

KINETICS OF MESOPHASE FORMATION OF A LYOTROPIC AROMATIC POLYAMIDE

CHEN Shouxi (陈寿羲)

(*Institute of Chemistry, Academia sinica, Beijing*)

ABSTRACT

The kinetics of mesophase formation of a lyotropic aromatic polyamide from isotropic state has been studied by means of depolarized light intensity. Avrami type analysis of the data gives an exponent close to 1, which suggests the nucleation followed by one-dimensional growth. No influence of blending flexible chain from nylon 6 to the aromatic polyamide on the kinetics of mesophase formation was observed.

INTRODUCTION

The kinetics of mesophase formation of a liquid crystalline polymer has been a matter of interest in recent time. In the case of low molecular weight liquid crystalline compounds the transition from isotropic phase to mesophase was studied by Price and Wendorff^[1] about ten years ago. They have found that the kinetics of mesophase formation to be nucleation controlled which can be described by an Avrami type equation. In the case of liquid crystalline polymers the similar results have also been obtained. Bhattacharya et al.^[2] have studied the kinetics of phase transition of a thermotropic main chain polymer from isotropic phase to nematic mesophase by DSC and optical microscopy. It is found that the value of Avrami exponent is about 1, which means nucleation followed by rod-like growth. Pracella et al.^[3] have studied the kinetics of phase transition of a thermotropic side chain polymer from isotropic phase to smectic mesophase by DSC. The parameter n Avrami exponent has been found to be 3, which suggests nucleation followed by three-dimensional growth. The kinetics of mesophase formation of liquid crystalline polymers has also been reported by other authors^[4,5]. These results indicate that the mesophase formation of liquid crystalline polymers can be described by Avrami equation. To our knowledge, no kinetic study has been published so far concerning the mesophase formation occurring in lyotropic liquid crystalline polymers.

Poly(*p*-phenylene terephthalamide) (PPTA) is a lyotropic liquid crystalline polymer characterized by a nematic mesophase when the concentration of solution reaches a critical value. The first-order nematic to isotropic transition is accompanied by an appreciable heat absorption^[6] like thermotropic polymers. The mesophase formation of PPTA solution from isotropic state to nematic phase can take place with a certain degree of supercooling. The kinetics of mesophase formation at different temperatures can be conveniently investigated for PPTA/H₂SO₄ system.

In this paper we present the results of kinetic study of the mesophase formation from isotropic state to nematic phase of PPTA solution in H_2SO_4 by means of depolarized light intensity.

EXPERIMENTAL

The inherent viscosity of the poly (1, 4-phenylene terephthalamide) (PPTA) sample used in this study is 5.4 dl/g as measured at 30 °C in 96wt-% H_2SO_4 . The sample was dried for 24 hours in vacuum at 80 °C and then kept in a desiccator before use.

PPTA was dissolved in 100wt-% H_2SO_4 at a concentration of 16wt-% (anisotropic solution). Solution of 16wt-% PPTA blended with various contents of nylon-6 were also studied.

The kinetics of isothermal mesophase formation were carried out using a method of depolarized light intensity^[7]. In these experiments the solution sample was heated to 165 °C, and kept at that temperature for 2 min. and then rapidly quenched to a predefined temperature. Depolarized light intensity during the isothermal mesophase formation was recorded as a function of time. The reproducibility of results was satisfactory on repeating the running using fresh samples.

RESULTS AND DISCUSSION

Fig. 1 is the variation of depolarizing light intensity with time during the isothermal mesophase formation of a 16wt-% PPTA solution at 57 °C. The curve looks very similar to that of isothermal crystallization of polymers. At each chosen temperature the fraction conversion X_t of the isotropic phase into mesophase was calculated as a function of time using Avrami equation:

$$X_t = 1 - \exp(-kt^n)$$

In the case of depolarized light intensity measurements X_t could be expressed as

$$\frac{I_t - I_0}{I_\infty - I_0}, \text{ so that}$$

$$\frac{I_\infty - I_t}{I_\infty - I_0} = \exp(-kt^n)$$

where I_0 , I_t and I_∞ and the depolarized light intensity at time 0, t and ∞ respectively, n is Avrami exponent dependent on the modes of nucleation and on the geometry of growth and k is a constant.

Values of $\frac{I_\infty - I_t}{I_\infty - I_0}$ are plotted against $\log t$ for various temperatures as shown

in Fig. 2. All these curves are of the inverted 's' shape which are superimposable on each other by an appropriate shift along the time axis. This result indicates that the kinetics of the mesophase formation of lyotropic PPTA is in good agree-

ment with the Avrami equation. The plots of $\log\left(-\ln \frac{I_\infty - I_t}{I_\infty - I_0}\right)$ versus $\log t$ at

different temperatures are presented in Fig. 3. All experimental data conform to the Avrami equation. The values of the Avrami exponent n calculated from the slope of the straight lines in Fig.3 are 0.97, 0.99 and 1.04 for 57.0 °C , 70.0 °C and 79.5 °C respectively. All of the n values are close to 1, which can be interpreted in terms of athermal nucleation, followed by one-dimensional growth. Similar values of n have been reported by other authors from isotropic to nematic phase transition of thermotropic main chain polymers^[2]. The kinetic parameters of mesophase of 16wt-% PPTA solution are collected in Table 1.

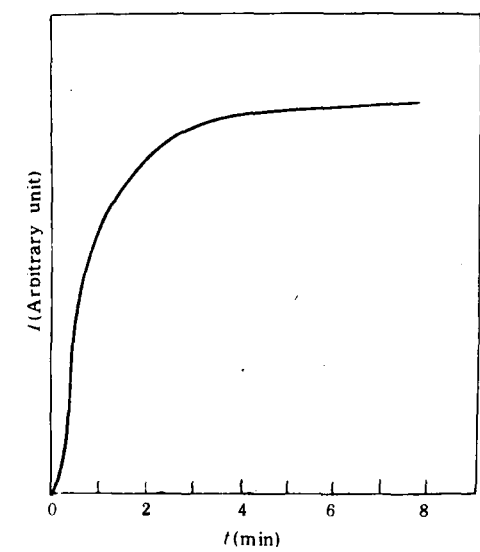


Fig. 1 The variation of the depolarizing light intensity with time for 16wt-% PPTA solution at 57 °C

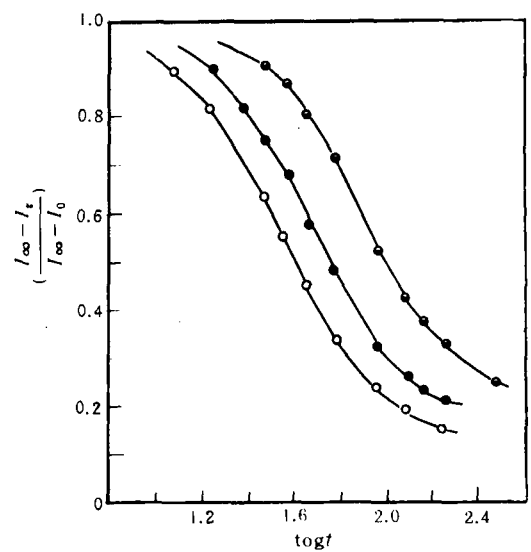


Fig.2The Plot of $\left(\frac{I_{\infty}-I_t}{I_{\infty}-I_0} \right)$ versus $\log t$ for 16wt-% PPTA solution at different temperatures
($\circ$) 57.0 °C ; ($\bullet$) 70.0 °C : ($\odot$) 79.5 °C

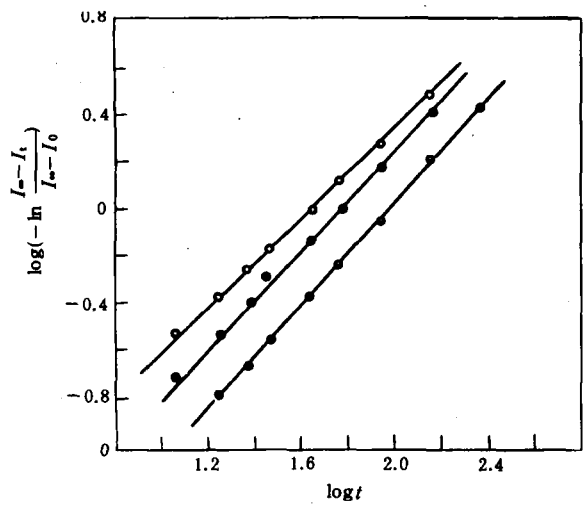


Fig. 3 The plot of $\log\left(-\ln \frac{I_{\infty}-I_t}{I_{\infty}-I_0}\right)$ versus $\log t$ for 16wt-% PPTA solution at different temperatures. PPTA blended with various contents of nylon-6
($\circ$) 57.0 °C ; ($\bullet$) 70.0 °C , ($\odot$) 79.5 °C

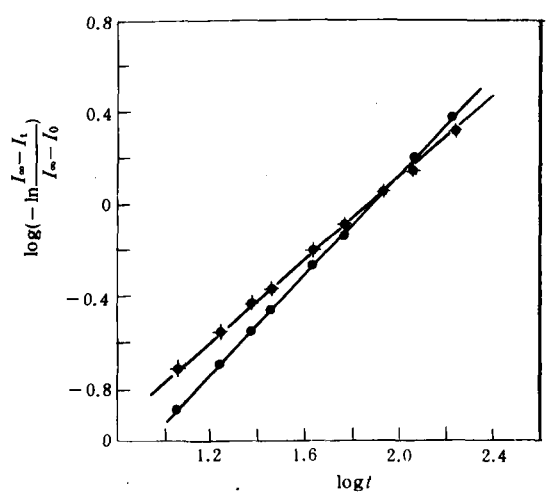


Fig.4 The plot of $\log\left(-\ln \frac{I_{\infty}-I_t}{I_{\infty}-I_0}\right)$ versus $\log t$ for PPTA blended with various contents of nylon-6
($+$) 5wt% ; ($\bullet$) 10wt% ; ($\circ$) 15 wt%

Table 1 The kinetic parameters of mesophase formation of PPTA

$T(^{\circ}\text{C})$	$t_{1/2}(\text{sec})$	n	$k(\text{sec}^{-1})$
57.0	44	0.97	1.98×10^{-2}
70.0	60	0.99	1.20×10^{-2}
79.5	100	1.04	5.76×10^{-3}

In order to study the influence of blending some flexible chain to PPTA on the mesophase formation, the kinetics of mesophase formation of 16wt-% PPTA in H_2SO_4 with the addition of various contents of nylon-6 was measured.

$\text{Log} \left(-\ln \frac{I_{\infty} - I_t}{I_{\infty} - I_0} \right)$ vs. $\log t$ plots for PPTA/nylon-6 blends are shown in

Fig. 4. The experimental data for these mixed system also follow Avrami equation. The values of the Avrami exponent n obtained are also close to 1, being independent of the content of nylon-6. It means that the mesophase formation of PPTA in H_2SO_4 is not influenced by the presence of a flexible chain polymer in the solution, i. e. the flexible chains will be excluded from the PPTA domains during its mesophase formation.

Keywords:

Kinetics; mesophase formation; lyotropic aromatic polyamide; Poly (1,4-phenylene terephthalamide)

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