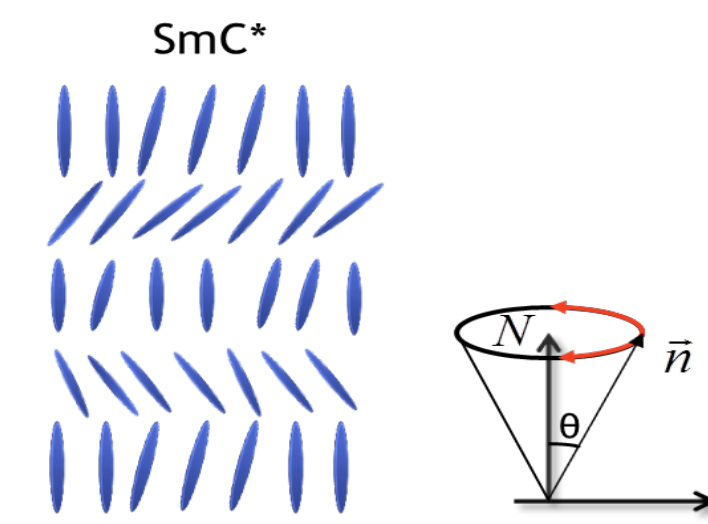


INVESTIGATION OF THE RELATIONSHIP BETWEEN THE STRUCTURE AND THE THERMAL STABILITY OF THE SMC PHASE FOR TWO SERIES OF CALAMITIC LIQUID CRYSTALS



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INTRODUCTION

The design of new ferroelectric mesogens for second harmonic generation is somewhat the holy grail of our research in the field of liquid crystals. The use of computations that predict theoretical models coupled with experiments enable us to determine relationships between molecular structures and the properties of materials. Employing this paradigm facilitates the proposal of new liquid crystalline candidates with improve properties for non-linear optic applications. In order to design new ferroelectric liquid crystals it is imperative to understand the factors that stabilize the SmC phase and therefore also stabilized a chiral SmC (SmC*) phase.

This poster focuses on a systematic study of the relationships between certain molecular parameters and the thermal stabilization of the SmC phase. The first series of homologs were synthesized and characterized by a former group member, M.-A. Beaudoin M.Sc. These were achiral bis(esters).¹ The goal of my project is to substitute an ester with a sulfinate ester in order to compare the liquid crystalline polymorphism of these two series of mesogens. Both series were studied using the intermediate of binary phase diagrams, thereby allowing us to probe the effect of the orientation of an internal molecular dipole over the thermal stability of the SmC phase. Aliphatic side chains were also varied to probe the effect of their length on the thermal stability and polymorphism of these smectogens.

Strong relationships have been established for these two molecular parameters. Interestingly we were able to demonstrate important similarities between the two series.

1) R. Vadnais, M.-A. Beaudoin, A. Beaudoin, B. Heinrich, A. Soldera, *Liquid Crystals*, 2008, 35, 357-364

PREVIOUS WORK : ACHIRAL BIS(ESTER) SMECTOGENS

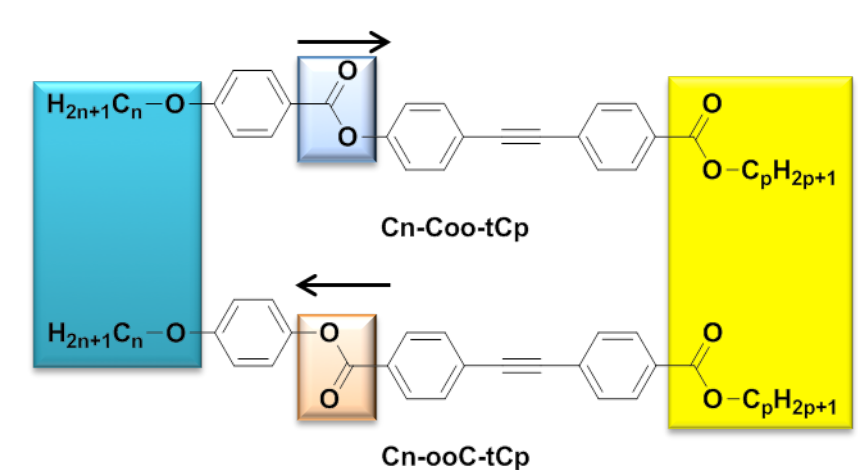
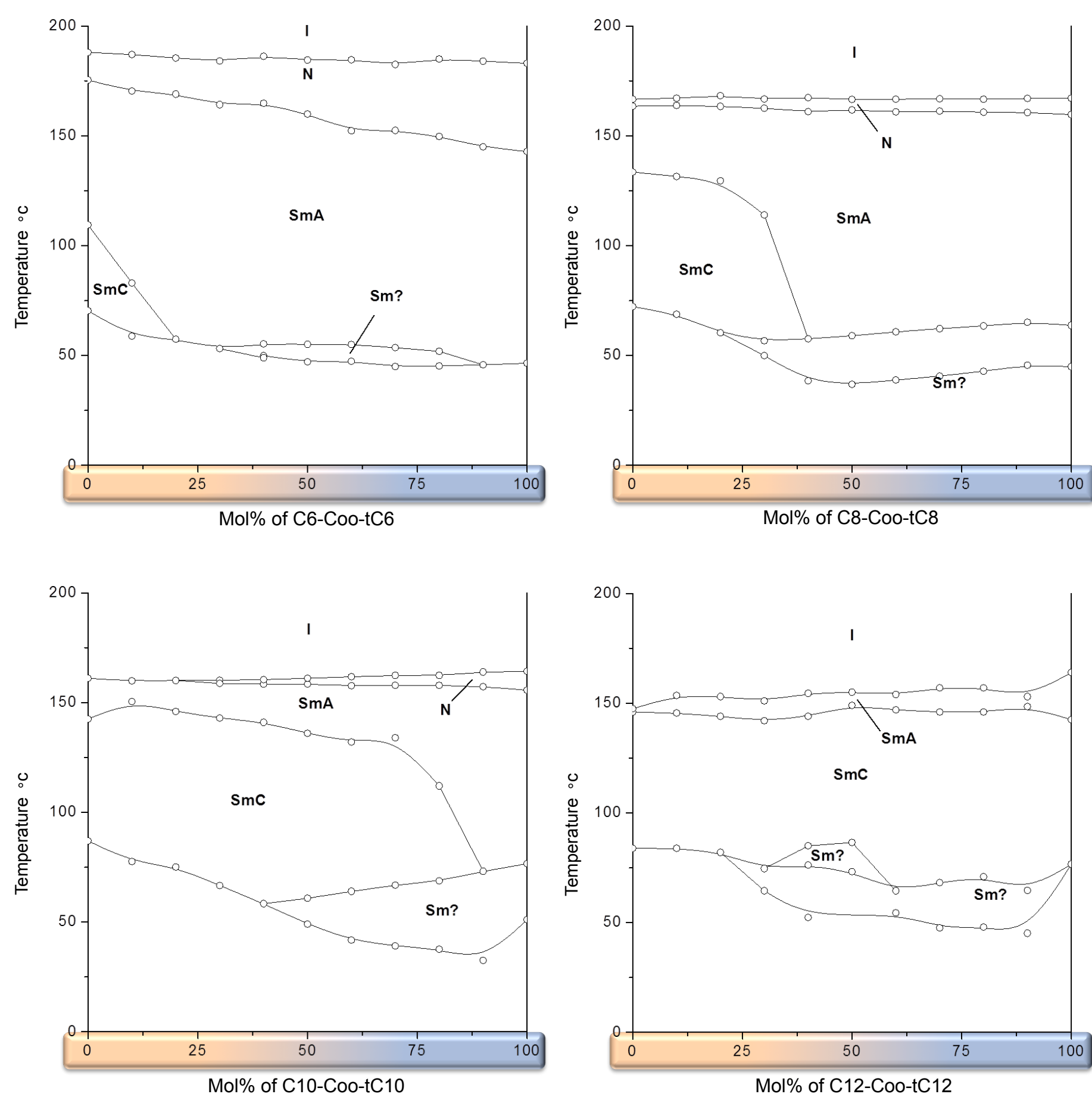


Table 1 : Side chains length and position for the bis(ester) series

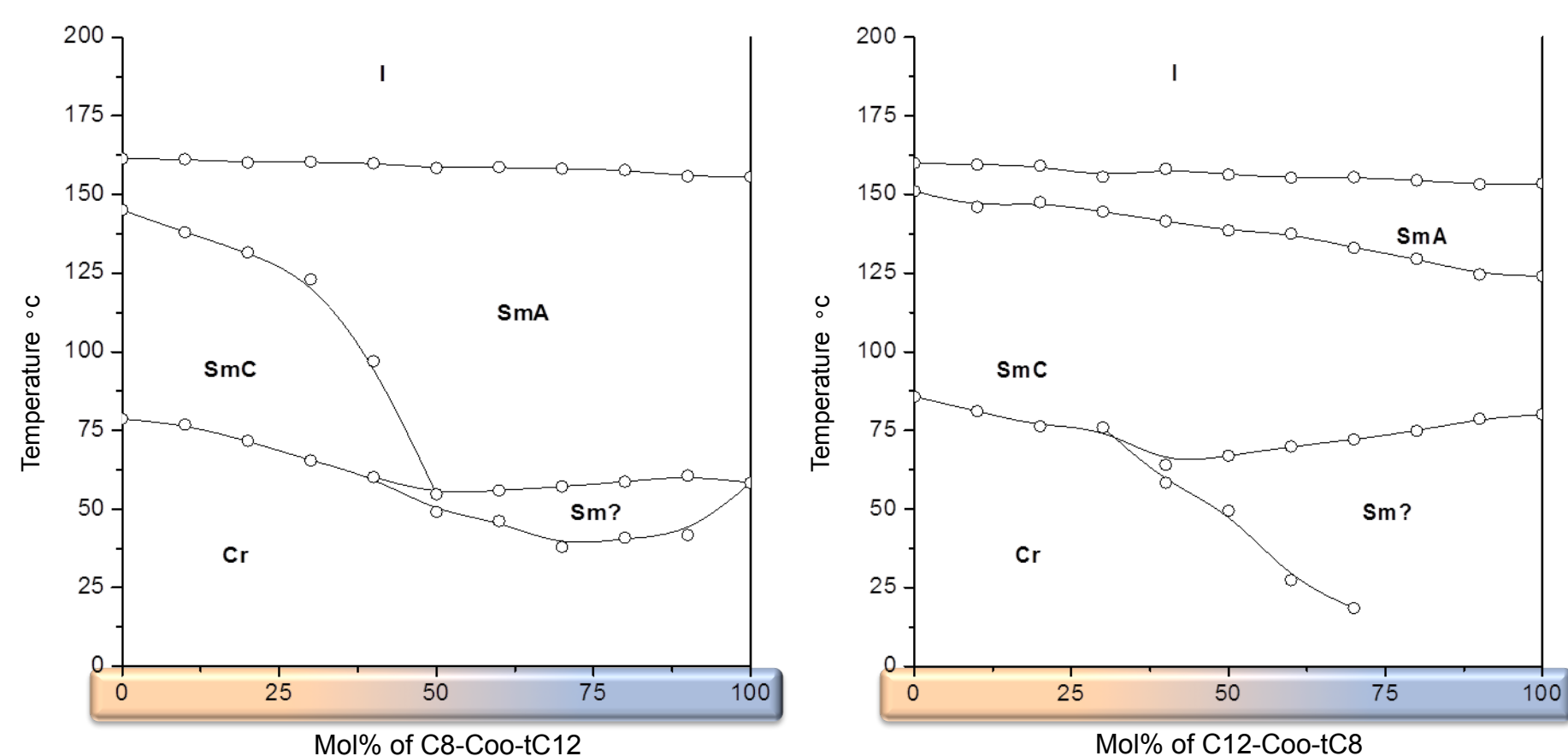
n	p
6	6
8	8 and 12
10	10
12	8 and 12

Series with symmetric aliphatic side chains



The SmC phase first arises from the homologs with two anti-parallel esters (ooC). As the aliphatic side chains are lengthened, the thermal stability of the SmC phase increases and the potential for the homologs with the parallel esters (Coo) to exhibit the SmC phase seems to increase as well. On the other hand, there is a decrease in the thermal stability of the liquid crystalline phases.

Series with asymmetric aliphatic side chains



Focusing on the side chains at the ether position, analogies can be made from these two phase diagrams if they are compared to those of mesogens bearing symmetric side chains with 8 and 12 carbons. The side chain at the ether position has a predominant effect over the thermal stability of the SmC phase as well as the liquid crystalline polymorphism of the binary mixtures.

PRESENT WORK : RACEMIC SULFINATE ESTER SMECTOGENS

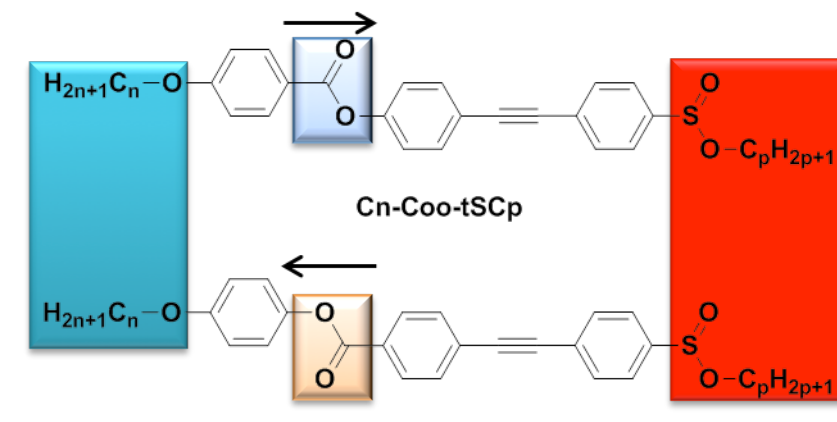
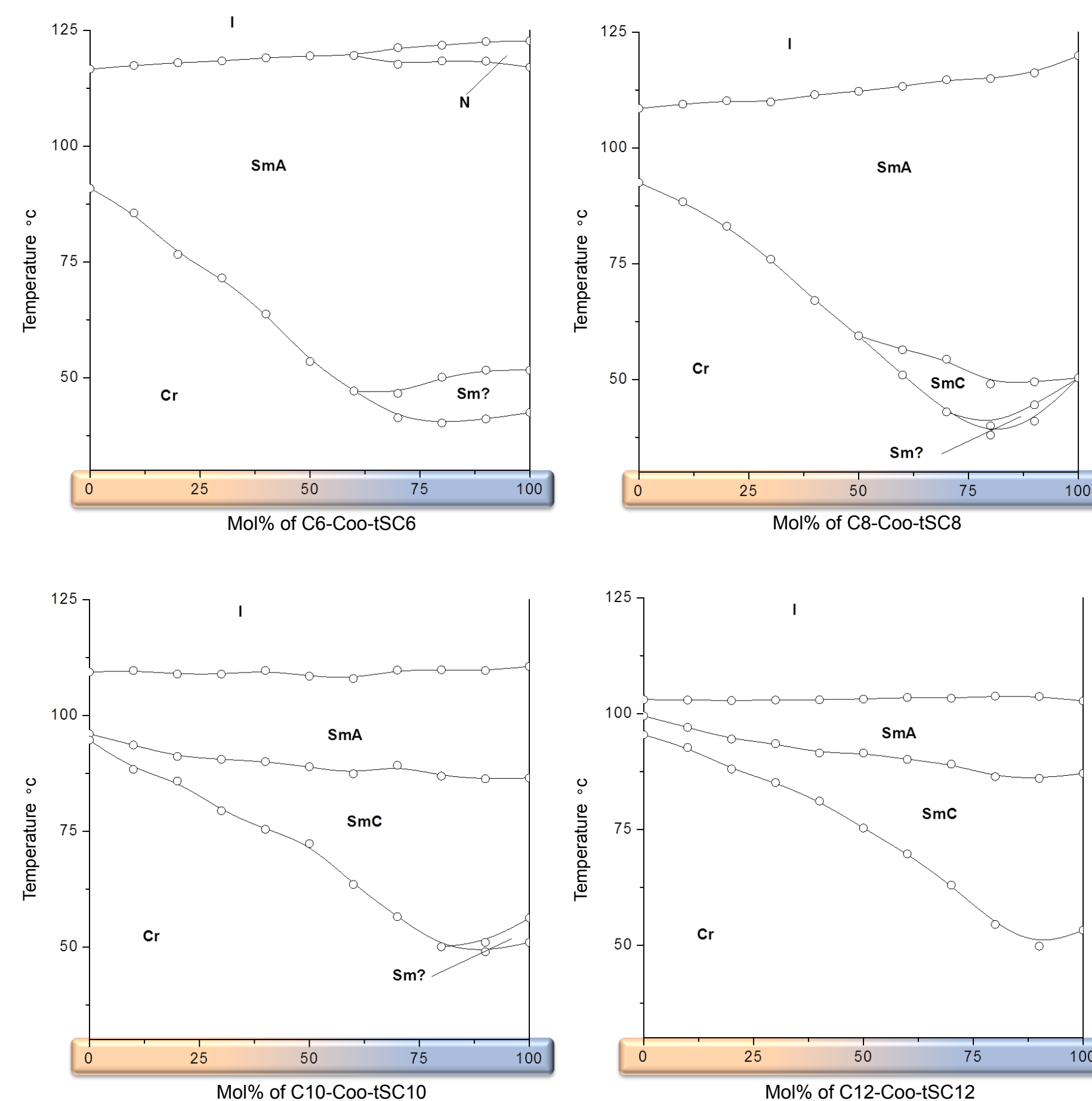


Table 2 : Side chains length and position for the sulfinate ester series

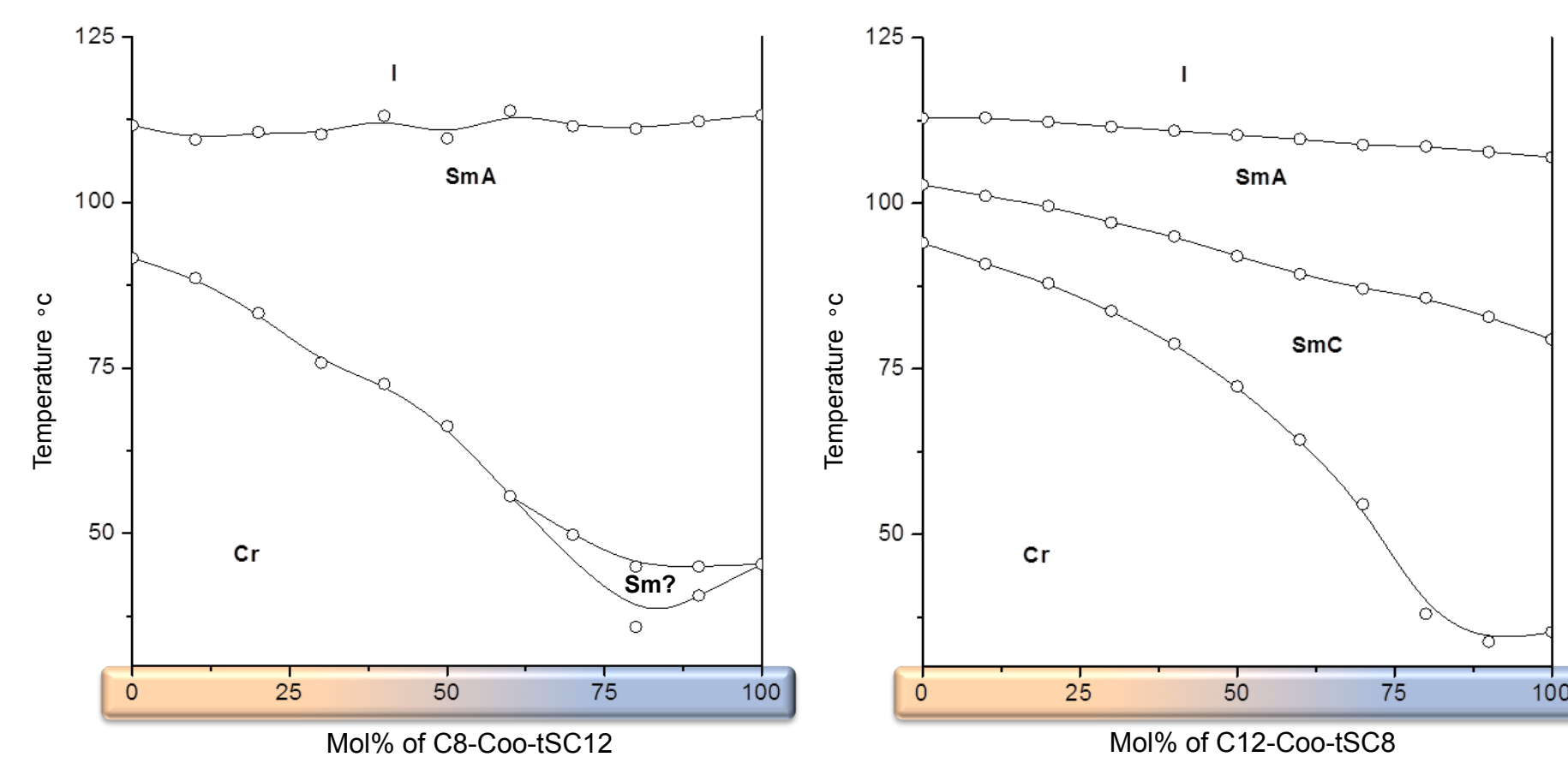
n	p
6	6
8	8 and 12
10	10
12	8 and 12

Series with symmetric aliphatic side chains



The SmC phase first emerges from the mixture of C8-Coo-tSC8 and C8-ooC-tSC8. Then as the length of the side chains increases, the thermal stability of the SmC phase increases for the 10 and 12 carbon homologs. In this series for both ester orientations, the potential to exhibit a SmC phase exists. The homologs with the antiparallel ester (ooC) crystallizes more readily. Finally, as the aliphatic side chains are lengthened, the liquid crystalline phase thermal stability decreases.

Series with asymmetric aliphatic side chains



From the phase diagrams, we can observe that the side chain at the ether position influences strongly the liquid crystalline polymorphism and the thermal stability of the SmC phase.

COMPARISON BETWEEN THE TWO SERIES

For the bis(ester) series, the orientation of the central ester influences strongly whether a stable SmC phase is exhibited. It has been shown that the SmC phase is stabilized for the homologs with the antiparallel ester (ooC) orientation. For the series containing a sulfinate ester the orientation of the central ester does not seem to be such a determining factor. For this latter series, both homologs have the potential to exhibit a stable SmC phase but crystallization occurs at a higher temperature for the homologs with the antiparallel ester (ooC) orientation.

Now looking at the first four phase diagrams of both series, the relationship between the liquid crystalline polymorphism and the aliphatic side chains length becomes evident. For both series, as the length of the side chains increases, the relative thermal stability of the SmC phase increases. On the other hand, increasing the chain length diminished the thermal range of liquid crystalline phases. These two relationships are shown in the Table 3.

For both series, there is a predominant effect over the liquid crystalline polymorphism with respect to the side chains at the ether position.

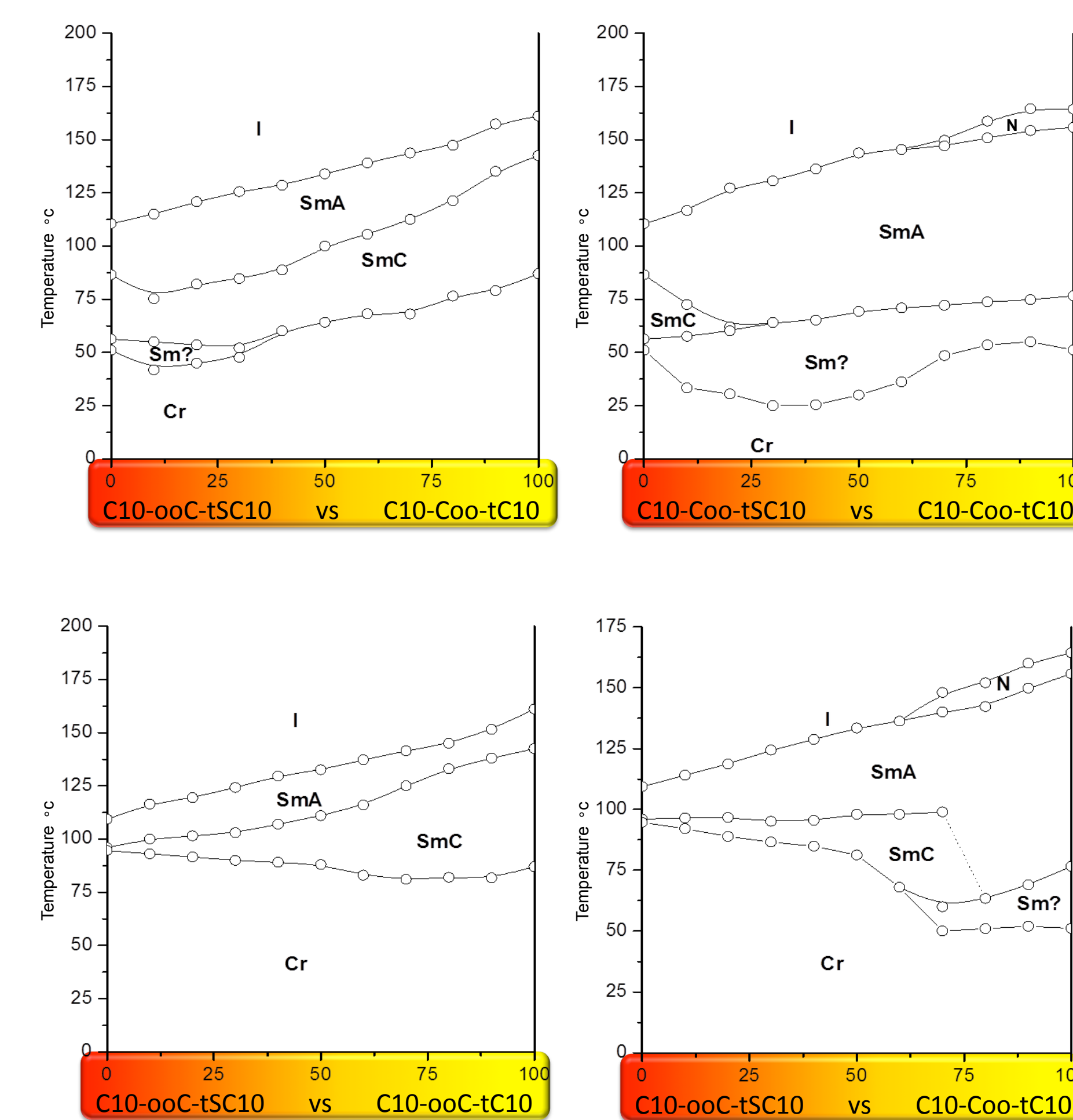
For a better understanding of the effect of the ester orientation and the influence of the nature of the peripheral moiety of these two series of homologs, binary mixtures have been made between homologs of the bis(ester) series and the sulfinate ester series

Table 3 : Total liquid crystalline area of symmetric side chains binary phase diagram of the two series of homologs and percentage of the SmC phase relative to the total liquid crystalline area

Values of n and p [# of carbons]	Total Liquid Crystalline Phases Area [T*mol%]		Percentage of SmC Area [%]	
	bis(ester) series	Sulfinate Ester Series	bis(ester) Series	Sulfinate Ester Series
6	134	61	3	0
8	118	51	18	6
10	107	40	54	49
12	87	30	90	60

MIXED BINARY PHASE DIAGRAMS

10 carbons symmetric aliphatic side chains



Phase diagrams on the left contain molecules that exhibits a SmC phase. When mixed together monotonic changes in phase transition temperatures are observed. These quasi-ideal mixtures exhibit a SmC phase for any combination of these three smectogens at any molar percentage.

On the other hand, phase diagrams on the right have a completely different behaviour. The top right has a SmC phase that rapidly disappears when the molar percentage of C10-Coo-tC10 is increased. In the bottom right phase diagram, the SmC phase is stable over a wider range of temperatures. Thus, there seems to be a greater ability for the molecule C10-ooC-tSC10 to stabilize the SmC phase.

CONCLUSIONS

For the bis(ester) series, the molecules with the antiparallel ester (ooC) orientation stabilize the SmC phase more readily and this effect increases as the side chains are lengthened.

For the series with the sulfinate ester, it is difficult to observe a trend for the influence of the orientation of the central ester. When the side chains are lengthened the SmC phase becomes stable over the entire range of molar percentages, regardless of the orientation of the central ester. The monotonic transition curves between the SmA and SmC phases for these phase diagrams mean that for this series, the SmC phase is an ideal mixture at any molar percentage.

When binary mixtures are made from molecules of both series, the ambiguities about the effects of the orientation of the central ester for the series with the sulfinate ester vanish. Comparing sulfinate ester mesogens C10-Coo-tSC10 and C10-ooC-tSC10 that exhibit a SmC phase in binary phase diagrams versus C10-Coo-tC10 bis(ester) mesogens, which do not exhibit a SmC phase, it is possible to see which ester orientation in the sulfinate ester series will stabilize more the SmC phase. Starting with the C10-Coo-tSC10, the SmC phase stability decreases rapidly with increasing molar percentage of C10-Coo-tC10. The decrease in SmC phase stability is less important when compared to the homolog C10-ooC-tSC10. It can then be concluded that for the series with the sulfinate ester, the homologs with the antiparallel ester (ooC) have a greater potential to stabilize a SmC phase than the homologs with the parallel ester.

Finally, comparing both series together, we can state that there are strong similarities between the effects of the orientation of the central ester and the potential to show a stable SmC phase. For both series the antiparallel ester orientation promotes the SmC phase.

Looking to the general potential to exhibit a SmC phase independent of the central ester orientation, it seems like the series with the sulfinate ester will form a SmC phase more easily even for the parallel ester orientation.

ACKNOWLEDGEMENTS AND FUNDING