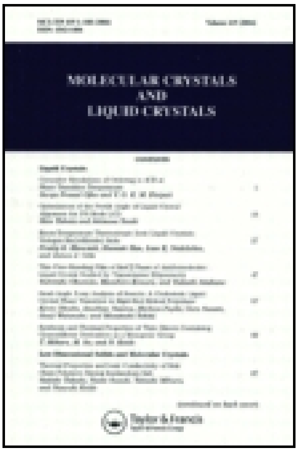

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Study of the Surface and Interfacial Tensions in Systems containing a Low Molar Mass Liquid Crystal

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Study of the Surface and Interfacial Tensions in Systems containing a Low Molar Mass Liquid Crystal

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ABSTRACT

The surface tension of a low molar mass liquid crystal (LMMLC), 4-cyano-4'-*n*-heptyloxybiphenyl (7OCB), was measured in the nematic and isotropic phases using the pendant drop method. Also the contact angles formed by drops of 7OCB in the nematic and isotropic phases on plates of polystyrene (PS) and of a liquid crystal polymer (LCP), were measured. Using those obtained values the interfacial tension between 7OCB and PS and between 7OCB and LCP were evaluated. The results were analysed from a thermodynamical point of view.

Keywords Surface tension, Interfacial tension, Pendant drop method, Liquid crystal.

INTRODUCTION

There has been an increasing interest in the study of composite systems involving liquid crystals and thermoplastics. The properties of such heterogeneous materials are greatly influenced by the interfacial interaction between their components.

In the case of nematics, the surface tension is expected to depend strongly on the alignment of the molecules in the surface [1]. Therefore it is expected that the order of the liquid crystalline molecules affect the interfacial interaction between the liquid crystalline and non-liquid-crystalline materials, turning the study of interfacial tension between a LMMLC and thermoplastics of great interest.

In the present work the surface tension of a LMMLC, 4-cyano-4'-*n*-heptyloxybiphenyl (7OCB), and the contact angles, formed by droplets of 7OCB on surfaces of polystyrene or of a liquid crystal polymer (copolymer of 4-hydroxybenzoic acid and 6-hydroxy-2-naphtoic acid) were measured as a function of temperature. The experimental values were used to evaluate the interfacial energy between 7OCB and the two different polymers. The results were analysed from a thermodynamical point of view.

EXPERIMENTAL

Materials

The 7OCB 4-cyano-4'-*n*-heptyloxybiphenyl was obtained from Aldrich Chemicals and used without further purification. Commercially available polystyrene, PS, (Lustrex HH-101 from Estireno do Brasil) and a liquid crystal polymer (a copolymer of 4-hydroxybenzoic acid and 6-hydroxy-2-naphtoic acid, namely VECTRA A-910 from Ticona Polymers) were also used.

Methods

The surface tension of 7OCB was measured with the pendant drop method which involves the determination of the geometrical profile of a pendant drop of a liquid. Pendant drops of 7OCB were formed in the sample chamber and the temperature was decreased from 89°C to 56 °C. The contact angles of 7OCB were determined on discs of PS and VECTRA A910. The accuracy of contact angle measurement was of ± 0.5^{o}. The interfacial tension between 7OCB and the polymers were obtained using Young's equation, and the values for the surface energy of PS and for VECTRA were obtained from the literature [2].

RESULTS AND DISCUSSION

Surface Tension of 7OCB

It can be observed from Figure 1 that γ_{7OCB} decreases when temperature increases, for temperatures ranging from 56.0 °C to 75.0 °C. A clear discontinuity of γ_{7OCB} can be observed nearby the nematic to isotropic transition temperature, T_{NI}. The nematic to isotropic transition is a first order transition and discontinuities of physical properties such as specific volume, heat capacity, index of refraction and surface tension are expected for those temperatures. For temperatures ranging from T_{NI} to 89.0 °C, γ_{7OCB} increases with increasing temperature.

The entropy of surface or interphase formation can be easily [3] inferred from the values of surface tension and interfacial tension, respectively, as a function of temperature. At constant volume the entropy per unit area of surface or interphase formation, ΔS”, and the corresponding enthalpy, ΔH", are given by:

$$\Delta S'' = -\frac{d\gamma}{dT} \qquad \Delta H'' = \gamma - T\frac{d\gamma}{dT} \tag{1}$$

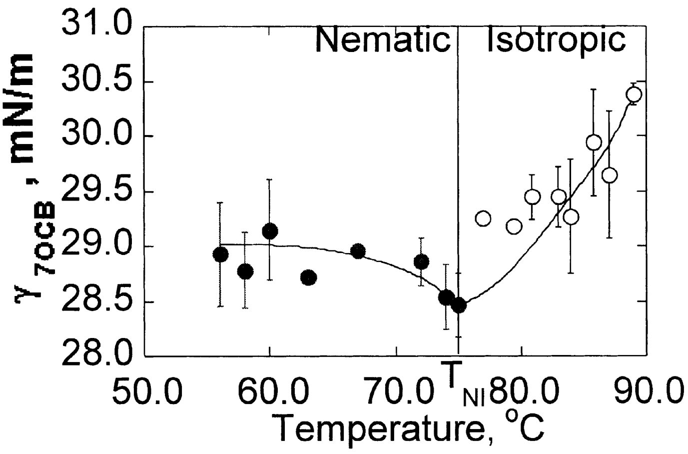

FIGURE 1 Surface tension of 7OCB as a function of temperature.

According to Croxton and Chandrasekhar [4], for liquid crystaline systems, -dγ/dt and therefore $\Delta S''$ results from a competition between the orientational ordering and the spatial disorder developed at the surface of the liquid crystal. It can be seen from Figure 1 that for the nematic phase of 7OCB, $(\Delta S'')_{7OCB}$ is positive; thus there is an increase of disorder going from bulk to surface of the drop. Also $(\Delta S'')_{7OCB}$ increases with increasing temperature. This may be due to the fact that NI phase transition and therefore the disordering begins and increases in the surface, propagating to the bulk. In the isotropic phase γ_{7OCB} increases with increasing temperature and $(\Delta S'')_{7OCB}$ is negative, corresponding to an decrease of disorder from bulk to surface. These results suggest that in the isotropic phase there is some kind of ordering of the molecules in the surface, compared to the bulk, in order to accommodate the rod like molecules in the surface. In the nematic phase this ordering in the surface was apparently smaller than that of the bulk.

Contact Angles formed by Drops of 7OCB on Solid Polymers

The values of contact angles formed by drops of 7OCB on a surface of PS, θ_{PS}, and VECTRA, θ_{VECTRA}, were measured as a function of temperature. Both θ_{PS}, and θ_{VECTRA} were constant in the nematic and isotropic phases of 7OCB. However the average θ_{PS} depended on the phase of 7OCB (17.6° for the nematic phase and 14.5° for the isotropic phase) and the average θ_{VECTRA} was constant (7.2° for both phases), not depending on the phase of 7OCB. This suggests that the nematic order of the molecules of 7OCB at the interphase between 7OCB and the solid polymers has less influence on θ_{VECTRA} than on θ_{PS}. This is probably due to the higher affinity between 7OCB and VECTRA which are both polar. In the case of PS a smaller affinity, evidenced by a higher value of the contact angle, could allow the molecular order to have more influence on θ_{PS}.

Interfacial Tension between 7OCB and the Solid Polymers

It can be seen from Figure 2 that, for the nematic and isotropic phases of 7OCB, both $\gamma_{7OCB/VECTRA}$ and $\gamma_{7OCB/PS}$ decreases linearly with increasing temperature. Therefore, $(\Delta S'')_{i/j}$ (where i and j are the components of the system) is positive. This indicates that there is a decrease in the order of the molecules of the 7OCB going from the bulk of the drop to the interphase. Also $(\Delta S")_{i/j}$ is larger in the isotropic phase indicating that the difference in ordering is larger in the isotropic phase in relation to that in the nematic phase. Near T_{NI}, both $\gamma_{7OCB/VECTRA}$ and $\gamma_{7OCB/PS}$ show a clear discontinuity most likely due to the first order transition from the nematic to the isotropic phase of 7OCB. $(\Delta S")_{i/j}$ is positive just as in the case of most polymer pairs for which the interfacial tension was shown [5] to decrease linearly with temperature.

Also $\gamma_{7OCB/VECTRA}$ is lower than $\gamma_{7OCB/PS}$. Since $(\Delta S")_{i/j}$ is similar for both systems, it can be inferred from equation 4 that the absolute values of the enthalpy, $(\Delta H")_{i/j}$ are larger for 7OCB/PS system than for 7OCB/VECTRA system. This indicates that, in 7OCB/PS system, there is a larger energy exchange for the interphase formation. These result are probably due to a better affinity between 7OCB and VECTRA than between 7OCB and PS.

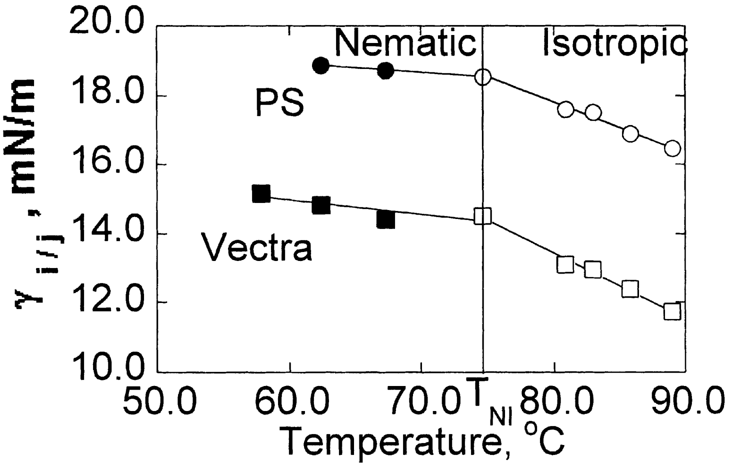

FIGURE 2 Interfacial tension between 7OCB and PS (circles) and 7OCB and VECTRA (squares)as a function of temperature.

CONCLUSIONS

The analysis of the behavior of the surface tension of 7OCB showed that in the nematic phase, the entropy of surface formation, $(\Delta S")_{7OCB}$, is positive, increasing with increasing temperature and that for the isotropic phase, $(\Delta S")_{7OCB}$ was negative the absolute value increasing with increasing temperature. For both 7OCB/PS and 7OCB/VECTRA systems the entropy of interphase formation, $(\Delta S")_{i/j}$, was positive for the nematic and isotropic phases of 7OCB. $\gamma_{7OCB/VECTRA}$ was lower than $\gamma_{7OCB/PS}$ and the absolute values of the enthalpy of interphase formation, for both phases of 7OCB, were larger for 7OCB/PS system than for 7OCB/VECTRA system. This was probably due to a better affinity between 7OCB and VECTRA than between 7OCB and PS.

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