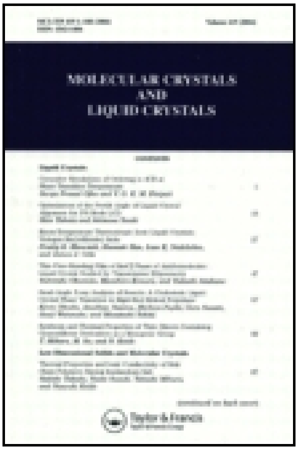

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Studies of Tails in Smectic Liquid Crystals. II. The Effect of a Butoxyethoxyethoxy Tail [1]

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Studies of Tails in Smectic Liquid Crystals. II. The Effect of a Butoxyethoxyethoxy Tail [1]

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In the previous paper [2], we studied the effect of a hybrid tail on the S_C^* phase range of a three-ring core mesogen. It is concluded that the ether tail has a small number of contorted, but energetically favored conformers. The hybrid tail has a slightly contorted minimum energy conformation but the fluorine substituents have raised the energy of the particular deep levels available to the ether tail. In brief, the ether substituents enable gauche conformers, and the fluorine substituent prevent the gauche conformers from becoming overwhelming. In an extension to further demonstrate the validity of our theory, we have examined the effect of a butoxyethoxyethoxy tail (BO tail). It is expected that this tail should display a significant effect on the smectic mesophase, especially the S_C^* phase because the rigidity of the tail increases with the extension of terminal carbon chain from two to four.

Keywords: Smectic liquid crystals; butoxyethoxyethoxy tail

RESULTS

The results are summarized in Tables II and III. It is demonstrated that the extension of an additional two carbons at the terminal ethoxy group of the ether tail increased the stability of the S_C^* phase dramatically. The stability of the BO tailed liquid crystal is in between that for the hybrid and ethoxyethoxyethoxy tails (EO tail). The following conclusions can be drawn from the experimental results.

1. Generally, the BO tailed liquid crystals have higher S_C^* stability than the corresponding EO tailed products. One exception is the liquid crystal

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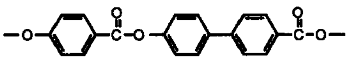
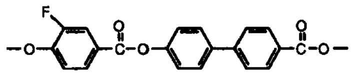
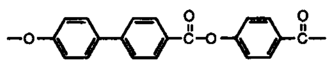
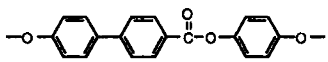
TABLE I Notations for chemical structures

STRUCTURE	TYPE	NOTATION
	CORE	PEPP
	CORE	PFEPP
	CORE	PPEP
	CORE	PPEPE
$-CH_2\overset{*}{C}H(CH_3)CH_2CH_3$	HEAD	C4*
$-CH_2\overset{*}{C}H(F)CH_3$	HEAD	C3F*
$-\overset{*}{C}H(CH_3)CH_2CH_3$	HEAD	C3*
$-CH(CH_3)CH_2CH_2CH_2CH_2CH_3$	HEAD	C7*
$-CH_2CH_2OCH_2CH_2OCH_2CH_3$	HEAD	BO
$-CH_2CH_2OCH_2CH_2OCH_2CH_2CH_2CH_3$	HEAD	EO
$-CH_2CH_2OCH_2(CF_2)_4H$	HEAD	HY

with both a fluorinated core and head with a EO tail (XIV) which has a broader S_C^* range than the BO tailed VI. The difference is attributed to the lower isotropic point resulted from the BO chain length. The S_C^* ranges for both liquid crystals are considered to be the same within the experimental error. The striking example is the comparison between VIII and XVII. The BO tailed liquid crystal, i.e. VIII, had a 2.5 times wider S_C^* range than the corresponding EO tailed XVII in the cooling cycle. It is interesting to note that XVII had no S_C^* phase at all in the heating cycle.

2. The S_C^* range remained wider for BO tailed liquid crystals than the corresponding EO tailed compounds with the four different head groups.

TABLE II Phase transition temperatures

				Cooling, °C					Heating, °C	
	Head	Core	Tail	I-S_A	I-Ch	Ch-S_A	S_A-S_C^*	S_C^*-K	K-S_C^*	S_C^*-S_A
I	C4*	PPEP	BO	129			90	−4	29	9
II	C3F*	PPEP	BO	159			82	27	63	82
III	C3*	PPEP	BO	118			77	−9	27	78
IV	C7*	PPEP	BO	94			69	−6	53	70
V	C4*	PFEPP	BO		85	82	68	5	60	70
VI	C3F*	PFEPP	BO	125			69	34	75	82
VII	C3*	PFEPP	BO	57			37	(1)		
VIII	C4*	PEPP	BO		98	90	76	−17	50	77
IX	C4*	PPEP	EO	140			85	29	32	86
X	C3F*	PPEP	EO	176			64	42(2)	60	66
XI	C3*	PPEP	EO	129			69	39	43	69
XII	C7*	PPEP	EO	108			55	38	42	57
XIII	C4*	PFEPP	EO		94	86	72	24	(3)	
XIV	C3F*	PFEPP	EO		139	134	82	35	64	82
XV	C3*	PFEPP	EO	71			65	62	(4)	
XVI	C4*	PEPP	EO		112	92	77	43	(5)	
XVII	C4*	PPEP	HY	165			141	22	64	142
XVIII	C3F*	PPEP	HY	213			119	61	87	118
XIX	C3*	PPEP	HY	159			140	24	81	141
XX	C7*	PPEP	HY	106			100	32	45	102
XXI	C4*	PFEPP	HY	141			109	15	75	110
XXII	C3F*	PFEPP	HY	197			93	30	69	94
XXIII	C3*	PFEPP	HY	136			113	11	72	114
XXIV	C4*	PEPP	HY	156			135	0	76	136
XXV	C4*	PPEPE	HY	131			126	82	93	127
XXVI	C4*	PPEPE	EO	142			130	85	96	129

(1) $S_C^* \overset{24^\circ}{\cdots} S_G \overset{1^\circ}{\cdots} K$ Other smectic states observed at 24° and 1°, with $K \cdots I$ in the heating cycle. (2) $S_C^* \overset{42^\circ}{\cdots} S? \overset{32^\circ}{\cdots} S? \overset{12^\circ}{\cdots} K$ (3) $K \overset{75^\circ}{\cdots} SA \overset{87^\circ}{\cdots} Ch \overset{96^\circ}{\cdots} I$ (4) $K \overset{83^\circ}{\cdots} I$ (5) $K \overset{84^\circ}{\cdots} SA \overset{93^\circ}{\cdots} Ch \overset{112^\circ}{\cdots} I$

TABLE III S_C^* Phase temperature ranges

			Cooling			Heating			Supercooling		
	HD	Core	BO	EO	HY	BO	EO	HY	BO	EO	HY
I, IX, XVII	C4*	PPEP	94	56	119	62	54	78	33	3	42
II, X, XVIII	C3F*	PPEP	55	22	58	19	6	31	36	26	26
III, XI, XIX	C3*	PPEP	86	30	116	51	26	60	36	4	57
IV, XII, XX	C7*	PPEP	75	17	68	17	15	57	50	4	13
V, XIII, XXI	C4*	PFEPP	63	48	94	10	0	35	55	51	60
VI, XIV, XXII	C3F*	PFEPP	29	47	63	7	18	25	42	29	39
VII, XV, XXIII	C3*	PFEPP	13	3	124	0	0	42	60	11	61
VIII, XVII, XXIV	C4*	PPEP	93	34	135	27	0	60	67	41	76
XXV, XXVI	C4*	PPEPE	44	45	–	33	33	–	11	11	–

3. The trend continued to be true with the change of three different cores.
4. The BO tailed liquid crystals had a larger supercooling effect than the EO tailed materials. This effect varied with the molecular structure in comparison to the hybrid tailed products. The supercooling effect of

hybrid tailed liquid crystal showed a very broad range. For example, XXIV had almost six times the range than did XX. On the other hand, the corresponding BO tailed mesogens fall within a 2X multiple.

5. The fluorinated head gave a broader S_A than S_C^* range which is consistent with our previous observation.
6. There is little change in the stability of the S_C^* phase for BO and EO tailed liquid crystals in extending the chain length at the chiral head. Surprisingly, the difference for EO tailed liquid crystals between IX and XII was three times.
7. Generally, the BO tail is less effective in stabilizing the S_C^* phase than the "hybrid" tailed material with only one exception (IV vs. XX).
8. The migration of the chiral center of the head toward the core had little effect on the stability of the S_C^* phase.
9. It is interesting to note that the BO and EO tailed mesogens with an ether linkage to the head possess the identical S_C^* range for the cooling and heating cycle and identical in supercooling effect (XXV and XXVI).

DISCUSSION

The effect of tail chain length on the stability of mesophases is reported by numerous investigators [3, 4, 5, 6]. The dramatic increase in S_C^* phase stability by replacing a butoxy with ethoxy group at the end of a five atom chain is very surprising. This observation can not be explained by the enhancement of the population of gauche conforms alone. It is impossible to account for the fact that the increase of only two methylene group, especially at the terminal end of a tail, will alter significantly the population of the gauche conformers. The average gauche bonds per tail is expected to be similar for both the hybrid and EO-ether tailed crystals based on the results of MNDO calculations of the model tails. The n-butyl group may prevent the gauche conformers from overwhelming the distribution of the low energy conformers. In summary, the "curled" EO tail is being released by introducing two methylene group at the end of the ether tail.

In contrast to the liquid crystal with the ester head, the ethereal headed compounds, i.e. XXV and XXVI, have identical S_C^* range in the heating and cooling cycles. Furthermore, the supercooling effects are also identical. This result suggested that the carbonyl group plays an important role in stabilizing the S_C^* phase of the mesogem. The structures of XXV and I were schematically represented in Figure 1. The swept volume of rotation expands exponently as the tail is connected through an ester linkage in

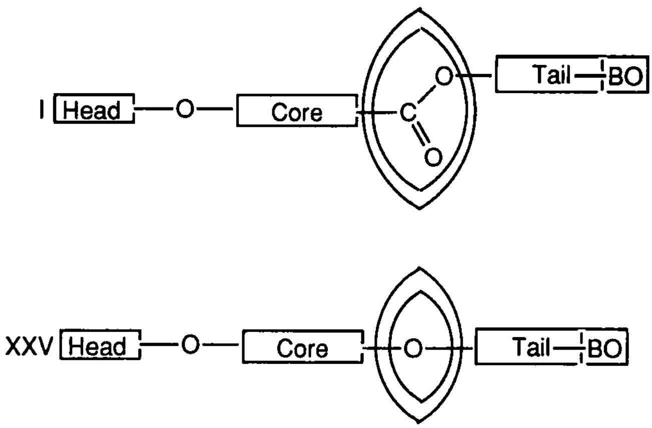


FIGURE 1

comparison to the ether group. In addition, the release of "curl", which originated from the increased rigidity of the tail with the introduction of two terminal carbons, is expected to have a profound effect on the mesophase due to its ability to enlarge the rotational manifold. These observations clearly suggested that a "balance" must be reached between head and tail within a given core in stabilizing the tilted S_C^* phase.

References

[1] The structures of the compounds are given in Table I the synthesis of representative compounds were described in reference 2 in the experimental section.

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