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Dissertation review

I was asked to make the review of PhD thesis written by Ms. Natalia Podoliak. This work is entitled „*Polar liquid crystals: structures, phase transitions and properties*". Before reading I have checked of "scientific parameters" of author. What can we learn from scientific data base (Scopus) about author of dissertation? She is the author of 11 scientific papers published in indexed scientific journals:

1. Kovářová, A., Světlík, S., Kozmík, V., Svoboda, J., Novotná, V., Pociecha, D., Gorecka, E., **Podoliak, N.**, Beilstein Journal of Organic Chemistry, 10, 794-807 (2014).
2. **Podoliak, N.**, Novotná, V., Kašpar, M., Hamplová, V., Glogarová, M., Pociecha, D., 41 (2), 176-183 (2014).
3. Novotná, V., Vejpravová, J., Hamplová, V., Prokleška, J., Gorecka, E., Pociecha, D., **Podoliak, N.**, Glogarová, M., RSC Advances, 3 (27), 10919-10926 (2013).
4. **Podoliak, N.**, Hamplová, V., Kašpar, M., Novotná, V., Glogarová, M., Pociecha, D., Gorecka, E., Liquid Crystals, 40 (3), 321-328 (2013).
5. Novotná, V., Hamplová, V., Kašpar, M., **Podoliak, N.**, Pociecha, D., Liquid Crystals, 40 (1), 14-21 (2013).
6. Novotná, V., Kašpar, M., Hamplová, V., **Podoliak, N.**, Glogarová, M., Pociecha, D., Liquid Crystals, 39 (4), 477-486 (2012).
7. **Podoliak, N.**, Novotná, V., Glogarová, M., Pociecha, D., Gorecka, E., Kašpar, M., Hamplová, V., Physical Review E, 84 (6), 061704 (2011).
8. Novotná, V., Hamplová, V., **Podoliak, N.**, Kapar, M., Glogarová, M., Pociecha, D., Gorecka, E., Journal of Materials Chemistry, 21 (38), 14807-14814 (2011).
9. Novotná, V., Hamplová, V., Kašpar, M., **Podoliak, N.**, Bubnov, A., Glogarová, M., Nonnenmacher, D., Giesselmann, F., Liquid Crystals, 38 (5), 649-655 (2011).
10. Kašpar, M., Novotná, V., Hamplová, V., **Podoliak, N.**, Nonnenmacher, D., Giesselmann, F., Glogarová, M., Liquid Crystals, 38 (3), 309-315 (2011).
11. **Podoliak, N.**, Novotná, V., Glogarová, M., Hamplová, V., Kašpar, M., Bubnov, A., Kapernaum, N., Giesselmann, F., Phase Transitions, 83 (10-11), 1026-1036 (2010).

Above mentioned papers have been cited 18 times (without self-citations). Author's Hirsch index is 3. Both scientific parameters are on good level in comparison with average level in Poland among PhD students finishing their dissertations. Natalia Podoliak is the first author for four publications. It conventionally means that she played the most important role in preparation of four mentioned papers.

This review is my first "external" one. At the beginning of reading I was a bit confused because in Poland reviewers check firstly the thesis of work and then they check if the thesis is proven or not. In reviewed work thesis is not presented explicitly. The

question arose: What does author want to confirm, prove or underline? After reading point *1.1 Objectives of the thesis*, I have formulated the thesis of read work for the purposes of my review: **The lactate units (one or more) used in synthesis of new liquid crystal compounds can give us very interesting materials with rich polymorphism and unique properties**. And, in my opinion, Natalia Podoliak has proven this thesis in her work.
This work consist of four main chapters. Chapter 2 presents all interesting for author liquid crystals phases. In chapter 3 there is short theory overview important for interpretation made in next chapters. Author presents in chapter 4 all experimental procedures used in her work. In chapter 5 all experimental results with interpretation are collected.
When we take into account that chapters 2, 3 and 4 are so called "literature overview" while chapter 5 is the presentation of author's own research one can conclude that 29 pages of "literature overview" in relation to 69 pages of author's own research, it is the classical ratio in PhD thesis.
Well-chosen references proves that author knows much about the current state of knowledge in the field explored by her.
Author presents investigation of more than 30 new compounds:
BFR6/6, BFR7/6, BFR8/6, BFR10/6, 7AHL, 8AHL, 9AHL, 11AHL, 8AHLL, 9AHLL, 10AHLL, 11AHLL, 12AHLL, 8AHLLL, 5BBLL, 7BBLL, 8BBLL, 9BBLL, 10BBLL, HZL12, HZLLL12, BBr6/6, BBr7/6, BBr8/6 BBr10/6, 5ZBL, 7ZBL, 8ZBL, 9ZBL, 10ZBL. All of studied compounds have been synthesized in Chemistry Department of Institute of Physics, Czech Academy of Sciences. This laboratory is well known abroad due to many new compounds containing lactic acid functional group, synthesized in this group.

This work takes up topics related to important question in chiral material chemistry physic and material engineering:
What is the role of chiral center in formation of chiral phases?
How can the properties and phase change if the number of chiral centers in molecule increases?
Dissertation, in my opinion is an experimental work. Author has used in her work many experimental techniques:

- Polarized Optical Microscopy (POM),
- Differential Scanning Calorimetry (DSC),
- Spontaneous polarization (P_S) measurements using Sawyer-Tower bridge and integration of polarization current methods,
- Tilt angle (θ) measurements,
- Frequency Domain Dielectric Spectroscopy (FDDS),
- Helical Pitch (λ) measurements,
- X-ray diffraction (XRD).

Interesting phenomena were observed in investigated compounds. Some of investigated materials are 'de Vries' type. Some of investigated liquid crystals are very close to be the orthoconic ones.
In some materials author observed 'classical' smectis phases: SmA*, SmC* and SmC_A*, while in another materials frustrated phases as TGBA and TGBC were found. In BBrn/6 homologous series re-entrant TGBA phase was found, while in nZBL series re-entrant SmA* phase appears. Some of them were observed for the first time.

It is also a very interesting idea, proposed by author, to investigate 9ZBL compound in mixtures with its nearest neighbors (8ZBL and 10ZBL) not creating re-entrant paraelectric SmA* phase. It was the way to observe increasing ability for creation of re-entrant phase. It was not make 'by chance' but it was made after observation that in some-how 10ZBL posses hidden potential to create re-entrancy...
In liquid crystal science there is many examples that there is a narrow border between materials showing, or not, interesting properties. And author is aware of this. I have read many PhD thesis where young authors write about pure experimental facts but no interpretation or model are coined. It is very good that author proposes in evaluated dissertation the model of mechanism of creation re-entrancy of SmA*, basing on her own experimental observations.
Electroclinic effect seems to be very promising one for potential applications. There is many works which study this effect. Author observes a big ecc in 9ZBL material and correctly links it with re-entrancy phenomena.

Editorial mistakes
Work is written clearly. I had no problems to understand all results and ideas presented in this dissertation. The English level is very good. I managed to find only a few typos, mistakes or inappropriate wording. Below you can find them listed:

- At the bottom of **page 56**, there is: [...] *TGBC phase is changes into* [...]. There should be: [...] *TGBC phase changes into* [...].
- At the bottom of **page 19**, there is [...] *it is about 0.8 K* [...]. There should be: [...] *it is about 0.8 deg* [...]. The same is at the top of page 27, there is [...] *accuracy of 0.1 K* [...]. There should be: [...] *accuracy of 0.1 deg* [...].
- In the middle of **page 30** there is: [...] *golden electrodes* [...]. There should be [...] *gold electrodes* [...]. I do not know why but when I wrote my own paper, the native English reviewer suggested me to change "golden" into "gold".
- Sometimes author write the abbreviation: SmC^*_A (e.g. **page 47**), sometimes SmC_A^* (e.g. **page 46**).
- In figure 48 in such presentation it is difficult to see anything related to dielectric response in TGBC and TGBA phases.
- I think it would be better if all molecular structures presented in this work were prepared in one style. For example the style of molecular structures presented in figures 17, 31, 36, 46 and 60 differ from the style of structures shown in figures 22, 52 and 72.
- There is no scale for relaxation frequency in inset of figure 50 on **page 62**.
- On **page 26**, author uses there the term 'Polariz**ing** Optical Microscopy'. In my opinion is it better to use 'Polariz**ed** Optical Microscopy' instead.

Questions and suggestions
After this dissertation reading I have to ask a few question or comment some part of this work.

Equations (34) and (35) on **page 30** are of course true. Every impedance analyzer can measure impedance in two equivalent circuit (parallel or serial) and can measure different parameters (C, R, G, L, etc.). Author should clarify that resistance R and capacitance C are measured in parallel equivalent circuit. Could author clarify which kind of parameters is used in equations (34) and (35)?

To calculate real and imaginary parts of electric permittivity we need to know (according equations (34) and (35) on **page 30**) the cell thickness d and active electrode area S. How to measure them? In my laboratory we just measure (not calculate) capacity of empty cell C_0 (before cell filling). Then real ε' and imaginary ε'' parts of electric permittivity are calculated as follows: $\varepsilon' = \frac{C}{C_0}$, $\varepsilon'' = \frac{1}{2\pi f C_0 R}$. And we have no problem with measuring of dimensions of measuring cell. Next problem is that sometimes thickness d through the sample is not homogenous... Please comment my doubts.

Page 37 figure 20. Why the layer thickness versus temperature plots p(T) has steps. Such shape of this plot suggests a discrete character of this function. Is it true?

Page 39. In nAHL series compounds with n=7,8,9,11 were investigated. Why compound with n=10 was omitted?

Page 39. All compounds nAHL, nAHLL and nAHLLL contain photo-sensitive azo group. Did author take into account the fact that this material is photosensitive and behavior can depend on light illumination? Did author notice any change in properties when material is illuminated or not?

Page 48. Author, basing on figure 34 has written: relaxation frequency of high frequency mode (anti-phase motion) is almost temperature independent. In my opinion it is difficult to say anything on behavior of P_H mode when the temperature range (where mode is observed) was just 5 deg. The second problem is that this mode as well as P_L one are quite covered by parasitic effects (low frequency losses caused by ions and high frequency losses caused by ITO low conductivity. To say anything certainly figure 34 should show results with removed both low and high frequency parasitic effects. It is well known that relaxation frequency of P_H mode changes a lot with temperature – even 4-5 orders but the temperature range of such observation is more that 100 deg.

Page 49 figure 35. Author wrote that in this figure: For 11AHLL no anomaly is observed at SmC* - SmC_A* transition. Plot for 11AHLL starts at temperature 76°C and according diagram shown in figure 32 the phase transition SmC* - SmC_A* for 11AHLL appears at 74°C so simply speaking we cannot see any anomaly for 11AHLL in figure 35.

Pages 48 and 50. There are two different interpretations of modes observed in nAHLL series. On **page 48** there is written: [...] *the lower frequency mode being associated with the in-phase rotation of the c-director in adjacent layers, and the higher frequency mode with the anti-phase motion* [...]. On **page 50** there is written: [...] *We suggest that the lower frequency mode is the anti-phase collective mode and the higher frequency mode corresponds to the molecular rotation around the short axes* [...]. Which interpretation is valid in this case?

Page 62. Author shows dielectric response at TGBA-SmC_A* phase transition. What kind of relaxations give the dielectric response shown in figure 50?

Page 66. Author shows that in hexatic phase spontaneous polarization is difficult to measure due to the fact that hexatic phase motions are slowed down. My question is: how slow AC electric field, in author opinion, can be used for spontaneous polarization (P_S) measurements?

Page 76. In figure 68 author shows X-ray intensity versus azimuthal angle. What does this azimuthal angle mean?

Page 84. In figure 79 only right full arrows indicate SmA* - SmC* phase transition, while left full arrows indicate crystallization temperature from SmC* -phase for 10ZBL and crystallization temperature from SmA_{RE}* for 9ZBL. Above mentioned temperatures do not coincide with values shown in table 6 (third column in this table).

Conclusion

Summarizing I would like to underline, that all my mentioned above critical comments and doubts do not change my positive evaluation of this dissertation. Such is the reviewer task that must be in the opposition to the evaluated work and try to find weak sides of dissertation.

In my opinion according to this work Ms. Natalia Podoliak is ready for creative scientific work. She is ready:

- to ask herself questions,
- to define scientific problems,
- to use literature and existing knowledge,
- to organize experimental work,
- to cooperate with other scientists,
- to analyze results and draw conclusion,

and finally

- to forward clearly her ideas to other scientists.

The results of this work develop knowledge how create materials on demand with special set of parameters.

Recommendation

I would like to recommend accepting this work as a doctoral thesis and allowing it for the next stages of defending procedure.