

STATISTICS OF A NOVEL CLASS OF LIQUID CRYSTAL POLYMERS

WANG Xinjiu (王新久) and ZHAO Jingan (赵静安)

(Department of Physics, Tsinghua University, Beijing)

ZHOU Qifeng (周其凤)

(Department of Chemistry, Peking University, Beijing)

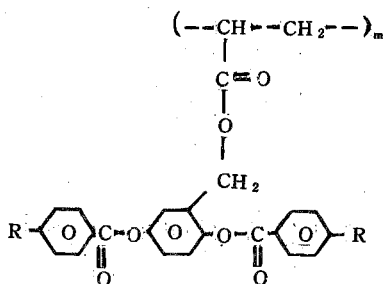
ABSTRACT

A novel class of the liquid crystal polymers with mesogens laterally attached to flexible main chain backbones has been synthesized recently by us. While the flexible backbones tend to take configuration of maximum entropy the mesogenic side groups tend to orientate because of the anisotropic soft dispersion forces. A mean field theory is presented to describe the competition between these two trends which makes it possible for this class of polymers to show anisotropic (liquid crystal) phase within certain temperature range where the polymer main chains and the side chain mesogens will take approximately parallel arrangement, which is different from the normal side chain liquid crystal polymers. The temperature range of the liquid crystal phase, its ordering and phase transition all depend on the flexibility of the backbone, the strength of the anisotropic forces of the side groups and the hinge elasticity. The results show that the liquid crystal-isotropic phase transition is of the first order. The phase diagram, i.e. the dependence of the transition temperature on the structure of the polymers is also given.

INTRODUCTION

In the last years, a lot of the polymers with the thermotropic or lyotropic liquid crystal (LC) phases have been synthesized. It is found that there are two kinds of LC polymers, the linear polymers with main chain mesogenic groups and the flexible spacers, and the side chain polymers with the side chain mesogenic groups. The presence of the mesogenic groups can be the rod-like, the disc-like, and even the alternative of both of them. We can see the occurrence of the mesogenic group brings into strong effects on the conformation, the statistics and the phase behaviour of the polymers^[1-8].

Recently, a new class of the side chain polymers has been synthesized by us. The main chain is flexible, but the side chains at regular intervals along the main chain consist of the rod-like mesogenic groups. The side chains are linked with the main chain via short linkages. The geometry of the hinge makes the side chain to tend not to be perpendicular to the main chain as that the conventional side chain LC polymers do, but to be parallel to it. The polymers are poly(2, 5-bis (4-alkoxybenzoyloxy) benzyl acrylates), the chemical formulas of which are shown below:



$$\text{R} = \text{R}' = \text{OC}_n\text{H}_{2n+1} \quad n = 1, 2 \text{ and } 4.$$

The optical experiment shows that the polymers exhibit the birefringence and the form of a Maltese cross under the cross polars, as shown in the Figure 1. Such behaviour is interpreted in terms of the typical nematic liquid crystal texture.

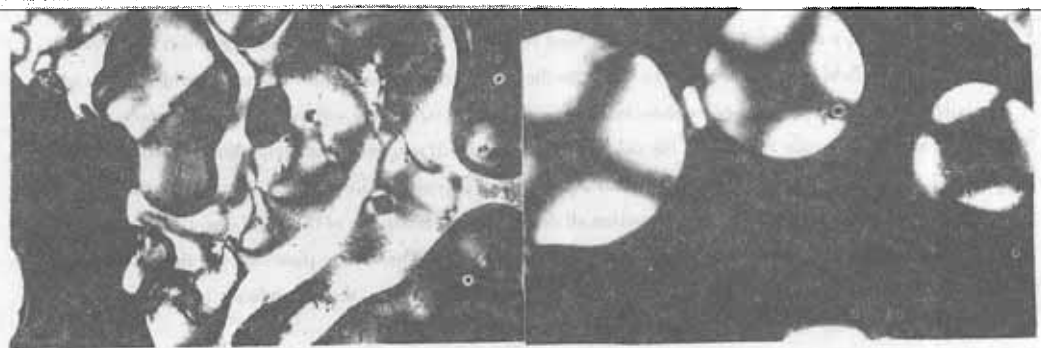


Fig. 1 The optical texture of the side chain LC polymers under cross-polar microscope. $T = 150^\circ\text{C}$, 100X.

A theoretical model is presented here to describe the nematic-isotropic phase transition of this new kind of the side chain polymer, which depends upon the flexibility of the main chain, the coupling of the side groups, the hinge elasticity, and the length of the side group as well as the side chain volume fraction. The two order parameters are presented to describe the ordering of the main- and side chains respectively. The dependence of the order parameters on the temperature is calculated.

MODEL

The main chain of the side chain polymer is linear. In general, the main chain is not complete flexible and has more or less rigidity. We will describe the properties of the main chain in terms of the semi-rigid chain theory^[3,4].

The conformation of the main chain in the absence of the external fields would be the random walk coil. Meanwhile, the side groups are actual low molecular weight liquid crystal nematogens, they tend to align parallel to each other. The Maier-Saupe (M-S) theory^[9] and the Onsager model^[10] have shown that either the anisotropic dispersion force or the steric repulsion of the elongated shape of rigid rods can make the mesogens to show the anisotropic phase, the nematic LC.

The new side chain polymer mentioned above can be thought to be a binary mixture of the typical linear polymers, the main chains, and the typical low molecular weight LC, the side chains,

with the hinge elasticity as the interaction between them.

Figure 2 shows schematically the side chain polymer. It is of interest to note that in such polymers the side chain groups tend to be parallel to the main chain because of the hinge interaction. The length of the main chain is L when it is fully extended. l is designated as the arc length from one end of the main chain, $\vec{u}(l)$ is the tangent of the main chain at l , the unit vector. The long axis of the rigid elongated side group is labelled by a unit vector $\vec{s}$, the magnitude s is the axial ratio of the side group. The uniaxial direction of the side chain polymer is defined $\vec{n}$, i.e. the director.

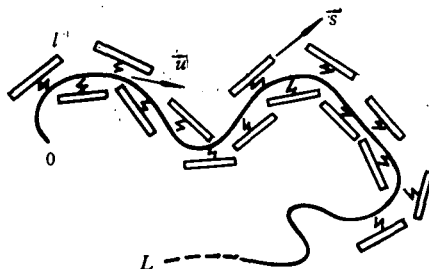


Fig.2 The schematic of the new side chain polymer. $\vec{s}$ is the long axis vector of side group, L is the total length of main chain, l is the arc length from one end of main chain, $\vec{u}(l)$ the tangent of main chain at l .

The interaction of the main chain and the side groups attached to it is obviously dependent on the relative orientations of $\vec{u}(l)$ and $\vec{s}$. As mentioned above, the hinge of the main- and side chains proposes that it be the lowest energy state when $\vec{u}(l)$ and $\vec{s}$ are parallel to one another.

In the mean field approximation, the interaction is proportional to the square of the scalar product of the vectors $\vec{u}$ and $\vec{s}$, it takes the form

$$-(\vec{s} \cdot \vec{u})^2 \quad (1)$$

Let us choose a Cartesian co-ordinates with the z axis along the director $\vec{n}$. We will define the $\vec{s}$ and $\vec{u}$ by their polar angles, θ , φ and θ' , φ' , respectively. As a result of the equal azimuthal distribution of the $\vec{s}$ and $\vec{u}$, we can assume the system behaviour is independent of φ and φ' , and thus the statistical average of $(\vec{s} \cdot \vec{u})^2$ is given by

$$\begin{aligned} \overline{(\vec{s} \cdot \vec{u})^2} &= \cos^2 \theta \cos^2 \theta' + \frac{1}{2} \sin^2 \theta \sin^2 \theta' \\ &= \frac{2}{3} P_2(\cos \theta) P_2(\cos \theta') + \frac{1}{3} \end{aligned} \quad (2)$$

where $P_2(x)$ is the second-rank Legendre polynomial, i.e. $P_2(x) = 3x^2/2 - 1/2$. In the equation (2), the constant $1/3$ does not contribute to the statistics of the system we concern with, and may be omitted. The factor $2/3$ of first term may be combined with the hinge elasticity c .

The flexible main chain is to make the conformation of random walk coil to get the maximum configuration entropy. Meanwhile, the side mesogens tend to align to be an ordered arrangement. So that there is the competition of the two tendencies through the hinge interaction.

In the mean field theory, the potential of each side chain will take the form which is similar to the Maier-Saupe expression

$$U_s = -xas S_s P_2(\cos\theta) - c S_m P_2(\cos\theta) \quad (3)$$

Here the subscripts s and m are designated for the side chain and main chain respectively. The first term comes from the dispersion force of the side groups themselves with (as) as the material-dependent coefficient. As a result of the existence of the main chain, the coupling of the diluted side chains will be multiplied by the volume fraction x of the side chain. S_s is the order parameter of side chains.

S_s is defined as follows:

$$S_s = \langle P_2(\cos\theta) \rangle \quad (4)$$

The bracket represents a thermal average over all the orientation of the side chains. The second term in equation (3) is related to the interaction from the main chain, where S_m is defined as the average result of each segment of the main chain, i.e.

$$S_m = \int_0^L \langle P_2(\cos\theta') \rangle dl / L \quad (5)$$

The main chain can be taken as a continuous semi-rigid, long chain with the bend modulus ϵ . So that we have the bend elastic energy

$$1/2\epsilon \int_0^L \left(\frac{d\bar{u}}{dl} \right)^2 dl \quad (6)$$

Here ϵ is dependent on the flexibility of the main chain, the more the flexibility, the less the modulus ϵ , in other words, the less the rigidity. The bend deformation of the main chain is expressed by $\frac{d\bar{u}}{dl}$. In addition to the elasticity of the main chain itself, the interaction from the side chain adds hinge elastic energy. If we assume that the N side mesogens are attached to a main chain, the hinge energy will be given by, after the average along the main chain,

$$-\frac{N}{L} \int_0^L c S_s P_2(\cos\theta') dl \quad (7)$$

As the result, the partition function of each main chain is given by

$$Z_m = \int d\bar{u} \exp \left[-\beta \frac{\epsilon}{2} \int_0^L \dot{u}^2 dl + \beta \frac{N}{L} c S_s \int_0^L P_2(\xi) dl \right] \quad (8)$$

where $\dot{u} = \frac{d\bar{u}}{dl}$, $\xi = \cos\theta'$, $\beta = 1/k_B T$, k_B is the Boltzmann constant. We follow the method proposed by Warner et al.^[3] and Wang and Warner model^[4] in the following calculation. It is known that the path integral in equation (8) is equivalent to a diffusion equation of a particle on the surface of an unit sphere, which is called Brownian walk equation,

$$\left[\frac{\partial}{\partial l} - D \nabla_u^2 - \Delta^2 (1 - \cos^2\theta') + \frac{2}{3} \Delta^2 \right] G(\bar{u}, \bar{u}'; l, l') = \delta(\bar{u}, \bar{u}') \delta(l, l'). \quad (9)$$

Here $D = 1/2\beta\epsilon$ is the rotational diffusion coefficient, D^{-1} has the dimension of length, in fact, it is the step of random walk when the main chain is in the isotropic phase. For convenience, we normalize all the length, e.g. L and l by D^{-1} which can be measured by small angle X-ray or

neutron scattering. $\Delta^2 = -3 \frac{N}{L} c \epsilon \beta^2 S_s \cdot \nabla_u^2$ is the angular part of the Laplace operator. The Green function $G(\vec{u}, \vec{u}'; l, l')$ is the propagator taking the $\vec{u}(l)$ along the main chain from initial direction $\vec{u}'$ at the point l' to the final $\vec{u}$ at the other point l . δ is the Delta function. Suppose the l dependence of the propagator G , $e^{-\lambda_n l}$, thus the equation (9) becomes

$$\left[\Lambda_n + \frac{1}{\sin \theta'} \frac{d}{d\theta'} (\sin \theta' \frac{d}{d\theta'}) + \Delta^2 (1 - \cos^2 \theta') \right] W(\theta') = 0, \quad (10)$$

The eigenvalue $\Lambda_n = \lambda_n - \frac{2}{3} \Delta^2$. If the main chain is a free semi-rigid chain, thus $\Delta^2 = 0$, equation (10) will be the Legendre equation with the eigenvalue $\Lambda_n = n(n+1)$. For a long flexible chain, the conformation of the main chain is the typical random walk coil, and no orientation order will occur. When $S_s > 0$, the definite Δ^2 makes the flexible chain to walk in an uniaxial, anisotropic potential which takes the maximum at the equator and the minimum at the region of two poles. As the result, the segments of the main chain are forced to orientate towards two poles.

Equation (10) is the standard form of the Spheroidal wave equation of zero-order^[11]. The propagator G can be obtained as follows:

$$G(\xi, \xi'; l, l') = \frac{2n+1}{2} \sum_{n=0}^{\infty} S_p_n(\xi') S_p_n(\xi) e^{-\lambda_n |l-l'|} \quad (11)$$

where $S_p_n(x)$ is the Spheroidal wave function of zero-order. For a very long chain, only the lowest term is dominant because of the exponent, hence the partition function Z_m and the order parameter S_m will be obtained as

$$\begin{aligned} Z_m &= \int d\xi d\xi' G(\xi, \xi'; L, 0) = \sum_{n=0}^{\infty} \frac{2n+1}{2} \left[\int d\xi S_p_n(\xi) \right]^2 e^{-\lambda_n L} \\ &\doteq \frac{1}{2} \left[\int d\xi S_p_0(\xi) \right]^2 e^{-\lambda_0 L}, \end{aligned} \quad (12)$$

and

$$\begin{aligned} S_m &= \frac{1}{L} \int_0^L \left[\int d\xi d\xi' P_2(\xi) G(\xi, \xi'; L, 0) / Z_m \right] dl \\ &\doteq \frac{1}{2} \int_{-1}^1 d\xi [S_p_0(\xi)]^2 P_2(\xi). \end{aligned} \quad (13)$$

Meanwhile, for a side mesogen, the partition function Z_s is

$$Z_s = \int_{-1}^1 \exp [\beta(xas S_s + c S_m) P_2(z)] dz, \quad (14)$$

where $z = \cos \theta$. And the order parameter S_s is given by

$$S_s = \int_{-1}^1 P_2(z) \exp [\beta(xas S_s + c S_m) P_2(z)] dz / Z_s \quad (15)$$

Obviously, equations (13) and (15) are the self-consistence equations about S_m and S_s .

The numerical method can be called to solve the equations. For the qualitative demonstration of the behaviour of the system, we will asymptotically expand the parameters S_s and S_m . First of all,

we reduce the form of S_s into the Dawson function, denoting $\alpha = \frac{3}{2} \beta (xas S_s + c S_m)$, thus we get

$$S_s = \frac{3}{2} \cdot \frac{\partial}{\partial \alpha} \ln \left[\frac{e^\alpha}{\sqrt{\alpha}} D(\sqrt{\alpha}) \right] - \frac{1}{2}, \quad (16)$$

where $D(x)$ is the Dawson function. Subsequently, we expand the Dawson function in first approximation. Consequently, the order parameter S_s takes the form

$$S_s = 1 - \frac{3}{2\alpha} + O\left(\frac{1}{\alpha^2}\right) \doteq 1 - \frac{k_B T}{xas S_s + c S_m} \quad (17)$$

Warner et al.^[3] have obtained the asymptotical expression of the Spheroidal wave function. Introducing the asymptotical expression, after the simple algebra, the order parameter S_m of the main chains becomes

$$\begin{aligned} S_m &= 1 - \frac{3}{2|\Delta|} + O(1/|\Delta|^{3/2}) \\ &= 1 - \frac{\sqrt{3}}{2} \cdot \frac{k_B T}{\sqrt{\frac{x}{1-x} \frac{\varepsilon}{s} S_s}} \end{aligned} \quad (18)$$

If we assume that the main- and side chains have the equal cross-section, it is found to be a good approximation, thus it yields the volume fraction as follows:

$$x = \frac{N_s}{N_s + L}, \quad 1 - x = \frac{L}{N_s + L} \quad (19)$$

Equation (19) means implicitly the limit on the value of x . Because the side chain of the axial ratio s is at least connected to one segment of the main chain, the volume fraction has the maximum, i.e.

$$x_{\max} = \frac{1}{1 + 1/s} \quad (20)$$

Suppose the free energy of the isotropic phase of the side chain polymer F_I is zero, the free energy of the nematic LC must be less than F_I for the stable nematics. It is convenient to set a normalization temperature T_0 which is the nematic (N)-isotropic(I) phase transition temperature of the pure side mesogens alone. From the equations (17) and (18), we get the solution of both S_s and S_m versus the reduced temperature $T^* = T/T_0$ with the coupling constants of the ratio of $as:c:\varepsilon/s$. According to the calculation of Wang and Warner^[4], the free energy per persistence length D^{-1} of the main chain is given by

$$F_m/L = -k_B T \lambda_0 + \frac{1}{2} \frac{x}{1-x} S_s S_m \frac{D^{-1}}{s} \quad (21)$$

where the eigenvalue λ_0 is given by

$$\lambda_0 = -\frac{2}{3} |\Delta|^2 + 2|\Delta| - 1 + O(1/|\Delta|) \quad (22)$$

Meanwhile, the free energy per side mesogen is

$$\begin{aligned}
 F_s &= -k_B T \ln(Z_s/2) + \frac{1}{2}(xas S_s^2 + c S_s S_m) \\
 &= -k_B T \left(\frac{2}{3}\alpha - \ln\alpha - \ln 2 \right) + \frac{1}{2}(xas S_s^2 + c S_s S_m)
 \end{aligned} \quad (23)$$

Here the first term is taken from the expansion of the Dawson function in the similar way as that in the equation (17). Consequently, the total free energy per side chain polymer molecule becomes

$$F_N = F_m + N F_s = (Ns + L) \left(\frac{1-x}{D^{-1}} \cdot \frac{F_m}{L} + x \cdot \frac{F_s}{s} \right) \quad (24)$$

When the N-I transition occurs, the equation (24) must vanish, i.e. $F_N = 0$. It yields

$$(1-x) \left[2|\Delta| - 1 + \frac{2}{3}|\Delta|^2 (S_m - 1) \right] + x^2 a \varepsilon \beta^2 S_s^2 - 2\beta x \frac{\varepsilon}{s} \left(\frac{2}{3}\alpha - \ln\alpha - \ln 2 \right) = 0 \quad (25)$$

In the isotropic phase, $S_s = S_m = 0$. At the N-I transition, the order parameters jump simultaneously to zero from definite values, which corresponds to the definite heat content. Thus N-I transition of the side chain polymer is of the first order type.

Similarly to those of Wang and Warner^[4,6], the entropy S per unit volume is

$$S/k_B = -(1-x) \frac{2}{3} S_m |\Delta|^2 - 2x\beta \left(\frac{2}{3}\alpha - \ln\alpha - \ln 2 \right) \frac{\varepsilon}{s} \quad (26)$$

And the heat content thus is

$$Q = T_c S_c \quad (27)$$

where T_c is the N-I transition temperature, S_c the entropy change at the transition.

SUMMARY

As mentioned above, we choose T_0 the normalization temperature which is given by, in the Maier-Saupe theory,

$$k_B T_0 / (as) = 0.2202 \quad (28)$$

where the constant (as) is equivalent to a in the Maier-Saupe expression.

The formulas in §2 show that the statistics of the system depends upon the flexibility ε of the main chain, the coupling a and the axial ratio s of the side mesogen, and the hinge elasticity c . It is found that the statistics of the system depends equivalently upon the following ratio

$$K = as : c : \varepsilon / s.$$

Figure 3 shows the dependence of the parameters S_s and S_m on the temperature with a typical $x = 0.7$, and with two sets of K , $K = 1:0.2:0.2$ and $K = 1:0.2:0.05$. One can see that at the absolute temperature, i.e. $T^* = 0$, $S_s = S_m = 1$. The results are expected, but it is only important in the theoretical sense. In fact, no materials can keep the nematic order until $T \rightarrow 0$ K. As the temperature increases, the order parameters decrease smoothly until the critical values S_{sc} and S_{mc} at the N-I transition. In the Figure 3, the S_s is not concised with S_m , which means that the main- and side chains have different orientational order, it is the reason that we propose two order parameters separately for main- and side chains.

It needs to point out that the asymptotical equations (17) and (18) suggest the α and Δ are

large enough as to neglect the high terms of α^{-1} and Δ^{-1} . They are working well as the temperature T is far from the N-I transition T_c , but when the T is close to T_c , the high terms will become significant, so the order parameters S_c 's at T_c are not very precise.

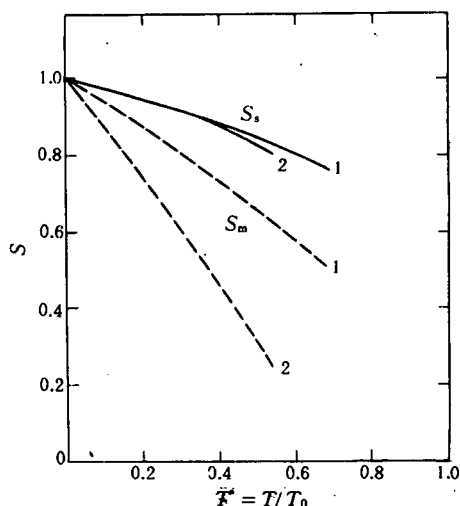


Figure 3 The order parameters S_s and S_m as the function of reduced temperature $T^* (T/T_0)$.

T_0 is the N-I transition temperature of pure side mesogens. The solid curves correspond to S_s ,

the dashed curves correspond to S_m .

1, the coupling constants of the ratio

$$K = as : c : \epsilon / s = 1 : 0.2 : 0.2; 2,$$

$$2, K = 1 : 0.2 : 0.05.$$

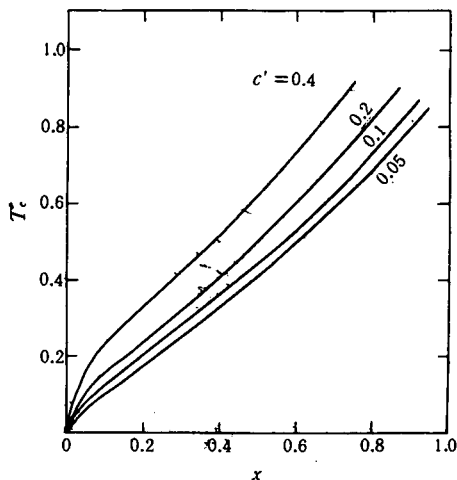


Figure 5 The phase diagrams with the reduced temperature T_c^* against the volume fraction x of side chain (II) The curves correspond:

$$c' = 0.4, 0.2, 0.1, 0.05 \text{ with } K = 1 : c' : 0.2.$$

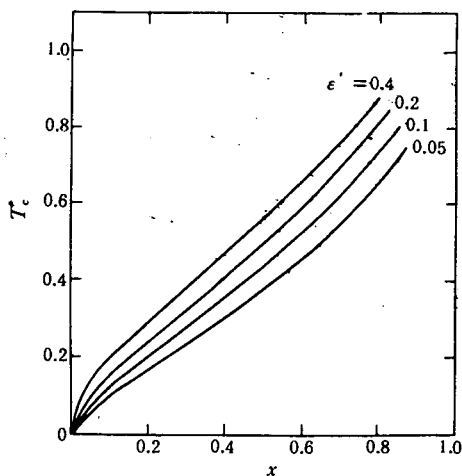


Figure 4 The phase diagrams with the reduced temperature T_c^* against the volume fraction x of side chain (I). The curves correspond:

$$\epsilon' = 0.4, 0.2, 0.1, 0.05 \text{ with } K = 1 : 0.2 : \epsilon'.$$

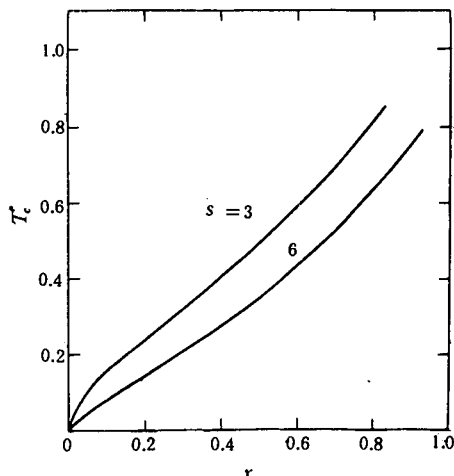


Figure 6 The phase diagrams with the reduced temperature T_c^* against the volume fraction x of side chain (III). The curves correspond:

$K = 1 : 0.2 : 0.2$ which is equivalent to $s = 3$,
and $K = 1 : 0.1 : 0.05$ which is equivalent to $s = 6$.

Figure 4 shows the phase diagrams, the dependence of the N-I transition temperature T_c^* on the volume fraction x . With the increase of x , T_c increases, but it is always less than T_0 . As a result of the limit of x , the calculation is suitable below the certain value of x for various s . For example, $x_{\max} = 0.75$ for $s = 3$. As x approaches zero, the nematic order vanishes. The result is expected for the flexible linear polymers. Actually, there should be a minimum limit $x_{\min}$ for x because of the crystallization or glassifying of the polymer. The curves in Figure 4 correspond to different bend modulus. As ϵ increases, the curves rise up.

Figure 5 shows the phase diagrams with reduced temperature T^* against the volume fraction x of side chain corresponding to different hinge elasticity c . It is through the hinge elasticity c that the side mesogens force the main chain to align.

Figure 6 shows the influence of the axial ratio s of side chain on the N-I transition, where two curves corresponding to $s = 3$ and $s = 6$ were drawn. It is noted that the T_0 will change simultaneously with s , as shown in the equation (28).

COMPARISON WITH THE EXPERIMENTS

We take into account the bonds of the hinge, as shown in the Figure 7, one can find that the local main chain segment and side group are almost parallel to each other. The case is the same as what the article described.

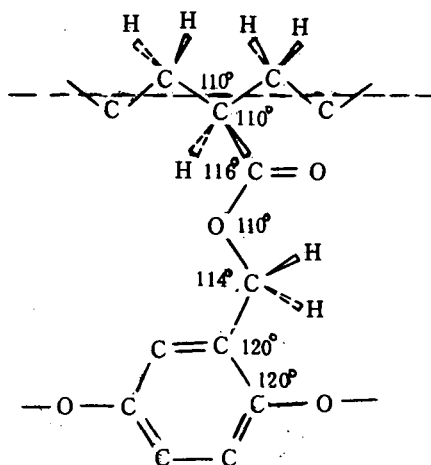
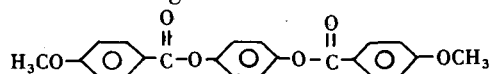


Figure 7 The bonds at the hinge of the side chain polymers.

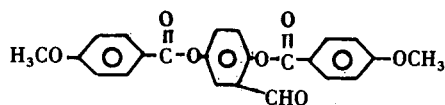
The paper has assumed that the dimension of the cross-section of the main chain is about the same as that of the side chain. The assumption is supported by X-ray diffraction. The experiment shows, in the range of the diffraction angle from 10 to 60 degrees, only a diffuse ring at 20.04 degrees, which is attributed to the liquid-like positional correlation, corresponding to around 4 to 5 Angstroms of the diameter of the cross-section.

The side chains of the side chain polymer consist of the mesogenic groups, which are similar to the following low molecular weight LCs. One of them is



which exhibits the N-I transition at 297°C^[12].

The chemical formula of another low molecular weight LC is



The later is measured by the DSC experiment which shows the N-I transition temperature of 224°C.

Meanwhile, the side chain LC polymer shows the reduction by a few tens degrees to the N-I transition which is 170°C by the DSC. If we choose arbitrarily the former low molecular weight LC as the side mesogens of the side chain polymer, we will have $T_c^* = 0.76$. The corresponding volume fraction of the side chain is found to be 0.75. The result is qualitatively in agreement with the theoretical expectation.

The question of interest remains whether there is a helical conformation in the side chain LC polymer which is likely expected. Some experiments are being carried out on it.

Keywords

Side chain liquid crystal polymer; Poly(2, 5-bis (4-alkoxybenzoyloxy) benzyl acrylates); Brownian walk

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REFERENCES

- [1] Ten Bosch, A., Maissa, P., Sixon, P., *Phys. Lett.*, **1983**, 94A, 299; *J. Chem. Phys.*, **1983**, 79, 3462.
- [2] Jahnig, F., *Mol. Cryst. Liq. Cryst.*, **1981**, 63, 157.
- [3] Warner, M., Gunn, J. M. F., Baumgartner, A., *J. Phys.*, **1985**, A18, 3007.
- [4] Wang XinJiu, Warner, M., *J. Phys.*, **1986**, A19, 2215.
- [5] Wang XinJiu, Warner, M., *Phys. Lett.*, **1986**, 119A, 181.
- [6] Wang XinJiu, Warner, M., Rutherford Appleton Laboratory Report, RAL-1986-037.
- [7] 王新久, Warner, M., 全国高等院校高分子化学与物理学术讨论会论文集 (Proceeding of Symposium on Polymer Chemistry and Physics of National Institutions of High Learning, Guangzhou), **1986**, p.26.
- [8] Renz, W., Warner, M., *Phys. Rev. Lett.*, **1986**, 56, 1268.
- [9] Maier, W., Saupe, A., *Z. Naturforsch.*, **1959**, 14A, 882; **1969**, 15A, 287.
- [10] Onsager, L., *Ann. N. Y. Acad. Sci.*, **1949**, 51, 627; Zwanzig, R., *J. Chem. Phys.*, **1963**, 39, 1714.
- [11] Meixner, J., Schafke, F. M., *Mathieusche Funktionen und Spharoidfunktionen*, Springer-Verlag, Berlin, **1954**.
- [12] Kelker, H., Hatz, R., *Handbook of Liquid Crystals*, Verlag Chemie, **1980**, Ch.2.