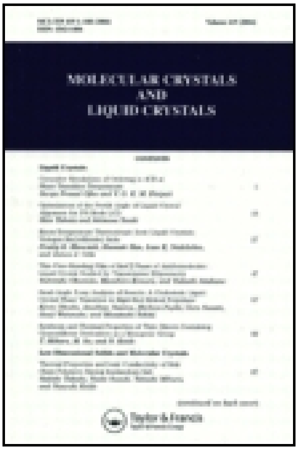

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Monte Carlo Studies of Model Systems of Rodlike Molecules with Partially Flexible Terminal Groups and/or with Side Groups

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Monte Carlo Studies of Model Systems of Rodlike Molecules with Partially Flexible Terminal Groups and/or with Side Groups

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The results of Monte Carlo simulations performed for model systems of rodlike molecules are compared with those of the same rodlike molecules with semiflexible end groups and/or with side groups. The presence of side groups perturbs the packing of the rigid cores and lowers the nematic/isotropic transition temperature. This effect is higher when the side groups are more exposed.

Keywords: simulation; liquid crystals; terminal groups; side groups

INTRODUCTION

In spite of the everyday increasing technological importance of liquid crystals[1,2], the relationships between molecular shape and thermal properties of these fascinating materials are still far from being completely understood. For this reason, we have recently started a systematic Monte Carlo study of the simulated phase behavior of simple molecules consisting of properly linked Lennard-Jones centers. At variance with systems simulated in the recent literature[3-6], our model molecules are simple enough to allow equilibrating the large systems required to approximate thermodynamic stability, but their shape can be

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* <www http://www.dichi.unina.it>

easily adapted to embody constitutional features found in real mesogenic molecules, such as pendant flexible or semiflexible terminal groups and/or side groups. Groups of this kind are required to lower the melting temperature such that liquid anisotropic phases may develop, and are good sites for chemical modifications designed to tune the anisotropic/isotropic transition temperature for a given application. Although the inclusion of these groups may change the molecular anisotropy of polarizability, it appears that in most cases their efficiency is mainly related to sterical hindrance[2,7]. In order to understand the effects of changes of the molecular shape due to inclusion of terminal and side groups, we compare in this paper the results obtained in the following simulations:

a) a reference system of rigid linear molecules of four units (system RC) at a density similar to that of the rigid cores in real mesogenic materials;[8,9]
b) system RC with an added pendant terminal group fixed at various angles with respect to the long axis of the rigid core;[9]
c) system RC with an added pendant terminal group free to assume various orientations, with or without a restricting bending potential; [9]
d) system RC with an added side group linked perpendicular to the long axis of the rigid core to a terminal unit or to an internal unit.

MODELS AND METHODS

The model molecules studied in this work consist of five Lennard-Jones centers connected by links of length σ (Figure 1). The first four units are rigidly aligned, mimicking the rigid core of mesogenic molecules, while the position of the fifth unit is changed in the various simulations.

We denote with R and F systems containing model molecules with a terminal group added to the rigid core in which the angle τ (see Figure 1) is restricted by a quadratic potential $E_\tau = (1/2)k_\tau\tau^2$ or fixed, respectively. Simulations have been performed for systems R_0, $R_{1.0}$ and $R_{3.5}$ in the first case (the subscripts indicating the value of k_τ in kJ·mol^{-1}·rad^{-2}), and for systems F_{15}, F_{30}, F_{45}, F_{60} and F_{75} in the second case (the subscripts indicating the fixed value of τ in degrees). Systems of model molecules with a side group added perpendicular to the rigid core are denoted with S_3 or S_4 (see Figure 1; note that S_4 is equivalent to F_{90}), while the reference system of rigid cores without the fifth unit is denoted with RC (see before).

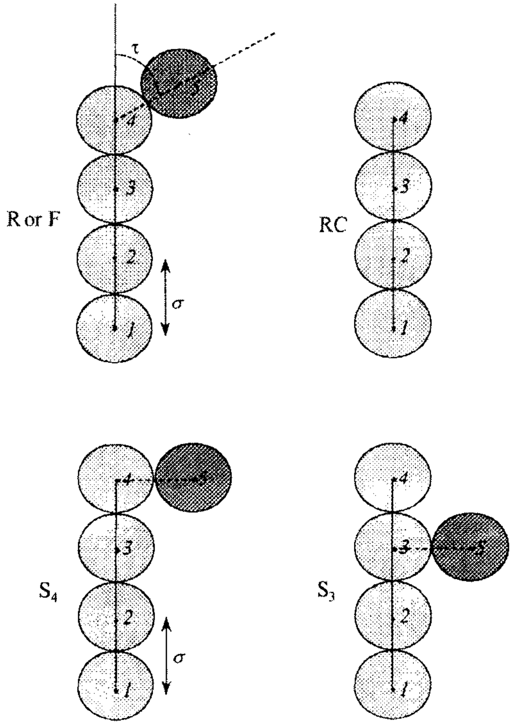

FIGURE 1 The model molecules utilized in this work (see text)

Non-bonded centers interact through a shifted 12-6 Lennard-Jones potential $E_{nb} = \varepsilon[(\sigma/r)^{12}-2(\sigma/r)^{6}+1]$, truncated at the distance σ such to include repulsive interaction only. According to current theories[10,11], attractive anisotropic interactions among rigid cores are modelled in the mean field form $E_{mf} = -As(3\cos^2\theta - 1)/2$, with s the order parameter and θ the angle between the rigid core and the nematic director. Values of 416 J/mol and 7.6 kJ/mol are used for ε and A, respectively[8,9]. Calculations have been performed with 10667 model molecules in a tridimensionally periodic cubic cell of edge 40σ (the molecular number density being ρ = 1/6 molecules/σ^3). Systems S_4 and S_3 have been also simulated at a lower density, i.e. with 9143 molecules in the same cell (ρ = 1/7 molecules/σ^3) and with the correspondingly reduced value of A = 6.5 kJ/mol[11].

The mean field approximation adopted for the attractive anisotropic interactions simplifies several aspects of the calculations. For instance, it allows establishing *a priori* the direction of the nematic director, taken in our simulations to be coincident with the z axis. All simulated systems have been then initialized with rigid cores randomly positioned parallel to this axis, the fifth terminal group being placed at τ = 45° in the case of systems R. We have then used the Monte Carlo algorithm with periodic boundary conditions in the canonical (NVT) ensemble in order to equilibrate the simulated systems at various increasing temperatures. After isotropization, partly equilibrated configurations with order parameter ≈0.3 have been utilized as starting points for cooling runs. The theoretical basis for this method, as well as further details on the simulation procedure and parameters, are described in Refs. 8 and 9.

RESULTS AND DISCUSSION

For each molecular constitution (Figure 1), we have performed Monte Carlo calculations at various temperatures and with various starting configurations, carrying out both heating and cooling runs. In all cases, anisotropic phases and the isotropic liquid have been reversibly observed by changing the temperature. Table 1 summarizes the transition temperatures for all systems investigated. Among the others, Table 1 shows that:

a) the transition temperatures of systems R_0, $R_{1.0}$ and $R_{3.5}$ are very close to those of F systems with τ = 60°, 55° and 45°, respectively; also, the transition temperatures of systems $R_{1.0}$ and RC are practically coincident;

b) the transition temperature of systems F decreases strongly with increasing τ for τ between 15° and 45°; the dependence becomes much weaker when $\tau > 60°$, for which T_{NI} is confined in the 280-300 K range;

c) the transition temperature of systems S_3 and S_4 is always lower than that of RC; the decrease is relatively small when $\rho = 1/6$, and much higher when $\rho = 1/7$; at a given density, T_{NI} is 10-15° lower for S_4 than for S_3.

System	T_{NI} (K)	System	T_{NI} (K)	System	T_{NI} (K)
RC	300-305	R_0	295-300	F_{15}	460-470
S_4, $\rho = 1/6$	280-285	$R_{1.0}$	300-305	F_{30}	380-385
S_4, $\rho = 1/7$	225-230	$R_{3.5}$	320-325	F_{45}	320-325
S_3, $\rho = 1/6$	295-300			F_{60}	290-295
S_3, $\rho = 1/7$	235-240			F_{75}	280-285

TABLE 1 Nematic-isotropic transition temperatures (T_{NI}) for all systems investigated; the molecular number density is $\rho = 1/6$ molecules/σ^3, unless otherwise indicated.

In order to rationalize the observed behavior, we have calculated several properties of the various systems in the isotropic and anisotropic phases close to the transition points. It is remarkable that all properties of interest, including the orientational distribution of the rigid cores, are practically coincident for systems RC and $R_{1.0}$ at all temperatures. In other words, flexible or slightly inflexible end groups can be treated as *bonded solvent* in thermodynamic calculations. Also, the average values of τ in systems R_0, $R_{1.0}$ and $R_{3.5}$ at the transition points are approximately equal to the values of τ in F systems with the same transition temperature. However, it is interesting to point out that the distribution of τ in the isotropic liquid of system $R_{1.0}$ is quite different from the distribution for a gaseous model molecule at the same temperature, indicating that packing effects favor more compact conformations in condensed phases. Furthermore, the distribution in the nematic phase is shifted toward lower values of τ with respect to the distribution in the isotropic liquid, showing that the nematic/isotropic transition is coupled with a conformational transition favoring more extended conformation in the ordered phase. This latter finding is in excellent agreement with the results of NMR experiments[12].

The effect of flexibility has been investigated in previous studies[13,14] (see also Ref. 9 and references therein). In particular, flexible tails are known to stabilize smectic layering[13]. Since our interest was focused on the anisotropic/isotropic transition behavior, we have carefully checked the nematic nature of systems obtained in a 20-30 K range below the transition. More structured phases are certainly possible for our model molecules at lower temperatures and/or higher densities.

The *bonded solvent* behavior of the end groups in system $R_{1.0}$ implies that system RC is equivalent to a dense liquid of rigid cores linked to two semiflexible end groups of this kind, while systems F can be considered to derive from RC by substituting one of such end groups with a fixed bent group. In a similar way, systems S_3 and S_4 can be considered to derive from RC by substituting one of the semiflexible end groups with a side group when $\rho = 1/6$, and by simply adding a side group when $\rho = 1/7$ (adding a side group increases the molecular volume and decreases the molecular number density). The finding that T_{NI} decreases much more in the second case is then obviously explained by the reduced intensity of the mean field related to the dilution of the rigid cores, while the decrease of T_{NI} observed when $\rho = 1/6$ confirms that side groups interfere with the packing of the rigid cores.

On the other hand, the simulation result that at each density T_{NI} is 10-15° lower for S_4 than for S_3 is only related to the different shape of the model molecules. We have examined the intermolecular radial distribution function of the side groups in systems S_4 and S_3 with $\rho = 1/6$ in the nematic phase. The side groups in S_4 are more exposed to intermolecular interactions than those in S_3, producing a greater interference on the packing of the rigid cores and a higher lowering of T_{NI} with respect to system RC. This is in good agreement with experimental results showing that side groups in sterically shielded positions are less effective[2].

Though relatively simple, our model takes into account the two factors commonly believed to regulate the onset of long range order in liquid crystals: molecular shape and anisotropic attractive interactions.

Approximating the latter factor as a mean field simplifies the calculations and allows comparing the results with the predictions of available theories[8,9]. Of course, the thermal behavior of the simulated systems is partly governed by the mean field itself (in the absence of repulsive interactions, all systems would show a transition at 201 K when A = 7.6 kJ/mol and $\rho = 1/6$). On the other hand, Table 1 indicates that the model can be quite sensitive to relatively small changes of molecular shape. This is shown, for instance, by the transition temperatures of F systems with $\tau < 60^{\circ}$, also considering that the mean field is only applied to the rigid cores (i.e. terminal and side groups do not interact with the mean field). The weaker consequences of adding terminal groups with $\tau > 60^{\circ}$ or adding flexible or slightly inflexible end groups are due to a compensation of two opposing effects. These are the tendency of terminal groups to increase the transition temperature when aligned to the rigid core and the tendency of side groups to disturb the packing in the nematic phase.

In conclusion, it appears that the model can be utilized in this easily manageable form to investigate the general aspects of the relationships between molecular shape and thermal properties of liquid crystalline materials. We are presently extending the study to other cases of interest, such as dimers and trimers constituted by terminally linked rigid cores.

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