

STATISTICAL MODELS FOR SEMI-RIGID NEMATIC POLYMERS*

WANG Xinjiu (王新久)

(*Department of Chemistry, Peking University, Beijing 100871*)

ABSTRACT

Semi-rigid liquid crystal polymer is a class of liquid crystal polymers different from long rigid rod liquid crystal polymer to which the well-known Onsager and Flory theories are applied. In this paper, three statistical models for the semi-rigid nematic polymer were addressed. They are the elastically jointed rod model, worm-like chain model, and non-homogeneous chain model. The nematic-isotropic transition temperature was examined. The pseudo-second transition temperature is expressed analytically. Comparisons with the experiments were made and the agreements were found.

INTRODUCTION

First mesomorphic polymer was discovered in 1937 in solution of the tobacco mosaic virus, a rigid long polymer^[1]. A few efforts have since been made to establish the theoretical basis for this class of liquid crystal polymers, among those the most important theories were the virial expansion by Onsager in 1949^[2] and the lattice model by Flory in 1956^[3]. In their theories, liquid crystal phases arise from purely steric reasons, relatively dense systems of long rigid rods easily form a liquid crystal phase. Twenty years later, the liquid crystal phase was observed in semi-rigid main chain polymers as well. Those polymers are composed of rigid mesogenic units with flexible spacers. The application in high modulus fiber has aroused research interest in this respect. Since then tremendous efforts have been made to synthesize the liquid crystal polymers and many experiments have been performed to investigate their properties. Meanwhile, the theoretical study has been made as well.

* The work was supported by the Foundation of State Education Committee of China

Received September 1, 1994

The Maier-Saupe theory^[4], a suitable mean field theory for low molecular weight liquid crystals, was proposed to describe the simplest model of these polymers, i. e. , the freely-jointed-rod model. In this model each repeated mesogenic unit models as a rod subject to a nematic field, while the successive rods rotate freely. Therefore, the nematic-isotropic (N-I) transition of the polymer occurs at the temperature $T_c = 0.2202 a/k_B$, where a is the nematic coupling constant and k_B is the Boltzmann's constant.

Because of its simplicity, the rods have no effect on orientation of successive rods so that random-walk conformation is obtained, but one expects the rod behavior as the nematic field is strong. Actually, the rods are not freely hinged. To overcome the drawback of the freely-jointed-rod model, the following statistical models were presented for such semi-rigid nematic polymers. Among them are elastically-jointed-rod model^[5]; worm-like chain model^[6-8]; non-homogeneous chain model^[9-11].

ELASTICALLY-JOINTED-ROD MODEL

There are two parts of energy of a set of jointed rods, one is from nematic mean field

$$U_n = - \sum_i p S P_2(\cos\theta_i) \quad (1)$$

where the order parameter $S = \langle P_2(\cos\theta) \rangle$, P_2 is the second Legendre polynomial. p is the nematic coupling constant of a mesogenic rod and θ_i is the angle of rod axis with respect to the director. The other part of energy arises from bending of successive rods

$$U_b = \sum_i \frac{1}{2} q (\theta_{i+1} - \theta_i)^2 \quad (2)$$

Where q is the bend elastic const. The first term favors both anti-parallel and parallel alignment. But the second term favors only the parallel alignment of two neighboring rods.

There is a characteristic length λ that balances the two effects. When the repeated unit length of the polymer l_o is greater than λ , the repeated unit along the polymer might be able to change abruptly its orientation and the polymer behaves as jointed rods. If l_o is less than λ , the polymer chain is worm-like.

The former case is treated by the elastically-jointed-rod model^[5], which

examines the liquid crystal polymers in terms of the transfer matrix approach, originally applied in one-dimensional Ising model. For simplicity, only discrete orientations are taken into account, that is, up($n=1$), down($n=-1$) and 4-fold degeneracy orientations on the perpendicular plane to the nematic director ($n=0$). The partition function of a set of jointed rods is then

$$Z = M_{\eta}^{(i+1)} M_{\eta}^{(i)} M_{\delta}^{(i-1)} \quad (3)$$

where the 6x6 matrix M is

$$M_{\eta}^{(i)} = \langle n_{\xi}^{(i)} | \exp(-H) | n_{\eta}^{(i-1)} \rangle \quad (4)$$

and the hamiltonian H is

$$H = -\frac{\alpha}{2} [P_2(n_{i+1}) + P_2(n_i)] + \frac{\beta}{2} (n_{i+1} - n_i)^2 \quad (5)$$

where $\alpha = pS/k_B T$, and $\beta = q/k_B T$. Actually, β is the ratio of persistence length to repeated unit length of polymer. M can be reduced to a 3×3 matrix by considering the 4-fold degeneracy of orientations in the perpendicular plane to director. Because of their identical form of each matrix M in equation (3), the partition function Z is the trace of the product of the N matrices M

$$M = \begin{Bmatrix} e^{-\alpha} & 2e^{-\alpha/4-\beta/2} & e^{-\alpha-2\beta} \\ 2e^{-\alpha/4-\beta/2} & (1 + 2e^{-\beta/2} + e^{-2\beta})e^{\alpha/2} & 2e^{-\alpha/4-\beta/2} \\ e^{-\alpha-2\beta} & 2e^{-\alpha/4-\beta/2} & e^{-\alpha} \end{Bmatrix} \quad (6)$$

and is dominated by the largest of its three eigenvalues, λ_{max} , and thus the partition function becomes

$$Z = \lambda_{max}^N \quad (7)$$

The free energy of a polymer is obtained from the partition function, $F = -k_B T \ln Z$, and can be expanded in the Landau-de Gennes' form. It is found from the expansion that the N-I transition is of typical first order. We analyze below the pseudo-second transition temperature T^* instead of T_c . The difference between two temperatures is small, experimentally within a few Kelvin.

The pseudo-second transition temperature T^* for this polymer of infinite length is given by the coefficient of quadratic term of free energy

$$T^* = (1 + e^{\beta/2} + e^{3\beta/2})/6 \quad p/k_B \quad (8)$$

where β is the ratio of persistence length to rod length, for typical value of the ratio, e. g., $\beta=4$, $T^*/T^*(\beta=0)=2.8$, where $T^*(\beta=0)$ is the value of freely jointed rods or that of corresponding monomers. The prediction is qualitatively in agreement with experiments^[12].

WORM-LIKE CHAIN MODEL

If the extended length of the polymer chain is fixed, but the building rods become very short the elastic discrete chain evolves into a worm-like chain, i. e., an elastically inextensible homogeneous chain. The path integral approach is then naturally applied^[6-8].

The partition function is then expressed by^[7,8]

$$Z = \sum_{n=0}^{\infty} 2(2n+1) \left[\int_0^1 dz S p_n(z) \right]^2 \exp(-\lambda_n L/l) \quad (9)$$

where L is the total length of polymer chain and l is the chain persistence length. $S p_n$ and λ_n are the Spheroidal wave functions and their eigenvalues, respectively, which are associated with $S a \epsilon / (k_B T)^2$. a and ϵ are the nematic coupling constant per unit length of chain and chain bend elasticity.

Substituting Z into free energy and adding the mean field term, the free energy per polymer is written as^[8]

$$F = -k_B T \ln Z + \frac{1}{2} a S^2 L \quad (10)$$

Expanding the free energy in the form of Landau-de Gennes theory the pseudo-second transition temperature can be obtained in the similar way as that in the second section

$$T^* = \left[\frac{2}{15} \left(1 - \frac{1 - e^{-6L/l}}{6L/l} \right) \right]^{1/2} \sqrt{a \epsilon / k_B} \quad (11)$$

This formula describes the effect of chain length on the N-I transition. T^* disappears when L/l approaches to zero and saturates as L is above the persistence length. It is in good agreement with the experiments^[13].

NON-HOMOGENEOUS CHAIN MODEL

Most main chain liquid crystal polymers are composed of mesogenic units linked by spacers with varying degree of flexibility, such as repeated methylene, oxyethylene, or siloxane groups. In the non-homogeneous chain model, the polymer chain is modeled in sequence of rods and spacers^[9-11]. The numerical results can be found in our early work^[11], and the analytical expression of the pseudo-second transition temperature for this polymer with infinite long chain may be obtained by

$$k_B T^* = (3a^2 v_{aa} + 2al \sqrt{v_{aa} v_{bb}} + b l v_{bb}) / 15(a + b) \quad (12)$$

where a , b and l are lengths of rod-like mesogenic unit, semi-flexible spacer, and its persistence length; v_{aa} and v_{bb} are the interaction between mesogenic units and spacers, respectively. Here we suppose interaction between mesogen and spacer is approximately equal to geometric mean of v_{aa} and v_{bb} .

Comparison with experiments was made in Ref. [11] and agreement was found. One of advantages of this model is its connection of transition temperature and the molecular parameters.

SUMMARY

Many efforts have been made to describe statistical behavior of the semi-rigid liquid crystal polymers. A few works improved the Onsager or Flory model, originally designed for rigid rod systems, to illustrate the solution of semi-rigid liquid crystal polymers^[14,15]. The basic idea is the introduction of persistence length. The above-mentioned models in this paper are three of models developed recently. Each of them has its advantages. In this paper we only concerned with the N-I transition temperature. Other properties of semi-rigid liquid crystal polymers, such as critical order parameter, entropy change at N-I transition, and conformations are also interests of theories. Theoretical study on the semi-rigid liquid crystal polymers is continuing.

Keywords:

Semi-rigid nematic polymer; Statistical model; Elastically-jointed rods; Worm-like Chain; Non-homogeneous chain

REFERENCES

- [1] Bawden, F. C. and Piri, N. W., *Proc. Roy. Soc. London*, **1973**, B123, 274.
- [2] Onsager, L., *Ann. N.Y. Acad. Soc.*, **1949**, 51, 627.
- [3] Flory, P. J., *Proc. Roy. Soc. London*, **1956**, A234, 73.
- [4] Maier, W. and Saupe, A. Z., *Naturforsch.*, **1959**, 14a, 882.
- [5] Warner, M. and Wang, X. J., *J. Phys. A*, **1992**, 25, 2831.
- [6] Jahmig, F., *Mol. Cryst. Liq. Cryst.*, **1981**, 63, 157.
- [7] Warner, M.; Gunn, J. M. F. and Baumgartner, A., *J. Phys. A*, **1985**, 18, 3007.
- [8] Wang, X. J. and Warner, M., *J. Phys. A*, **1986**, 19, 2215.
- [9] Matheson, R. R. Jr. and Flory, P. J., *Macromolecules*, **1981**, 14, 954.
- [10] Yurasova, T. A. and Semenov, A. N., *Mol. Cryst. Liq. Cryst.*, **1991**, 199, 301.
- [11] Wang, X. J. and Warner, M., *Liquid Crystals*, **1992**, 12, 385.
- [12] Blumstein, R. B.; Stickles, E. M.; Garthier, M. M., et al., *Macromolecules*, **1984**, 17, 177.
- [13] Griffin, A. C.; Hill, J. S. and Hughes, W. E., *Liquid Crystals*, **1989**, 4, 677.
- [14] Khokhlov, A. R. and Semenov, A. N., *Physica, A*, **1981**, 108, 546.
- [15] Ronca, G. and Yoon, D. Y., *J. Chem. Phys.*, **1984**, 80, 925.