with the Young equation and neglecting the spreading pressure, yields

$$\gamma_{LV}(1 + \cos\theta) = 2(\gamma_S^d\gamma_L^d)^{1/2} + 2(\gamma_S^p\gamma_L^p)^{1/2} \tag{7}$$

From equation (7) the components of the surface tension of the solid (and its total surface tension) can be obtained from the contact angles measured with a pair of testing liquids whose surface tension components (dispersive and polar) are known. On the other hand, van Oss *et al.* [33] considered an alternative decomposition of the surface tension:

$$\gamma = \gamma^{LW} + \gamma^{DA} \tag{8}$$

where the dispersion (London), orientation (Keesom) and induction (Debye) interactions are treated together as the Lifshitz-van der Waals (LW) contribution while the donor-acceptor (DA) contribution is associated with the processes involving transfer of electrons between an electron donor (Lewis base) and an electron acceptor (Lewis acid). van Oss *et al.* [38] postulated that the donor-acceptor term should be divided into an electron acceptor surface parameter γ^+ and an electron donor surface parameter γ^- such that for the substance i, $\gamma_i^{DA} = 2\sqrt{\gamma_i^+\gamma_i^-}$. In both components are negligible, the substance is considered *apolar*. When only one of the components is appreciable, the substance is *monopolar* and if both components have to be considered, the substance is *bipolar*. The solid/liquid interfacial tension is given by:

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 2(\gamma_{LV}^{LW}\cdot\gamma_{SV}^{LW})^{1/2} - 2(\gamma_{LV}^{+}\cdot\gamma_{SV}^{-})^{1/2} - 2(\gamma_{LV}^{-}\cdot\gamma_{SV}^{+})^{1/2} \tag{9}$$

which coupled with the Young equation, leads to the following expression:

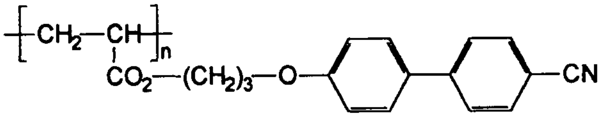
$$\gamma_{LV}(1+\cos\theta)=2(\gamma_{LV}^{LW}\cdot\gamma_{SV}^{LW})^{1/2}+2(\gamma_{LV}^{+}\cdot\gamma_{SV}^{-})^{1/2}+2(\gamma_{LV}^{-}\cdot\gamma_{SV}^{+})^{1/2} \qquad (10)$$

This equation allows the determination of the LW and DA components of the surface tension of a solid surface from contact angle measurements of three testing liquids with known surface tension components. One of the liquids should be purely Lifshitz-van der Waals type, i.e. $\gamma_{LV}=\gamma_{LV}^{LW}$, while the others should be bipolar.

EXPERIMENTAL

Materials

The studied side-chain liquid crystalline polyacrylate is from Merck (catalogue code LCP95) and has the following structure:



The phase-transition temperatures are reported to be 46.7°C for the glass transition and 82.9°C for the smectic A – isotropic transition. The number-average molecular weight, M_n, is 3790 and the polydispersity index, M_w/M_n, is 1.58.

Water, diiodomethane and glycerol are used as testing liquids to determine the surface tension of the solid substrate. Water was doubly distilled and deionized in a Milipore purification system, diiodomethane (Merck Schuchardt > 99%) was distilled under vacuum and glycerol (Aldrich > 99.5%) was used with no further purification.

Methods

For contact angle measurements, polymer films were prepared by spin coating on glass disks from a 4% (w/w) polymer solution in dicloromethane. The spinning velocity was 2000 rpm and the time of rotation was 30 seconds. After film deposition, the samples were kept inside a desiccator for 48 hours and dried inside a vacuum oven in two steps: 2 hours at 40°C and another 2 hours at 60°C. Then the samples were slowly cooled under vacuum till ambient temperature and kept inside a desiccator. The annealing at 60°C (i.e. in the liquid crystalline phase well above T_g) before the contact angle measurements was performed in order to eliminate eventual orientational effects induced by the spin coating procedure.

The glass disks used as substrates for the polymer films were 2 mm thick and had 22 mm of diameter. The analysis of the glass surface composition by X-Ray Photoelectron Spectroscopy revealed the presence of tin as the major impurity. Prior to film deposition, the glass disks were washed with a liquid detergent, deionized water and then submitted to isopropanol vapour for, approximately, 40 minutes.

The contact angles were obtained by the sessile drop method using a JVC Colour Video Camera mounted on a Wild M3Z microscope to record the drop image. The video signal was transmitted to a Video Pix Framegrabber from Sun Microsystems and a Sun Sparstation IPC was used to acquire the image from the image processor and to perform the image analysis. The program used to analyse the shape of the drop, ADSA-P (Axisymmetric Drop Shape Analysis – Profile) was developed by Neumann and co-workers [39,40]. With this algorithm it is possible to determine the contact angle from a set of coordinates taken along the drop profile. The first image was taken immediately after drop deposition and then one image was recorded every 10 s till 200 s, and every 100 s, thereafter. Approximately 4-μL drops were deposited with a micrometer syringe (Gilmont Instruments).

The contact angle measurements were carried out inside a thermostated chamber between 24°C and 73°C. The chamber, from Ramé-Hart, Inc. is built in stainless steel (with the exception of the two optical-quality glass windows) and has a double wall to allow for the circulation of the thermostatic fluid. Water was the chosen fluid for the temperatures studied. The temperature inside the chamber was measured against a reference temperature using a differential copper-constantan® thermocouple (39 μV/°C) connected to a digital multimeter Prema, model 6001. When measuring water and diiodomethane the chamber was previously saturated with the liquid under study. For glycerol, an hygroscopic substance, the chamber was kept as dry as possible through the use of silica gel.

To measure liquid surface tensions, the same program (ADSA-P) was applied to pendant drops generated at the end of a teflon tube introduced inside a metallic jacket to be kept in the vertical position. The teflon tube is connected to the micrometer syringe referred above and 22 μL drops were used, in general. The drops were suspended inside a quartz cell whose atmosphere was saturated with a pool of the liquid sample. The measurements were carried out with the quartz cell and the Teflon tube enclosed inside a thermostatized environmental chamber which contacts the metallic jacket in order to minimize the temperature gradients.

The polymer films were characterised by atomic force microscopy (Humboldt University in Berlin) and by optical second harmonic generation (FOM Institute for Atomic and Molecular Physics in Amsterdam).

RESULTS AND DISCUSSION

The temperature dependence of the contact angles of the three testing liquids, water, diiodomethane and glycerol, is presented in Figures 1, 2 and 3, respectively. The experimental points are averages over the results obtained from a set of, at least, ten experiments.

Each experiment was carried on for a period of time as long as possible (depending on the stability of the drop) and, since no plateau was achieved, the final value for the contact angle was obtained by extrapolation to time

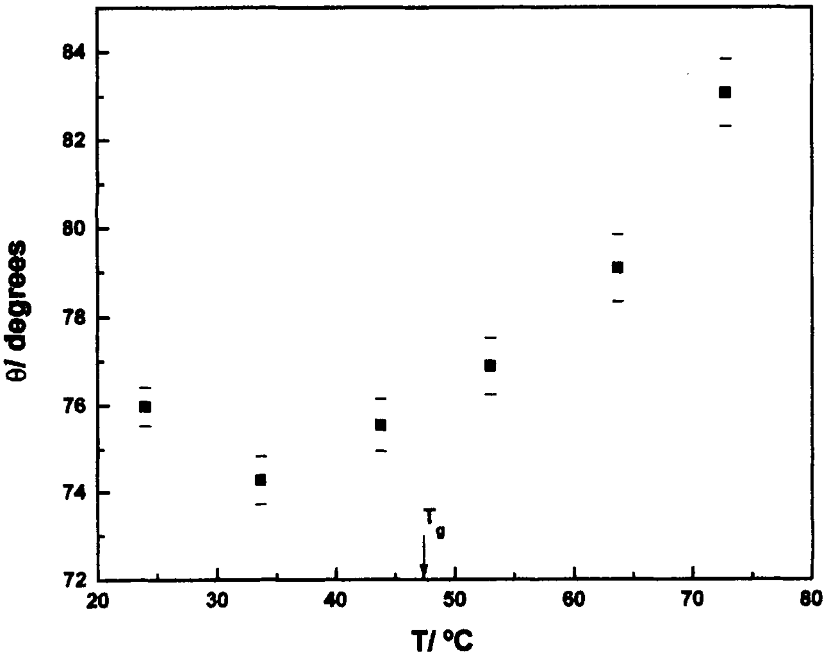


FIGURE 1 Temperature dependence of the contact angle, θ, of water on the polymeric surface. The glass transition temperature, T_g, of the polymer is indicated by an arrow.

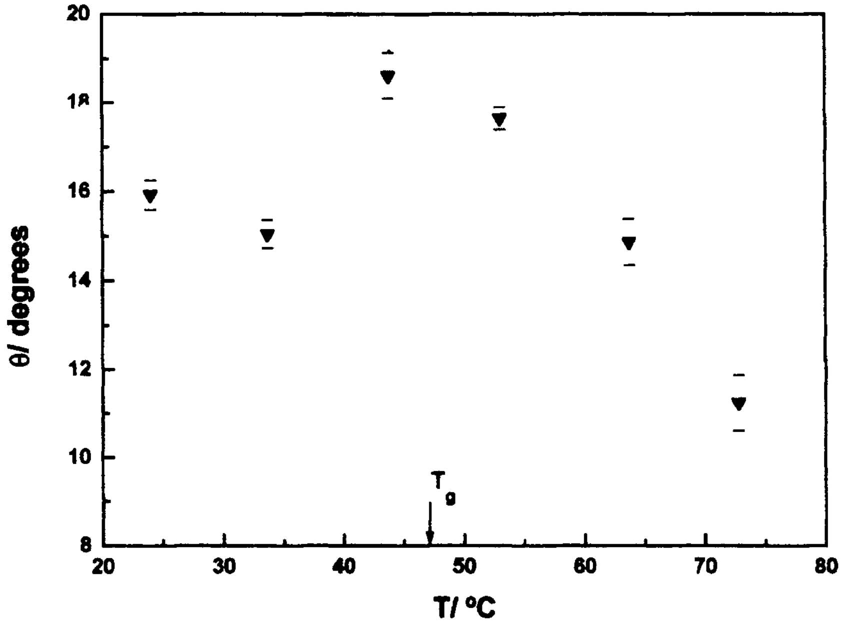


FIGURE 2 Temperature dependence of the contact angle, θ, of methylene iodide on the polymeric surface. The glass transition temperature, T_g, of the polymer is indicated by an arrow.

$t = 0$ s. The error bars represent the limits of 95% confidence interval assuming a Student distribution. Both water and diiodomethane which yield, respectively, the maximum and the minimum values for the contact angles, feel the phase transition of the solid substrate. For these two liquids, the temperature dependence of the contact angles changes significantly at a temperature slightly below T_g which is consistent with the fact that the molecules existing at the surface are able to move earlier than the bulk molecules. In contrast, the contact angle of glycerol increases slightly with increasing temperature over the whole range and does not exibit any special behaviour at the glass transition temperature.

The total surface tension of the liquid-crystalline polymer was calculated as a function of temperature from the reported values of the contact angles using the equation of state approach (Eq. 5) applied to water, diiodomethane and glycerol, and the geometric mean approach (Eq. 7) for the pair water/diiodomethane. The values of the total surface tension as well as its dispersive and polar components for water and diiodomethane, in the

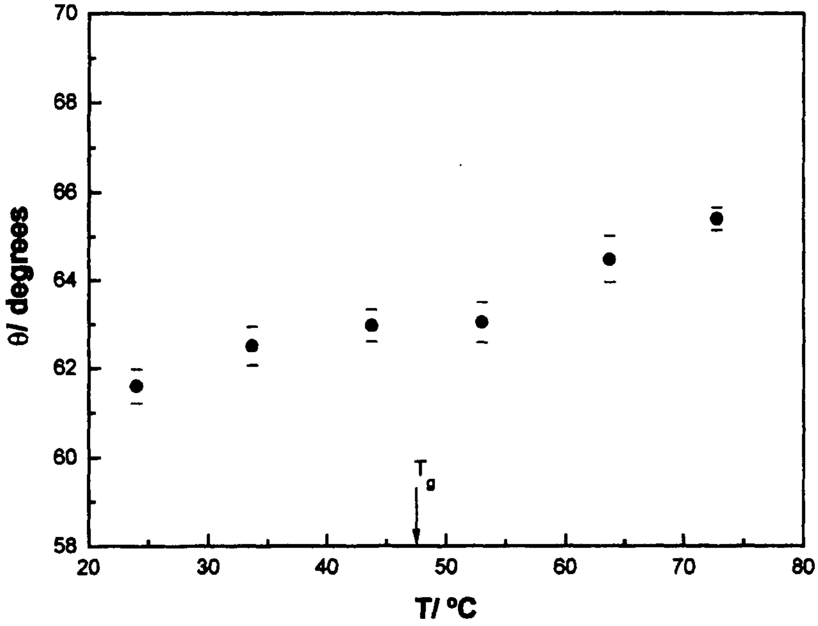


FIGURE 3 Temperature dependence of the contact angle, θ, of glycerol on the polymeric surface. The glass transition temperature, T_g, of the polymer is indicated by an arrow.

studied temperature range, were obtained from liquid-liquid interfacial tensions taken from the literature [30]. The reported experimental values for water/*n*-hexane and water/diiodomethane interfacial tensions were measured at temperatures varying from 20°C to 50°C but a linear extrapolation to 73°C was assumed to be valid. The surface tension components were calculated at each temperature using the equivalent of (Eq. 6) for the liquid/liquid interfacial tension γ_{ij}:

$$\gamma_{ij} = \gamma_i + \gamma_j - 2(\gamma_i^d \gamma_j^d)^{1/2} - 2(\gamma_i^p \gamma_j^p)^{1/2} \tag{11}$$

where γ_i and γ_j are the surface tensions of the liquids i and j; γ_i^d and γ_i^p are the dispersive and polar components of the surface tension of liquid i; γ_j^d and γ_j^p are the equivalent quantities for liquid j. If j is a purely dispersive liquid, the dispersive component of i is automatically obtained and the polar component results from $\gamma_i - \gamma_i^d$. This is the procedure used to calculate the surface tension components of water as a function of temperature from the interfacial tension water/*n*-hexane. Once these values were known, the surface tension components for diiodomethane were calculated in a similar way from the interfacial tension water/diiodomethane. Table I lists the surface tension and its components for water and diiodomethane at the various temperatures used in the experiments. The surface tension of glycerol is given by the equation $\gamma = 63.42 - 0.00269\ T^{1.66}$ obtained from our experimental value at 25°C and from the temperature dependence taken from the literature [41]. Since no interfacial tensions involving glycerol, above room temperature, were found in the literature, the dispersive and polar components could not be determined.

Figure 4 shows a comparison of the different values obtained for the total surface tension of the liquid-crystalline polymer using the referred approaches.

The first comment which arises from the observation of this figure is the discrepancy among the γ_S values derived from the equation of state. When the equation of state is applied to diiodomethane data, the agreement with the values obtained from the Owens-Wendt's approach is reasonable. However, as the polarity of the testing liquid increases, the calculated γ_S values increasingly deviate from the previous ones. From these results we may conclude that the Neumann equation for interfacial tensions lead to γ_S values which vary according to the liquid used in the calculations. This characteristic of the Neumann equation of state has been thoroughly discussed by several authors [42–44] according to whom the range of application of this equation of state is practically restricted to apolar liquids, which seems to be confirmed by our results. The fact that the γ_S values are dependent

TABLE I Surface tension and its dispersive and polar components (in mN m^{-1}) for water and diiodomethane at various temperatures

Liquid	*Temperature* °*C*	γ/mNm^{-1}	γ^d/mNm^{-1}	γ^p/mNm^{-1}
Water	24.0	72.15	21.49	50.66
	33.7	70.58	20.92	49.66
	43.8	68.95	20.34	48.61
	53.0	67.46	19.80	47.66
	63.7	65.73	19.18	46.55
	72.8	64.26	18.65	45.61
Diiodomethane	24.0	50.35	49.98	0.37
	33.7	49.24	48.89	0.35
	43.8	49.08	47.75	0.33
	53.0	47.02	46.71	0.31
	63.7	45.79	45.50	0.29
	72.8	44.75	44.48	0.27

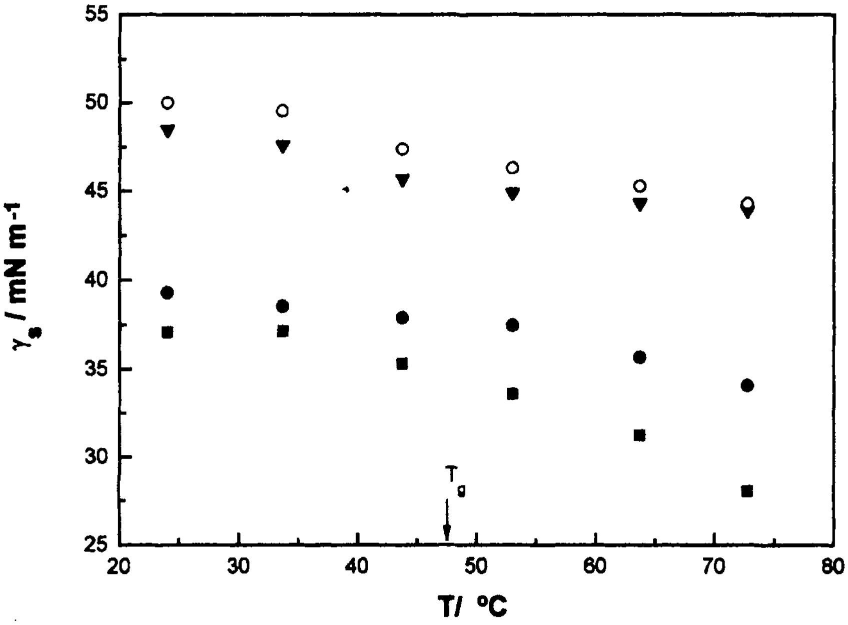


FIGURE 4 Surface tension of the liquid crystalline polymer calculated by Neumann's equation of state (for water (■); for glycerol (●) and for methylene iodide (▼)) and by the geometric mean method (○). The glass transition temperature, T_g, of the polymer is indicated by an arrow.

on the liquid used certainly reveals a weak point of Neumann's equation. As explained before, this equation (equation (5)) results from equation (4) which was chosen by Neumann as the definition of the interaction parameter of Good. The only reason presented to justify the choice of this function was that ϕ must approach unity when γ_{LV} and γ_{SV} become similar. In our opinion, this is a very questionable statement. In fact, ϕ is unity for regular interfaces [45], i.e. for interfaces where the cohesive and adhesive forces are of the same type and of similar intensities. The identity between γ_{LV} and γ_{SV} does not imply that the intermolecular interactions which operate across the solid-liquid interface must be of the same type as those present in the liquid and in the solid or, to put it differently, the interfacial tension between any two phases having the same surface tensions may not always be the same [46]. In fact, a pair liquid-solid may be chosen such that $\gamma_{SV} \sim \gamma_{LV}$, in which e.g. an associated liquid contacts an essentially dispersive or purely basic solid through an interface which is far from regular. As a result, the argument frequently expressed by Neumann [47], according to which all liquids with the same surface tension have the same contact angle on a given solid, is wrong and shall not thus be used to support the equation of state. We believe that the most serious drawback of Neumann's empirical equation is precisely the choice of the function which is supposed to describe the Good's interaction parameter. On the other hand, ϕ will take different discrete values for each pair of phases and we believe that, given the wide diversity of the interactions between unlike systems, the attempt of describing the deviations from the geometric mean by a continuous function of the properties of each phase is an unprofitable task. The results presented in this work strengthen the idea frequently expressed in recent research papers [42–44] according to which the Neumann equation is incomplete and not universal for interfacial tensions and that its application range is practically restricted to apolar liquids.

Focusing now our attention on the γ_S values which deserve more confidence, sets with triangles and open circles in Figure 4, one can conclude that the variation of γ_S with T shows the "normal" decreasing behaviour in the entire temperature range. On the other hand, no discontinuity is observed in the surface tension at the glass transition. Nevertheless, a slight change in the slope $d\gamma_S/dT$ is apparent when the glass transition temperature is crossed. This behaviour is in agreement with the thermodynamic considerations about the nature of the glass transition. This phase transition bears many characteristics of a second-order transition [29], namely, the first derivative of the Helmholtz surface energy with respect to the surface area is continuous at T_g:

$$\gamma_G = \gamma_{LC} \tag{12}$$

where γ_G is the surface tension of the glassy phase and γ_{LC} is the surface tension of the liquid-crystalline phase. Moreover, the second derivative of the Helmoltz surface energy with respect to the temperature, the surface heat capacity per unit area, is discontinuous at T_g which implies that:

$$\left(\frac{d\gamma_G}{dT}\right)_{T<T_g} \neq \left(\frac{d\gamma_{LC}}{dT}\right)_{T>T_g} \tag{13}$$

Since $-d\gamma/dT = (S_{\text{surface}} - S_{\text{bulk}})$, this means that the surface excess entropies per unit area of the solid and the liquid-crystalline phases are different. Figure 4 shows that for our liquid-crystalline polymer:

$$S_G^E > S_{LC}^E \tag{14}$$

which may be interpreted considering that the excess of disorder of the surface relatively to the bulk is lower in the liquid crystalline phase, probably due to a higher degree of long range orientational order of the surface's mesophase when compared with the surface of the glassy phase. Nevertheless, we must emphasize that these comments are speculative since the change in the behaviour of the function $\gamma(T)$ across the glass transition is indeed very slight.

The observation of the films by atomic force microscopy showed, on the other hand, that there is some degree of surface order in the glassy state of the polymer (at room temperature). In fact, it was observed that, after annealing at 85°C i.e. above the clearing temperature and cooling down to room temperature, the surface showed terrace steps corresponding to the thickness of a smectic layer indicating that the smectic layers tend to orient parallel to the surface (homeotropic alignement) [48]. This situation is probably at the origin of the slight modification of the global surface properties of our side-chain LCP films when the glass transition temperature is crossed. It should also be pointed out that the observation of the samples with optical second-harmonic generation in order to determine the orientation of the side-groups at the interface with the substrate did not show any significant signal, indicating that these side groups are oriented parallel to the solid substrate. This observation, which is consistent with other measurements made on liquid crystalline polmers similar to that studied in the present work [49], seems to show that the interfaces LCP/solid-substrate and LCP/air of our films have independent structures i.e. that are not influenced by each other.

In Figures 5 and 6 the dispersive and the polar components of the surface tension, obtained by the Owens-Wendt's approach, are plotted as a function of temperature, respectively.

It can be observed from the figures that the polar component of the surface tension, γ_S^p, is only a minor contribution to the total surface tension, despite the fact that the mesogenic side groups have strongly polar terminal cyano groups. On the other hand, the results in Figures 5 and 6 suggest that the dispersive and polar components of the surface tension show a very different behaviour in the two polymer phases although the total surface tension does not change appreciably across the glass transition. In fact, below the glass transition temperature, T_g, i.e. in the solid phase of the polymer, the dispersive component, γ_s^d, decreases with increasing temperature whereas the polar component, γ_s^p, remains nearly constant indicating that it is the dispersive component which is responsible for the decrease of the total surface tension with increasing temperature. In contrast, above T_g,

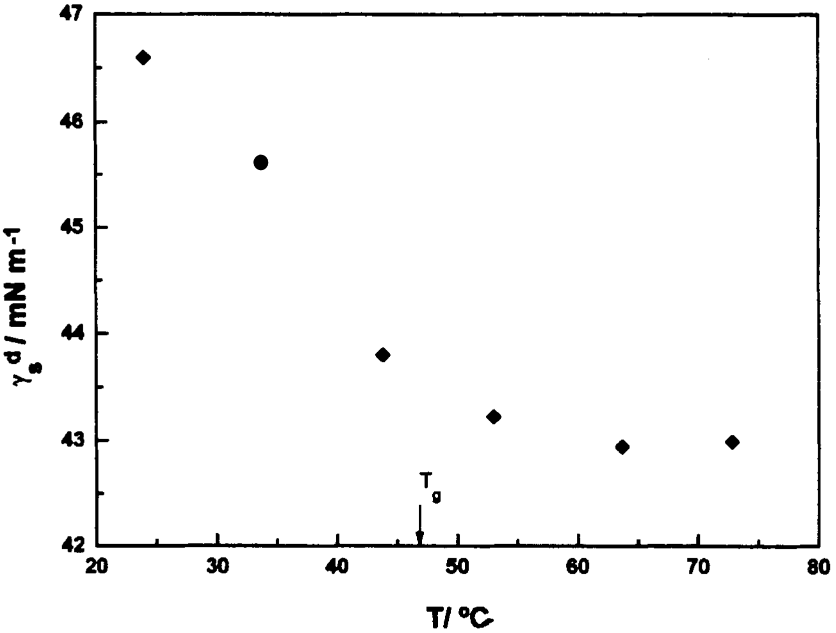


FIGURE 5 Temperature dependence of the dispersive component, γ_s^d, of the total surface tension of the polymeric substrate. The glass transition temperature, T_g, of the polymer is indicated by an arrow.

i.e. in the liquid crystalline phase, γ_s^p decreases with increasing temperature and nearly vanishes when the clearing temperature is approached, whereas the dispersive component remains nearly constant indicating that the decrease of the total surface tension with increasing temperature in the liquid crystalline phase arises from the behaviour of the polar component. Furthermore, the behaviour of γ_s^p in the liquid crystalline phase suggests that the molecular correlations are such that the polar groups in the mesogenic moieties tend to reorient from the surface to the bulk as the temperature increases, so that the surface of the liquid crystalline phase near the clearing temperature is mainly composed of segments of the polymeric main chain.

Finally, we should discuss the results obtained with the Lifshitz-van der Waals donor acceptor approach. In reference [34] the authors used this treatment to calculate the Lifshitz-van der Waals and donor-acceptor components of the surface tension of the liquid crystalline polymer under study from experimental values of the contact angles of water, diiodomethane and glycerol at $T = 20°C$. Different values for the surface tension components of

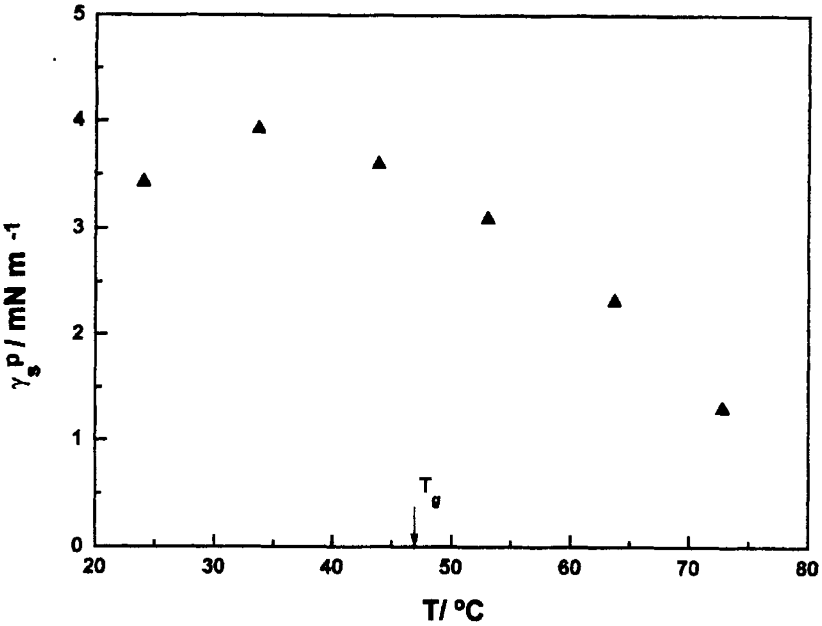


FIGURE 6 Temperature dependence of the polar component, γ_s^p, of the total surface tension of the polymeric substrate. The glass transition temperature, T_g, of the polymer is indicated by an arrow.

the testing liquids were found in the literature and, according to the choice, different results were obtained. Table II presents the Lifshitz-van der Waals and the donor-acceptor components of the surface tension obtained with the values proposed by van Oss [38].

The essentially electron donor character of the non-dispersive component is an expected result since there are no acidic protons in the molecular structure of the liquid-crystalline polymer but, in contrast, the nitrogen and oxygen atoms provide lone electron pairs which can constitute Lewis basic sites (electron donors) for charge transfer interactions. It is interesting to remark that the total surface tension obtained with this approach $\gamma_S = 50.19$ mN m^{-1} is in excellent agreement with the values obtained using the approach of Owens and Wendt, $\gamma_S = 50.2$ mN m^{-1}. The Neumann equation of state applied to diiodomethane yields $\gamma_S = 48.8$ mN m^{-1} which does not deviate much from the other two values. In order to know the temperature dependence of the electron donor and electron acceptor contributions to the non-dispersive component of the surface tension we need experimental

TABLE II Surface tension and its Lifshitz-van der Waals and donor-acceptor components (in $mN m^{-1}$) for the liquid-crystalline polymer at 20°C

γ	γ^{LW}	γ^{DA}	γ^{+}	γ^{-}
50.19	48.78	1.43	0.12	4.29

values for the liquid/liquid interfacial tensions of the pairs glycerol/diiodomethane and glycerol/*n*-alkane as function of temperature. Since these values are not available in the literature, we intend to carry out in the near future the experimental work which is necessary to elucidate this topic.

CONCLUSIONS

Contact angle measurements were used in order to determine the temperature dependence of the surface tension of a side-chain liquid crystalline polymer across the glass transition and in the liquid crystalline phase. Different methodologies were used for this purpose, namely the approach based on the Neumann equation and those which postulate the decomposition of the surface tension into independent components (Owens-Wendt approach and donor-acceptor approach). Neumann's equation led to values for γ_S which depend on the testing liquid: only diiodomethane yielded a γ_S value in reasonable agreement with the values obtained using the other methods. The decomposition of the surface tension into its dispersive, γ_S^d, and polar, γ_S^p, components showed that the temperature dependence of these components is remarkably different for the glassy state of the polymer and for its liquid crystalline phase. In fact, it was observed that the temperature variation of the total surface tension below the glass transition temperature is driven by the dispersive component, whereas the polar component is the determinant factor in the liquid crystalline phase. In order to interpret this behaviour at the molecular level an experimental study of the temperature dependence of the acidic and basic components of the non-dispersive component of the surface tension is planned for the near future.

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