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Takahiro Sato [a] & Toshiyuki Shimizu [a]

[a] Department of Macromolecular Science, Osaka University, 1-1 Machikaneyama-cho, Toyonaka, Osaka, 560-0043, Japan

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Kinetics of Phase Transition in a Lyotropic Liquid-Crystalline Polymer System

TAKAHIRO SATO* and TOSHIYUKI SHIMIZU

Department of Macromolecular Science, Osaka University 1–1 Machikaneyama-cho, Toyonaka, Osaka 560–0043, Japan

The radius R, the radius distribution function, and the number density of growing cholesteric droplets in metastable solutions of cellulose tris-(phenyl carbamate) (CTC) were measured as function of time t after quench, by polarizing microscopy. From the R dependence of the growth rate of cholesteric droplets, we concluded that the rate-determining process in the cholesteric droplet growth is the orientation of CTC molecules at the isotropic-cholesteric interface.

Keywords: lyotropic liquid crystal; polymer; cholesteric phase; kinetics of phase transition; growth rate; polarizing microscopy

INTRODUCTION

When lyotropic liquid-crystal systems are transformed from the isotropic to liquid-crystal phase, both concentration c and orientational order parameter S increase simultaneously. During this first-order phase transition, c is conserved but S is not conserved in the whole system. Since the two order parameters obey different kinetic equations, the kinetics of phase transition in lyotropic liquid-crystal systems is more involved than thermotropic liquid-crystal systems or binary mixtures undergoing liquid-liquid phase separations,[1] and have recently attracted considerable interest.[2-8]

In this study, we have investigated the kinetics of the cholesteric phase separation from metastable isotropic solutions of a cellulose derivative, cellulose tris(phenyl carbamate) (CTC), after brought into the biphasic region. As shown in Figure 1, the isotropic–cholesteric phase

* Also at CREST of Japan Science and Technology

boundary concentrations (c_I and c_A) for the CTC–tetrahydrofurane (THF) system slightly depend on temperature T, so that we can bring the system into the biphasic region by quench.[9] After the quench, cholesteric droplets appear and grow in the metastable isotropic phase. We have measured the growth rate of the droplets by polarizing microscopy to reveal the rate-determining process of this phase separation.

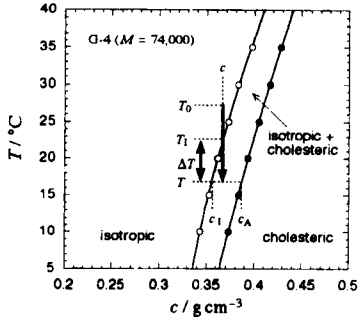

FIGURE 1. Phase diagram of a system of CTC and THF.

EXPERIMENTAL

Three fractionated CTC samples from our stock[10] were dissolved in THF to use for quench experiments. Table 1 lists the viscosity average molecular weights M and the polydispersity indices (the ratio of weight- to number-average molecular weight M_w/M_n) of the three samples as well as the initial polymer mass concentrations c_0 of the test THF solutions use in quench experiments. Each test solution was filled into a drum-shaped cell with a 15-mm inner diameter and 2-mm thickness, and left at a temperature T_0 above the phase boundary temperature T_I until quench experiments.

Quench experiments were made by transferring the cell to a cell holder on the stage of a polarizing microscope (Olympus, BHS-P) which was thermostated at T below T_I. After quench, polarizing micrographs for the same portion of the solution were taken by a CCD camera

TABLE 1. Molecular characteristics and diffusion coefficients

sample	$M/10^4$ [a]	M_w/M_n [b]	c_0 / g cm^{-3} [c]	D_m/μm^{2}s^{-1} [d]
Q11-4	9.9	1.05	0.379	158
G-4	7.4	1.05	0.365	207
H-4	4.9	1.07	0.404	271

[a] Determined from the intrinsic viscosity–molecular weight relation obtained by Kasabo *et al.*[10] [b] Determined by size-exclusion chromatography. [c] At 25 °C. [d] Determined by dynamic light scattering.

(Hamamatsu Photonics, 4742-95) attached to the microscope (× 20 or 40) at different times t. Radii R of same cholesteric droplets arbitrarilychosen in the micrographs taken at different t were measured using an image analyzing software. Furthermore, R of all the droplets (30 – 90 droplets) in an area (ca. 0.2 mm × 0.2 mm) in the micrographs were measured to determine the droplet-size distribution. The number density n of droplets was estimated by the average of the asymptotic radius cubed $\langle R(\infty)^3 \rangle$ and the initial supersaturation x_0 [$\equiv (c_0 - c_I)/(c_A - c_I)$] at $t = 0$ using the equation

$$(4\pi/3)\langle R(\infty)^3 \rangle n = x_0 \tag{1}$$

The quench depth was expressed in terms of the supercooling temperature ΔT ($\equiv T_I - T$) in what follows. From the phase diagram determined (*e.g.* Figure 1 for sample G-4), x_0 for each quenched solution can be related to ΔT by[9]

$$x_0 = \begin{cases} \Delta T/[11.3 + 0.050(T/^\circ C)] & \text{(sample H-4)} \\ \Delta T/[13.9 + 0.035(T/^\circ C)] & \text{(sample G-4)} \\ \Delta T/[16.8 - 0.006(T/^\circ C)] & \text{(sample Q11-4)} \end{cases} \tag{2}$$

RESULTS

Typical results of the time evolution of R are shown in Figure 2 for a THF solution of the CTC sample Q11-4. Cholesteric droplets in the solutions grow rapidly at early stage and level off at late stage. The growth rate dR/dt at early stage does not strongly depend on ΔT, which was observed also for other CTC samples. Figure 3 compares the growth of cholesteric droplets in solutions of three CTC samples with different molecular weight M. The growth rate seems to decrease with increasing M.

Figure 4 shows the time evolution of the radius distribution function of cholesteric droplets growing in a solution of sample G-4 at $\Delta T = 0.4$ °C. While the average radius of the droplets increases with t, the width of the distribution is almost unchanged during the phase separation. Similar trend of the time evolution of the distribution was observed for other quenched experiments.

Number densities n of droplets in three quenched solutions are plotted against t in Figure 5. Except at early stage, n is almost constant in all quenched solutions. Since very small droplets at short t cannot be seen by the microscope, n may be underestimated at early stage, and this

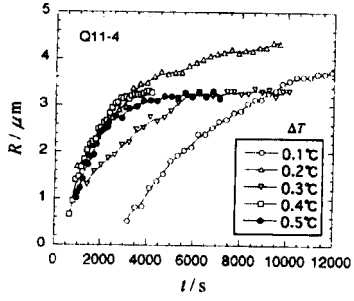

FIGURE 2. Time evolution of radii of cholesteric droplets growing in a metastable isotrop ic solution of sample Q11-4.

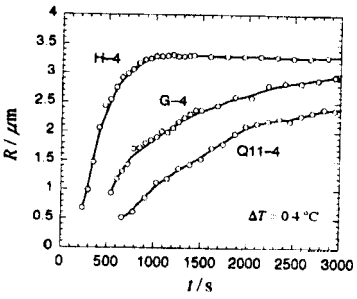

FIGURE 3. Cholesteric droplet growth in solutions of three different molecular weight CTC samples.

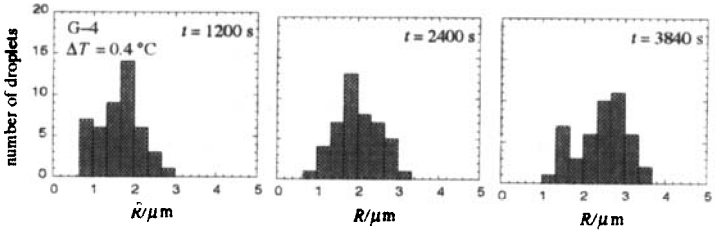

FIGURE 4. Radius distribution function of cholesteric droplets growing in a solution of sample G-4 at $\Delta T = 0.4$ °C.

may be the reason for small n at short t for solutions of sample Q11-4 shown in Figure 5. We have never observed the decrease of n at late stage of phase separation before sedimentation of droplets due to gravity. Therefore the present isotropic–cholesteric phase transition occurring in CTC solutions does not exhibit the *Ostwald ripening* process often observed in phase separation for some small molecular systems,[1,11] and each droplet in metastable isotropic solutions seems to grow independently.

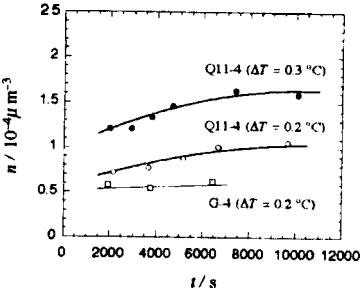

FIGURE 5. Number densities of droplets in three quenched solutions plotted against t.

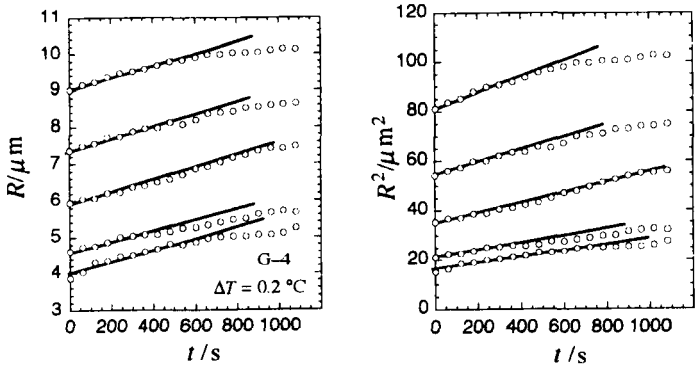

FIGURE 6. Time evolution of radii of cholesteric droplets with different sizes growing after the double quench for sample G-4 at ΔT = 0.2 °C; (a) plots of R vs. t, and (b) plots of R^2 vs. t.

We have also studied the growth of cholesteric droplets in CTC solutions after the "double quench," explained as follows. A deeply quenched solution including considerable amount of the cholesteric phase was stirred using a small magnetic tip in the drum-shaped cell, upon heating above T_I. Then the most of cholesteric phase was transformed to the isotropic phase and a small number of cholesteric droplets with a broad size distribution remain in the solution. This solution is quenched again below T_I to make the remaining droplets grow. The growth of droplets of different sizes after the double quench for sample G-4 at ΔT = 0.2 °C is shown in Figure 6; in Panels a and b, R and R^2 are plotted against t, respectively. In the former plot, data points for different size droplets almost follow lines with similar slopes at early stage. On the other hand, in the latter plot, data points for larger droplets obey steeper lines. The R independence of dR/dt was observed for other doubly quenched solutions of three CTC samples examined. As will be explained in the following section, those results give us information what the rate-determining step of the cholesteric droplet growth is.

DISCUSSION

In order that a cholesteric droplet grows, CTC molecules in the metastable isotropic phase must translationally diffuse into the droplet phase and orient to the direction parallel to the director at the interface of the droplet. If the molecules can align to the director at the interface immediately when they arrive at the interface, the translational diffusion of the molecules is the rate-determining process (the diffusion-controlled

growth). On the other hand, when the concentration gradient relaxes much faster than the orientation at the interface, the orientation of the molecules controls the growth rate of the droplet (the orientation-controlled diffusion).

We can formulate growth rates of the droplet at both diffusion-controlled and orientation-controlled growths, as explained in Appendix. If the quench is shallow and also the phase separation is not at a late stage, growing droplets fulfill the condition $2d_0/x \ll R \ll R_b$. Under this condition, Eq. (A3) in Appendix for the diffusion-controlled growth can be approximated to $dR^2/dt \approx 2D_m x$. Mutual diffusion coefficients D_m for isotropic CTC solutions at $c = c_I$ were estimated using dynamic light scattering[10] (*cf.* Table 1). The growth rate dR^2/dt calculated from Eq. (A3) using the results of D_m at the early stage ($x = x_0$) are two order magnitude faster than the experimental growth rate, calculated from plots shown in Figure 6b and also for other quenched solutions. Therefore, the kinetics of the isotropic–cholesteric phase transition in CTC solutions cannot be explained by the diffusion-controlled mechanism.

Under the condition $2d_0/x \ll R \ll R_b$, Eq. (A3) predicts that dR^2/dt is independent of R. On the other hand, Eq. (A10) for the orientation-controlled growth predicts the R independence of dR/dt in the same condition. It can be seen from Figure 6 that the latter prediction is correct for the cholesteric droplet growth in metastable isotropic CTC solutions. Thus we conclude that the orientation of CTC molecules is the rate-determining process in this phase transition. It is however noted that since we have made only rather shallow quench experiments in this study, the rate-determining process at a deep quench is still open question.

APPENDIX

Diffusion–Controlled Growth

Let us consider the concentration distribution $c(r)$ in the metastable mother phase in the vicinity of a growing droplet. Here, r represents the distance from the center of the droplet. If there are many growing droplets in the mother phase, we can define a "watershed" between two growing droplets. We denote the average distance of the watershed from the center of the droplet into consideration as R_b and the concentration at R_b as c_b. In this subsection, we assume that liquid-crystalline polymer molecules can orient to the director at the interface immediately when they arrive at the interface; *i.e.*, the orientation of polymer chains is much faster than their translational diffusion.

If the metastable mother phase is in equilibrium with the droplet phase at the interface $r = R$ during the growing process, the concentration $c(R)$ at the interface is written as[12]

$$c(R) = c_I + \frac{2d_0(c_A - c_I)}{R} \tag{A1}$$

where d_0 is the "capillary length" defined by[13]

$$d_0 \equiv \frac{\gamma}{(\partial\Pi/\partial c)_{c_I}} \frac{c_I}{(c_A - c_I)^2} \tag{A2}$$

with the interfacial tension γ and the osmotic pressure Π. Using Eq. (A1), the growth rate of the droplet is given by

$$\frac{dR^2}{dt} = 2D_m \frac{c_b - c(R)}{1 - R/R_b} = \frac{2D_m}{1 - R/R_b}\left(x - \frac{2d_0}{R}\right) \tag{A3}$$

where D_m is the translational mutual diffusion coefficient in the mother phase, and x is supersaturation defined by

$$x \equiv \frac{c_b - c_I}{c_A - c_I} \tag{A4}$$

From the mass conservation rule, c_b is determined by

$$c_b = \frac{2(c_0 - c_A\rho^3) - c(R)\rho(1-\rho)(1+2\rho)}{(1-\rho)(2+\rho)} \tag{A5}$$

where c_0 is the initial concentration at $t = 0$, and $\rho \equiv R/R_b$.

Orientation–Controlled Growth

If the orientation of polymer chains at the interface is the rate-determining process in the phase transition, the liquid-crystalline droplet phase should grow in a different manner from the above diffusion-controlled growth. We here assume that the concentration gradient relaxes much faster than the orientation at the interface. In this case, the concentration in the mother phase near the growing droplet is regarded to be uniform, and the time evolution of the the orientational order parameter S governs the droplet growth as for themotropic liquid crystal systems.

Chan[14,15] formulated the growth rate of the liquid-crystalline droplet phase for thermotropic systems by assuming that the profile of the orientational order parameter at the interface are in a steady state

during the droplet growth, and also that the excess free energy density f^{ex} for the uniform system is expressed by a quartic equation of S according to the Landau–de Gennes theory,[16] *i.e.*,

$$\partial f^{ex}/\partial S = 2AS + 3BS^2 + 4CS^3 = 4CS(S - S_2)(S - S_A) \quad \text{(A6)}$$

Here A, B, and C are the expansion coefficients, S_A is the equilibrium order parameter in the liquid-crystal bulk phase, and S_2 is the order parameter at the local maximum of f^{ex}. His final result is written as[14]

$$\frac{dR}{dt} = 2\Lambda\sqrt{\kappa C}(S_A - 2S_2) - \frac{4\kappa\Lambda}{R} \quad \text{(A7)}$$

where Λ is the rotational mobility and κ is the coefficient of the gradient free energy.

Originally, Chan obtained the above equation (A7) for thermotropic liquid crystal systems where S_2 and S_A depend on temperature. For lyotropic liquid crystal systems which we are now concerned with, S_2 should depend on the concentration c in the metastable mother phase. When c is equal to $c(R)$ given by Eq. (A1), the droplet phase is in equilibrium with the mother phase, so that $dR/dt = 0$. Furthermore, if the supersaturation x is not so high, we may write S_2 as the function of x (or c) in the form

$$S_2 = \frac{S_A}{2} - \frac{\sigma}{2}x + \frac{d_0\sigma - \sqrt{\kappa/C}}{R} \quad \text{(A8)}$$

where σ is the linear expansion coefficient. Furthermore, according to the Cahn–Hilliard theory,[17] the coefficient κ can be related to the interfacial tension γ between the two phases, as

$$\kappa \approx \gamma^2/C \quad \text{(A9)}$$

Using Eqs. (A7) – (A9), we finally obtain

$$\frac{dR}{dt} \approx 2\Lambda\sigma\gamma\left(x - \frac{2d_0}{R}\right) \quad \text{(A10)}$$

In this equation, x can be calculate from Eqs. (A4) and (A5).

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