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ARTICLE

Photoresponsive helical nanofilaments of B₄ phaseCite this: DOI: 10.1039/x0xx00000x Anna Zep,^a Kaja Sitkowska,^a Damian Pocięcha,^a Ewa Gorecka^{a,*}Received 00th January 2012,
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New dimeric compounds forming Helical Nanofilament phase (B₄) are reported. It is shown that filaments can be aligned in macro-scale when grown from aligned smectic phase. Due to the photosensitivity of the mesogenic material the patterning of the sample is possible by selective UV irradiation, which reversibly melts the B₄ phase and in result locally changes alignment of nanofilaments. Also photosensitive composite materials are reported, in which nano-filaments encapsulate smectic phase. In such composites, as the UV melting of filaments occurs, the layer spacing of smectic matrix is shorten or lengthen depending whether cis or trans conformation of dimers enrich the matrix.

Introduction

The bent-core compounds form large number of mesophases, sometimes with complex hierarchical structure, that are specific for this group of materials. The smectic layers made of bent core molecules have a strong tendency for layers to have negative curvature^[1] that might lead either to torical focal conic domains arranged into strongly distorted 'plumber nightmare' network (sponge-like phase)^[2] or to the formation of helical nanofilaments, HNFs.^[3] In both cases the size of the topological objects is few hundred nanometers. The torical focal conic structure is usually referred in literature as a 'dark conglomerate' (DC) phase, while the helical filament structure is referred as B₄ phase.

The B₄ phase is one of the most unusual phases; it is chiral, strongly optically active, despite it is built of achiral molecules.^[4] In nanoscale it is made of densely packed saddle-splay deformed ribbons, each ribbon being made of few layer membrane with crystalline in-plane order. Generally, thermotropic LC materials are well miscible, the property of the mixture results from the properties of components, e.g. layer spacing in smectic phases of the mixture is an average of the values found for pure components, spontaneous polarization of the ferroelectric SmC mixture is linearly dependent on the concentration of chiral component. The B₄ phase behaves differently, having very limited solubility for other compounds.^[5] When filaments are formed they separate from the mixture. The membranes building the B₄ phase repel from their structure 'alien' molecules and when B₄ material is mixed with other mesogenic molecules forming nematic or smectic phase, the filaments become separated in space and voids between them are filled with 'alien' material.^[6] Our recent

results show that also an isotropic liquid can fill the voids, and such mixtures form physical gels with thermally reversible sol-gel phase transition.^[7] Moreover, it seems that by an appropriate choice of the solvent the twisted ribbons, characteristic for thermotropic B₄ phase, can transform into the chiral tubules.^[7] Here we describe the homologue series, D-n, of azo-dimers forming B₄ phase, and show that because of their photosensitivity they might serve as photoactive matrix to confine other materials. Moreover the sequence of phases observed for dimers – the B₄ phase is formed below SmC phase – enables obtaining good alignment of HNFs over large length scale. This gives significant progress toward application of HNF phase, as previously used aligning technics were rather elaborated and expensive.^[8]

Results and Discussion

The studied dimeric compounds containing azo units (Figure 1) exhibit strong odd-even effect regarding mesophase sequence as a function of carbon atom number, n, in the spacer. The LC properties for all studied homologues were confirmed by optical, DSC and X-ray studies (Figure 2, and Table 1 in SI). Dimers with even number of carbon atoms in the spacer form N, SmC and SmJ phases, typical for rod-like molecules.

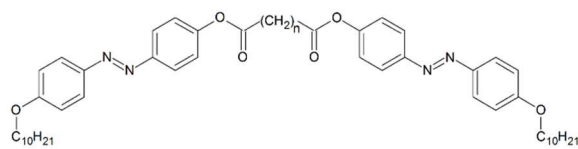
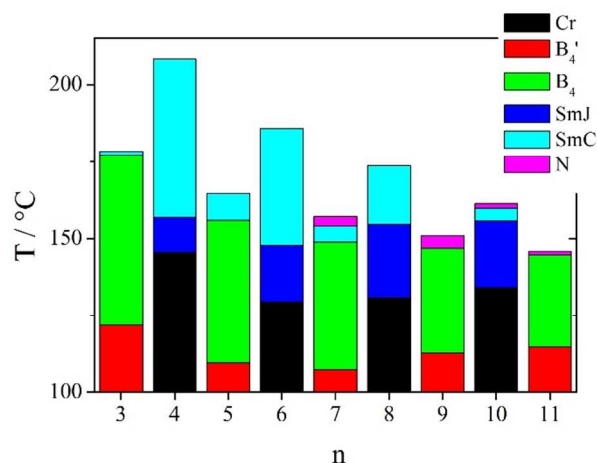


Figure 1. Molecular structure of studied dimers D-n, n = 3-11.**Figure 2.** Phase diagram for studied homologue series.

Odd spacer dimers with short alkyl chains between mesogenic units (n=3,5) exhibit Iso-SmC-B₄-B₄' phase sequence, for compounds with long alkyl spacer (n=9,11) Iso-N-B₄-B₄' sequence is observed. Intermediate homologue n=7 shows both the SmC and N phases above B₄ phase. There was no texture change at the B₄-B₄' phase transition; also the x-ray diffraction measurements revealed robust lamellar structure with nearly the same layer spacing in both phases. The observed strong broadening of xrd signals related to lamellar structure is consistent with finite thickness of the smectic layer stacks,^[9] from which the filaments of B₄ phase are formed (see SI). The relatively sharp reflections observed at high diffraction angles (see SI) confirm that the molecules have long range positional order within the layers^[10]; two B₄ phases differ slightly in crystallographic unit cell.

Interestingly, if the mixture of two odd homologues is prepared, they are completely miscible in liquid or liquid crystalline phases, while they separate in B₄ phase; in the x-ray pattern the series of reflections coming from crystallographic lattices of each homologue are detected, showing that filaments are always built from pure compounds, even in case of close chemical similarity of mixture components (see SI).

In homotropic cells the phase transition from SmC to B₄ phase is manifested by disappearance of schlieren texture and formation of non-birefringent texture with optically active domains, the size of these domains varies upon the sample cooling rate; apparently in such cells the filaments of the B₄ phase are preferably oriented perpendicular to the surfaces. In planar cells, in SmC phase the domains with opposite tilt are formed (Figure 3). Careful observation of the texture shows that domains have molecules almost parallel to rubbing direction while the smectic layer normal is tilted from the rubbing direction (by ~ 27 degree for homologue D-7). Between crossed polarizers domains can be brought into light extinction condition through the rotation of the sample by few degrees, such rotation positions director in the given domain along polarizer. The tilt in the SmC phase deduced from optical studies (~ 30 degree for D-7, few degrees below N-SmC phase transition temperature) agrees well with the value measured by x-ray method, assuming non-tilted molecules in B₄ phase. The transition to B₄ phase, in the planar texture, is accompanied by sudden decrease of birefringence, the domains persist with the

same boundaries, however they interchange brightness, those observed in SmC phase between polarizers as dark become bright and vice versa (Figure 3), the observation is in line with drastic decrease of tilt in the layers at transition from SmC to B₄ phase. The lower birefringence of the B₄ phase shows that averaging of the molecular positions takes place, that is due to formation of twisted filaments. The direction of filaments is inclined from the rubbing and defined by the layer direction in the smectic C phase. Apparently filaments of the B₄ phase can be very well aligned over macro lengthscale if grown from aligned SmC phase in the cell with strong planar anchoring. If the B₄ phase is formed from nematic phase (D-3, D-5), no preferable orientation of filaments can be achieved, randomly oriented filaments are formed.

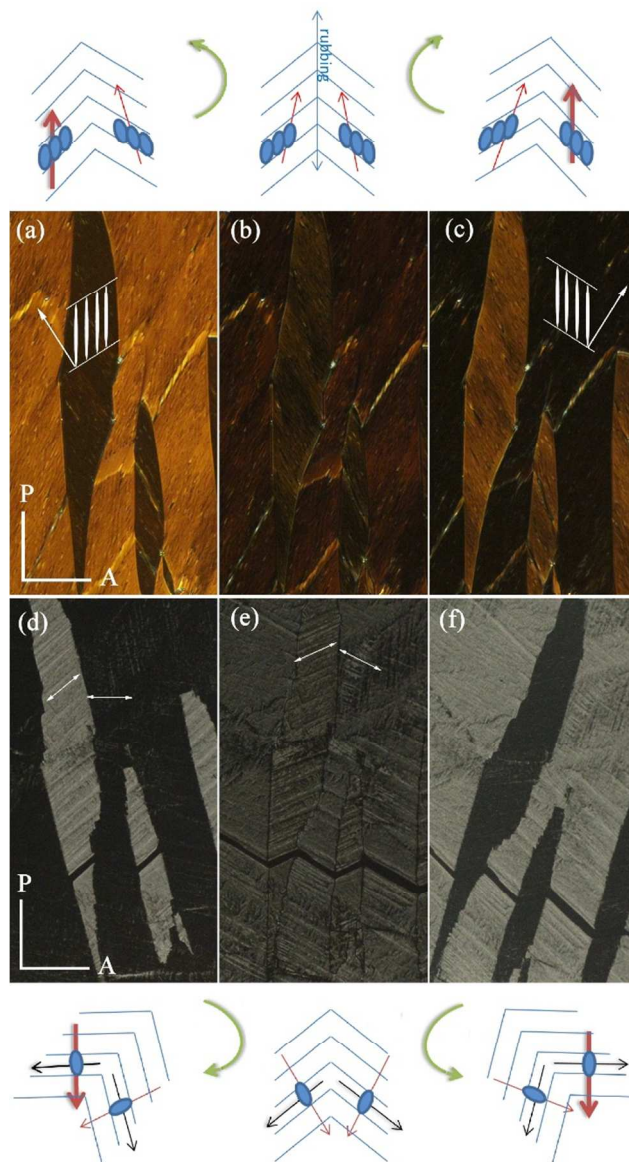


Figure 3. (a,b,c) Texture of smectic C phase for D-7 viewed between crossed polarizers, in (a) and (c) director in given domains is oriented along the polarizer, in (b) rubbing direction is along polarizer. (d,e,f) Texture of B₄ phase viewed between crossed polarizers, in (d) and (f) filament axes are oriented along the analyzer, in (d) rubbing direction is along polarizer. Arrows in (d,e,f) indicate filament orientation in domains. Above and below, schematic drawing showing

average orientation of smectic layers, molecules (represented as ellipsoid with red arrow) and filaments of B_4 phase (represented by black arrows). Thick arrows mark the domain being in extinction condition after rotating the sample vs. polarizers.

Since the studied compounds contain in molecular structure photoactive azo groups^[11], the UV irradiation (wavelength 365 nm) induces the melting of the B_4 phase structure to isotropic liquid by the isomerization of azo molecular units from trans to cis conformation. Turning off the light results in direct transition from isotropic to B_4 phase, the N and smectic phases are not observed, and B_4 phase is restored with orientation of filaments perpendicular to the glass surface even in the cells with planar anchoring. The change of filaments orientation changes locally the birefringence of the sample. Irreversible change of filament orientation under UV illumination allows for selective patterning of the sample (Figure 4), the resulting grating is stable unless the temperature is increased and B_4 phase molten.

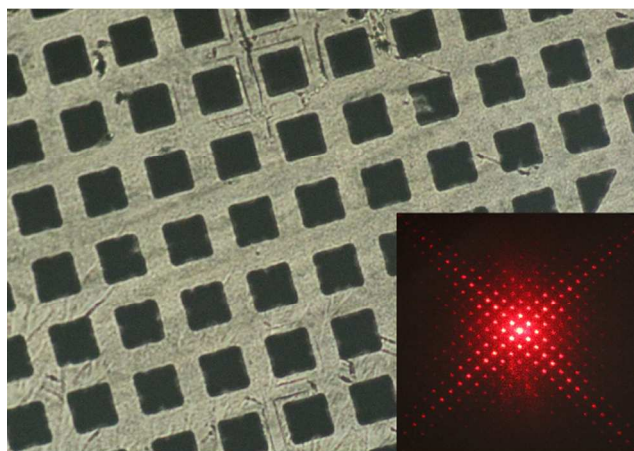


Figure 4. Micro-pattern obtained by selective irradiation of aligned filaments of the B_4 phase in **D-7** material by UV light (irradiated places have zero birefringence), the mesh size is ~ 50 micron. In the inset diffraction of laser beam on the micro-pattern.

In the studied homologue series the odd-even effect was observed also regarding the gelation ability of materials. The compounds with even number of carbon atoms in the spacer did not form gels neither with organic solvents nor with water. Instead of gel, the micro-sized crystallites precipitated from the solution (Figure 5).

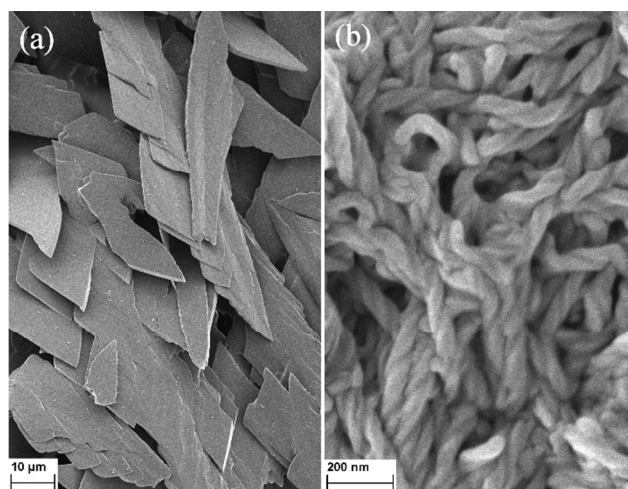


Figure 5. SEM images showing different morphologies of (a) micro-crystallites of dimer **D-6** precipitated from the menthone solution and (b) xerogel formed by dimer **D-7** in menthone.

Contrary, all odd spacer homologues show a strong gelation ability for various organic solvents, the gels were formed already at low concentrations ($\sim 2\%$ wt.) of dimer. The gel and sol states are thermo-reversible with phase transition temperature slightly dependent on organic solvent (Table 2 in SI).

The gel-sol transition could be also induced by illumination of the sample with the UV light, the resulting sol state is stable for hours after switching off the light, by monitoring the sample absorption in visible range it is apparent that cis form is very stable in such a solution (see SI). At room temperature the mixture returns to gel state only after irradiation with visible light ($\lambda \sim 400$ nm) that restores trans conformation of azo units. For the dried xerogel the SEM imaging revealed formation of three-dimensional network composed of long, entangled fibrous aggregates (Figure 5).

The average diameter of the nanofilaments is ~ 50 nm and twist angle ~ 35 deg. The x-ray pattern of gel (as well as xerogel) is identical to that of B_4' phase, apparently the local crystallographic lattice is not affected by gel formation.

The gelation ability of studied dimers was also examined for mesogenic solvents forming smectic phases. Miscibility studies were performed with rod-like compounds showing a phase sequence Iso-SmA-SmC (compounds 1 and 2, see SI). It was observed that rod-like and dimeric materials are fully miscible in temperature range above which B_4 phase is formed, at B_4 phase appearance the separation of mixture components takes place. Growing of B_4 filaments in SmA or SmC phase host matrix can be observed as a change in the optical texture, stripes are formed that are oriented perpendicular to the smectic layer normal, the density of stripes is dependent on mixture composition (Figure 6).

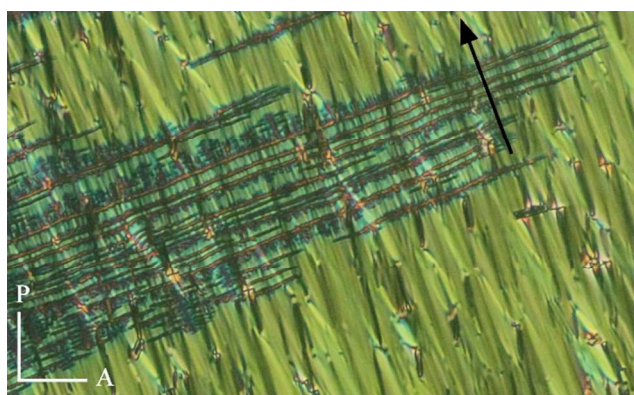


Figure 6. Ordered filaments of the B_4 phase growing from aligned SmA phase (20%wt mixture of **D-5** dimer with compound **1**), viewed between crossed polarizers. Arrow indicated smectic layer normal (rubbing direction).

De-mixing process can be also monitored by analysis of smectic layer thickness evolution with temperature. Upon formation of B_4 filaments the layer spacing of the smectic host suddenly decreases (Figure 7) because molecules of dimeric component, which length is larger than of rod like molecules, are extracted from smectic phase as HNFs are formed. Just below phase transition to B_4 phase, the layer thickness in smectic phase is higher than in pure rod-like compound, pointing that some dimer molecules still remain in smectic matrix. With decreasing the temperature molecules of dimer are gradually 'taken' from smectic mixture and are transferred into HNFs, in result the observed layer thickness in smectic C phase reaches at low temperature the same value as for pure rod-like compound.

The influence of light irradiation was studied for the mixtures with compound **2** having better stability upon UV radiation than compound **1**. The mixture with azo component concentration 20% was studied by x-ray diffraction method; it exhibited Iso-SmA-SmC phase sequence, and the B_4 phase appeared within the SmA temperature range.

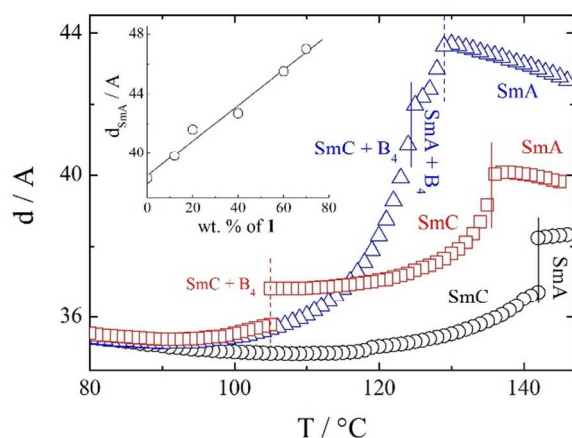


Figure 7. Layer spacing vs. temperature for compound **1** (black) and mixtures of compound **1** with dimer **D-5**: 20% (red) and 40% (blue). In the inset layer spacing in SmA phase vs. concentration of dimer in the mixtures.

The UV irradiation applied to the mixture above the transition to B_4 phase resulted in pronounced decrease of layer thickness, below the value for the pure host material. The change was caused by photoswitching of azodimeric molecules from trans to cis conformation, which shortens its length below that of the

host rod-like molecule. Turning off the UV light immediately restores the initial layer thickness of the mixture, showing that in anisotropic environment linear, trans conformation of dimer molecule is strongly favoured over kinked, cis conformation, and no illumination with visible light is even necessary to restore the trans conformation of azo groups. At the temperature range in which smectic phase is confined between HNFs, under UV irradiation the xrd signals related to B_4 phase disappear and signal coming from smectic layers of the matrix is shifted to the larger diffraction angle corresponding to smaller layer periodicity than before irradiation (Figure 8). Directly after turning off the UV light, x-ray pattern show only one signal at small angle region coming from smectic layers having periodicity larger, than in matrix before irradiation, indicating that the smectic layers are enriched with trans form of dimer molecules. It takes ~120 seconds after turning off the light to restore initial value of the smectic layer thickness of the mixture and for the signal of the B_4 phase to re-appear, the measured time for restoring B_4 filaments agrees with microscopic observation.

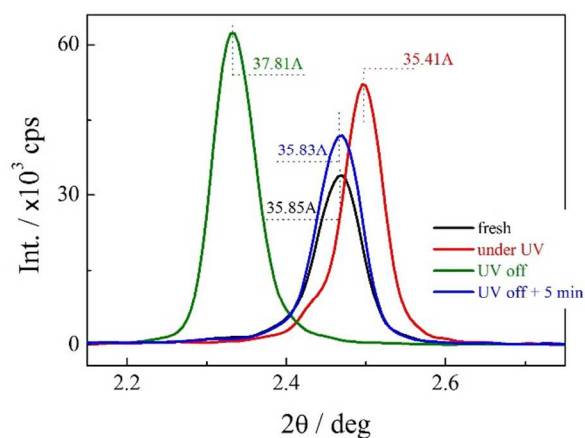


Figure 8. Xrd signal related to layer spacing in smectic C phase for mixture of compound **2** and dimer **D-5** (16%wt.); before UV irradiation (black), under UV irradiation (red), immediately after turning off the UV light (green) and ~200s after turning off the UV light (blue).

Conclusion

Formation of the B_4 phase by photosensitive molecules gives possibility for obtaining new type of nano-system controlled by light. It was found that for materials having SmC- B_4 phase sequence, macroscopic domains of oriented filaments are formed, if the B_4 phase is grown from well aligned smectic phase in the cell with planar anchoring conditions. The direction of filaments growth is governed by position of smectic layers. As the UV light induces cis molecular conformation, the filaments melt, despite their crystal nature. Interestingly, upon termination of UV light the system returns from isotropic phase to the B_4 phase directly, although in the temperature sequence between Iso and the B_4 phases also N and SmC phases were observed. Apparently recovering of trans conformation is not full, and in the mixture of trans and cis forms the nematic and smectic phases are suppressed as the cis molecules do not have linear shape compatible with formation of such phases. The B_4 phase formed directly from isotropic phase has its fibers oriented differently than when it is formed from SmC phase, this gives the possibility to pattern the

samples by selective illumination of sample with UV light. Since the B₄ phase is nearly crystalline phase it can coexist with smectic phase, creating new type of composite materials. The B₄ filaments in such composites can align by interactions with the smectic phase matrix, and the density of filaments can be controlled by mixture composition. Moreover, the filaments built of photo-sensitive molecules can be selectively molten in the matrix, in result the layer spacing of matrix is shorten or lengthen depending whether cis or trans conformation dimers enrich the matrix. Studied dimers easily form gels, photosensitive nature of filaments encapsulating the solution makes possible to control the gel-sol transition by light.

Acknowledgements

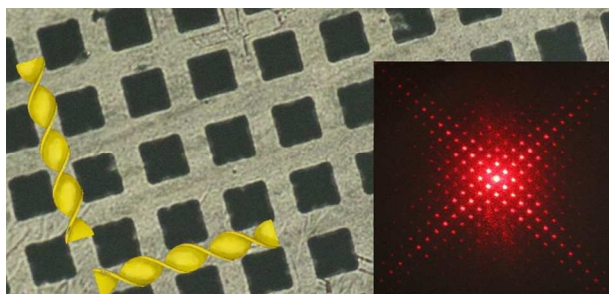
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Notes and references

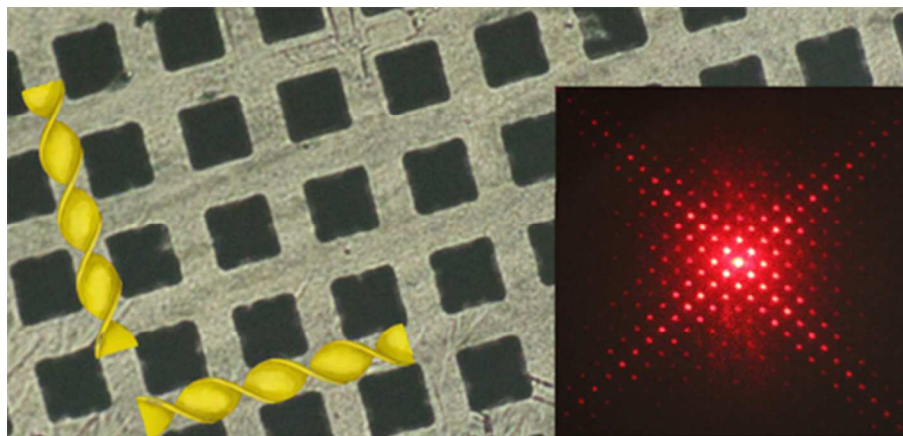
^a Department of Chemistry, University of Warsaw, 02-089 Warsaw, Poland.

Electronic Supplementary Information (ESI) available: Experimental details, synthesis scheme, characterization of new compounds, additional results of xrd, dielectric and UV-Vis spectroscopic studies. See DOI: 10.1039/b000000x/

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It is shown that the nanofilament structure of B₄ made of azo-dimers can be easily re-structured by UV light.



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