Smectic A Formation by Twin Dimers Assuming U-shaped Conformation

Yu Naito, Ryohei Ishige,* Manabu Itoh, Masatoshi Tokita, and Junji Watanabe
Department of Organic and Polymeric Materials, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152-8552

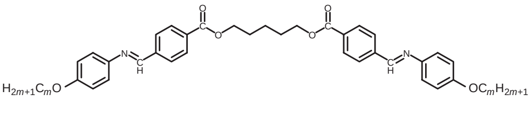
(Received April 30, 2008; CL-080446; E-mail: rishige@polymer.titech.ac.jp)

Twin dimers with 3-methylpentane spacers behave as U-shaped (folding) molecules if the carbon number of alkyl tail group is longer than 12 and form an S_A phase. This behavior is in contrast to that in dimers with linear pentane spacers which assume extended conformation and form the antiferroelectric $S_{CA}{}^{b}$. Folding of twin molecules, hence, is another way to accommodate tail groups fairly longer than the spacers, suggesting new potentiality in spontaneous molecular organization.

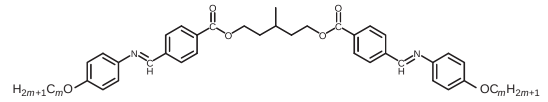
The twin dimer has three different skeletal units: an alkyl tail, an aromatic mesogen and an alkyl spacer. The mesogenic groups form layer as in the monomeric molecules, but it is important to know how the alkyl groups in the tail and spacer are accommodated into a smectic layer.[1–4] The most reliable smectic structure will be constructed by random mixing of the spacer and tail groups because of the gain of mixing entropy. However, what happens when there is a large difference in length between them? If the two aliphatic groups are still mixed randomly, the smectic structure would be significantly damaged, and then transform to the nematic one. On the other hand, if the molecules strongly tend to form the smectic phase, a segregation of the two groups occurs because of their steric incompatibility, which results in a bilayer smectic phase with two mesogen layers included in a repeat length.

The bilayer S_{CA} phase, so called $S_{CA}{}^{b}$, which is formed from dimers with odd-carbon-numbered spacers is interesting. In this $S_{CA}{}^{b}$, molecular axes lie perpendicular to the layer but the mesogenic groups are tilted to the layer normal with opposite tilt direction of mesogens between neighboring layers.[5] Each bilayer then has polar C_{2v} packing symmetry, in other words, spontaneous polarization arises parallel to the layer and along the tilt direction of mesogen, resulting in ferro- or antiferroelectricity even in an achiral system.[6,7] Such polar phases have been discovered in the following dimers, *m*OAM5AMO*m* (Scheme 1),[8] here, 5 and m are the carbon numbers of spacer and tail alkyl groups, respectively. In this homologous system, three types of fluid smectic phases are formed, the single-layer smectic phase ($S_{CA}{}^{s}$) with a random mixing of spacer and tail groups, the bilayer $S_{CA}{}^{b}$ with a microsegregation of the two groups, and the intermediate frustrated smectic phase ($S_{CA}{}^{f}$). It is found that $S_{CA}{}^{b}$ is formed from molecules with m larger than 12 and found to show antiferroelectric switching with opposite polarization between neighboring bilayers.[8]

It should be noted here that there is another type of smectic phase which can accommodate comfortably alkyl tail groups fairly longer than the spacer group. It is constructed by molecules with U-shaped conformation; twin molecules are folded so that the alkyl tails are neighbored together within a molecule. In this study, we report an example of a layer association of U-shaped molecules in the following dimers, *m*OAM5(3-Me)AMO*m* (Scheme 2), which are homologous to *m*OAM5AMO*m*, but have methyl substitution in the pentane spacer.



Scheme 1.



Scheme 2.

Figure 1 shows the phase behavior of *m*OAM5(3-Me)-AMO*m* with $m = 4$–22. The thermodynamic data are listed in Table 1. All the materials form the enantiotropic smectic phases. Two kinds of fluid smectic phase are formed depending on the carbon number of alkyl tail, m. When m is 4 and 8, $S_{CA}{}^{s}$ is formed as expected, whereas when m is longer than 12, unusual S_A is formed.

S_{CA} structure for dimers with $m = 4$ and 8 was identified from optical microscopy and X-ray methods.[8] Its decisive evidence is the microscopic observation of a strong birefringence with Schlieren textures of $s = 1$ and $1/2$ singularities in homeotropically aligned sample.[5] S_{CA} can be also identified from the X-ray pattern taken for the same sample with a beam parallel to the layer. The geometric relationship of the outer and inner reflections is characteristic; the inner layer reflections arise on a meridian, and the outer broad reflections attributable to the liquid-like association of mesogens are split into two portions lying above and below the equator.[5]

Comparison of the layer spacing with the calculated molecular length in a trans (extended) conformation (see Figure 2a) allows us to describe how the molecules are accommodated into the layer. Spacings of the first layer reflection (d_{obs}) and calculated lengths are listed in third and fourth columns of Table 1, respectively. The layer spacing for dimers with $m = 4$ and 8 corresponds roughly to half a molecular length, indicating that

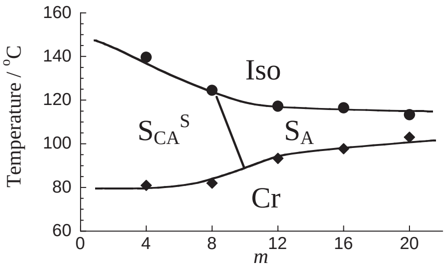


Figure 1. Phase behavior of *m*OAM5(3-Me)AMO*m* homologues.

Table 1. Transition temperatures and smectic layer spacings of *m*OAM5(3-Me)AMO*m*

	Transition temperature/°C						Layer spacing		
		ΔH/kJ mol^{-1}			ΔS/J mol^{-1} K^{-1}				
m	Cr		$S_{CA}{}^{S}$	U-S_A		I	d_{ob}/Å	$d_{cal}{}^{a}$/Å	$d_{cal}{}^{b}$/Å
4	●	81.1	●	—	139.7	●	20.4	37.0	23.4
		1.6 4.2			12.1 29.7				
8	●	81.9	●	—	124.5	●	23.9	46.3	28.8
		20.5 58.2			14.6 36.4				
12	●	93.4	—	●	117.3	●	33.1	55.1	33.9
		63.2 172.0			13.8 35.1				
16	●	97.8	—	●	116.5	●	39.0	64.2	38.8
		99.6 267.8			15.9 40.6				
20	●	102.9	—	●	113.3	●	44.7	73.3	43.8
		113.8 302.9			15.9 41.0				

[a]Based on the all-trans conformation in Figure 2a. [b]Based on the folding conformation in Figure 2b.

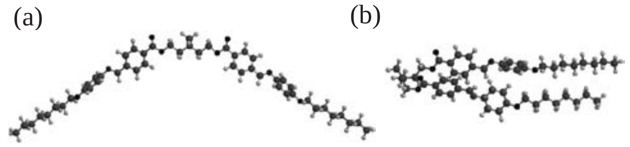


Figure 2. Molecular models adopting (a) all-trans conformation and (b) U-shaped conformation.

the smectic layer is formed by random mixing of the tail and spacer groups. The smectic phase is thus assigned to a single layer S_{CA}, so called $S_{CA}{}^{s}$.

The smectic phase in compounds with $m = 12$, 16, and 20 appears as typical batonnets upon cooling from the isotropic melt and coalesce to form well-defined fan textures. The homeotropically aligned sample shows completely dark domain which identifies the S_A phase. The oriented X-ray pattern shows the inner reflection on the meridian and outer reflections on the equator, which also supports the S_A structure. As found in Table 1, the elucidated layer spacings are significantly smaller than the molecular length, but larger than half a molecular length.

The resulting phase behavior is thus illustrated in Figure 1. By comparing with that in *m*OAM5AMO*m* homologues (Figure 2 of Ref. 8), one can recognize that the antiferroelectric bilayer $S_{CA}{}^{b}$ phase in the longer tail homologues is replaced to the S_A phase. Here, a question arises on how the twin molecules with odd-numbered spacer can form the S_A phase. Two possible models are likely. One is constructed by unusual extended conformation in which two mesogenic groups within a molecule are parallel to each other. Here, the random mixing of the tail and spacer groups is required from the observed layer spacing nearly equal to half a molecular length, but it may be impossible because the spacer group is too much shorter than the tail group to sustain the layer association of mesogens.[1] Most likely S_A model is constructed by a U-shaped folding molecules (refer to Figure 2b) as illustrated in Figure 3. The U-shaped molecules can behave similarly to the monomeric molecule and then form the S_A phase.[9] It should be noted that such a U-shaped conformation is not unusual; the conformational analysis by isomeric-state model has shown that it is possible for the dimers with an odd-numbered carbon spacer.[5] Since the molecules with a linear pentane spacer do not assume such a U-shaped conformation, the methyl substitution plays an important role to induce it. The molecular length was calculated for one possible conformation given in Figure 2b and listed in the fifth column of Table 1. It is found to correspond to the layer spacing.

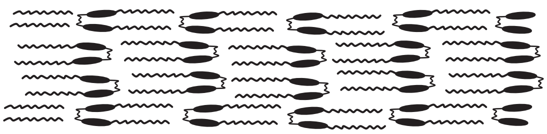


Figure 3. Schematic representation of smectic A structure which is formed by U-shaped molecules.

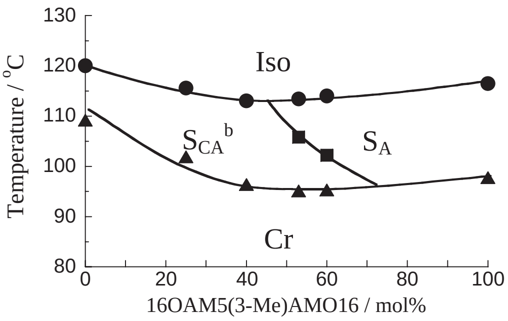


Figure 4. Phase behavior for mixtures of 16OAM5(3-Me)-AMO16 and 16OAM5AMO16.

The miscibility test was examined between the compounds in two mixture systems. Figure 4 shows the phase behavior in mixtures of 16OAM5AMO16 and 16OAM5(3-Me)AMO16 which form the antiferroelectric bilayer $S_{CA}{}^{b}$ phase and the S_A phase, respectively. Obviously, these two phases are not miscible. Mixtures with intermediate contents show the polymorphism forming S_A in the higher-temperature zone and $S_{CA}{}^{b}$ in the lower-temperature zone. A similar test was examined between S_A of 12OAM5(3-Me)AMO12 and $S_{CA}{}^{s}$ of 8OAM5-(3-Me)AMO8, showing that the S_A is the higher-temperature phase than $S_{CA}{}^{s}$. In twin dimers, thus, the phase sequence in order of increasing temperature is as following.

$$S_{CA}{}^{b} \rightarrow S_{CA}{}^{f} \rightarrow S_{CA}{}^{s} \rightarrow S_A \qquad (1)$$

Even if the constituted molecules assume a U-shaped conformation which might be entropically unfavorite, the normal conclusion is thus obtained that the S_A phase is the highest-temperature mesophase among smectic phases.

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Published on the web (Advance View) July 19, 2008; doi:10.1246/cl.2008.880