Kinetics of Mesophase Transition of Lyotropic Chitosan in Dichloroacetic Acid

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ABSTRACT: The mesophase transition and its kinetics of chitosan in the solutions of chitosan/dichloroacetic acid (DCA) were investigated by means of DSC and depolarized light intensity technique, respectively. The mesophase formation of chitosan in DCA involves nucleation and growth. The isothermal kinetics of mesophase formation from isotropic phase were described by Avrami using the equation with an exponent n close to 1, which suggests that the formation of chitosan mesophase is a process of instantaneous nucleation and one-dimensional rod-like growth in the temperature range investigated. This was confirmed by small angle light scattering Hv patterns of the mesophase. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1770–1775, 2001

Key words: chitosan/dichloroacetic acid solution; lyotropic liquid crystal; cholesteric; isothermal mesophase transition; kinetics; SALS Hv pattern

INTRODUCTION

In 1982, Ogura et al.[1] first demonstrated that chitosan, hydroxypropyl chitosan, and acetoxypropyl chitosan can form lyotropic chiral nematic ordered materials at suitable concentrations, which opened a new field for studies of chitosan. Terbojevich et al.[2] reported that the persistence length is about 220 Å for chitosan with a degree of acetylation of 42% and 15% in 0.1M acetic acid–0.2M sodium chloride aqueous solution, which implied that the chitosan chains are rigid enough for the formation of mesophase at adequately high concentrations of the polymer. Sakurai et al.[3–5] tried to make chitosan fibers from lyotropic liquid crystalline solutions of chitosan/formic acid that had been concentrated from dilute solutions. Other research has been carried out on the structure and properties of mesophases for chitosan derivatives.[6–9]

In recent years, the kinetics of phase transition of liquid crystalline polymers has become an interesting topic of study, with one of the goals being to understand the mechanism of the mesophase formation correctly.[10–18] Bhattacharya et al.[10] studied the kinetics of phase transition of a thermotropic polyester from isotropic to nematic mesophase and reported that the Avrami exponent is about 1. Chen[16] studied the kinetics of phase transition of lyotropic aromatic polyamide from the isotropic to the nematic mesophase and obtained similar results. Pracella et al.[13] studied the transformation from the isotropic to the smectic phase of a side chain LCP and found the Avrami exponent n is about 3, which indicates the growth of mesophase is three-dimensional. Chen
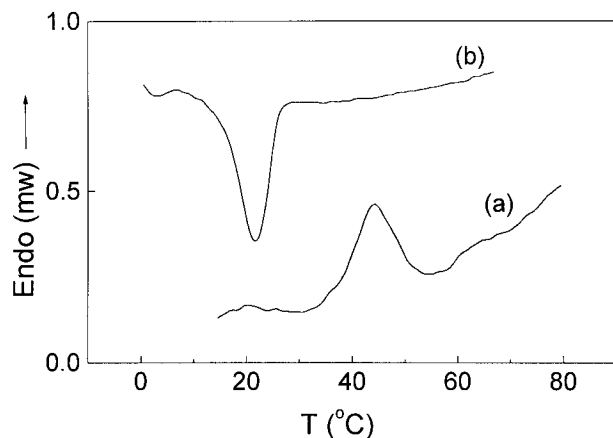
Figure 1 Thermograms of chitosan/DCA solution with a concentration of 18 wt % in heating (curve a) and cooling (curve b) processes.

et al.[17] and Huang et al.[18] studied the mesophase formation of thermotropic hydroxyethyl cellulose acetate from the isotropic to the cholesteric mesophase isothermally and nonisothermally, respectively. It was found in their work that the Avrami exponent n is close to 1.

As far as we know, little has been published on the mesophase transition of chitosan, which is a lyotropic cholesteric LCP, and its transition kinetics. In fact, the study of the chitosan/dichloroacetic acid (DCA) system has been insufficient. Our previous article discussed phase transition behavior, which was determined by differential scanning calorimetry (DSC) and polarized light microscopy (PLM).[19] The purpose of the present work is to explore the phase transition kinetics of chitosan in DCA.

EXPERIMENTAL

The sample of chitosan was obtained from KEXIN Chemical Company. The degree of deacetylation was 82%, as determined by FTIR. M_η was approximately 1.6×10^6.[19] DCA was provided by the China Military Medical Science Academy.

The chitosan/DCA solutions were prepared by mixing chitosan and DCA at room temperature and then sealing the mixture tightly for storage. The solutions were used within 2 days after they were prepared. All solution concentrations are given in the weight percent (wt %).

Thermal transitions were determined with a Perkin-Elmer DSC-2 differential scanning calorimeter purged with high purity N_2. The calibration was done with standard In. The sample weight was in the range 10–20 mg and the scanning rate was 10°C/min.

The isothermal kinetics of mesophase formation were determined using the method of depolarizing light intensity.[20] The solutions were pressed into a thin film between cover slides, which were sealed with acrylate at room temperature. The solutions of 18 and 20 wt % were first heated to 45 and 46.5°C, respectively, for 180 s, and then rapidly transferred to a predefined temperature for the mesophase formation. The variation of the depolarizing transmittance intensity during the isothermal mesophase formation was recorded as a function of time.

The small angle light scattering experiments were performed with a He-Ne gas laser (λ = 6328 Å), and scattering patterns were recorded photographically.
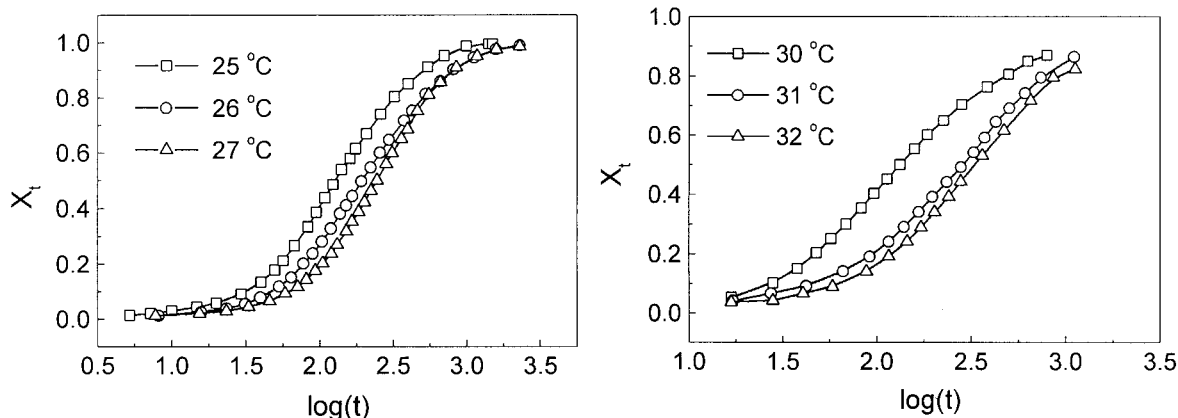

Figure 2 The plots of X_t versus $\log(t)$ for solutions of chitosan/DCA with concentrations of 18 (left) and 20 wt % (right) at the indicated temperatures.
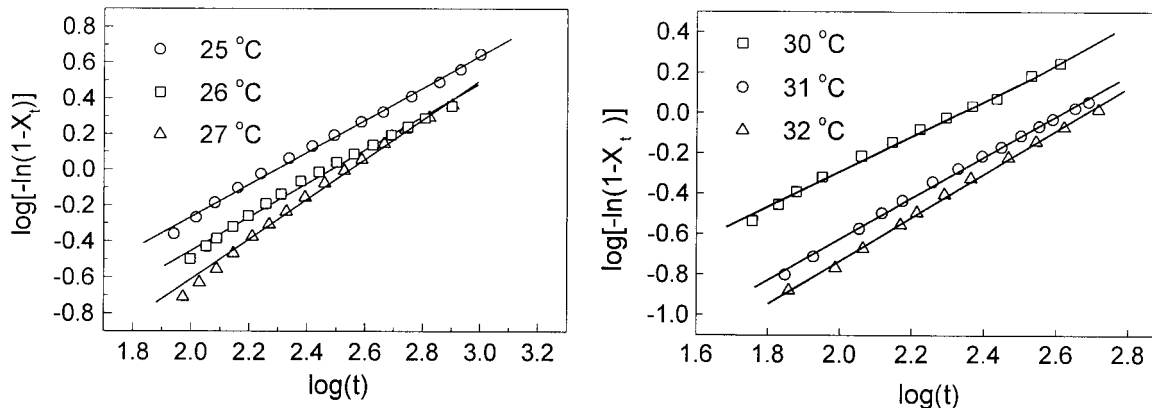
Figure 3 The plots of $\log[-\ln(1 - X_t)]$ versus $\log(t)$ for solutions of chitosan/DCA with concentrations of 18 (left) and 20 wt % (right) at the indicated temperatures.

RESULTS AND DISCUSSION

Figure 1 shows the thermograms of the chitosan/DCA solution with a concentration of 18 wt %. One main endothermal peak is observed at 45°C in the heating process. According to our previous report,[19] this peak is attributed to the transition from the cholesteric to the isotropic phase, which is supported by the polarized optical microscopy (POM) observations using hot stage at the same heating rate. Similarly, the exothermal peak for the liquid crystallization is detected at about 23°C during cooling of the isotropic solution.

There is a temperature difference of around 20°C between the endothermal and the exothermal peaks, similar to the supercooling of crystalline materials. It was demonstrated by our previous article[19] and an early work by Miller et al.[21] that this could be due to a nucleation and growth mechanism of the formation of the ordered phase.

For measurements of the isothermal liquid crystallization in chitosan/DCA solutions, the capability of most popular techniques, such as the DSC method, was restricted because the response time of the instrument was quite large in contrast with the overall time for mesophase formation. It was found in this work that the depolarizing transmittance method was suitable for monitoring the rapid isotropic-anisotropic transition.

In the case of depolarizing transmittance measurement, the fraction X_t of the conversion of the isotropic phase into mesophase at time t can be expressed as the following equation:

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

where I_∞, I_0, and I_t represent the depolarizing transmittance intensity at long time $t = \infty$, at initial time $t = 0$, and at any specified time t, respectively. Figure 2 shows X_t versus $\log(t)$ for the chitosan/DCA solution with a concentration of 18 and 20 wt % at different liquid crystallization temperatures. All the curves have an "S" shape, which are able to overlap on each other by an appropriate shift along the time axis with the variation of liquid crystallization temperatures. This indicates that the mesophase formation in chitosan/DCA is also nucleation-controlled, and the kinetics are in good agreement with the Avrami equation. The results are analyzed using the Avrami equation:

$$1 - X_t = \exp(Kt^n) \qquad (2)$$

where K is the kinetics constant of the liquid crystallization process, and n is the Avrami exponent depending on the type of nucleation and liquid crystal growth geometry.

Table I Kinetics Parameters of Liquid Crystallization of Solution of Chitosan/DCA

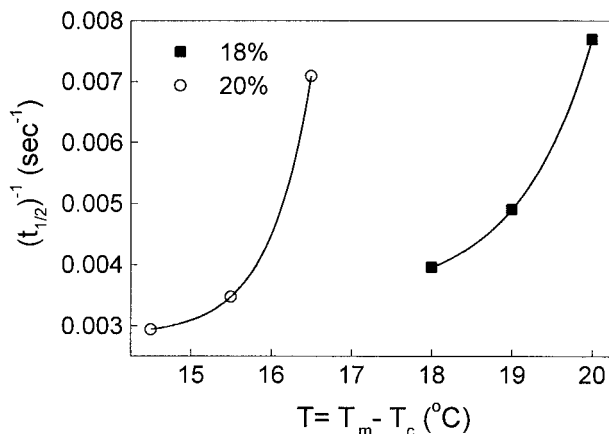| Concentration (wt %)	T_c (°C)	$t_{1/2}$ (sec)	n	K (sec^{-n})
18	25	130	0.9	8.62×10^{-3}
	26	204	0.9	4.72×10^{-3}
	27	253	1.1	1.48×10^{-3}
20	30	141	0.9	9.22×10^{-3}
	31	288	1.0	2.20×10^{-3}
	32	340	1.1	1.28×10^{-3}

Figure 4 The inverse half-time $(t_{1/2})^{-1}$ versus the supercooling degree, ΔT, for liquid crystallization of chitosan.

The kinetics parameters, n and K, for the mesophase formation of chitosan in solutions are determined from the slope and intercept of the straight lines, respectively, in Figure 3. They are also listed in Table I. The values of the half-time, $t_{1/2}$, in Table I are calculated using eq. (3):

$$t_{1/2} = (\ln 2/K)^{1/n} \qquad (3)$$

All the values of n are in the range of 1 ± 0.1, which indicates that lyotropic cholesteric mesophase of chitosan in chitosan/DCA solutions is formed in the manner of instantaneous nucleation, and is followed by one-dimensional rod-like growth in the temperature ranges in-

vestigated. Chen et al.[17] and Huang et al.[18] obtained similar results in their studies on a thermotropic cholesteric cellulose derivative. The characteristics of cholesteric mesophase formation were also similar to that of nematic mesophase formation in thermotropic aromatic polyester[10] and in a lyotropic aromatic polyamide.[16] In terms of the alignment structures for their molecules, the cholesteric and nematic phases are very similar. By a simple explanation the former is thought to be a variation form of the latter, i.e., the twisted nematic structure. Therefore, it is not surprising that the values of n for the mesophase formation of cholesteric chitosan are close to 1, which means that the kinetic characteristics are similar for cholesteric and nematic mesophase formations.

The half-time, $t_{1/2}$, of the mesophase transition process for chitosan in solutions shows a strong dependence on temperatures. Within the range of 2–3°C, the value of $t_{1/2}$ decreases by two to three times, which further supports the nucleation-controlled mechanism theory. It should be noted that $(t_{1/2})^{-1}$ is proportional to the transition rate. Relationships between the inverse half-time $(t_{1/2})^{-1}$ and the supercooling degree ($\Delta T = T_M - T_C$) are illustrated in Figure 4. It is shown that the increase in the supercooling degree accelerates the transition rate sharply, which means that the nucleation plays a dominating role in such a mesophase transition. Therefore, the higher concentration is beneficial for the nucleation and increases the transition rate further. This conclusion is confirmed
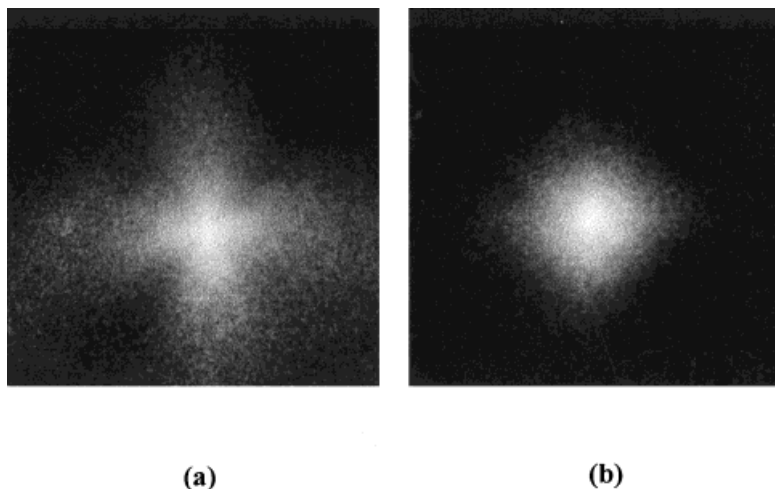

Figure 5 The SALS Hv patterns of liquid crystal formed in 18% solution of chitosan/DCA at (a) 22°C and (b) 26°C.
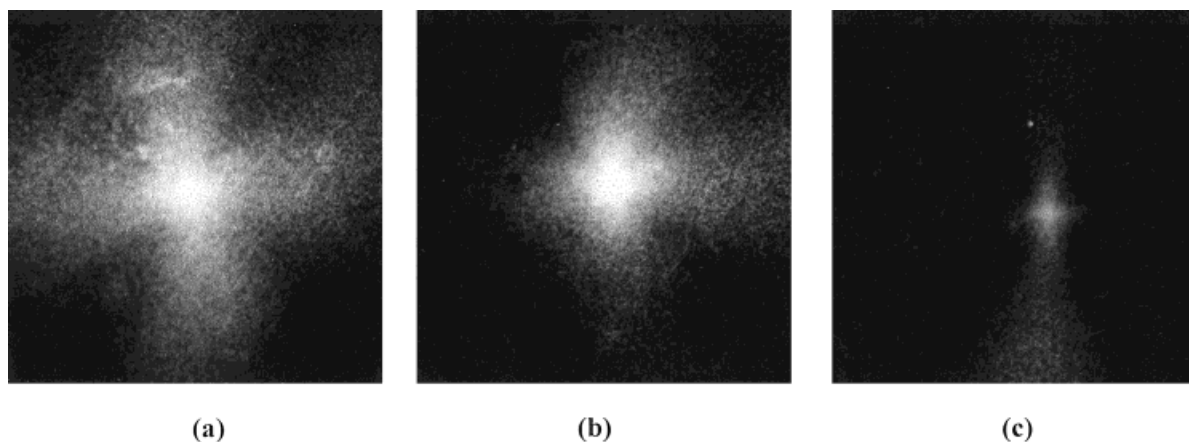
Figure 6   The SALS Hv patterns of liquid crystal formed in 20% solution of chitosan/DCA at (a) 22°C, (b) 26°C, and (c) 30°C.

by comparing two curves, illustrated in Figure 4, of the inverse half-time $(t_{1/2})^{-1}$ as a function of the supercooling degree.

Figures 5 and 6 show the results of SALS patterns for chitosan/DCA solutions quenched to different temperatures for the mesophase formation from their isotropic state. All the resultant mesophases exhibit a typical SALS Hv pattern of cross type, indicating developments of a rod-like aggregation in the systems. Considering these morphological and kinetics results of mesophase formation, one may find that these morphological observations conform to the Avrami analysis, which indicates that the growth mechanism of liquid crystal is one-dimensional. Furthermore, the influence of temperature on the size of the formed domain is obvious. With increasing the temperature of the isothermal transition, the Hv pattern shrinks in scattering angles, which indicates an increase in the size of the domains in the liquid crystals of rod-like aggregation. It is instructive to compare the isothermal transition of the mesophase with the isothermal crystallization. Generally speaking, such a feature is common in the isothermal crystallization of flexible polymers. The higher the crystallization temperature, the larger the formed crystal. In the case of chitosan mesophase, as the temperature increases, the nucleation becomes more difficult, or the nucleus (domain) less stable. As a consequence, at higher temperatures, the density of nuclei is lower, but the growth rate is higher.

CONCLUSIONS

1. The Avrami equation can be used to describe the isothermal kinetics of mesophase formation from isotropic phase to cholesteric for lyotropic chitosan. The obtained values of the Avrami exponent, n, are in the range 1 ± 0.1. The formation of the chitosan mesophase is a process of instantaneous nucleation and one-dimensional rod-like growth in the temperature range investigated.
2. The transition rate of mesophase formation obviously becomes faster for the lyotropic chitosan solution with the higher concentration.
3. The mesophase formed exhibits crossed SALS Hv patterns, which confirms the Avrami analysis on the growth dimensionality of liquid crystals. The size of mesophase domains formed in the lyotropic chitosan solution depends on the temperature, and it increases with increasing temperature.

REFERENCES

1. Ogura, K.; Kanamoto, T.; Sannan, T. In Chitin Chitosan Proceeding Int Conf 2nd, Tottori, Japan, 1982.
2. Terbojevich, M.; Cosano, A.; Conio, G.; Marsano, E.; Bianchi, E. Carbohydr Res 1991, 209, 251.
3. Sakurai, K.; Shibano, T.; Kimura, K.; Takahashi, T. SEN-IGAKKAISHI 1985, 41, T-361.
4. Sakurai, K.; Takahashi, T. SEN-IGAKKAISHI 1988, 44, 149.

5. Sakurai, K.; Miyata, M.; Takahashi, T. SEN-IGAK-KAISHI 1990, 46, 79.

6. Rout, D. K.; Pulapura, S. K.; Gross, R. A. Macromolecules 1993, 26, 5999.

7. Rout, D. K.; Pulapura, S. K.; Gross, R. A. Macromolecules 1993, 26, 6007.

8. Rout, D. K.; Barman, S. P.; Pulapura, S. K.; Gross, R. A. Macromolecules 1994, 27, 2945.

9. Dong, Y. M.; Li, Z. Q. Acta Polymerica Sinica (in Chinese) 1998, 3, 282.

10. Bhattacharya, S. K.; Misra, A.; Stein, R. S.; Lenz, R. W.; Hahn, P. E. Polym Bull 1986, 16, 465.

11. Liu, X. P.; Hu, S. R.; Xu, M. Polymer 1989, 30, 273.

12. Hans, K.; Zugenmaier, P. Makromol Chem 1988, 189, 1189.

13. Pracella, M.; Petris, S-De.; Frosini, V.; Magagnini, P. L. Mol Cryst Liq Cryst 1984, 113, 225.

14. Tsukrak, V.; Shilov, V.; Lokhonya, O.; Lipatov, Y. Polym Bull 1984, 11, 561.

15. Papkov, V. S.; Svistunov, V. S.; Godovsky, Yu-K.; Zhdanov, A. A. J Polym Sci Polym Phys Ed 1987, 25, 1859.

16. Chen, S. X. Chinese J Polym Sci 1989, 7, 379.

17. Chen, S. X.; Sun, Z.; Song, W. H.; Jin, Y. Z.; Huang, Y. Chinese J Polym Sci 1996, 14, 86.

18. Huang, Y.; Wang, H. L.; Tan, Q.; Zeng, J. Mol Cryst Liq Cryst 1996, 281, 27.

19. Hu, Z. M.; Li, R. X.; Wu, D. C.; Sun, Y. S.; Liu, H. B.; Wu, L. H. Chem J Chinese University (in Chinese) 1999, 20, 153.

20. Xu, Z. M.; Chen, S. X. Polym Commun (in Chinese) 1979, 3, 129.

21. Miller, W. G.; Kou, L.; Tomyama, K.; Voltaggio, V. J Polym Sci Polym Symp 1978, 65, 91.