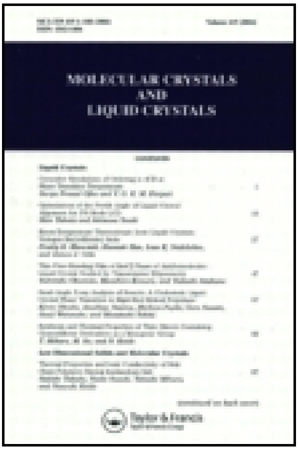

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The Anchoring Energy Coefficient of Dye Guest-Host Ferroelectric Liquid Crystals

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The Anchoring Energy Coefficient of Dye Guest-Host Ferroelectric Liquid Crystals

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This study investigated the polarization anchoring energy coefficient (W_p) and the dispersion anchoring energy coefficient (W_d) of Dye Guest-Host Ferroelectric Liquid Crystal (DGH-FLC) cells. The results showed that the polarization anchoring energy coefficient (W_p) and the dispersion anchoring energy coefficient (W_d) increased with increasing dye concentration, and decreased with increasing temperature. The rotational viscosity and memory effect of red dye guest-host ferroelectric liquid crystals were also studied. The experimental results showed that the rotational viscosity and memory effect increased with increasing dye concentration.

Keywords: FLC; Anchoring Energy Coefficient; DGHFLC; Rotational Viscosity; Memory effect

INTRODUCTION

Heilmeier and Zanoni first reported on guest-host displays[1] in 1968, and in 1969, Heilmeier, Castellano, and Zanoni[2] discussed them in greater detail. Dye guest-host liquid crystal displays (DGHLCDs)[1-7] have many advantages over twisted nematic (TN)[8] mode and super twisted nematic (STN) mode LCDs. These advantages include fewer polarizers, a wider viewing angle, more tolerance for alignment and cell spacing, easier construction and in some cases greater brightness.

Clark and Lagerwall[9] first demonstrated the concept of ferroelectric liquid crystal displays (FLCDs). FLC displays offer more potential advantages over the widely used TN and STN displays, due to their bistability, memory effect and fast response capability. For these purposes, these devices require uniform molecular alignment on the glass surfaces[10]. Since interfacial interaction plays an important role between the liquid crystal molecule and the substrate surface, we were interested in the anchoring energy between the liquid crystal molecule and the substrate surface and measured anchoring energy by optic-electric method[11].

Guest-host type display devices have been investigated since the 1980's for ferroelectric liquid crystals[12-13]. There are several advantages to these devices which include the possibility of omitting a polarizer with the cell gap effect, increased brightness, and a wider viewing angle. This study investigated the dichroic dye guest-host effect for ferroelectric liquid crystals[14-15], and we were able to determine which electro-optical properties of ferroelectric liquid crystals are strongly dependent on the alignment and anchoring energy of ferroelectric liquid crystal molecules.

In this study, we used red dichroic dye to fabricate the dye guest-host ferroelectric liquid crystals (DGHFLC) device to determine anchoring energy coefficient. Memory effect, and rotational viscosity are also discussed.

EXPERIMENT

(A) Experimental Material

The host material for the dye guest-host ferroelectric liquid crystals used was SCE13, produed by E. Merck Ltd. It has good chemical, thermal and photochemical stability, a broad smectic C* phase range and appropriate phase sequence, a negative $\Delta\varepsilon$ for dielectric stabilization and fast switching times. The physical properties of ferroelectric liquid crystals are summarized in TABLE I.

TABLE I Physical properties of ferroelectric liquid crystal SCE13.

Phase sequence	$K \xrightarrow{<0℃} SmC^{\bullet} \xrightarrow{61℃} SmA^{*} \xrightarrow{86℃} N^{*} \xrightarrow{103℃} I$
Spon.Polar. (20℃)	+30.6 nC/cm^2

The guest material for the dye guest-host ferroelectric liquid crystals was a red dichroic azo dye which was synthesized in the laboratory[16]. The molecular structure of the red dichroic azo dye is shown in FIGURE 1.

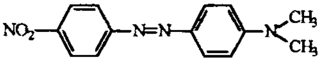

FIGURE 1 The molecular structure of red dichroic azo dye.

(B) Experimental Method

To measure dye solubility in the ferroelectric liquid crystal host, the dye guest-host ferroelectric liquid crystal mixture was fabricated as follows: Dichroic dye was dissolved into the ferroelectric liquid crystal at the desired intervals of ca. 0.5% by weight. A small amount of dye guest-host ferroelectric liquid crystal mixture was placed on a glass slide, covered by a glass coverslip, and inspected for phase separation with an optical microscope. If no phase separation was observed, the dichroic dye was considered soluble in the ferroelectric liquid crystal at that weight percent. The dichroic dye concentrations were 0%, 0.5%, 1%, 1.5%, and 2.0%.

The cells were fabricated from glass substrates coated with an indium tin oxide (ITO) conducting surface and a nylon66 anti-parallel rubbed alignment layer. Electrode spacing was maintained using 8μm glass fibers and the cell was sealed using a quick heat curing epoxy resin. 10cm wire leads were attached to the exposed ITO surfaces using a conductive solder. The cells were capillaries filled at the elevated temperature with the desired dichroic dye guest-host ferroelectric liquid crystal mixture and sealed with UV curing resin to prevent leakage. The cells were placed on a Mettler hot stage FP900 and the temperature was ramped at 0.1℃/min while applying a 5Hz square wave signal with a ±10V amplitude to switch the FLC between its bistable states.

(C) Measurement of Rotational Viscosity in the DGHFLC

The rotational viscosity γ_ϕ which mainly determines the switching time of the director is one of the most important parameters of ferroelectric liquid crystal materials. The relationship between electro-optical switching, memory effect and dye concentration of the DGHFLC can be determined. In this experiment, the standard evaluation relation which has been employed to determine the rotational viscosity in the SmC* phase associated with the motion of the tilted molecule along the cone of the azimuthal angle is normally written as[17-18]

$$\gamma_\phi = \frac{P_s \cdot E \cdot \tau_{10-90}}{1.8} \qquad (1)$$

where $\tau_{10\text{-}90}$ is the response time, E the applied switching field and P_s is the magnitude of the spontaneous polarization.

The electro-optical response time was studied with a microscope setup. FIGURE 2 shows the measurement arrangement in used. We used a He-Ne laser to measure the switching time which is 10% to 90% of change in transmitted intensity by photodiode which has a fast response (rise time is 10ns). The measurements were made with a square wave voltage with an amplitude of 10V and a frequency of 60Hz.

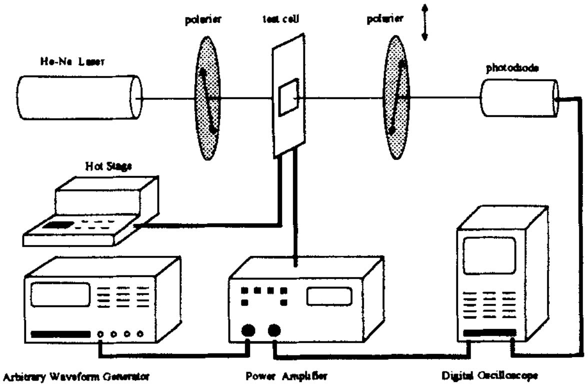

FIGURE 2 Experimental setup for response time measurement.

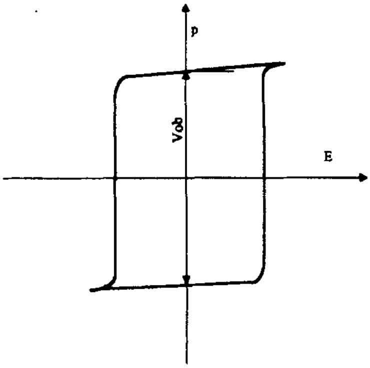

FIGURE 3 Hysteresis loop for ferroelectric liquid crystals.

The spontaneous polarization was measured with the Diament bridge method which consists of two Sawyer-Tower circuits in parallel. The spontaneous polarization was determined from the hysteresis loop. FIGURE 3 shows the hysteresis loop for FLCs. The evaluation P_s is written as[9]

$$P_s = \frac{C_o \cdot V_{ob}}{2A} \tag{2}$$

where A is the active area of the DGHFLC cells, V_{OB} is the magnitude of the y-axis of the hysteresis loop, and C_o is the fixed capacitor of the Sawyer-Tower circuit.

All of the test temperatures of the DGHFLC cell were controlled to within ±0.1℃ by the Mettle temperature control system FP900.

(D) Anchoring Energy Coefficients of DGHFLC

The anchoring energy in an FLC plays an important role in influencing the properties of molecule alignment and memory effect, bistability. The anchoring energy of FLC was determined using the free energy. The FLC free energy includes the surface terms, which are the polarization and dispersion contributions and they are written as[5]

$$F = \int_S \left(\tilde{W}_p + \tilde{W}_d\right) d\sigma \tag{3}$$

$$\tilde{W}_p = -W_p(P\nu) \tag{4}$$

$$\tilde{W}_d = -W_d(P\nu)^2 \tag{5}$$

where W_p and W_d are the corresponding anchoring strength coefficients, ν is the layer normal, and P is the FLC polarization.

We can evaluate the dispersion anchoring strength coefficient by measuring the free relaxation times τ_d for the bistable states for the FLC director[11]

$$W_d = \frac{\gamma_\phi d}{4\tau_d} \tag{6}$$

where γ_ϕ is the rotational viscosity, and d is the cell gap.

The polarization anchoring strength coefficient is written as[19]

$$W_p = \sqrt{P_s \cdot W_d^{1/2}} \tag{7}$$

where P_s is the spontaneous polarization of ferroelectric liquid crystals.

RESULTS AND DISCUSSION

(A)Rotational Viscosity(γ_ϕ)

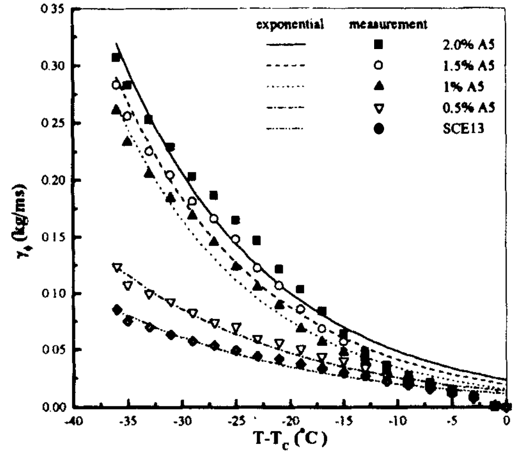

FIGURE 4 Results of the measurement and exponential fit of the rotational viscosity γ_ϕ as a function of temperature (T-T$_C$) for different dichroic dye (A5) concentrations. The T$_C$ of host FLC SCE13 is 61℃.

The rotational viscosity γ_ϕ is an important parameter in studying the dynamic behavior of FLCs and DGHFLCs. FIGURE 4 shows the rotational viscosity increased with increasing dichroic dye concentration, and decreased with increasing temperature (T-T$_C$). T$_C$ is the transition temperature of SmC* to SmA*. FLC, the rotational viscosity start to vanish, becomes smaller with changes in temperature due to the cone which is zero at the SmC* to SmA* phase transition[20]. For DGHFLC, the rotational viscosity increased due to the interaction between dye molecules and FLC. This interaction increased as dye concentration increased.

The rotational viscosity has more or less an exponential behavior with temperature[17]. FIGURE 4 also shows the result of exponential fitting relationship using the following:

$$y \propto A_1 e^x \tag{8}$$

where y is rotational viscosity, A_1 is the exponential fitting constant, x is the temperature, $T-T_C$. TABLE II shows the values of the fitting parameter.

TABLE II The exponential fitting parameter values of rotational viscosity versus temperature.

	A_1 (kg/ms)
2% A5	0.31965
1.5% A5	0.29004
1% A5	0.26602
0.5% A5	0.12351
SCE13	0.08483

(B) Anchoring Energy Coefficient

The coefficient of proportionality measures the ease with which the FLC orientation can deviate from the anchoring direction and is called the anchoring strength or anchoring energy coefficient. Generally, the anchoring strength can define two anchoring strengths which are polarization and dispersion. Polarization anchoring is due to the electrostatic forces between the dipole moments of the surface and the liquid crystal molecules[21]. Almost all liquid crystal molecules have permanent dipole moments at the molecular level, but they are averaged out in the bulk except in ferroelectric liquid crystal phases. Dispersion anchoring covers the non-electrostatic portion of the interaction (Dispersion or Van Der Waals forces) between the surface and the liquid crystal[3-6,22]. FIGURE 5 shows the dispersion anchoring energy coefficient versus temperature at different dichroic dye concentrations. FIGURE 6 shows the dispersion anchoring energy coefficient while temperature is near T_C. FIGURE 7 shows the relationship between the polarization anchoring energy coefficient and temperature. FIGURE 8 shows the relationship between the polarization anchoring coefficient and dispersion anchoring energy coefficient at different dichroic dye concentrations.

In FIGURE 5 to FIGURE 7, the anchoring energy coefficient increased with increasing dichroic dye concentration and decreased with increasing temperature. The overall profiles of the temperature dependence are as expected except for the phase transition temperature between the SmC* and SmA* phases, T_C, where an electroclinic effect prevents an accurate determination of the dispersion anchoring energy coefficient[23]. It was found that the dispersion anchoring energy coefficient decreases as the concentration of dichroic dye A5 of the mixture decreased. The linear

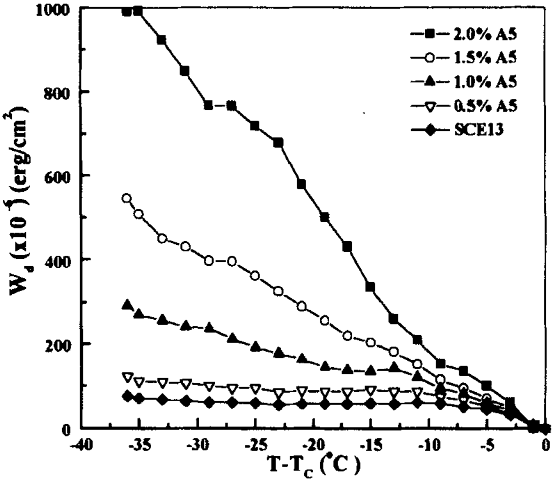

FIGURE 5 The dispersion anchoring energy coefficient versus temperature at different dichroic dye concentrations.

dependence of the dispersion anchoring energy coefficient on the temperature is shown in FIGURE 7. Generally, this is reasonable as the dipole moments cancel out, resulting in a smaller dispersion anchoring energy coefficient.[18] Simultaneously, the dispersion anchoring energy was proportional to temperature while temperature was near the SmC* to SmA* phase transition temperature as shown FIGURE 7. The proportional relation is as follows:

$$W_d \propto B(T - T_C) \qquad (9)$$

where B is the fitting slope. TABLE III summarizes the results of the dispersion anchoring energy coefficient versus temperature by linear fit.

TABLE III The slope of the dispersion anchoring energy coefficient versus temperature by linear fitting.

	B (erg/cm^{2}K)
2% A5	-1.93668×10^{-5}
1.5% A5	-1.40161×10^{-5}
1% A5	-1.09398×10^{-5}
0.5% A5	-8.60369×10^{-6}
SCE13	-6.69968×10^{-6}

FIGURE 7 shows the relationship between the polarization anchoring energy coefficient and temperature. It was found the polarization anchoring energy coefficient decreased with increasing temperature, but increased with increasing concentration of dichroic dye A5. Generally, this can be explained because the enthalpy of the molecule increased with temperature and broke the interaction barrier.

The relationship between the polarization anchoring energy coefficient and the dispersion anchoring energy coefficient at different dichroic dye concentrations is shown in FIGURE 9. It can be seen that the curve is near the polarization anchoring energy coefficient axis, and when the dichroic dye concentration increased, the curve is closer and closer to the dispersion anchoring energy coefficient axis. This means that the dispersion anchoring energy coefficient increased with an increase in the dichroic dye. Ferroelectric liquid crystals behave similarly to other liquid crystals in regards to surface anchoring, however, their spontaneous bulk polarization may perhaps imply a little larger contribution to polarization anchoring[3-6].

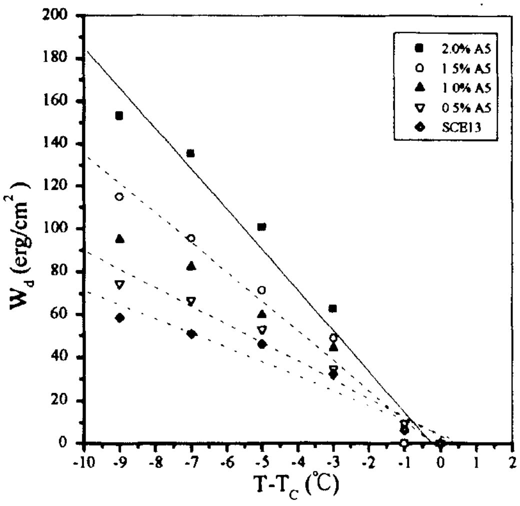

Figure 6 The dispersion anchoring energy coefficient near phase transition temperature at different dichroic dye concentrations.

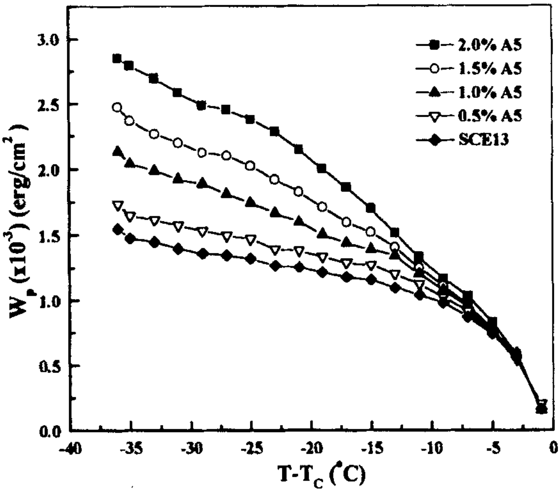

FIGURE 7 The polarization anchoring energy coefficient versus temperature at different dichroic dye concentrations.

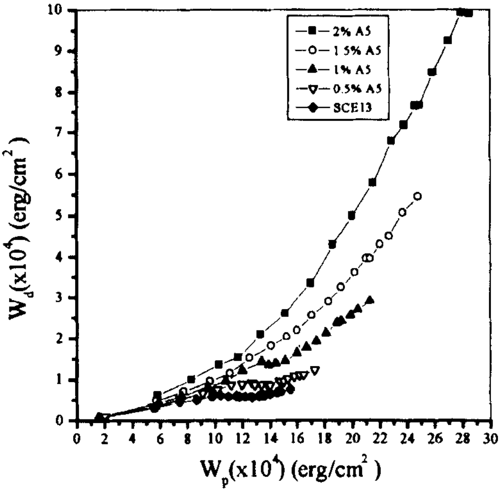

FIGURE 8 The polarization anchoring energy coefficient versus temperature at different dichroic dye concentrations.

(C) Memory Effect

In order to investigate how the FLC would react to partial switching pulse sequences we used a very simple two pulse slot addressing scheme. In this case the pulse sequences applied to the cell consisted of a +10V, 2ms duration to reset the pulse (to put the cell into a uniform black state), followed by a 77.8ms delay (to allow the black state to relax) and a 2ms duration −10V pulse (to switch partially towards the white state). Memory effect was measured as light intensity through the DGHFLC or FLC cell which applied bipolar pulses.

Memory effect was studied while the bipolar pulse voltages were turned off and a photo-diode was uesd to detect the V-T curve. The V-T curve, optical response, of the cell is shown in FIGURE 9. FIGURE 9-(A) to FIGURE 9-(E) shows the V-T curves for various dichoric dye concentrations with different temperatures. In FIGURE 9-(A), the memory effect incresed with increasing dichroic dye concentration and decreased with increasing temperature. The memory effect increased due to the rotational viscosity and anchoring energy also increaed. In this case, where the rotational viscosity and anchoring energy increased, the V-T curve can maintain brightness and can achieve a better memory effect. But as the dichroic dye concentration decreased, the rotational viscosity and anchoring energy could not play an important role in maintaining the brightness.

In other words, while the dichoring dye concentration decreased, the potential due to the rotational viscosity and anchoring was not able to keep the liquid crystal molecule in the same position, so the brightness decreased and the memory effect worsened. The results showed that memory effect increased with increasing dichroic dye concentration, and decreased with decreasing test temperature.

CONCLUSION

In this study, we mixed dichroic dye into ferroelectric liquid crystal to fabricate the dichroic dye guest-host ferroelectric liquid crystal (DGHFLC). The study results showed that dichroic dye concentration could make a slight, but not important influence on the properties of the ferroelectric liquid crystal. The response time was still fast ,and the light transmission will rise due to the DGHFLC can omit a polarizer.

For the evaluation of rotational viscosity, it was discovered that dichroic dye increased the rotational viscosity, and the intrinsic property temperature decreased rotational viscosity were due to the stereo configuration between the dye and liquid crystal molecule. We think the interactions like the Van Der Waal's force which played an important role between the dye and liquid crystal molecule.

For the anchoring energy measurement, it appears the influence was due to polarization and dispersion. The increase in dichroic dye concentration will increase both the polarization and dispersion anchoring energy coefficient, however the polarization anchoring energy coefficient was more than one order greater than the dispersion anchoring energy coefficient in this study. FLCs behave similarly to other liquid crystals concerning surface anchoring, however, their spontaneous bulk polarization may perhaps imply a little larger contribution to polarization anchoring.

Greater dichroic dye concentration will produce better memory effect and viewing quality. Regarding the viscoelastic property of the ferroelectric liquid crystal, the elastic property played an important role when the ferroelectric liquid crystal was not mixed with dichroic dye. However, when the dichroic dye concentration increased, the elastic property of the ferroelectric liquid crystal did not play an important role but the viscous property of the ferroelectric liquid crystal became more and more important. Therefore, the memory effect will become increasingly better.

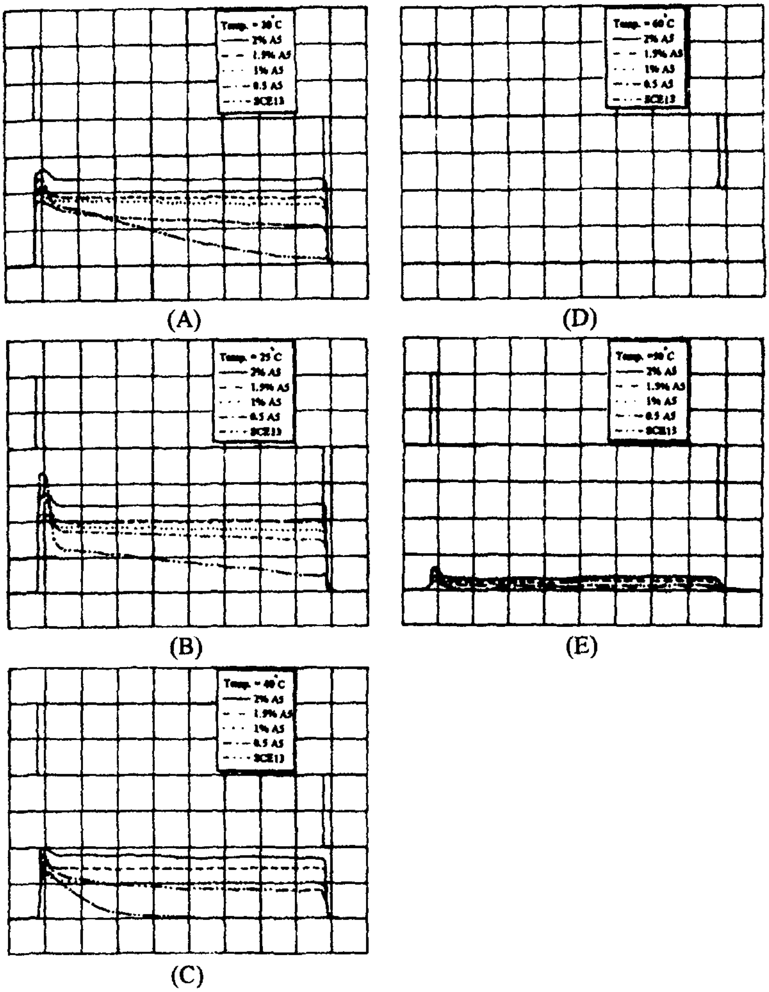

FIGURE 9 The memory effect of DGHFLC with dichroic dye A5 at different measuring temperatures. (A) at 25℃ (B) at 30 ℃ (C) at 40℃ (D) at 50℃ (E) at 60℃.

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