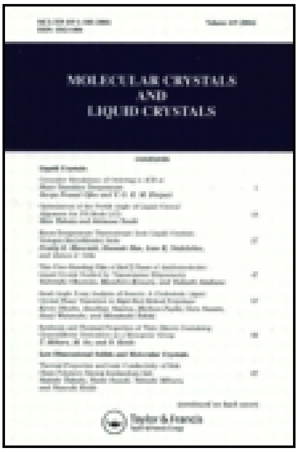
This article was downloaded by: [University of California, San Diego]
On: 07 August 2012, At: 12:21
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Effect of Enantiomeric Excess on the Smectic- - Smectic-C* Phase Transition

Yuji Sasaki [a], Kenji Aihara [a], Mariko Isobe [a] & Kenji Ema [a]
[a] Department of Physics, Tokyo Institute of Technology, Meguro, Tokyo, Japan

Version of record first published: 16 Jun 2011

To cite this article: Yuji Sasaki, Kenji Aihara, Mariko Isobe & Kenji Ema (2011): Effect of Enantiomeric Excess on the Smectic- - Smectic-C* Phase Transition, Molecular Crystals and Liquid Crystals, 546:1, 209/[1679]-214/[1684]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.571163

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., Vol. 546: pp. 209/[1679]–214/[1684], 2011
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.571163

Taylor & Francis
Taylor & Francis Group

Effect of Enantiomeric Excess on the Smectic-C_{α}^{*} – Smectic-C^{*} Phase Transition

YUJI SASAKI, KENJI AIHARA, MARIKO ISOBE, AND KENJI EMA

Department of Physics, Tokyo Institute of Technology, Meguro, Tokyo, Japan

Downloaded by [University of California, San Diego] at 12:21 07 August 2012

Calorimetric investigation on the effect of enantiomeric excess on the smectic-C_{α}^{*} (SmC_{α}^{*}) – smectic-C (SmC*) phase transition has been carried out using a high-sensitivity differential scanning calorimetry in an antiferroelectric liquid crystal compound. For highly optically pure samples, the SmC_{α}^{*} – SmC* transition is found to be first-order accompanying a thermal hysteresis, while the decrease in the optical purity weakens the first-order nature of the transition and eventually moves towards continuous behavior through the critical point. Our results indicate that the enantiomeric excess dramatically influences the nature of the SmC_{α}^{*} – SmC* transition.*

Keywords Antiferroelectric liquid crystal; critical behavior; enantiomeric excess; high-sensitivity dsc; SmC_{α}^{*}– SmC^{*} transition

1. Introduction

Tilted smectic-C^{*} (SmC^{*}) phases formed of chiral rod-like molecules provide an interesting area of researches not only from fundamental but also from technological points of view due to their polar nature. Since the discovery of the smectic-C_{A}^{*} (SmC_{A}^{*}) phase [1], several intermediate SmC^{*} subphases have been found below the non-tilted smectic-A (SmA) phase and their physical properties were characterized through extensive experimental researches [2]. All these SmC^{*} variant phases are specified by the tilt azimuthal direction (i.e., helical modulation of the azimuth) from layer to layer. When the temperature is lowered the general sequence of the phases so far reported is SmC_{α}^{*} – SmC^{*} – SmC_{FI2}^{*} – SmC_{FI1}^{*} – SmC_{A}^{*}. However, it is also known that the appearance of several subphases is influenced by the optical purity of the system, which implies that the enantiomeric excess can play an important role in the stabilization of the phases.

Among these subphases, the SmC_{α}^{*} phase is similar to the SmC^{*} phase in structure except for the short helical pitch, which was characterized by resonant X-ray diffraction (RXRD) studies [3]. Since the difference between both phases lies only

Address correspondence to Yuji Sasaki, Department of Physics, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro, Tokyo, 152-8551, Japan. Tel.: +81-(0)3-5734-2731; Fax: +81-(0)3-5734-2705; E-mail: sasaki.y.ak@m.titech.ac.jp

in the pitch of the helix, the transition can be continuous and discontinuous. In fact, Liu *et al.* [3] measured the temperature dependence of the pitch near the SmC_α^* – SmC^* phase transition using a homologue series of antiferroelectric liquid crystals and their mixtures, and revealed the existence of a critical point. From the thermal perspective, ac calorimetric measurements were also expected to yield important information on the critical behavior associated with the SmC_α^* – SmC^* phase transition. However, since the thermal relaxation process due to the helical modulation is thought to be very sluggish, the frequency-domain measurement by an ac calorimetry at a low-frequency operation (0.03125 Hz) could not detect noticeable heat capacity response even close to the critical point [3]. To overcome this problem, recently, calorimetric studies have been performed using a high-sensitivity differential scanning calorimetry (DSC) for several liquid crystalline samples exhibiting the SmC_α^* – SmC^* phase transition [4]. In that work, the obtained heat anomalies clearly exhibited different types of behavior, which agrees with the results of the earlier RXRD measurements. Nevertheless, there still remains the question of what gives rise to the difference between the types of the heat anomaly at the SmC_α^* – SmC^* transition.

In this study, high-sensitivity DSC measurements have been carried out for racemic mixtures of (R)- and (S)-MHPOBC samples to investigate the effect of the optical purity on the SmC_α^* – SmC^* phase transition.

2. Experimental Methods

The liquid crystal MHPOBC purchased from Sigma-Aldrich is used without further purification. The commercial products provide (S)-enantiomer (99% purity) and (R)-enantiomer (98% purity). The phase behavior of highly optically pure compounds is reported as SmC_α^* – SmC_{FI2}^* – SmC_{FI1}^* – SmC_{A}^* [5]. When the optical purity is slightly lowered, the SmC_{FI2}^* phase disappears and the SmC^* phase appears between SmC_α^* and SmC_{FI2}^*. Moreover, further racemization causes the SmC_{FI2}^* phase to disappear. In this paper, hereafter, we use the weight fraction of the commercial (S)-enantiomer, x, to describe mixtures, because there remains an ambiguity concerning the true enantiomeric excess due to impurities in the commercial sample.

High sensitivity differential scanning calorimetry (DSC) has been performed to measure the phase transition temperatures of the sample. To detect the difference in heat flow between the sample and reference, the thermo-electric modules (Ferrotec Co. 9502/023/012 M) have been used. The temperature scan rate for a standard operation is 0.1 K/min and sometimes a slower scan rate of 0.05 K/min is also tried to check the influence on the shape of the anomaly. For all measurements both scan rates give essentially the same results.

3. Results

Figure 1 shows the temperature variation of the excess heat capacity near the SmA and SmC^* subphases for the $x = 1.00$ sample (i.e., the commercial (S)-enantiomer sample with 99% purity) on heating and cooling, with the scan rate of ± 0.05 K/min. Five peaks are seen on heating, while four peaks are observed on cooling. This observation is in accordance with the result for a mixture obtained by Gorecka *et al.* [5]. The heat anomaly associated with the SmA – SmC_α^* phase transition shows a

Downloaded by [University of California, San Diego] at 12:21 07 August 2012

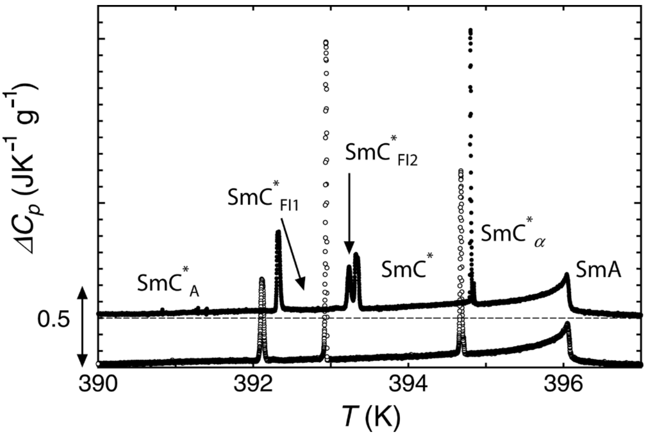


Figure 1. Temperature variation of the excess heat capacity for the $x = 1.00$ sample near the SmA and SmC^* subphases obtained by DSC. Closed circles (upper Figure) and open circles (lower Figure) show the data obtained on heating and cooling, respectively. The dashed line shows the baseline for the background heat capacity on heating. The temperature scan rate is ± 0.05 K/min.

Downloaded by [University of California, San Diego] at 12:21 07 August 2012

substantial C_p wing due to pretransitional fluctuation and no thermal hysteresis is observed, which is consistent with the earlier report of ac calorimetric measurement [6]. On the other hand, the SmC^*_α – SmC^* transition shows a delta-function like singularity as a result of a discontinuity of the free energy with a clear hysteresis of 0.2 K indicating that the transition is first order.

Figures 2 and 3 present the temperature dependence of the excess heat capacity for samples $x = 0.97$ and $x = 0.94$. Peaks corresponding to the SmA – SmC^*_α, SmC^*_α – SmC^*, and SmC^* – SmC^*_A phase transitions are clearly seen. The observed heat anomalies at the SmC^*_α – SmC^* and SmC^* – SmC^*_A transitions exhibit thermal hysteresis of 0.06 K and 0.03 K for $x = 0.97$ and 0.94, respectively, implying the first-order

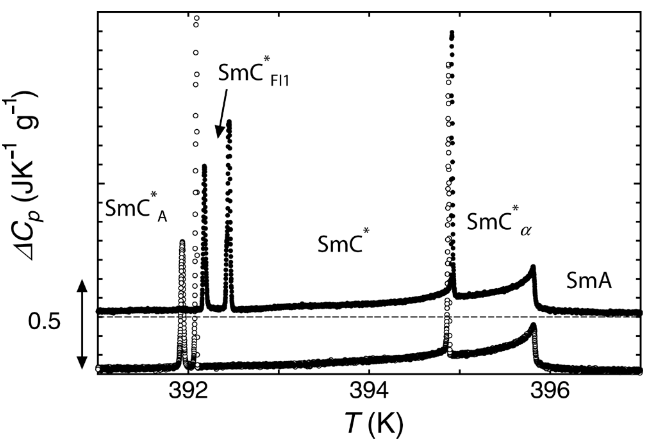


Figure 2. Temperature variation of the excess heat capacity for $x = 0.97$. For further details see caption to Figure 1.

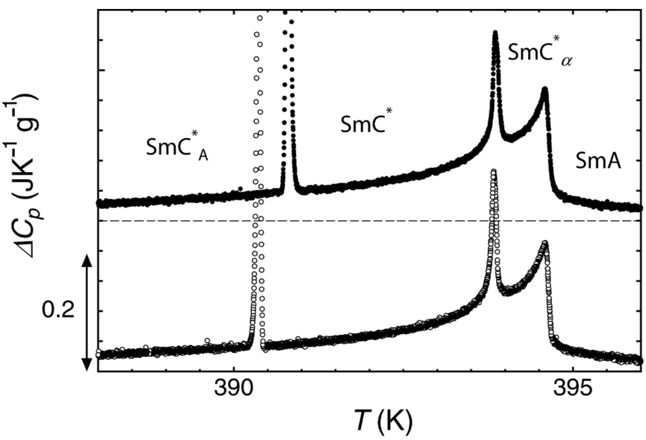


Figure 3. Temperature variation of the excess heat capacity of the $x = 0.94$. For further details see caption to Figure 1.

nature of the transitions. When compared with the results obtained for the $x = 1.00$ sample, the thermal hysteresis at the SmC^*_α – SmC^* phase transitions clearly diminishes as the increase in the racemization. Moreover, the heat anomaly at $x = 0.94$ exhibits a divergent behavior with a pretransitional wing of the heat capacity.

Figures 4 and 5 present the data obtained for $x = 0.90$ and 0.87 compounds, respectively. As observed in 0.97 mixture, three heat anomalies corresponding to the SmA – SmC^*_α, SmC^*_α – SmC^*, and SmC^* – SmC^*_{A} phase transitions are clearly seen. In addition to the SmA – SmC^*_α phase transitions, no thermal hysteresis is observed at the SmC^*_α – SmC^* phase transition. The heat anomaly for $x = 0.90$ is almost divergent but slightly rounded in the vicinity of the transition temperature. On the other hand, heat capacity for $x = 0.87$ exhibits a more rounded peak than that of $x = 0.90$.

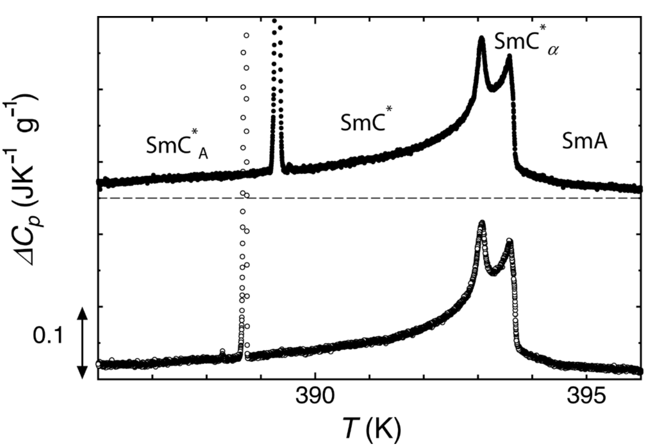


Figure 4. Temperature variation of the excess heat capacity of the $x = 0.90$. For further details see caption to Figure 1.

Downloaded by [University of California, San Diego] at 12:21 07 August 2012

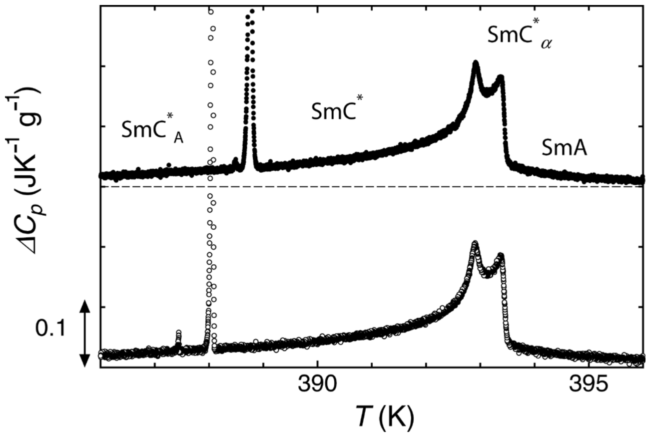


Figure 5. Temperature variation of the excess heat capacity of the $x = 0.87$. For further details see caption to Figure 1.

4. Discussion

As shown above, high-sensitivity DSC measurements reveal the solid evidence that the heat anomaly at the SmC^*_α – SmC^* transition is significantly influenced by the variation of the optical purity. Our results indicate that a slight racemization dramatically influences the nature of the critical behavior near the SmC^*_α – SmC^* transition. From earlier reports [5] it is known that the SmC^*_α, SmC^*_{FI2}, and SmC^*_{FI1} phases are very sensitive to the enantiomeric excess of the racemic mixture. Moreover, recently, Chang *et al.* [7] reported that mixing a chiral dopant stabilizes the SmC^*_α phase. Therefore, the observed behaviors demonstrate that increasing the opposite enantiomer ((R)-enantiomer) weakens the stability of the SmC^*_α phase and the first-order nature of the transition eventually leads to the supercritical evolution through the critical point. This is also strongly supported by the reduction of the thermal hysteresis. Recently, the corresponding behavior changing from a first-order to a continuous transition is also measured in pure enantiomers of the different compounds as shown in Figures in ref [4]. This can also be explained by taking the chiral strength of the compounds into account, which is expected to give rise to the different behavior. In this sense, measurements of (R)- and (S)-mixtures are suitable for the study of the critical behavior associated with the SmC^*_α – SmC^* transition. To obtain further information, a variety of mixtures should be measured.

Acknowledgment

This work was supported by the Global Center of Excellence Program by MEXT, Japan through the "Nanoscience and Quantum Physics" Project of the Tokyo Institute of Technology.

References

[1] Chandani, A. D. L., Gorecka, E., Ouchi, Y., Takezoe, H., & Fukuda, A. (1989). *Jpn. J. Appl. Phys.*, *28*, L1265–L1268.
[2] Takezoe, H., Gorecka, E., & Cepic, M. (2010). *Rep. Mod. Phys.*, *82*, 897.

Downloaded by [University of California, San Diego] at 12:21 07 August 2012

[3] Liu, Z. Q., Wang, S. T., McCoy, B. K., Cady, A., Pindak, R., Caliebe, W., Takekoshi, K., Ema, K., H. Nguyen, T., & Huang, C. C. (2006). *Phys. Rev. E*, *74*, 030702.
[4] Sasaki, Y., Aihara, K., Ema, K., Yao, H., & Huang, C. C. (2010). *Ferroelectrics*, *395*, 60.
[5] Gorecka, E., Pociecha, D., Cepic, M., Zeks, B., & Dabrowski, R. (2002). *Phys. Rev. E*, *65*, 061703.
[6] Ema, K., Kanai, M., Yao, H., Takanishi, Y., & Takezoe, H. (2000). *Phys. Rev. E*, *61*, 1585.
[7] Chang, H. S., Jaradat, S., Gleeson, H. F., Dierking, I., & Osipov, M. A. (2009). *Phys. Rev. E*, *79*, 061706.

Downloaded by [University of California, San Diego] at 12:21 07 August 2012