

# Liquid crystallization in lyotropic liquid crystalline polymers

Jiaping Lin\*, Jian Zhu, Dafei Zhou

*Department of Polymer Science and Engineering, East China University of Science and Technology, Shanghai 200237, People's Republic of China*

Received 27 October 1998; received in revised form 20 January 1999; accepted 29 January 1999

## Abstract

Kinetics of the phase transition from isotropic to liquid crystal state, which is by analogy termed as liquid crystallization, was reported for the poly(*p*-phenylene terephthalamide)/H<sub>2</sub>SO<sub>4</sub> system. Experimental results show that the effect of the temperature on the liquid crystallization process is marked while the polymer concentration within the experimental condition employed has a negligible influence. Some preliminary results also indicate that the liquid crystallization process is accelerated considerably after an external shearing is applied. Assuming that the liquid crystallization is a nucleation followed by the growth process, a theoretical approach was attempted in this work. The theory developed provides a reasonable interpretation of the liquid crystallization kinetics in the lyotropic liquid crystalline polymers. © 1999 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Lyotropic liquid crystalline polymers are of commercial interest due to their ability to form anisotropic state which yields good spinning properties and the possibility to form high strength fibers. They are also of interest academically since they provide an opportunity to study the nature of the liquid crystal polymeric materials. The kinetics of phase transitions of lyotropic liquid crystalline polymers has been a matter of interest in recent times [1–5]. The major phase transitions are crystallization from the anisotropic state, anisotropic–isotropic transition, and transition from the isotropic state to the liquid crystalline state, which may be by analogy termed as liquid crystallization.

As for the liquid crystallization, less attention has been paid so far especially from the theoretical aspect.

It is through investigation of the kinetics of the liquid crystallization that the information about the nucleation process and the growth of the liquid crystalline mesophase can be gained, and such information would be of great interest from both theoretical and technological standpoints. Recently, a study of liquid crystallization in a solution of a rigid-rod polyimide was performed by Cheng et al. [1,2]. In that system, during cooling, the hot and isotropic solutions first underwent a mechanical sol/gel transition through liquid–liquid phase separation, followed by a development of lyotropic liquid crystalline spherulites through a nucleation and growth mechanism. Lin et al. [4] have reported a kinetic study of liquid crystallization for poly(*p*-benzamide) (PBA)/H<sub>2</sub>SO<sub>4</sub> and PBA/Nylon 6/H<sub>2</sub>SO<sub>4</sub> systems. The results obtained by depolarized light intensity (DLI) measurement show that the mechanism of liquid crystallization in the lyotropics is a nucleation followed by the liquid crystal growth process. In the study, the well-known Avrami equation was also borrowed to

\* Corresponding author.

analyze the experimental data. The calculated Avrami exponent is about 1 for both PBA/H<sub>2</sub>SO<sub>4</sub> and PBA/Nylon 6/H<sub>2</sub>SO<sub>4</sub> systems.

In the present work, the liquid crystallization of PPTA was investigated by the DLI technique which has been proved to be a valuable method in following the phase transitions in lyotropic liquid crystalline polymers [3–5]. The influence of temperature and polymer concentration on the liquid crystallization process has been studied. Assuming that the liquid crystallization is a nucleation followed by the growth process, a theoretical consideration was proposed. It presents a reasonable explanation to the isotropic–anisotropic transition kinetics in the lyotropic liquid crystalline polymers.

## 2. Experimental

PPTA sample used in the experiments has intrinsic viscosity of 0.67 dL g<sup>-1</sup> measured in 96% H<sub>2</sub>SO<sub>4</sub> at 25°C. The molecular weight was estimated to be 5700 according to the Schaeffgen et al. relation [6]. The polymer was dried in a vacuum oven at 80°C for 72 h before use. Liquid crystal solutions were prepared by dissolving the polymer sample in 100% H<sub>2</sub>SO<sub>4</sub> under dry N<sub>2</sub> atmosphere at 60°C for about one day. In each case about 2 ml of solution was made. The polymer concentration expressed in volume fraction in the present study was estimated from the density (1.44 g/cm<sup>3</sup>) of PPTA.

Isothermal experiments to study the liquid crystallization were conducted with the DLI apparatus designed by the Institute of Chemistry, Academia Sinica and Leitz-Ortholux II polarized light microscope. The detailed description of the DLI apparatus is available in the literature [7,8]. DLI sample preparation was processed in a dry box under N<sub>2</sub> atmosphere to avoid the moisture contamination. The anisotropic solution was put between two cover glass slides and sealed. The sample was heated in a built-in hot stage to 80°C at which the anisotropic–isotropic transition occurred, kept at this temperature for 15 s to destroy the anisotropic phase completely and then quenched the sample to a desired temperature to follow the liquid crystallization process by detecting the DLI changes at these temperatures. The temperature range of interest is between 30 and 50°C, where pure anisotropic phase can be observed. The effect of external shearing on the liquid crystallization was examined by shearing the isotropic solution at 80°C between two slides and subsequently quenching to the isothermal liquid crystallization temperature. The shear rate is of magnitude of order 100 s<sup>-1</sup>.

## 3. Results and discussion

### 3.1. Experimental results

It is well known that PPTA molecules take rigid-rod conformation [9]. As viewed by microscope, PPTA/H<sub>2</sub>SO<sub>4</sub> solution shows typical nematic texture above a critical volume fraction  $v_p$  of 0.184 for the sample used in the present studies. Heating the lyotropics to about 80°C, anisotropic–isotropic transition results in a uniform isotropic phase. Quenching such isotropic solution to a temperature where anisotropic phase can be stable, first anisotropy is observed in the form of specks of light in the dark field of vision, then the anisotropic domains with nematic texture are gradually developed from the specks. For the PPTA/H<sub>2</sub>SO<sub>4</sub> with  $v_p$  from 0.196 to 0.231, a pure nematics can be formed with time as it is quenched to a temperature range from 30 to 50°C.

The intensity of transmitted depolarized light is quite sensitive to the appearance of ordered texture during the formation of the nematic mesophase. The intensity of depolarized light ( $I$ ) is recorded as a function of time  $t$  in the isothermal liquid crystallization experiments. Assuming that  $I$  is proportional to the fraction of liquid crystals formed at time  $t$ , at any stage of the transition, the fraction of the liquid crystalline component can be expressed as

$$X_t = (I_t - I_0)/(I_\infty - I_0) \quad (1)$$

where  $I_t$  is the intensity of the depolarized light at time  $t$ , and  $I_0$  and  $I_\infty$  are the intensity values before and after the transformation. Fig. 1 shows a typical plot of the fraction of liquid crystals formed versus time for PPTA/H<sub>2</sub>SO<sub>4</sub> with concentration of  $v_p = 0.207$  at various temperatures where stable anisotropic phase is observed. The effect of temperature on the liquid crys-

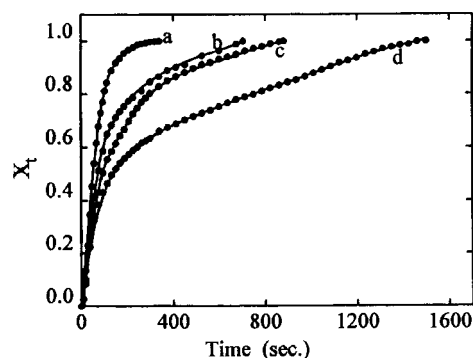


Fig. 1. Isothermal curves for the liquid crystallization of PPTA/H<sub>2</sub>SO<sub>4</sub> system at 30°C (a), 35°C (b), 40°C (c), and 45°C (d).

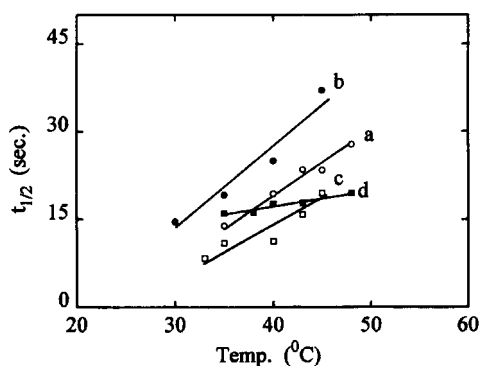


Fig. 2. Dependence of half-time of liquid crystallization on the temperature for PPTA/H<sub>2</sub>SO<sub>4</sub> system with various concentrations,  $v_p = 0.196$  (a), 0.207 (b), 0.219 (c), and 0.231 (d).

tallization process within the experimental temperature range employed is marked. As temperature is increased, the liquid crystal forming process slows down.

The half-times of the liquid crystallization for the samples with different concentrations are given in Fig. 2 as functions of temperature. The values of  $t_{1/2}$  increase with isothermal crystallization temperature for all the concentrations examined. However, it can be seen that there is no evident influence of the concentration on the isothermal liquid crystallization rates.

A typical result of the external shearing effect on the liquid crystallization is demonstrated in Fig. 3 for a lyotropics of  $v_p = 0.202$  with and without shearing treatment. The liquid crystallization process is accelerated considerably after an external shearing treatment is applied.

### 3.2. Theoretical consideration

If an isotropic solution is temperature-jumped across

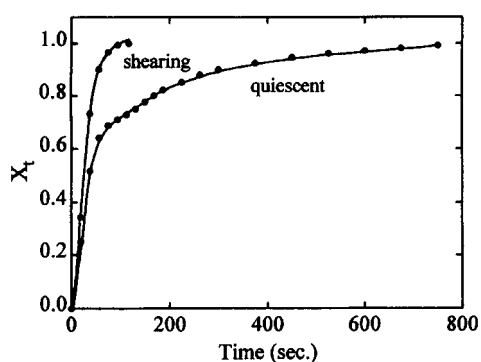


Fig. 3. Isothermal liquid crystallization curves for PPTA/H<sub>2</sub>SO<sub>4</sub> system of  $v_p = 0.202$  with and without shearing treatment.

the biphasic phase into the region where the pure ordered phase can be formed, an isotropic to liquid crystal transition may take place. Let  $dW'_1$  be the mass that is transformed during time  $dt$ , in the approximation that there is no impingement of growing centers. The expected actual liquid crystal mass formed can be given by

$$dW'_1 = (W_t/W_0) dW'_1 \quad (2)$$

where  $W_t/W_0$  is the fraction of the mass untransformed at time  $t$ ,  $W_0$  is the total mass of the system and  $W_t$  is the mass untransformed at time  $t$ . As revealed by the experimental studies [10], the transforming mass in the liquid crystal system may not expand with constant rate due to the restriction of previously formed substance. In the present study, the liquid crystal growth rate,  $G$ , is assumed not only to be diffusion controlled as in the case of crystallization [11,12], but also slows down with respect to time and being proportional to  $t^{-1}$ . According to the literature [11,12], the diffusion-controlled  $G$  may be given by

$$G = G_0 \exp(-Ed/RT) \quad (3)$$

where  $G_0$  is a constant.  $Ed$  is the apparent activation energy of viscous flow per molecule, serves as an approximation for the energy of activation for transport across the isotropic–anisotropic interface.  $Ed$  is assumed to be temperature independent for the temperature intervals of present interest, but it is function of concentration for lyotropic liquid crystalline polymers. Since the liquid crystal growth rate is also considered to be proportional to  $t^{-1}$ ,  $G$  should be replaced by

$$G' = Gt^{-1} \quad (4)$$

In accordance with the one-dimensional (1D) order of the nematic liquid crystals which are confined to grow between two cover glasses, it is reasonable to postulate that the liquid crystal growing centre takes cylindrical shape and is restricted to grow in one dimension. Then, in the approximation of no impingement, the volume  $V(t,z)$  at time  $t$  of a given cylindrically growing center which was initiated at time  $z$  is

$$V(t,z) = \pi r^2 \int_z^t G_0 \exp(-Ed/RT) t^{-1} dt \quad (5)$$

where  $r$  is the radius of the cylinder. The mass  $W'_1$  transformed at time  $t$  in the approximation of no impingement can be given by

$$W'_1 = (W_0/\rho_1) A \rho_2 \int_0^t V(t,z) dz \quad (6)$$

where  $A$  is the rate of the formation of nuclei per unit

of volume, the density of the isotropic phase is  $\rho_1$  and that of the liquid crystalline phase is  $\rho_2$ .

By substituting Eq. (5) into Eq. (6) and the resultant into Eq. (2), one obtains by integration

$$\ln(1/(1 - X_t)) = \pi r^2 AG(\rho_2/\rho_1)t = kt \quad (7)$$

where  $X_t = W_t/W_0$  is the fraction of the mass transformed at time  $t$ ,  $k$  is defined as the rate constant of liquid crystallization. If the isothermal liquid crystallization temperature is adjusted so that the final state is biphasic region, Eq. (7) can be further improved in consideration with the fact that the systems do not transform completely.

The variation of the liquid crystallization rate constant with either temperature or concentration is governed by the dependence of the growth and nucleation rate on these variables. The free energy change required for the formation of a small nucleus within the bulk of a mother liquor is the resultant of the contributions of two terms: the bulk free energy which is negative and the surface free energy which is positive. The free energy,  $\Delta F$ , of the formation of a cylindrical nucleus of length  $l$  and radius  $r$  is given by

$$\Delta F = 2\pi r l \sigma_1 + 2\pi r^2 \sigma_2 - \pi r^2 l \beta \Delta f \quad (8)$$

where  $\Delta f$  is the free energy difference between isotropic and anisotropic state,  $\beta$  is a scaling constant, and  $\sigma_1, \sigma_2$  are the interfacial free energies per unit area for the cylindrical surface and the two end surface, respectively. In the classical development of nucleation theory [13], the free energy of the formation of liquid crystal may possess a maximum with respect to nucleus size. The maximum value of the free energy of formation,  $\Delta F^*$ , is the height of the free energy barrier that must be surmounted in order for stable nuclei to be formed. Maximizing Eq. (8) with respect to  $l$  and  $r$ , we obtained

$$\Delta F^* = 8\pi \sigma_1^2 \sigma_2 / \beta^2 \Delta f^2 \quad (9)$$

In the formation of liquid crystals, the driving force  $\Delta f$  can be obtained according to the explicit formula derived by Flory [14,15]. The energy expression applicable to a polymer chain with large axial ratio which may form anisotropic state is given by

$$f_{\text{aniso}} = (1 - v_p) \ln(1 - v_p) + v_p \ln v_p + 2(1 - v_p)/y - v_p [\ln(xy^2) - y - 1] \quad (10)$$

where  $v_p$  is the volume fraction of polymer component,  $x$  is the axial ratio,  $y$  is the disorder index and it can be obtained by iteration at a given polymer concentration [14]. For the isotropic phase  $y = x$  [14], hence

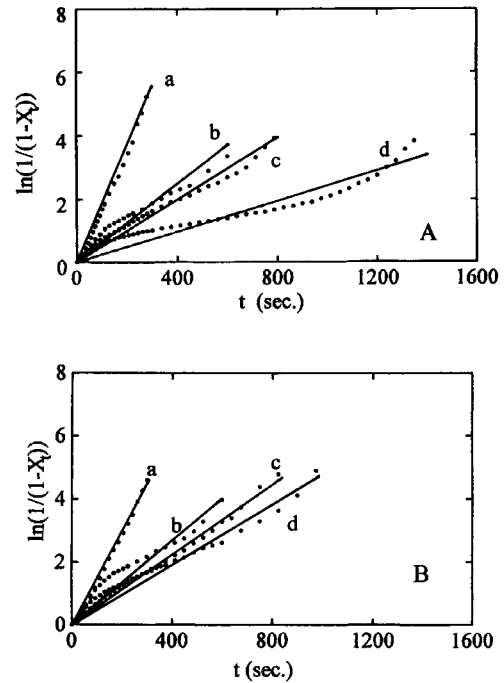


Fig. 4. (A): Plots of  $\ln(1/(1 - X_t))$  versus  $t$  for isothermal liquid crystallization of PPTA/H<sub>2</sub>SO<sub>4</sub> with concentration of  $v_p = 0.207$  at 30°C (a), 35°C (b), 45°C (c), 50°C (d). (B): plots of  $\ln(1/(1 - X_t))$  versus  $t$  for isothermal liquid crystallization of PPTA/H<sub>2</sub>SO<sub>4</sub> with concentration of  $v_p = 0.231$  at 35°C (a), 38°C (b), 43°C (c), 48°C (d).

$$f_{\text{iso}} = (1 - v_p) \ln(1 - v_p) + v_p \ln v_p + 2(1 - v_p)/x - v_p [\ln(x^3) - x - 1] \quad (11)$$

The driving force,  $\Delta f$ , can now be readily obtained and is found to be

$$\Delta f = 2(1 - v_p)/x - v_p [\ln(x^3) - x - 1] - 2(1 - v_p)/y + v_p [\ln(xy^2) - y - 1] \quad (12)$$

Adopting the formula written by Turnbull and Fisher [16], the steady state rate of nucleation in the isotropic solution may be expressed as

$$A = A_0 \exp(-Ed/RT - \Delta F^*/RT) \quad (13)$$

where  $A_0$  is a constant.

For the formation of nematic phase with 1D order, it is found from Eqs. (3), (7) and (14) that

$$k = \pi r^2 (\rho_2/\rho_1) A_0 G_0 \exp(-2Ed/RT - \Delta F^*/RT) \quad (14)$$

Eq. (14) can be further written in form of

$$\ln k = B - C/RT - D/\Delta f^2 RT \quad (15)$$

where  $B = \ln(\pi r^2 \rho_2 / \rho_1) A_0 G_0$ ,  $C = 2Ed$ ,  $D = 8\pi\sigma_1^2\sigma_2/\beta^2$ . Eq. (15) is of immediate interest, since it predicts a linear dependence of  $\ln(k)$  on  $1/T$ .

### 3.3. Comparison with experimental results

The theory developed above is ready to analyze the obtained experimental data. Typical plots of  $\ln(1/(1 - X_t))$  versus  $t$ , according to Eq. (7), are shown in Fig. 4 for lyotropic solutions with concentrations of  $v_p = 0.207$  (A) and  $v_p = 0.231$  (B). As it can be seen from the plots, linear fittings are obtained at lower liquid crystallization temperatures, indicating the theory works well in describing the development of the liquid crystallinity. At higher temperatures, some deviations from the linear agreements are noted. In the present work, the liquid crystal growth rate is assumed to be proportional to  $t^{-n}$ , where  $n$  equals 1. However,  $n$  may be time-dependent due to the restriction of the formed substance. On the other hand, the growth of the liquid crystals is also possible to deviate from 1D growth model, since the orientation order of the liquid crystal polymer is usually not perfect especially at higher temperatures and decreases with temperature [17,18]. All these effects may contribute to the discrepancy between the theory and the experimental results. Fitting of  $\ln(1/(1 - X_t))$  versus  $t$  also allows us to determine the rate constant of the liquid crystallization. The obtained  $k$  values for all polymer concentrations examined were used to construct a plot where  $\ln(k)$  is plotted against  $1/T$ . As predicated by Eq. (15), the result demonstrated in Fig. 5 shows that approximately a straight line is obtained. The  $\ln(k)$  increases linearly with  $1/T$  for all samples studied.

The effect of polymer concentration on the liquid crystallization process can be discussed on the basis of Eqs. (14) and (15). As the diluent is added to the solutions, the activation energy  $Ed$  becomes lower due to

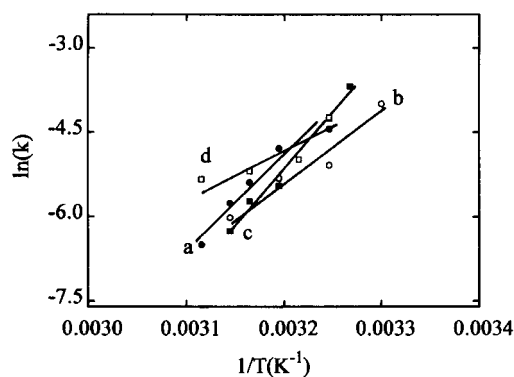


Fig. 5. Plots of  $\ln(k)$  versus  $1/T$  for PPTA/H<sub>2</sub>SO<sub>4</sub> with various concentrations,  $v_p = 0.196$  (a),  $0.207$  (b),  $0.219$  (c),  $0.231$  (d).

the decrease of viscosity of the medium. This would be expected to result in an increase in the crystallization rate. However, the steady-state nucleation will decrease with increasing diluent concentration because of the dependence of  $\Delta f$  on the concentration according to Eqs. (9) and (12). These opposing effects appear to counteract each other over the concentration range examined in which the rate constant appears to be independent of concentration as it is noted in Fig. 5.

Preliminary studies show that the liquid crystallization process can be accelerated considerably with a shearing treatment. It is most likely that the shearing force which may induce higher orientations of the formed liquid crystals might lower the free energy barrier for the nucleation, i.e. an extra term associated with the shearing energy should be added to Eq. (12) to increase the value of  $\Delta f$ . It is readily deduced from Eq. (9) that a higher value of  $\Delta f$  gives rise to a smaller value of  $\Delta F^*$ .

A plot of  $\ln(1/(1 - X_t))$  versus  $t$  is shown in Fig. 6 for the liquid crystallization experimental data of Fig. 3 where a shearing treatment is applied. For comparison, the result for the corresponding quiescent sample is also shown. It is noted that better agreement between experimental and theory is achieved for the liquid crystallization with a shearing treatment. This indicates that the nucleation and liquid crystal growth more exactly follow the proposed model after an external shearing treatment is applied. The result seems justified as the shearing can reduce the deviations from 1D growth and giving rise to higher degree orientation of the formed liquid crystals.

The effect of the external force on the liquid crystal forming process presents an interesting problem in relation to the fabrication of stiff-chain polymers. To our knowledge, no kinetic study has been reported so far concerning such effects. Some further attempts are being made and the results relating to this topic will be reported in the near future.

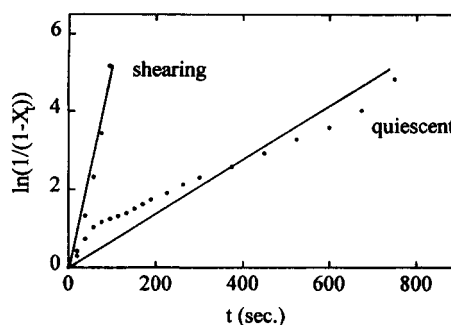


Fig. 6. Plots of  $\ln(1/(1 - X_t))$  versus  $t$  for PPTA/H<sub>2</sub>SO<sub>4</sub> system of  $v_p = 0.202$  with and without shearing treatment.

### Acknowledgements

Authors are grateful to the East China University of Science and Technology for financial assistance. Support from the National Science Foundation of China (Grant No. 59803002) is also greatly appreciated.

### References

- [1] Cheng SZD, Lee SK, Barley JS, Hsu SLC, Harris FW. *Macromolecules* 1883;1991:24.
- [2] Cheng SZD, Lee SK, Wu Z, Lee CJ, Harris FW, Kyu T, Yang JC. *Polym Int* 1993;30:115.
- [3] Lin J, Wu H, Li S. *Polym Int* 1993;32:339.
- [4] Lin J, Wu H, Li S. *Polym Int* 1994;34:141.
- [5] Lin J, Xi S, Wu H, Li S. *Eur Polym J* 1997;33:1601.
- [6] Schaeffgen JR, Soldi VS, Logullo FM, Gold VH, Culrich LW, Killian KL. *Polym Prepr, Am Chem Soc, Div Polym Chem* 1967;17:69.
- [7] Barrall EM, Gallegos EJ. *J Polym Sci, Part A* 1967;25:113.
- [8] Xu ZM, Chen SX. *Gaofenzi Tongxun* 1979;3:129.
- [9] Ciferri A, Krigbaum WR, Meyer RB. *Polymer liquid crystals*. New York: Academic Press, 1982.
- [10] Cheng SZD. *Macromolecules* 1988;21:2475.
- [11] Mandelkern L, Quinn FA, Flory PJ. *J Appl Phys* 1954;25:830.
- [12] Mandelkern L. *J Appl Phys* 1954;26:443.
- [13] Mandelkern L. *Crystallization of polymers*. New York: McGraw-Hill, 1964.
- [14] Flory PJ. *Proc R Soc London, Ser A* 1956;234:73.
- [15] Flory PJ. *Adv Polym Sci* 1984;59:1.
- [16] Turnbull D, Fischer JC. *J Chem Phys* 1949;17:71.
- [17] Ciferri A. *Liquid crystallinity in polymers*. New York: Verlag chemie, 1991.
- [18] Lin J, Li S. *Eur Polym J* 1994;30:671.