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Effect of Reheating and Ramp Rates on Phase Transitions of 5OCB Liquid Crystal using Logger Pro

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Abstract:
This research focuses on the effect of ramp rates on phase transitions of pentyl-oxy-cyanobiphenyl (5OCB) Liquid Crystal (LC). It also reports how reheating can bring changes in the shape and size of phase transitions of 5OCB. It is observed that when 5OCB is heated and cooled with different ramp rates, each phase transition shows temperature dynamics. They shift with temperature as ramp rates are changed. In heating, all transitions move towards higher temperature and in cooling all transitions move towards lower temperatures when ramp rates are increased. It is also observed that as an effect of reheating, a new transition appears in 2nd heating called 'heat crystallization'. So, from the 2nd heating and cooling, 5OCB shows two crystallizations: one in heating and another in cooling. We like to call heat crystallization as "Krystallization" and cool crystallization as "Crystallization" to show differences between them. The 5OCB shows three phase transitions during heating which are Krystallization, melting, and nematic; and three phase transitions in cooling as nematic, and a double cool crystallization peak labeled #1 and #2. Each transition shows the presence of activation energy. We are reporting their values in this paper as well.

Keywords:
Heating and Cooling, Differential Scanning Calorimetry, DSC, 5OCB, Liquid Crystal, Specific Heat Capacity, Crystalline, Krystalline, Melting, Phase transitions, Heating rate, Cooling rate, Ramp rate, Enthalpy, Temperature, LoggerPo.

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I. Introduction:

Research in material science is always full of varying types of materials with this research bringing remarkable results. For decades, Liquid Crystals (LCs) have been the material of interest in research, showing multiple states in between solid and liquid states. Liquid crystals (LCs) are being used in the modern world in multiple ways. Some examples of their application can be seen in Liquid Crystal Displays (LCDs), medicines, pure and applied research etc. [1-17]

Some research materials are used up completely, which means when they are heated, they are gone completely and never come back to their original state again that was observed when they are cooled; a common example of this is a cooked egg. When you heat up a beaten egg, it cooks. When you cool it down, it never comes back to the beaten egg form it was in before cooking. This is called irreversible reactions or transition or chemical reactions. There are some materials that come back to their initial state when they are cooled after heating, for example ice to water. This is called reversible transition or physical change. It becomes more interesting when some material behaves in between these two types. They are reversible or show physical change, but at some point, they also show some new features or facts based on heating and cooling. Another good example can be given with ice cream. A scoop of ice cream straight from the freezer will be solid, cold, and creamy. As the ice cream is kept at room temperature for some time, it gets softer or melts. If you refreeze it and check it again, it is not going to be as creamy as it was before, but you may find some parts crunchy with ice in it. The reason is it was amorphous before and now it is semicrystalline. A similar phenomenon can be seen in some LCs when they are cooled to a lower temperature very quickly and then reheated. [4]

Heating the same sample repeatedly, like what was done in this case, allows for in-depth research into the behavior of the substance being used. Heating a sample once will give a predictable graph, but multiple heating's allows for one to observe how the sample may behave in real world applications. For example, if you use an LC in an LCD screen and turn that LCD device on and off multiple times, this effect is like multiple heating and cooling. Our interest is to see the effect of multiple heating and cooling on pentyl-oxy-cyanobiphenyl (5OCB) LC and how it behaves when it is heated and cooled multiple times. Does it give the same phase transitions every time or do some new features appear in it?

Living in the modern age, the ability to control the temperature in one's home is simple. In the winter, the heat is turned on to keep the house from getting too cold. While in the summer, the air conditioning is turned on to prevent the house from getting too hot. Unfortunately, some areas in the world cannot afford this technology and are at the mercy of nature. A house that has an LCD and does not have heating in the winter, will affect the LCs inside that LCD. The LCs will be cooled or heated because of the weather outside. Then the LCs can be heated or cooled as a result of turning on or off the device. This phenomenon is like the effect of reheating and recooling, which is being studied extensively in this paper. The goal of this paper, and the experiments performed, was to see how the 5OCB would react if it was reheated and cooled and how this may affect it as a possible material for smart technology. In addition to studying the effect of reheating and cooling, the ramp rate at which the LC was heated and cooled is being studied. This is the speed at which the temperature rises and decreases; four separate rates were studied in this paper: 25°C/min, 20 °C/min, 15°C/min and 10°C/min.

In terms of LC, it is a material that stays in its crystalline state, which is its first state and resembles the solid state of matter. Then when heated, it goes to a melting state. Usually, any solid melts when it is heated, but LCs show intermediate states that are called phase transitions and they are not just solid and liquid but more than that. The 5OCB LC shows a crystalline state, nematic state and isotropic state during heating and cooling. It is also important to see how the speed of heating and cooling can bring changes in the material's behavior, which is called the effect of ramp rates in the language of calorimetry. In this research paper, we are using Differential Scanning Calorimetry (DSC) to run 5OCB four times with four different heating and cooling rates and find some hidden effects of 5OCB melting and crystallization transitions. [5-14]

II. Materials and Experiments:

Pentyl-oxy-cyanobiphenyl (5OCB) is the youngest liquid crystal in the family of Alkyl-oxy-cyanobiphenyl (nOCB). Its molecular weight is 265.350 g/mol. It usually shows a crystalline state (C), nematic state (N) and isotropic state (I) in heating, which can be seen in our first paper of this series.[13] Differential Scanning Calorimetry (DSC) is one of the important instruments that uses heat flow to detect any transitions in the material as the material heats up or cool down. The detailed thermal study of the material can be seen when it is cooled from the higher temperature to the lower temperature. DSC is one of the most powerful techniques from decades to study thermal behavior of the material in science and research areas. [13]

To study thermal behavior of the 5OCB liquid crystal, a small amount of this sample was used to run in a DSC instrument from TA instruments company, model number MDSC 2920 that was present in the Chemistry and Biochemistry department of WPI to study its phase transitions. The 5OCB is heated from -40 ℃ to 80 ℃ and then cooled from the same temperature: 80 ℃ to -40 ℃, with a constant heating and cooling rate. Then, the same sample of 5OCB is heated again and then cooled for the same temperature range as mentioned above for three more times with three different heating and cooling rates. The ramp rates used for this study are 25°C/min, 20 °C/min, 15°C/min and 10°C/min.

The data obtained from DSC show some cool features that appeared in 5OCB when it was heated and cooled multiple times. 5OCB shows endothermic peaks on heating and exothermic peaks on cooling for its 1st heating and cooling. However, a strange exothermic peak appears in the 2nd heating, along with two endothermic peaks and then two exothermic peaks in cooling where one peak was not a single peak, but it was a double peak. The strange new exothermic peak that appeared in heating started changing its shape and place when the sample was heated a 3rd and 4th time. The exothermic double peak appeared in cooling, and it also changed its shape and place for the 3rd and 4th cooling. All these details are shown in the result section of this paper.

To get detailed analysis of each of these phase transitions of 5OCB, Logger Pro is used as data analysis software for this study. Logger Pro is proven a good tool for data analysis. Theory used to plot graphs in Logger Pro is a simple DSC theory to get specific heat capacity from heat flow as a function of temperature and can be seen in our first paper of this series. [13]

A drawing of a 5OCB LC can be seen in Figure 1 and three typical states of 5OCB can be seen in Figure 2.

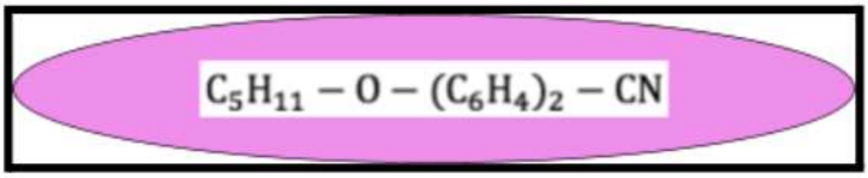

Figure 1: Molecular Formula of 5OCB.

The molecular formula for 5OCB is shown in Figure 1 inside a drawn liquid crystal. The LC structure is shown to be a rod-like shape and contains the formula for the liquid crystal. The 5-carbon chain is apparent on the left and the distinctive oxygen connecting the phenyl group and the carbon chain.

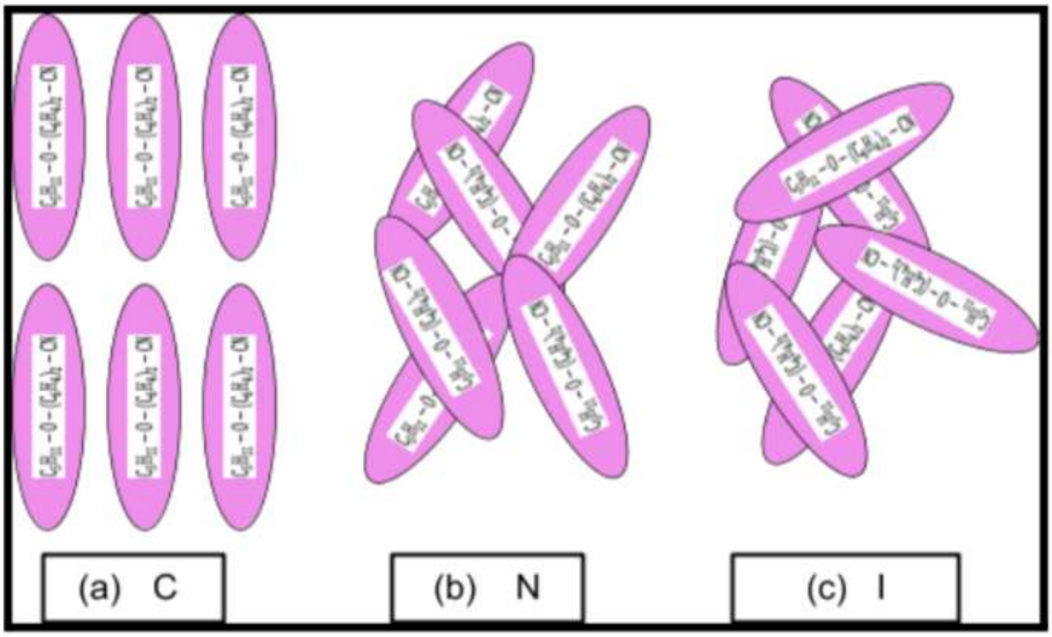

Figure 2: Molecular arrangement of 5OCB liquid crystal molecules in (a) Crystalline phase (C), (b) Nematic phase (N), (c) Isotropic phase (I).

The molecular alignment and molecular arrangement of 5OCB liquid crystal shows the existence of three states that is shown in Figure 2. At cooler temperatures, the liquid crystal would be in the (a) crystalline (C) phase and then would progress to the (b) nematic (N) phase as the temperature rises. At the highest temperatures, the LC will be in the (c) isotropic phase (I). It is clearly seen as 5OCB moves from C to I, its molecular alignment shows less ordered and organized states.

III. Theory:

The Arrhenius equation, which relates the rate of a reaction to its activation energy, is given as follows:

$$k = Ae^{\frac{-Ea}{RT}} \quad (1)$$

where k is the rate of the experiment, A is a pre-exponential factor, Ea is the activation energy, R is the universal gas constant, and T is the temperature. This equation can be applied to this research as:

$$\beta = \beta_o e^{\frac{-Ea}{RT}} \quad (2)$$

where β is the ramp rate, β_o is a constant, Ea is the activation energy, R is the universal gas constant, and T is temperature. The natural log of equation 2 will yield a straight line for the data to be analyzed. Equation 3 shows the natural log of equation 2 and how it relates to the equation of a line.

$$ln\ (\beta) = ln\ (\beta_o) - \frac{-Ea}{RT} \quad (3)$$

The rearrangement of equation 3 leaves:

$$ln\ (\beta) = (\frac{-Ea}{R}) * \frac{1}{T} + ln\ (\beta_o) \quad (4)$$

Equation 4 begins to resemble the equation of a line, which is shown as equation 5:

$$y = -mx + b \quad (5)$$

with y being the vertical-axis value, m being the slope of the line, x is the value of the horizontal axis, and b is the intercept of the vertical/ y-axis. Since equation 4 and equation 5 are similar, the slope and intercept of equation 4 is:

$$m = \frac{Ea}{R}, \quad b = \ln\ (\beta_o) \qquad (6)$$

Finally, the activation energy can be determined using equation 7.

$$Ea = m * R \qquad (7)$$

IV. Results:

The data obtained from the DSC instrument is plotted in Logger Pro to show how 5OCB changes in states as it is heated and cooled.

Figure 3 shows the first heat and cool run of 5OCB through the DSC instrument. The sample was heated and cooled at a rate of 20°C/min, with the sample being heated first and then cooled back down. The resulting peaks have been labeled as melting (TM), Nematic (TN) and Crystalline (TC) for the 1st run in DSC. The ranges of the crystal are labeled as well with crystalline, nematic, and isotropic. The letters C, N, I represent as Crystalline state, Nematic state and Isotropic state.

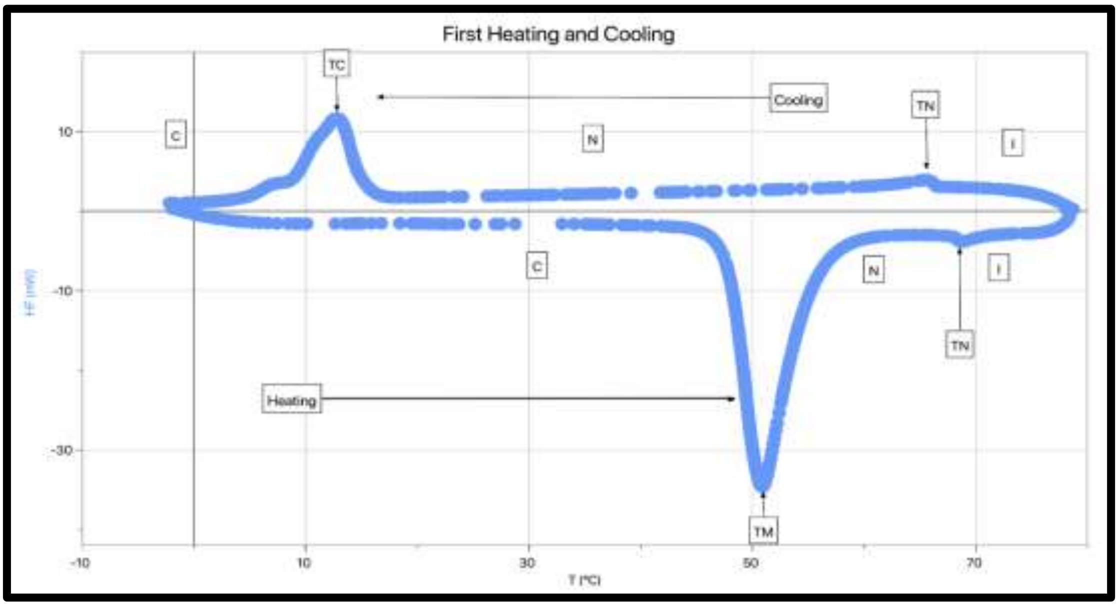

Figure 3: The first heating and cooling of 5OCB liquid crystal.

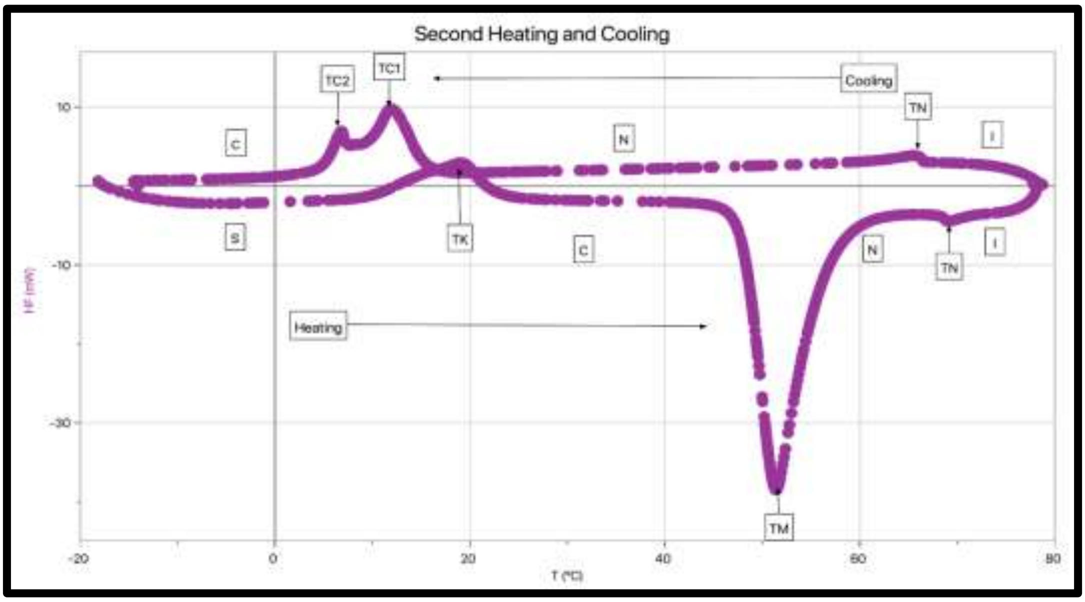

Figure 4: The second heat and cool of 5OCB.

The purple graph in Figure 4 shows the second run of 5OCB with 25 ℃/min ramp rate, where after the first run, the same sample was reheated and cooled again. The reheating and cooling caused the addition of a new peak in the heating portion; this peak is heat crystallization labeled as 'TK' and we like to call it as "Krystallization". This peak appears from a mixed solid-state peak that arose from reheating. The crystalline peak in the cooling portion of the graph shows a double peak labeled as 'TC1' and 'TC2'. Since after cooling for the 1st time, the entire sample doesn't go to a crystalline state, we call that state a mixed state that has crystalline and other types of solid too. The mixed solid state is called in the graph as "Solid" with a letter of S.

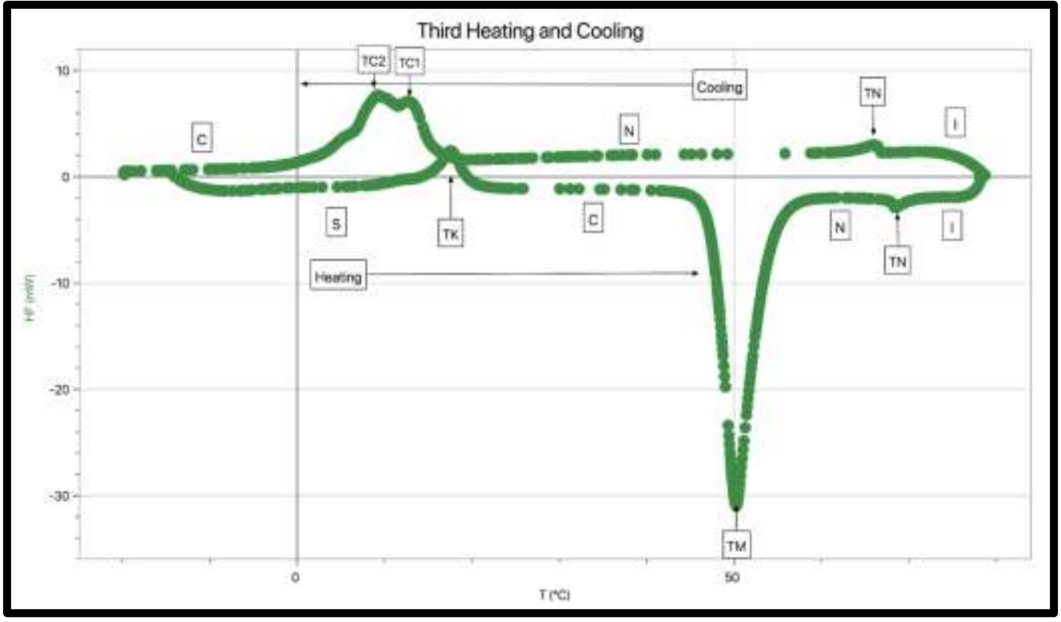

Figure 5: The third heat and cool of 5OCB.

5OCB was heated and cooled again for a third time by reheating and cooling the same sample used in Runs 1 and 2, which is shown in Figure 5. The rate of this run was 15 °C/min and the Krystalline peak is still present in this graph as well. The crystalline peak with two peaks begins to shift to the same spot as the Krystalline peak in heating. All states have been abbreviated: 'S' for mixed solid state, 'C' for crystalline, 'N' for nematic, and 'I' for isotropic and 'C1' and 'C2' are multiple peaks in cool crystallization.

Figure 6 is the final run of the 5OCB sample through the DSC instrument and it was heated and cooled at a rate of 10°C/min. The same sample was used all throughout the four trials and the addition of the Krystalline peak was only seen in trials that reheated the sample. Now the Krystalline peak and the double crystalline peak, occur in the same place on the graph.

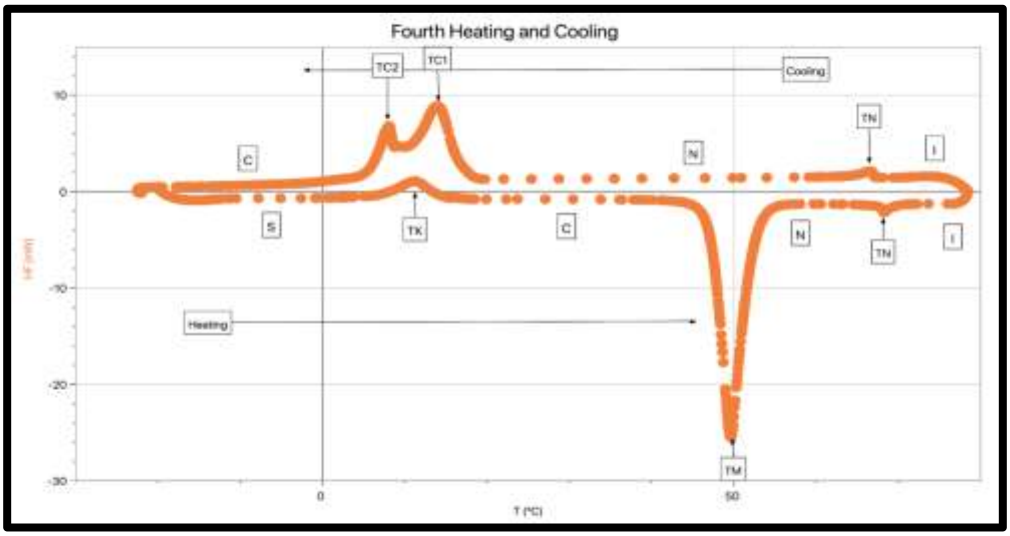

Figure 6: The fourth heat and cool of 5OCB.

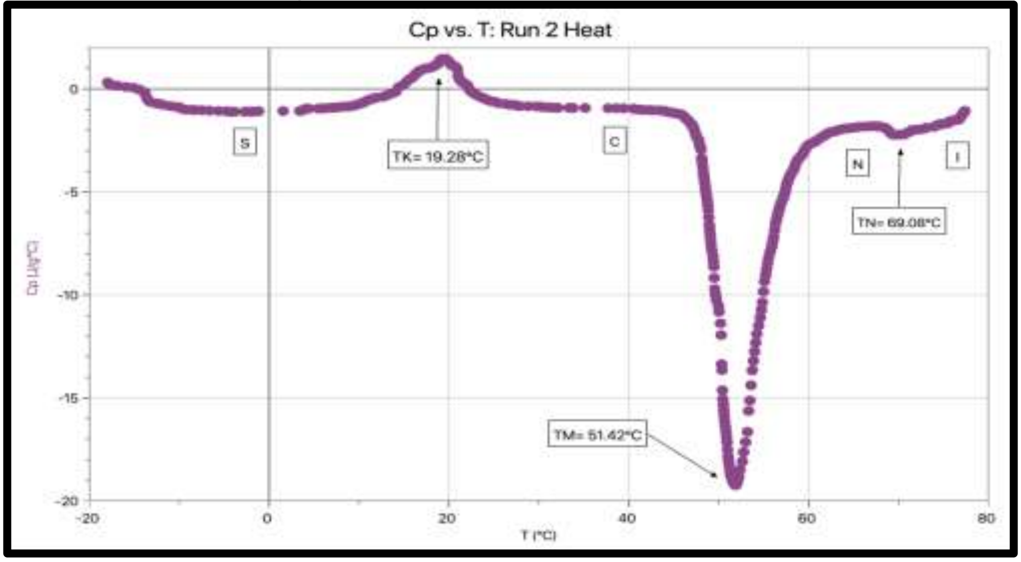

Figure 7: Zoomed in graph for the second heating of 5OCB.

Figure 7 shows the specific heat capacity vs. temperature of the run with a ramp rate of 25 °C/min. The second, third, and fourth run of the 5OCB crystal led to the addition of a new peak in the heating portion and a doublet instead of a singlet in the cooling portion. These characteristics can still be seen in the heat capacity graphs. The Krystalline peak in the heating portion is shown above more clearly. To see a clear effect of ramp rate on all three transitions of 5OCB, heat flow obtained from DSC is normalized by the mass of the sample and then their specific heat capacity is calculated to plot a graph for each ramp rate. A zoomed in figure for the second heat is shown as specific heat capacity vs temperature plot in Figure 7.

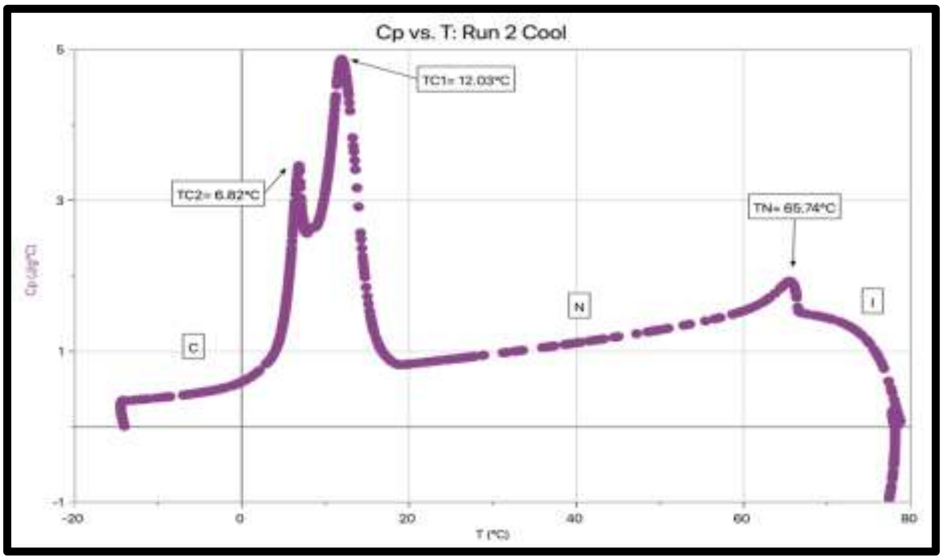

Figure 8: Zoomed in plot for the second run of cooling of 5OCB.

Figure 8 is the cooling of 5OCB for the second time at a rate of 25 °C/min, with the calculated specific heat capacity on the y-axis and temperature on the x-axis. The specific heat was calculated by multiplying the normalized heat flow by the reciprocal of the specific rate used in its trial. The peak displayed in Figure 8 is the double crystalline peak that arose from reheating and cooling.

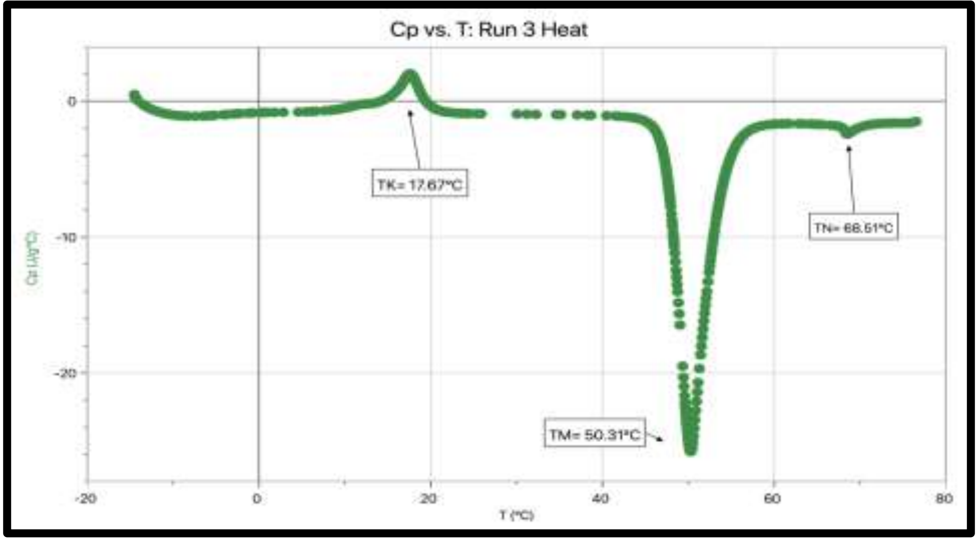

Figure 9: The specific heat capacity of 5OCB's third run heating through DSC.

The calculated specific heat capacity for the third run of 5OCB is in Figure 9; this trial means that the same sample from runs 1 and 2 was used and reheated and cooled at a ramp rate of 15 °C/min. The peaks of the graph are labeled, and the states were omitted since they are similar to those in run 2's graph.

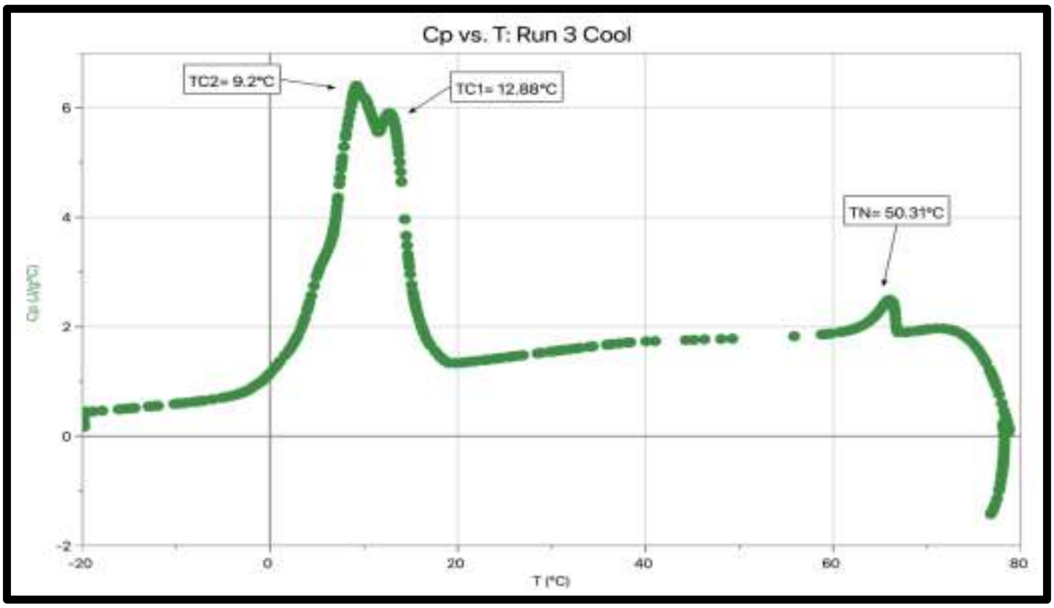

Figure 10: 5OCB's third run cooling and its specific heat capacity.

The cooling of the sample for the cooling of 5OCB at 15 °C/min is shown in Figure 10 with the nematic peak being labeled as 'TN' and the doublet peak being labeled as 'TC1' and 'TC2' to denote crystalline peak 1 and crystalline peak 2.

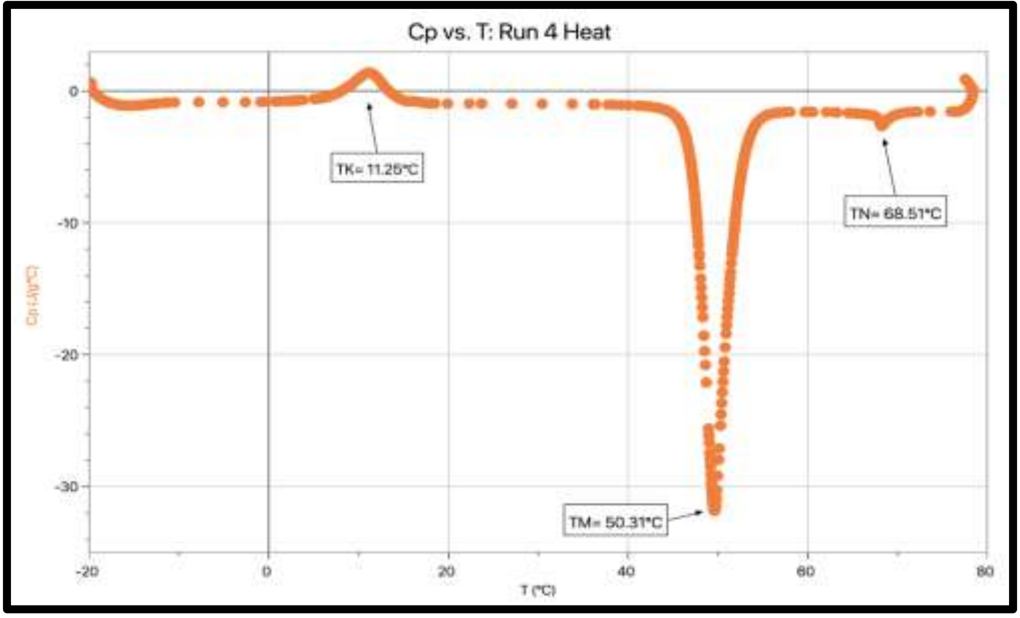

Figure 11: Fourth run of 5OCB heating using DSC.

The last reheating of the sample at a rate of 10 °C/min is shown in Figure 11, just showing the reheating of the sample and its resulting specific heat capacity. 'TK' denotes the additional peak seen in runs 2. 3, and 4 and will be analyzed along with the other peaks that occurred. This peak seems to decrease with each run that occurs.

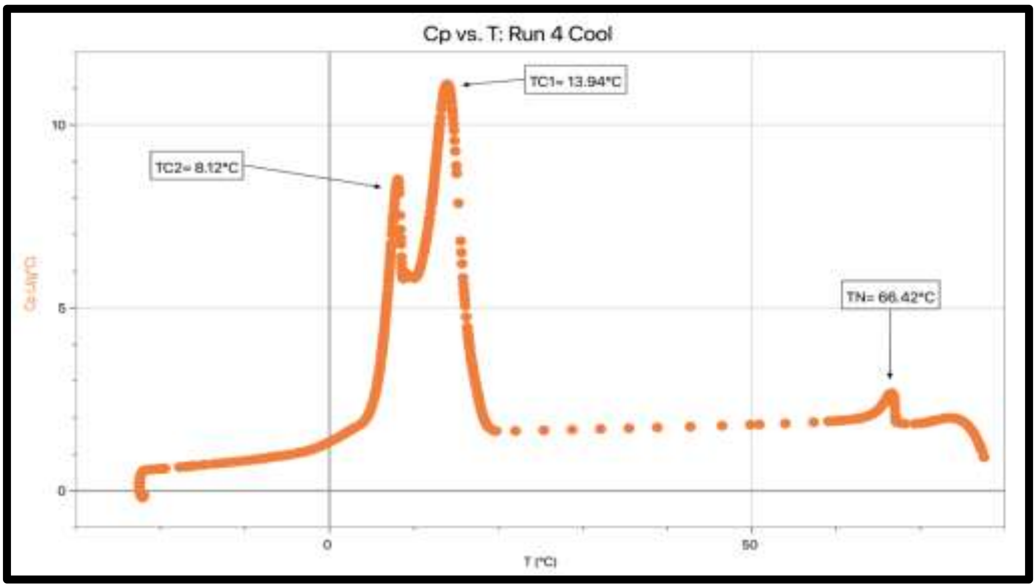

Figure 12: Specific heat capacity for just the cooling portion of the fourth run through the DSC.

The normalized heat flow of the cooling of 5OCB at 10 °C/min, which would look very similar to the figures showing run 2's normalized heat flow, was multiplied by the reciprocal of the rate and used to make Figure 12. This rate was 10 °C/min.

V. Discussion:

To understand the effect of ramp rates on all phase transitions of 5OCB liquid crystal, some summary graphs are plotted here showing a good comparison of the phase transitions of 5OCB for heat and cool for four different ramp rates from 10 ℃/min to 25 ℃/min.

The specific heat capacity vs temperature plots for each run's heating are shown in Figure 13 for all three phase transitions. Run 1 is in blue, run 2 is in purple, run 3 is in green, and run 4 is in orange and their corresponding ramp rates are given in the legend of the graph. Graphing all runs together allows for easy comparison between each run and how the sample behaved. The mixed solid-state peak is only present for runs 2-4 and run 4 has the biggest melting peak.

To see clear effects, a zoomed in graph is shown in Figure 14 for the specific heat capacity for each run's heating of 5OCB vs. its temperature for Krystallization and melting only. Graphing all runs together allows for easy comparison between each run and how the sample behavior changed from rate to rate. Run 4 has the biggest melting peak; all runs had a relatively similar nematic peak

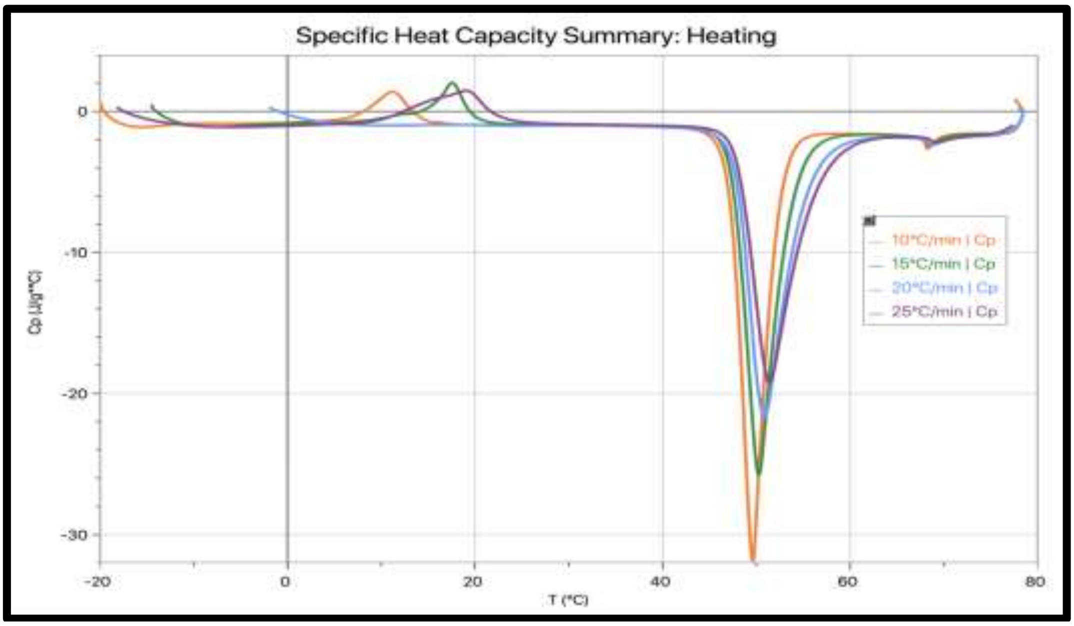

Figure 13: Summary of Specific heat for all four ramp rates of heating.

The graph seen in Figure 13 compares the specific heat capacity during heating of all runs, with their ramp rates denoted by color: orange is when 5CB was heated at 10 ℃/min, green is when the liquid crystal was heated at 15 ℃/min, blue is when the rate was 20 ℃/min, and purple is when the ramp rate was 25 ℃/min. The temperature is shown on the x-axis as the liquid crystal is heated; graphing the runs together shows how peaks move from rate to rate.

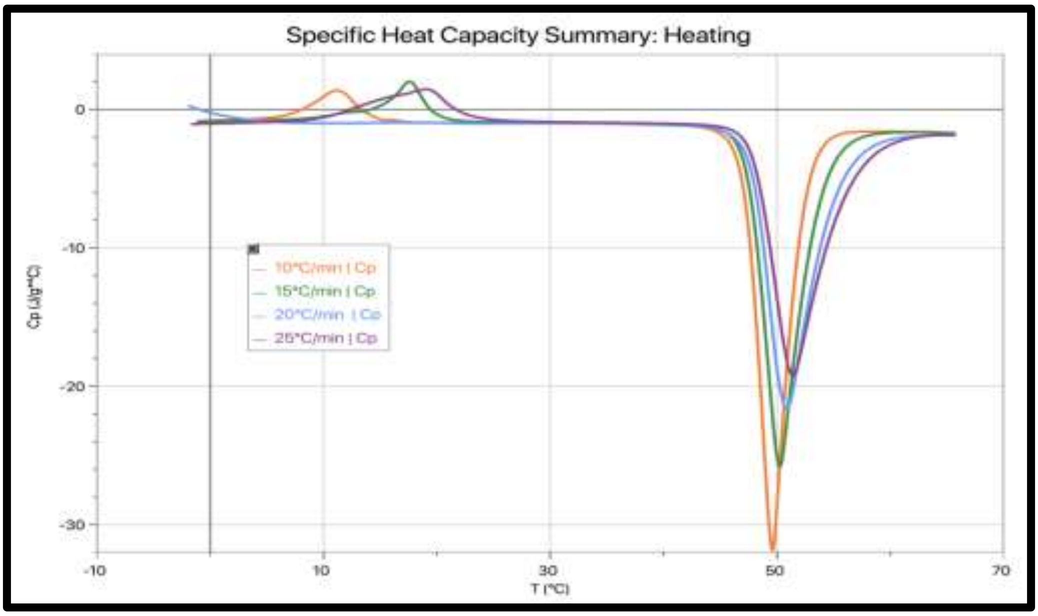

Figure 14: Zoomed in part of heat to show Specific heat capacity of 5OCB for all 4 runs for Krystallization and melting.

Figure 14 shows the summary of heating 5OCB for the four different ramp rates, the legend on the graph telling which rate belongs to which line. The peaks focused on in Figure 14 are the Krystallization peak or mixed solid-state peak, which occurs first, and the melting peak, which occurs second and is much bigger. The run with a ramp rate of 20 °C/min has no Krystallization peak.

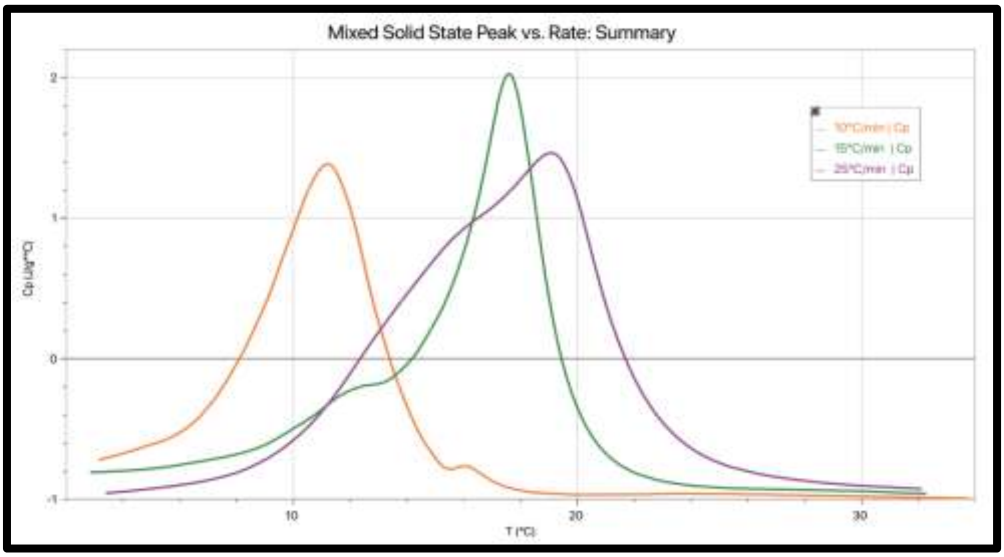

Figure 15: Zoomed in part of specific heat capacity vs Temperature plot of Krystallization peak in heating showing effect of ramp rates.

Figure 15 has three peaks for the rates of 10 ℃/min, 15 ℃/min, and 25 ℃/min; there is no peak for the rate of 20 ℃/min since this run did not show a mixed solid state or Krystallization peak. The mixed solid-state peak shifts its temperature range from rate to rate, with the 10 °C/min rate having an earlier temperature range, and 15 °C/min and 25 ℃/min having roughly the same range. However, the peak for the 25 °C/min rate is much broader than the mixed solid-state peak of the 15 °C/min rate.

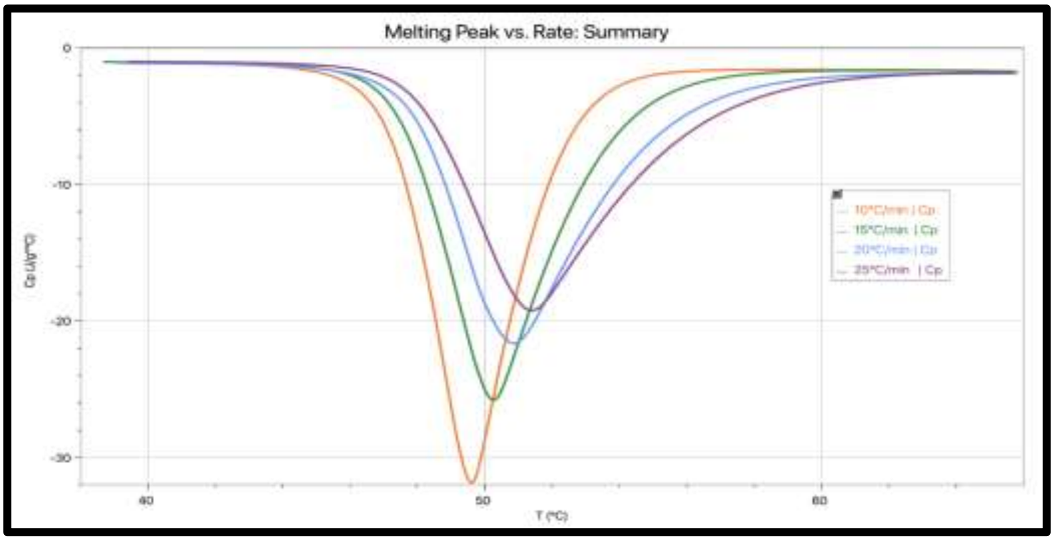

Figure 16: Zoomed in part of specific heat capacity vs temperature plot for melting peak in heating showing effect of ramp rates.

A close comparison of each rate's melting peak is graphed in Figure 15 with a legend to explain which line is which rate. The melting peaks of the runs line up together, falling between the same temperature range, and seem to have decreasing specific heat capacity as the rate increases. The biggest melting peak belongs to the ramp rate that heated 5OCB at 10 ℃/min and the smallest melting peak belongs to the rate of 25 ℃/min.

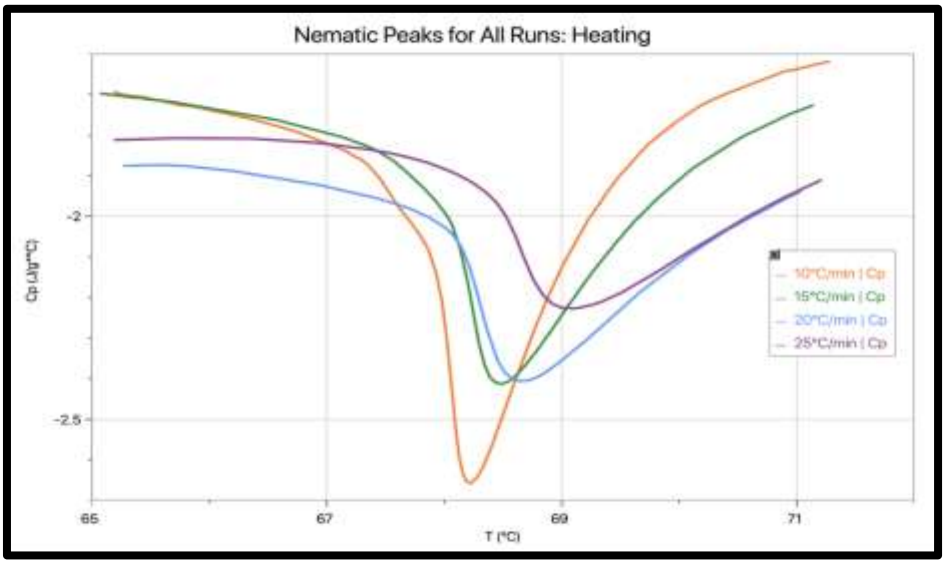

Figure 17: Zoomed in part of specific heat capacity vs Temperature plot of nematic peak in heating showing effect of ramp rates.

Figure 17 strives to compare the nematic peak of 5OCB while it is being heated to its rate at which it is being heated at. The legend on the graph provides color coordination for each rate. The peaks occurred around the same temperatures for each run of heating and repeated the trend that the specific heat capacity decreases as the rate increases. The run with the lowest ramp rate, 10 °C/min, had the biggest and deepest peak.

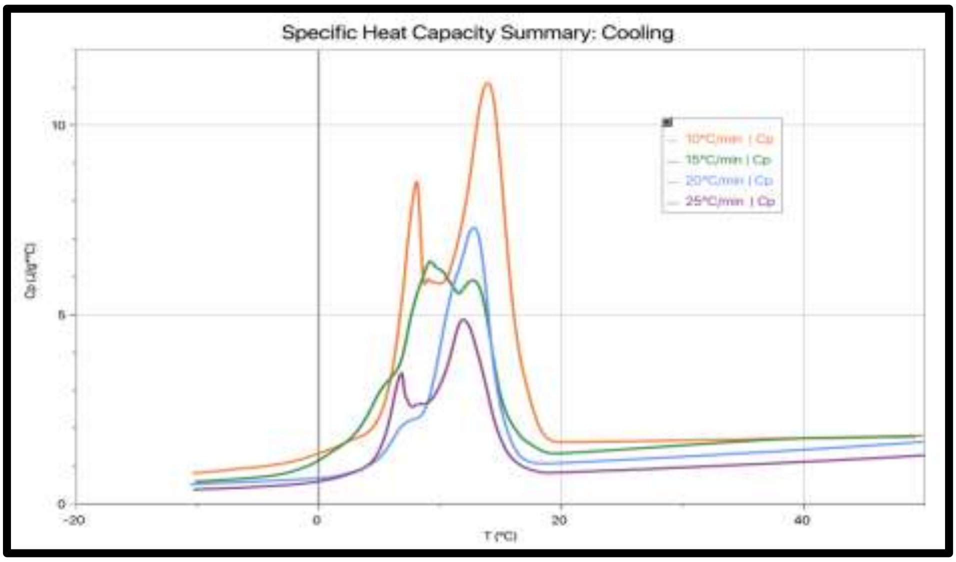

Figure 18: Specific heat capacity of 5OCB for all 4 runs for cooling.

The zoomed in graph for the specific heat capacity vs. the temperature plot of the cool crystallization of 5OCB for all four runs is shown in Figure 18, with a legend detailing the 10°C/min rate as orange, the 15 °C/min rate in green, the 20 °C/min rate in blue, and the ramp rate of 25°C/min in purple. 20 °C/min is the only singlet crystalline peak, while the others show a double peak. Again, the specific heat capacity decreases as the ramp rate increases.

The data details for all phase transitions appeared in 5OCB in heating and cooling for four ramp rates are shown in Figures 13-18. It can be seen clearly that as ramp rates move from 10 ℃/min to 25 ℃/min, the peak position of each phase transition appeared in heating move forward and peak position appeared in cooling move backwards in temperatures.

Table 1: Effect of ramp rates on each phase transition of 5OCB.

The important data of the peaks that occurred in the four runs of 5OCB are shown with the rate of their corresponding trial. The peak temperature and range of the heating and cooling were recorded and determined from the DSC. An uppercase ‘RM’ means the melting range was examined and an uppercase T means the peak temperature: ‘TK is the peak temperature of the Krystallization peak, ‘TM’ is the melting transition’s peak temperature, ‘TN’ is the peak temperature of the nematic heating transition, and ‘TC’ is the peak temperature of the crystalline transition.

Rate (℃/min)	TK (℃)	TM (℃)	TN Heat (℃)	TC1 (℃)	TC2 (℃)	RM (℃)
10	11.25	49.69	68.24	13.94	8.12	21.26
15	17.67	50.31	68.51	12.88	9.2	14.9
20	N/A	50.8	68.58	12.58	N/A	N/A
25	19.28	51.42	69.08	12.03	6.82	14.25

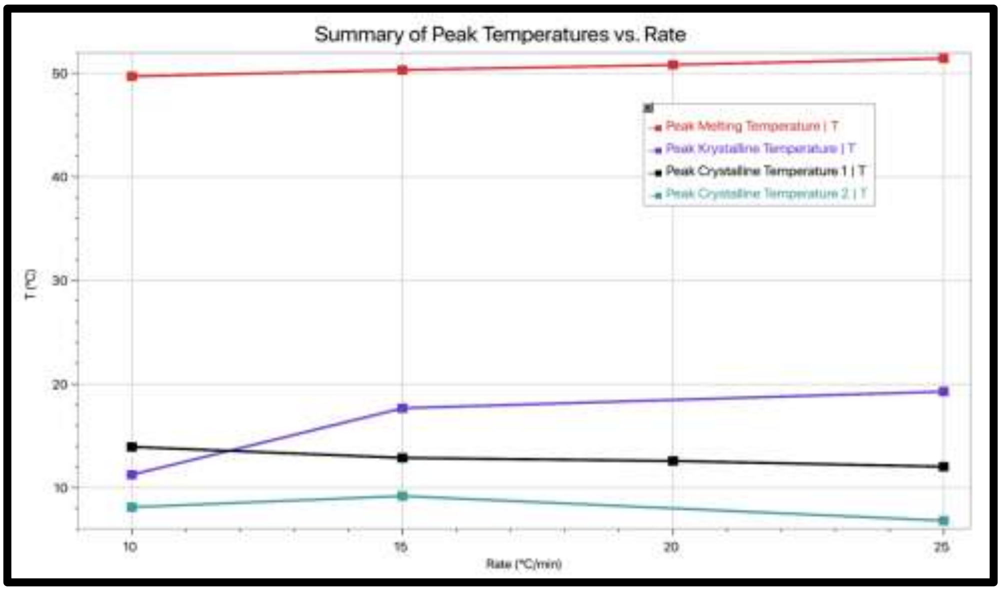

Figure 19: Effect of ramp rates on melting, Krystallization, and crystallization peak 1 and peak 2 of 5OCB.

Figure 19 shows a good comparison of how peak temperature of melting, Krystallization, and crystallization peak 1 and peak 2 are moving with ramp rates when ramp rate is increased from 10 ℃/min to 25 ℃/min. The peak melting temperatures remain relatively unchanged while the other peaks have temperature values that either had a minimum or maximum temperature value.

Explanation of Effect of Ramp Rates on Phase Transitions:

As shown in the Table 1 and Figure 19, as ramp rate increases, the peak temperature of Krystallization, melting and nematic move towards higher temperatures whereas the peak temperature of crystallization peaks # 1 and # 2 moves towards lower temperatures. Since K, M and N appear in heating and C1, C2 appear in cooling, they show movement in their peak temperature in the opposite directions.

Following equation # 4, 5, 6, and 7 from the theory section, a graph can be plotted between the natural log of the ramp rate and 1/T (peak temperature) that follows a line. From this line, a slope can be found; the value of the slope can be used to find activation energy of the transitions appearing in 5OCB in heating and cooling. Such types of graphs are plotted for Krystallization, melting, nematic, crystallization peak 1 and crystallization peak 2. These figures can be seen below with their brief descriptions.

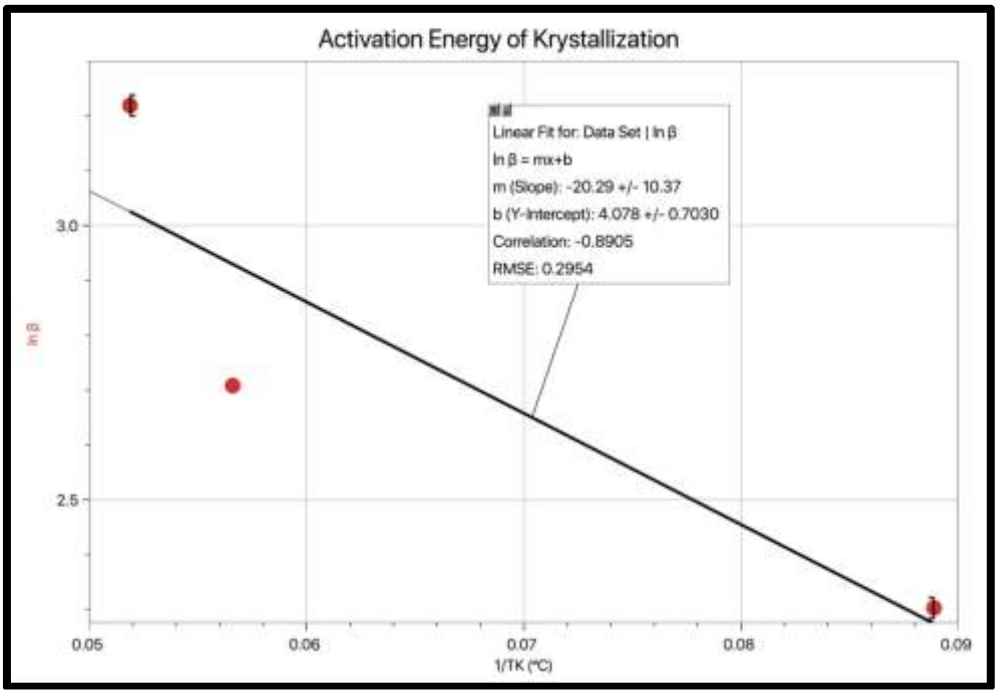

Figure 20: Activation energy graph for the Krystallization for each ramp rate.

The natural log of the ramp rate was graphed vs. the inverse of the Krystalline peak's highest temperature value in Figure 20. Graphing these two calculated values against each other allows for a linear curve to be fit to the data sets. The slope from the graph is used to calculate the activation energy, or the energy needed to begin the transition, and the y-intercept is equal to the natural log of the initial rate.

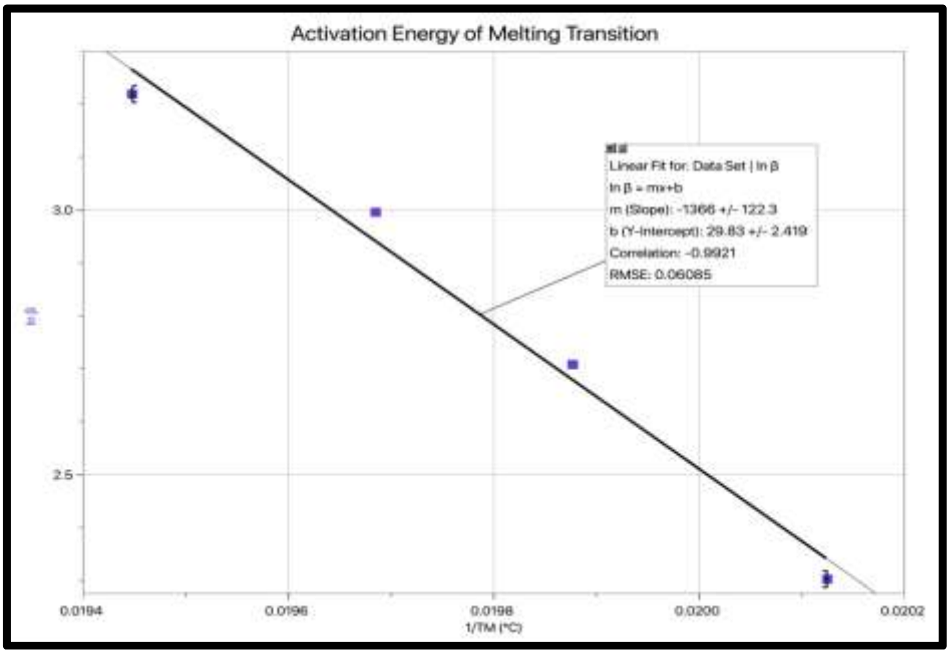

Figure 21: Melting transition's activation energy.

The natural log of the rate was again used in Figure 21, but now the inverse of the melting peak's greatest temperature values for each rate was used as the x-axis. The graph was given a linear trendline and the equation of the line is shown in the graph. The slope and y-intercept are recorded in **Table 2**.

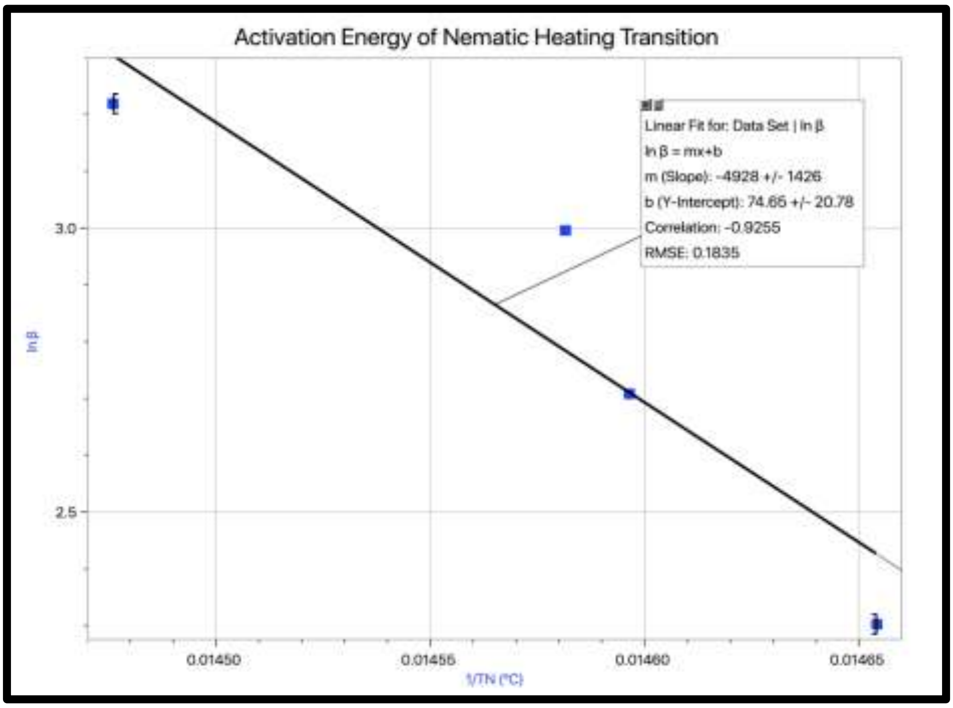

Figure 22: The activation energy of each ramp rate's nematic peak.

Figure 22 is similar to Figures 20 and 21, with the natural log of the ramp rate being plotted on the y-axis and the inverse of the nematic temperature peaks on the x-axis. So far, the slope of the activation energy graphs has been negative, however the absolute value of the slope and the intercepts are used in **Table 2**.

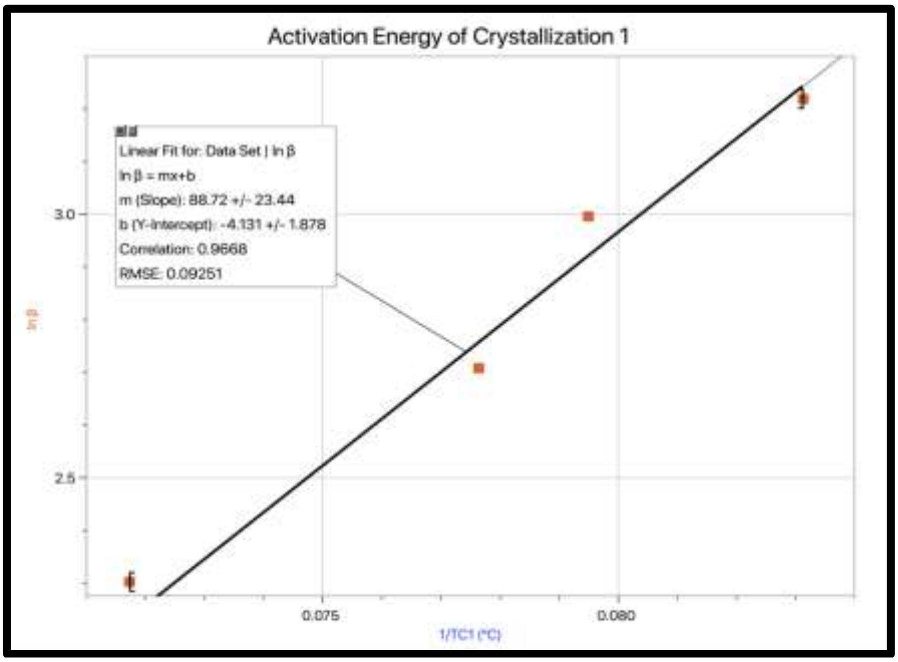

Figure 23: The activation energy plot for the crystalline peak 1 for each rate.

Figures 23 and 24 show the slope and line equation for the natural log of the rate vs. the peak temperatures of the crystalline 1 transition and the crystalline 2 transition respectively. Contrasting for the other activation energy graphs' slopes, Figures 23 and 24 have slopes that are positive. Crystalline 1 peak had data that closely followed the trendline, while crystalline 2 peak had data that stretched across the graph.

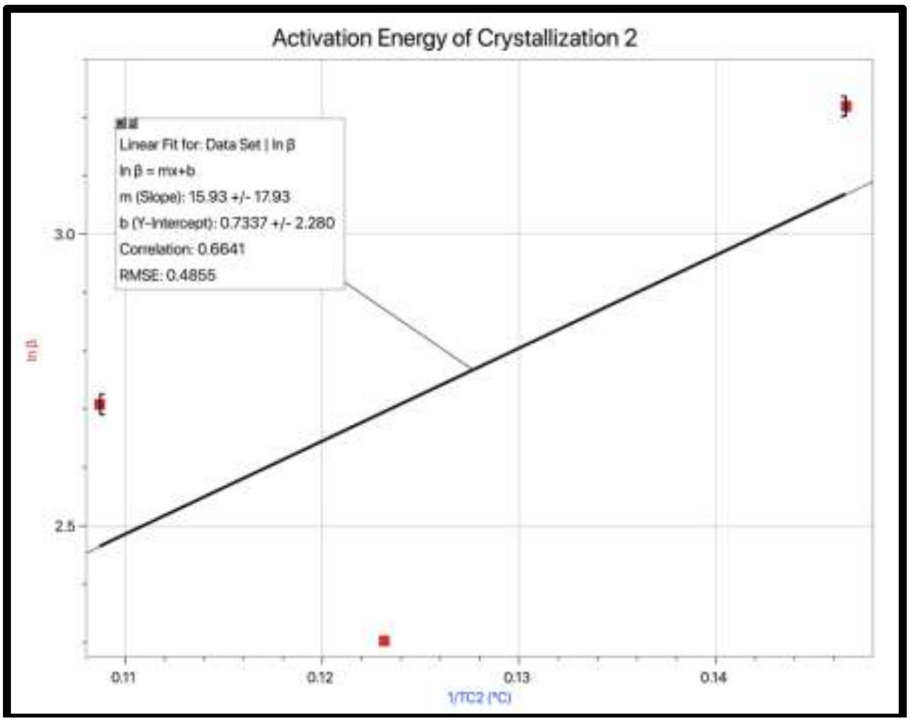

Figure 24: The crystalline peak 2's activation energy graph.

Details of analysis done of the peak temperatures of each run are shown in **Table 2**. The highest temperature for each peak transition for every run was graphed as a function of the varying rates. The inverse of the peak's temperature (1/T) was calculated and the natural log of the rate [ln(β)] was determined as well. These calculated columns were graphed together and the resulting slope, along with the gas constant (R=8.31 $\frac{J}{mol \ast K}$) was used to find the activation energy of the peak. The activation energy is shown in J/mol and kJ/mol. The y-intercept of those graphs was equal to ln (β_o) and recorded in **Table 2**. The uncertainties for the activation energies and intercepts are shown.

Transition	Slope = m	R ($\frac{J}{mol \ast K}$)	Ea (J/mol)	Ea (kJ/mol)	Uncertainty in Ea (kJ/mol)	ln (β_o)	Uncertainty in ln (β_o)
Krystallization	20.29	8.31	168.61	0.1686	+/- 0.0862	4.078	+/- 0.7030
Melting	1366	8.31	11,351.46	11.35	+/- 1.016	29.83	+/- 2.419
Nematic (Heat)	4928	8.31	40,951.68	40.95	+/- 0.3403	74.65	+/- 20.78
Crystallization 1	82.34	8.31	684.25	0.6843	+/- 0.0057	3.616	+/- 0.6493
Crystallization 2	15.93	8.31	132.38	0.1324	+/- 0.0011	0.7337	+/- 2.280

Table 3 is divided into four individual tables: **Table 3a**, **Table 3b**, **Table 3c**, and**Table 3d**. The data shown in the four tables is the width and depth of each peak transition, the peak specific heat capacity, and the wing jump value.

Table 3a displays the data for the specific peaks of the run with a rate of 10 ℃/min, Table 3b shows the data for the peaks of the run with the rate of 15 ℃/min, Table 3c records the data for the transition for the run with a rate of 20 ℃/min, and Table 3d shows the data for the transitions of the run with a rate of 25 ℃/min.

Table 3a: Data details for transitions of the run with a rate of 10 ℃/min.

10 ℃/min				
Transition Peak	ΔT (℃)	ΔCp (J/g*°C)	Cpp(J/g*°C)	WJ (J/g*°C)
Krystalline (Heat)	15.6	2.37	2.01	
Melting	12.89	-24.78	-32.3	-0.33
Crystalline 1	-22.15	7.64	11.26	0.29
Crystalline 2		5.57	8.61	

Table 3b: Data for transition peaks of run with rate of 15 ℃/min.

15 ℃/min				
Transition Peak	ΔT (℃)	ΔCp (J/g*°C)	Cpp(J/g*°C)	WJ (J/g*°C)
Krystalline (Heat)	14.7	2.88	2.4	-0.44
Melting	11.76	-29.54	-26.08	-1.52
Crystalline 1	-23.41	5.58	5.98	0.74
Crystalline 2		6.19	6.49	

Table 3c: Peak transition data for run with rate of 20 ℃/min.

20 ℃/min				
Transition Peak	ΔT (℃)	ΔCp (J/g*°C)	Cpp(J/g*°C)	WJ (J/g*°C)
Krystalline (Heat)	-	-	-	-
Melting	16.25	-20.51	-21.53	-0.54
Crystalline	-14.29	10.11	7.23	0.34

Table 3d: Data for peaks occurring during run with a rate of 25 ℃/min.

25 ℃/mn				
Transition Peak	ΔT (℃)	ΔCp (J/g*°C)	Cpp(J/g*°C)	WJ (J/g*°C)
Krystalline (Heat)	19.6	2.56	2.81	0.05
Melting	20.69	-18.3	-19.28	-0.75
Crystalline 1	-16.82	8.12	4.92	0.17
Crystalline 2		5.28	3.51	

Based on the figures shown from Figures 20-24 and data details in Tables 2-3, as ramp rate increases, peak temperature shows a shift in temperature showing the presence of activation energy. The activation energy found for each type of phase transition is shown in the Table 2, The Krystallization and crystallization have the lesser values of activation energy whereas the nematic transition has a higher value of activation energy, and the melting transition has the highest value of activation energy.

Explanation of Heat and Cool Crystallization:

When 5OCB is heated and cooled the 1st time, it shows its own typical phase transitions as melting and nematic in heating and then nematic and cool crystallization with a single peak in cooling. But material dynamics starts from the 2nd heat and cool. When 5OCB is heated, the molecular arrangement falls from 100% organized ordered state of crystalline to 0% organization of isotropic melting state showing two endothermic peaks in heating as a symbol of absorption of heat to the molecules of 5OCB. Then when 5OCB is cooled, the molecular arrangement starts going back to the ordered state by releasing thermal energy in terms of exothermic peaks and shows 5OCB goes back to a little ordered state from nematic to isotropic. It then goes to a more organized form of a crystalline state in cooling with a single peak in cool crystallization.

But when the same sample of 5OCB is heated again, it shows a heat crystallization, which is an additional transition in heat, and then when it is cooled, the cool crystallization starts showing double peaks. This is an indication that after the first cooling, the 5OCB molecules do not go back to 100% crystallization state but they go to a partial crystallization. Hence, they show a heat crystallization in the next heating and double crystallization in the next cooling. After the first cooling, since 5OCB goes to partial crystallization, we like to call that state as mixed solid state (S) as it has 5OCB in crystalline and non-crystalline state as well.
To explain 5OCB's thermal and alignment behavior, we used a model in Figure 16, that shows molecular alignment and molecular arrangement from the 2nd heating.

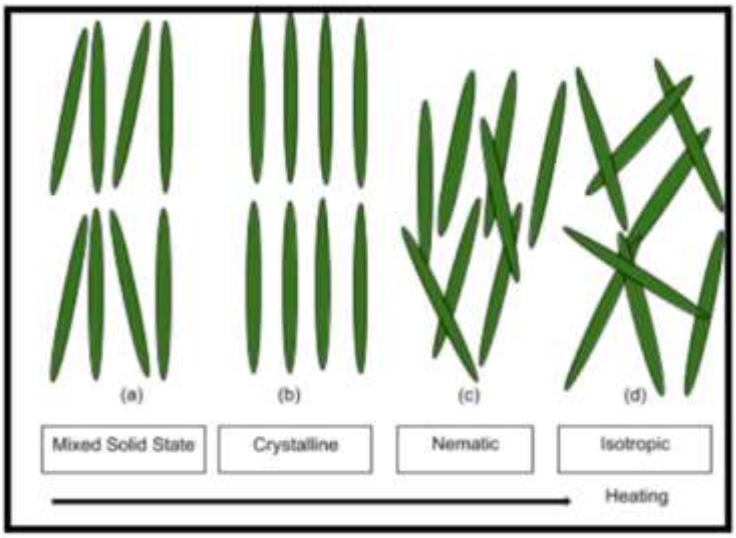

Figure 25: The stages of molecular arrangement for 5OCB molecules when being reheated through the (a) mixed solid state, (b) crystalline state, (c) nematic state, and (d) isotropic state.

The progression of the molecules' arrangement as it is being reheated is shown in Figure 25. As the liquid crystal is being reheated, it starts in (a) the mixed solid state and progresses to the (b) crystalline state as temperatures rise. After the crystalline phase, the state of the LC moves to the (c) nematic arrangement and finally (d) the isotropic phase. This drawing applies to the heating portions of runs 2,3, and 4. An extra solid state occurs before crystalline and can be referred to as the mixed solid state.

To understand why 5OCB shows a double peak in cool crystallization, we like to give our second model in Figure 26 a look, which indicates that from second heating when 5OCB is heated and cooled again, the mixed solid state of 5OCB goes to crystalline state in heating. Once 5OCB gets completely melted and then cooled, it releases energy in the form of exothermic peaks in cooling. When it reaches the crystalline state, it shows two energy levels for the molecular alignment, which appears as a double peak in cool crystallization. Molecules in the crystalline state have two levels of arrangement in Figure 26 as Crystalline 1 and Crystalline 2.

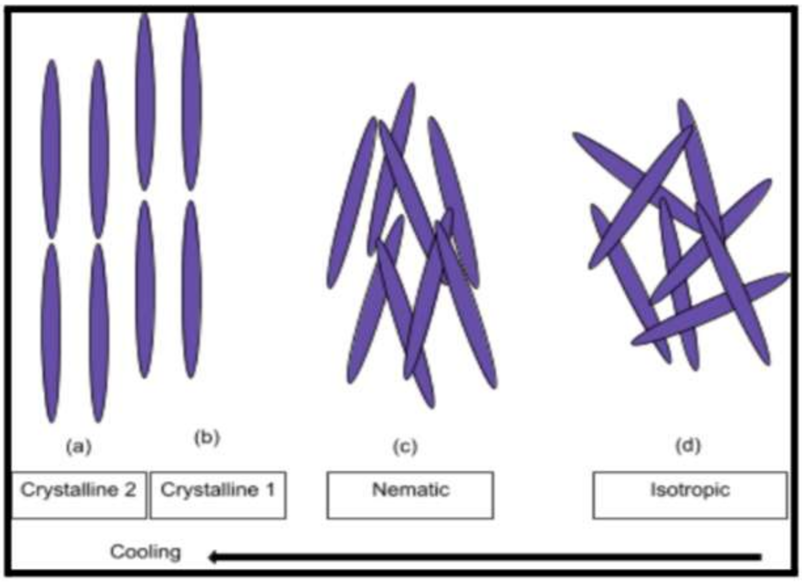

Figure 26: The stages of molecular arrangement for 5OCB molecules when being cooled from its reheated state as it goes through the (d) isotropic state, (c) nematic state, (b) crystalline 1 state, and (a) crystalline 2 state.

The organization of 5OCB molecules as they are being cooled down from reheating are illustrated in Figure 26. After being reheated, the liquid crystal was cooled down from its (d)isotropic state to (c) its nematic state, and then to crystalline arrangement. The crystalline stage however appears as a doublet on the DSC graphs and has been called (a) crystalline 1 and (b) crystalline 2.

VI. Conclusion:

In this paper, we are reporting the effect of ramp rates on phase transition of 5OCB liquid crystals as they appeared in heating and cooling. The 5OCB is used in DSC to run with four different ramp rates: 10 ℃/min, 15 ℃/min, 20 ℃/min and 25 ℃/min from -40 ℃ to 80 ℃ and then back to -40 ℃. As an effect of multiple heating and cooling, 5OCB shows an additional crystallization in heating after having been cooled to crystallization. All three transitions: melting, cool crystallization and heat crystallization show ramp effect and temperature dynamics. Transitions that occurred during heating move towards higher temperatures when ramp rates are increased. However, the transition that appears in cooling, moves towards lower temperatures as ramp rates increase. The activation energy found for each transition is reported in Table 2. The activation energy for K, C1, C2, M and N are 0.17, 0.68, 0.13, 11.35 and 40.95 kJ/mol respectively. The smallest activation energy is found for C2 and K. The highest is found for N. It means that it is easy to move from heat and cool crystallizations, whereas it is hard to move from a melting transition to a nematic phase when ramp rates are changed. That is one of the reasons why the nematic state is used in LCDs, as they are more stable when LCs are heated and cooled at different rates!

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