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FROM LIQUID CRYSTAL POLYMERS CONTAINING CROWN ETHERS TO
TAPERED BUILDING BLOCKS CONTAINING CROWN ETHERS WHICH
SELF-ASSEMBLE INTO TUBULAR SUPERMOLECULES
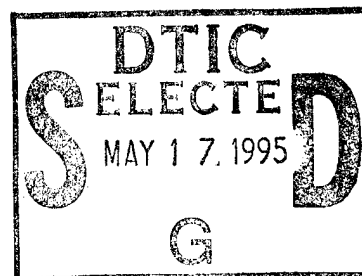
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Molecular recognition directed self-assembly of supramolecular architectures or noncovalent synthesis, and molecular recognition directed self-assembly of transition states or self-synthesis, are two of the most active topics of research in the area of supramolecular chemistry. We are concerned with the use of the simplest endo-receptor i.e., crown ether in the design of two classes of systems. The first one is a system which is externally regulated by molecular recognition processes via a crown ether endo-receptor. This system is based on various classes of liquid-crystalline polymers which exhibit phase transitions that are manipulated by the reversible complexation of the crown ether present in different parts of their repeat unit with metal salts. The information gained from these experiments is then exploited in the design of the second group of systems. This consists of self-assembling building blocks containing various combinations of crown ether as endo-receptor and a tapered group as exo-receptor. Upon complexation with metal salts, these building blocks self-assemble into tubular supramolecular architectures. Therefore, while the first system exhibits molecular recognition directed phase transitions, the second one self-assembles into tubular supramolecular architectures via various molecular recognition processes. These tubular supramolecular architectures display a thermotropic hexagonal columnar (Φ_h) liquid crystalline phase, which enables the structure of the self-assembled supramolecular architecture to be determined by X-ray diffraction experiments. Since the formation of a liquid-crystalline phase is a thermodynamically controlled process, its characterization eliminates many of the difficulties encountered in the characterization of self-assembled crystalline structures which are obtained by a kinetically controlled process. The goal of this paper is to discuss selected examples from these two groups of systems elaborated in our laboratory.

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FROM LIQUID CRYSTAL POLYMERS CONTAINING CROWN ETHERS TO TAPERED BUILDING BLOCKS CONTAINING CROWN ETHERS WHICH SELF-ASSEMBLE INTO TUBULAR SUPERMOLECULES

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INTRODUCTION

Molecular recognition directed self-assembly of supramolecular architectures or noncovalent synthesis (1), and molecular recognition directed self-assembly of transition states or self-synthesis (2), are two of the most active topics of research in the area of supramolecular chemistry (3). We are concerned with the use of the simplest endo-receptor i.e., crown ether in the design of two classes of systems. The first one is a system which is externally regulated by molecular recognition processes via a crown ether endo-receptor. This system is based on various classes of liquid-crystalline polymers which exhibit phase transitions that are manipulated by the reversible complexation of the crown ether present in different parts of their repeat unit with metal salts. The information gained from these experiments is then exploited in the design of the second group of systems. This consists of self-assembling building blocks containing various combinations of crown ether as endo-receptor and a tapered group as exo-receptor. Upon complexation with metal salts, these building blocks self-assemble into tubular supramolecular architectures. Therefore, while the first system exhibits molecular recognition directed phase transitions, the second one self-assembles into tubular supramolecular architectures via various molecular recognition processes. These tubular supramolecular architectures display a thermotropic hexagonal columnar (Φ_h) liquid crystalline phase, which enables the structure of the self-assembled supramolecular architecture to be determined by X-ray diffraction experiments. Since the formation of a liquid-crystalline phase is a thermodynamically controlled process, its characterization eliminates many of the difficulties encountered in the characterization of self-assembled crystalline structures which are obtained by a kinetically controlled process. The goal of this paper is to discuss selected examples from these two groups of systems elaborated in our laboratory.

LIQUID CRYSTALLINE POLYMERS CONTAINING CROWN ETHERS: SYNTHESIS AND MANIPULATION OF PHASE TRANSITIONS BY COMPLEXATION

Scheme 1 outlines the two major classes of liquid-crystalline polymers, i.e., main-chain and side-chain, and their architecture which is determined by the place of the repeat unit in which the crown ether endo-receptor is inserted. We have designed main-chain liquid-crystalline polymers containing crown ethers in their flexible spacer (4), and side-chain liquid-crystalline polymers containing crown ethers either in their backbone (5) or in their mesogenic side groups (6,7).
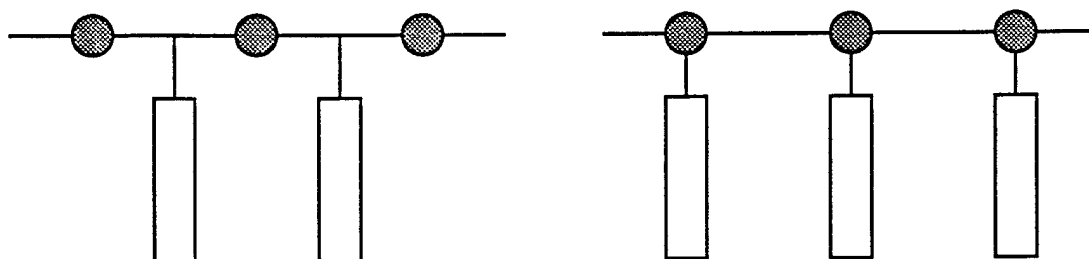
I. Main-Chain Liquid-Crystalline Polymers

II. Side-Chain Liquid-Crystalline Polymers

A. Crown ether ligand as part of the mesogenic unit

- crown ether ligand
- mesogenic unit
- interconnecting unit
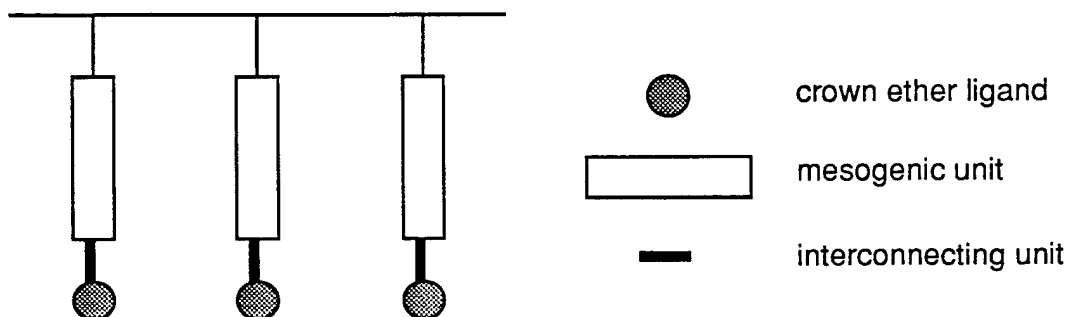
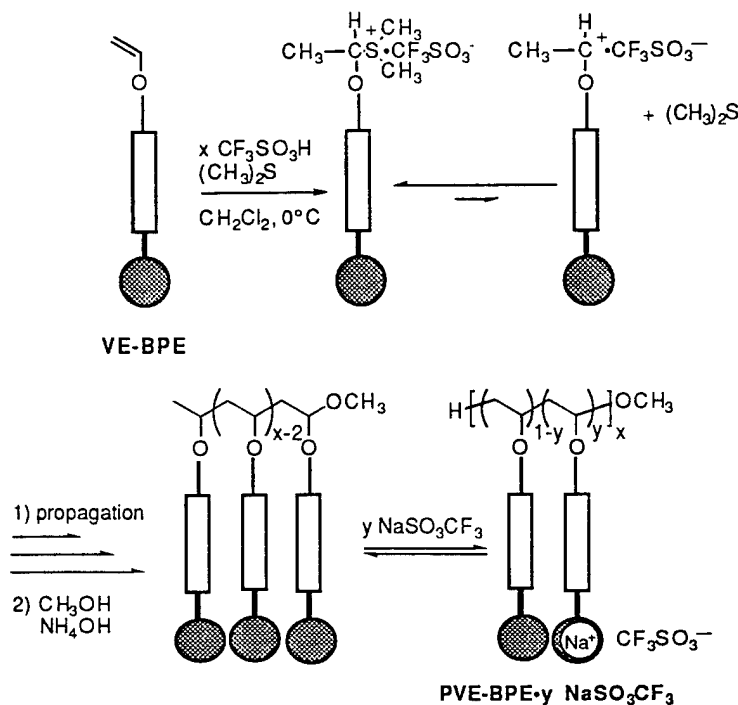## B. Crown ether ligand as part of the polymer backbone

Scheme 1. Various architectures of main-chain and side-chain liquid-crystalline polymers containing crown ethers

Scheme 2 outlines the synthetic procedure used in the preparation of the two monomers: 4-{2-[4'-(11-vinyloxyundecyloxy)biphenyl-4-yl]ethyl}benzo-15-crown-5 (**VE-BPE**) and 4-{2-[4'-(11-methacryloyloxyundecyloxy)biphenyl-4-yl]ethyl}benzo-15-crown-5 (**MA-BPE**) (7b). The synthetic details of this reaction scheme are available in the original publication (7b). **VE-BPE** was polymerized by a cationic mechanism employing an initiating system based on $CF_3SO_3H/(CH_3)_2S$ in methylene dichloride at 0°C. Under these conditions a "living" polymerization is achieved for this functional monomer. The selection of this cationic initiator was based on the use of the soft nucleophile/base, $(CH_3)_2S$, which reacts selectively with the growing carbenium species in a reversible way and therefore, avoids the reaction between the propagating carbenium ions and other nucleophilic functional groups of the monomer which exhibit a harder nucleophilic/basic character. Details of this polymerization and additional demonstrations of the ability of this initiator to generate living cationic polymerizations for a large variety of functional mesogenic vinyl ethers were reviewed elsewhere (8).

HO—⬡—Br

1

⬡—CH₂Cl
KOH / ethanol

⬡—CH₂O—⬡—Br   89 %

2

1) n-BuLi, -65 °C
2) (CH₃O)₃B, -65 °C
3) H⁺

⬡—CH₂O—⬡—B(OH)₂   88 %

3

HO(CH₂)₁₁Br

10

CH₂=CHO(CH₂)₃CH₃

⬡N–Pd(OAc)₂

CH₂=CHO(CH₂)₁₁Br   +   9

11   57 %

K₂CO₃
DMF, 80 °C

4

Br—⬡—CH₂COOH

polyphosphoric acid

Br—⬡—C(O)—⬡(crown)   **6**   70 %

(CH₃CH₂)₃SiH
CF₃COOH

Br—⬡—CH₂CH₂—⬡(crown)   **7**   75 %

toluene / ethanol
Na₂CO₃
(Ph₃P)₄Pd(0)

⬡—CH₂O—⬡—⬡—CH₂CH₂—⬡(crown)   **8**   74 %

H₂, Pd/C
CH₃COOH, 80 °C

HO—⬡—⬡—CH₂CH₂—⬡(crown)   **9**   73 %

HO(CH₂)₁₁Br
K₂CO₃
DMF, 80 °C

HO(CH₂)₁₁O—⬡—⬡—CH₂CH₂—⬡(crown)   **13**   73 %

(CH₃CH₂)₃N, THF, 0 °C
CH₂=C(CH₃)COCl

CH₂=C(CH₃)C(O)O—(CH₂)₁₁O—⬡—⬡—CH₂CH₂—⬡(crown)   43 %

MA-BPE

CH₂=CHO(CH₂)₁₁O—⬡—⬡—CH₂CH₂—⬡(crown)   75 %

VE-BPE

Scheme 2. Synthesis of **VE-BPE** and **MA-BPE**.

Figure 1a illustrates the cationic polymerization of **VE-BPE** and the structure of the resulted polymer (**PVE-BPE**). **PVE-BPE** with DP = 19 exhibits a crystalline melting followed by an enantiotropic smectic A (S_A) mesophase. Figure 1b presents the influence of complexation of **PVE-BPE** (DP = 19) with $NaSO_3CF_3$ on the phase behavior of the resulting complex. With the increase of the amount of $NaSO_3CF_3$ complexed by the 15-crown-5 moiety of this polymer, both the glass transition and the S_A-isotropic transition temperatures increase. At the same time the crystalline melting decreases. At higher concentrations of salt, a second smectic mesophase is uncovered.

(a)

VE-BPE

$x\ CF_3SO_3H$
$(CH_3)_2S$
$\xrightarrow{\quad CH_2Cl_2, 0°C \quad}$

$+ (CH_3)_2S$

1) propagation

2) CH_3OH
NH_4OH
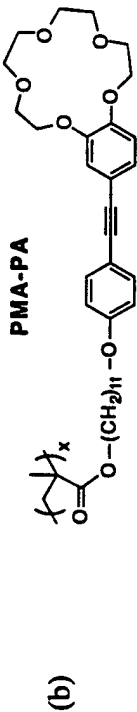
$y\ NaSO_3CF_3$

$CF_3SO_3^-$

PVE-BPE·y NaSO₃CF₃

(b)

Figure 1: (a) Cationic polymerization of **VE-BPE** and the complexes of **PVE-BPE** with $NaSO_3CF_3$. (b) The dependence of various transition temperatures of the complexes of **PVE-BPE** (**DP=19**) with $NaSO_3CF_3$ on the mole ratio $NaSO_3CF_3$/**PVE-BPE** (i=isotropic; S and S_A=smectic and smectic A; k=crystalline).

The S-S_A transition temperature decreases with the increase of the amount of complexed salt. Figure 2a outlines the radical polymerization of **MA-BPE**. The resulting polymer **PMA-BPE** also exhibits a crystalline and a S_A phase. The effect of complexation of **PMA-BPE** with $NaSO_3CF_3$ on its phase transitions is presented in Figure 2b. The trend obtained from this figure is quite similar to that observed from Figure 1a.

(a)
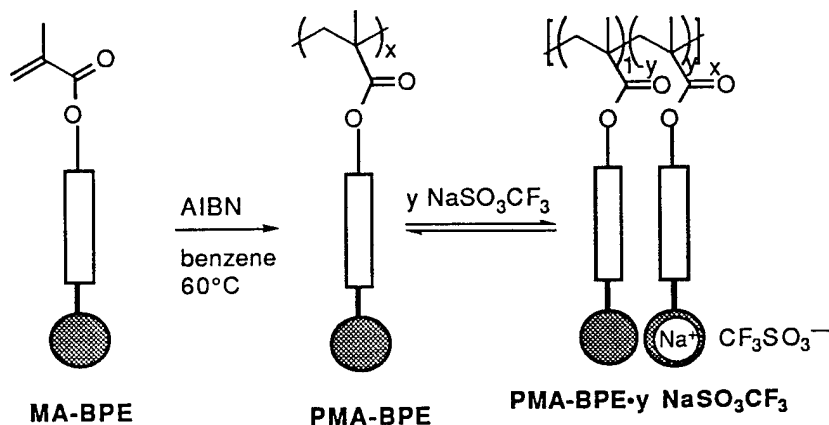
(b)
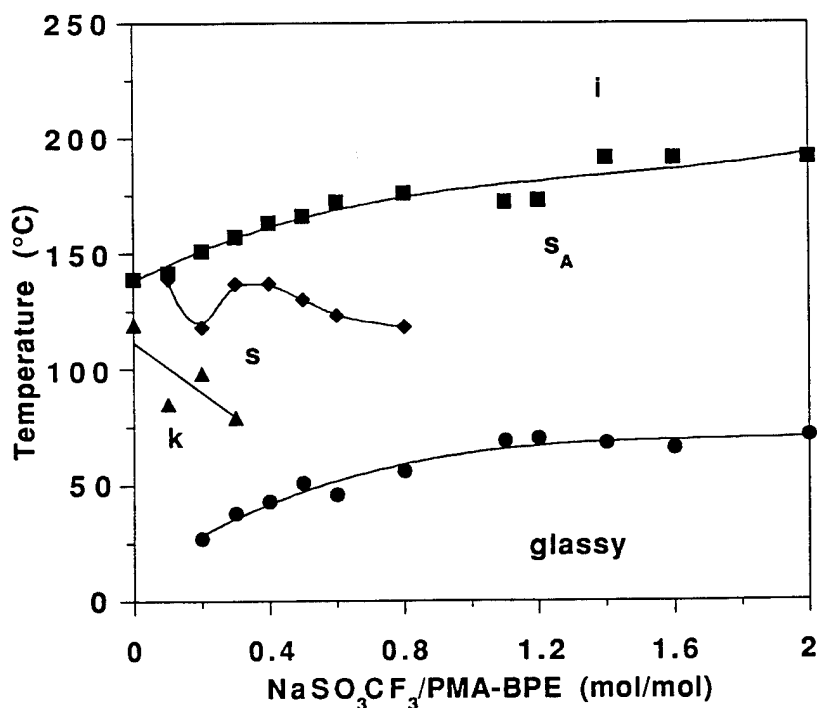
Figure 2:   (a) Radical polymerization of **MA-BPE** and the complexes of **PMA-BPE** with NaSO₃CF₃. (b) The dependence of various transition temperatures of the complexes of **PMA-BPE** with NaSO$_3$CF$_3$ on the mole ratio, NaSO$_3$CF$_3$ / **PMA-BPE** (i=isotropic, S and S$_A$=smectic and smectic A, k=crystalline).

The general message provided by these experiments is that complexation of the crown ether moiety of a side-chain liquid-crystalline polymer with metal salts enhances the stability of the lowest-order liquid-crystalline phase and decreases both the tendency towards crystallization as well as the tendency towards formation of higher-ordered liquid-crystalline phases. As a consequence, this molecular recognition effect can be expected to transform a crystalline polymer into a polymer displaying a monotropic or even an enantiotropic liquid-crystalline phase. For example, Figure 3a presents the heating and cooling differential scanning

PMA-PA

PVE-BPE

PVE-BPE (DP=8)

(a)

(b)
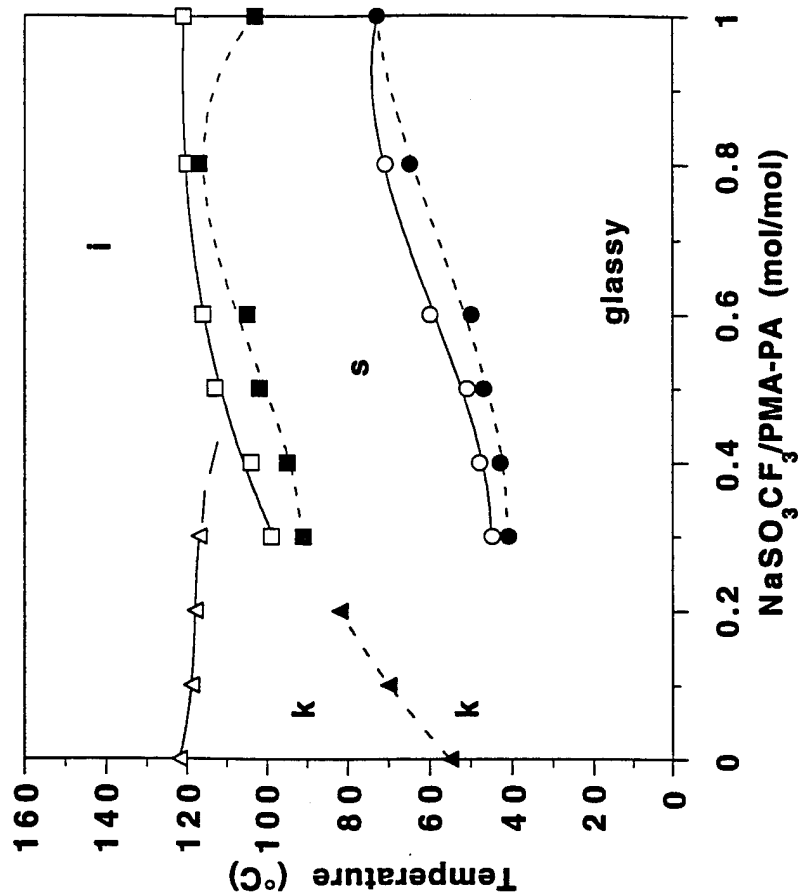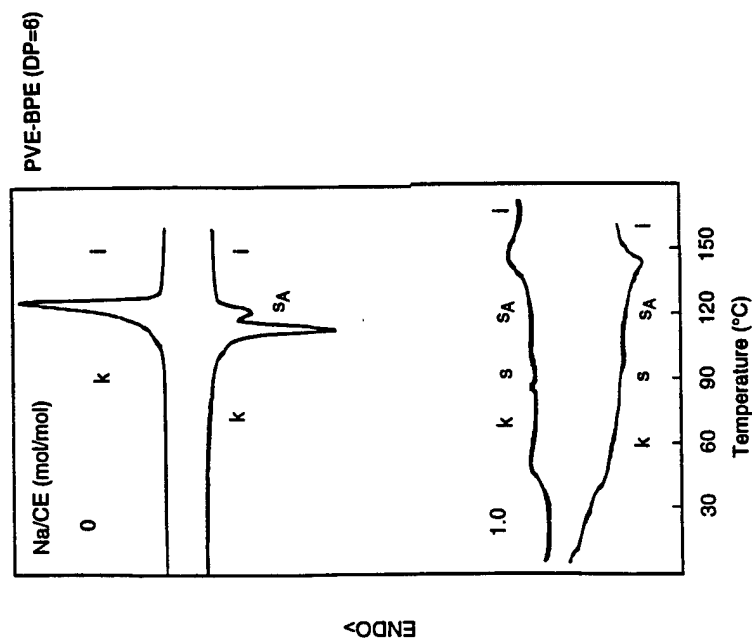
Figure 3: (a) DSC analysis of **PVE-BPE (DP=6)** and of its complex, NaSO₃CF₃/PVE-BPE (1.0/1.0, mol/mol); CE is crown ether. (b) The dependence of various transition temperatures of the complexes of PMA-PA with NaSO₃CF₃ on the ratio NaSO₃CF₃/PMA-PA (mol/mol). All data were obtained with $20°C \ min^{-1}$. Data from the second heating scan are: ○ - Tg; △ - T_{k-i}; □ - $T_{\phi h-i}$. Data from the cooling scans are: ● - Tg; ▲ - T_{i-k}; ■ - $T_{i-\phi h}$.

calorimetic (DSC) traces of **PVE-BPE** with DP = 6 which exhibits only a monotropic S_A phase. Upon complexation with 1.0 moles of $NaSO_3CF_3$, this polymer exhibits an enantiotropic S_A and an additional unidentified (S) smectic mesophase (7b). This experiment demonstrates the transformation of a monotropic S_A phase into an enantiotropic one and of a virtual smectic phase (S) into a monotropic one. Figure 3b demonstrates the transformation of the crystalline polymer, poly[4-(2-{4-[11-(methacryloyloxy)undecyloxy]-phenyl}ethynyl)benzo-15-crown-5] (**PMA-PA**) (6a), into a polymer which exhibits an enantiotropic S_A phase (7a). This experiment demonstrates that complexation can transform a virtual mesophase into an enantiotropic one.

The ability to manipulate and to stabilize liquid-crystalline mesophases by complexation is strongly dependent on the size of the crown ether, of the cation, and on the nature of the counteranion.

MOLECULAR-RECOGNITION-DIRECTED SELF ASSEMBLY OF TAPERED GROUPS CONTAINING CROWN ETHERS INTO TUBULAR SUPRAMOLECULAR ARCHITECTURES

Scheme 3 outlines the synthesis of a series of self-assembling building blocks containing 15-crown-5 based endo-receptors and 3,4,5-tris(p-alkoxybenzyloxy)benzoate (i.e., **12-ABG-B15C5, 4-ABG-15C5, 6-ABG-15C5** and **12-ABG-15C5**) or 3,4,5-tris(dodecyloxy)benzoate (**12-AG-15C5**)-tapered side groups as exo-receptors (9). All of these building blocks form lamellar crystalline phases. However, upon complexation with alkali metal salts those with twelve carbons in their alkyl tails self-assemble into tubular supramolecular architectures which generate a hexagonal columnar (Φ_h) thermotropic mesophase. Figure 4a presents a representative example of a series of DSC traces for the complexes of **12-ABG-B15C5** with KSO_3CF_3. The amount of salt in the complex is indicated on the figure. It is sufficient to add 0.1 moles of KSO_3CF_3 per crown ether to suppress the crystallization ability of **12-ABG-B15C5** and generate a supramolecular disordered structure which displays a glass transition temperature (Tg). The presence of a Tg indicates the creation of a polymer-like cooperative motion upon complexation. Addition of 0.2 moles of KSO_3CF_3 per crown ether produces a supramolecular tubular architecture. This amount of salt is sufficient to overcome the entropy loss required for the self assembly of **12-ABG-B15C5** into the tubular structure. Larger amounts of salt continue to stabilize the supramolecular tubular structure which is responsible for the formation of the Φ_h liquid-crystalline phase. Figure 4b plots the isotropic-hexagonal columnar ($T_{i-\Phi h}$) transition temperature as a function of the amount of salt in the complex for a series of four self-assembling building blocks. The values of $T_{i-\Phi h}$ for MSO_3CF_3/crown ether (mol/mol) ratios larger than 1.0 are less reliable (9) since in some cases the resulting structures start to decompose. These data demonstrate that the wider **12-ABG**-tapered groups produce a more stable tubular structure than the **12-AG** groups.
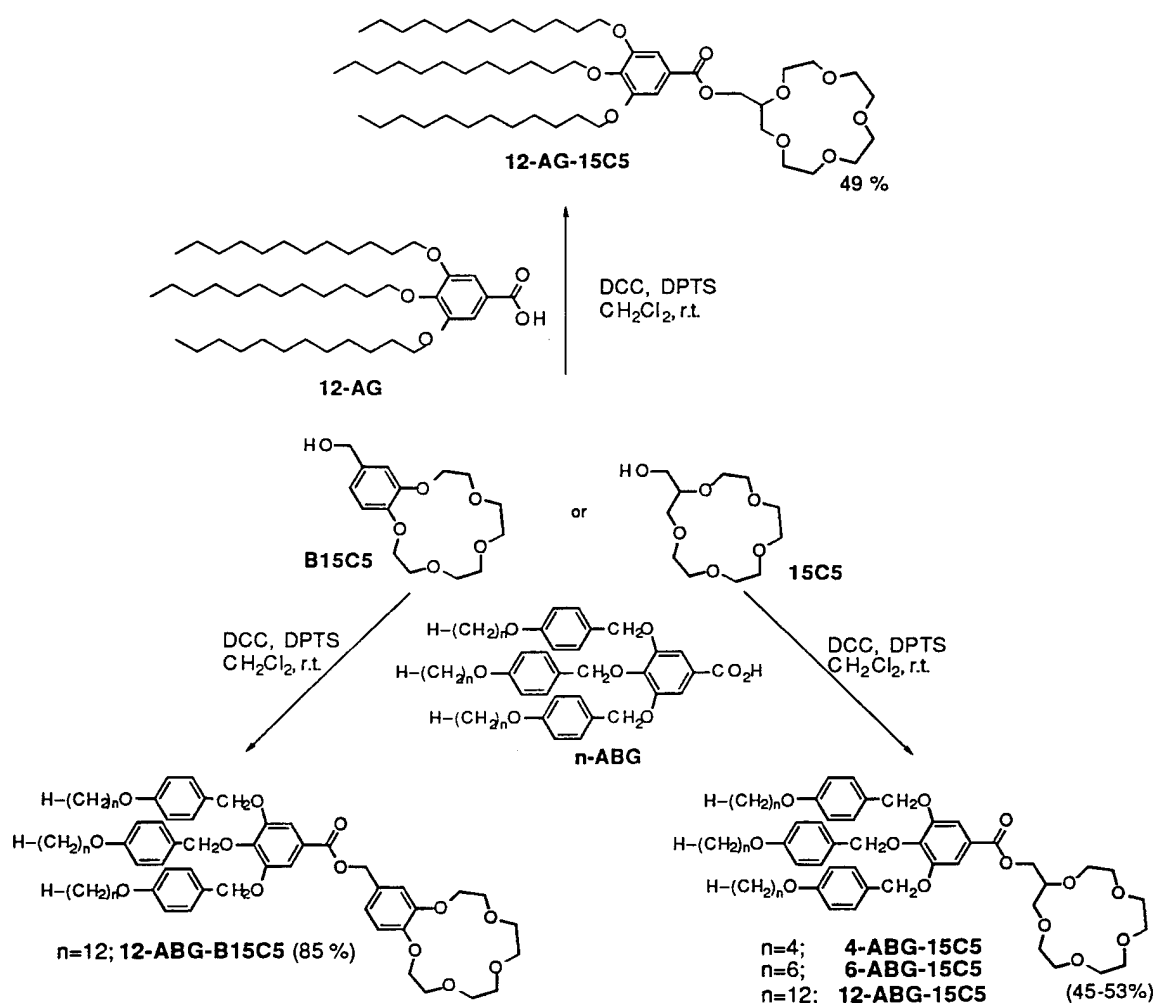
Scheme 3: Synthesis of **12-ABG-B15C5** and **n-ABG-15C5**

At the same time, for the same **12-ABG-B15C5** building block, complexation with cations which form 2/1 mol/mol crown/metal sandwich-like complexes (i.e., K^+) produce more stable columns than those which form 1/1 mol/mol crown/metal complexes (i.e., Na^+). The X-ray investigation of the Φ_h mesophase obtained from these supramolecular tubular architectures suggests the mechanism of self-assembly depicted in Figure 5. The crown ether endo-receptors are segregated in the center of the column with the tapered exo-receptors radiating towards the periphery of the column (9). The tapered shape of the exo-receptor of these building blocks determines the tubular shape of the supramolecular architecture. At the same time the endo-receptor (crown ether) is mainly responsible for the stability of the resulted column. The diameter of these tubular structures is determined both by the size of the tapered group and by the size of the crown ether. The alkyl tails of the tapered side groups are melted on the exterior surface of the tubular structure. The inner and outer diameters of these columns can be engineered via the size of the crown ether, the tapered side group, and the metal salt used in the complexation process. Therefore, the role of the exo-receptor is similar to that of a brick, while that of the endo-receptor is similar to that of the cement used in a construction.
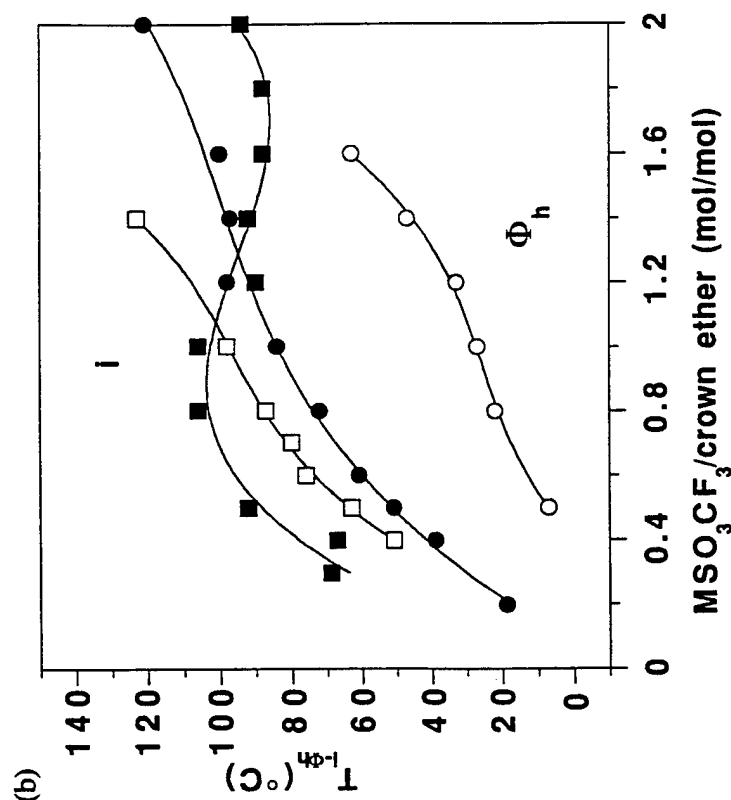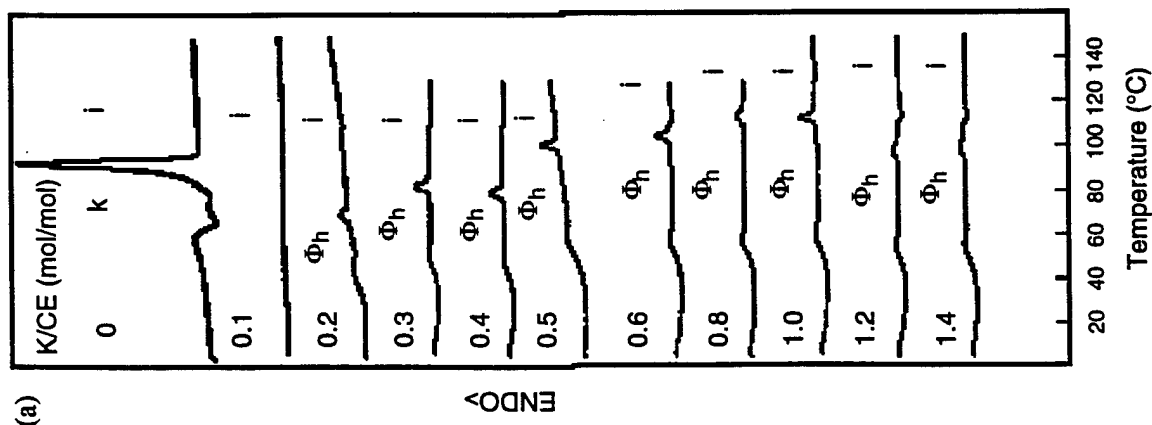
Figure 4: (a) Second DSC heating scans (20°C min^{-1}) of **12-ABG-B15C5** and of its complexes with KSO_3CF_3 in the ratio, KSO_3CF_3/**12-ABG-B15C5** (K/crown ether (CE), mol/mol). (b) The dependence of the isotropic-hexagonal columnar (T_i-Φ_h) transition temperatures of the complexes of various building blocks with $NaSO_3CF_3$ or KSO_3CF_3 on the ratio, MSO_3CF_3/crown-ether (mol/mol): □, **12-ABG-B15C5·$NaSO_3CF_3$**; ■, **12-ABG-B15C5·KSO_3CF_3**; ●, **12-ABG-15C5·$NaSO_3CF_3$**; ○, **12-AG-15C5-$NaSO_3CF_3$**.

Lattice parameter

NaSO$_3$CF$_3$

12-ABG-15C5

12-ABG-B15C5 · 1.4 eq. NaSO$_3$CF$_3$:   D= 57.7 Å

12-ABG-15C5 · 1.6 eq. NaSO$_3$CF$_3$:   D = 60.9 Å

12-AG-15C5 · 1.6 eq. NaSO$_3$CF$_3$:   D = 48.0 Å
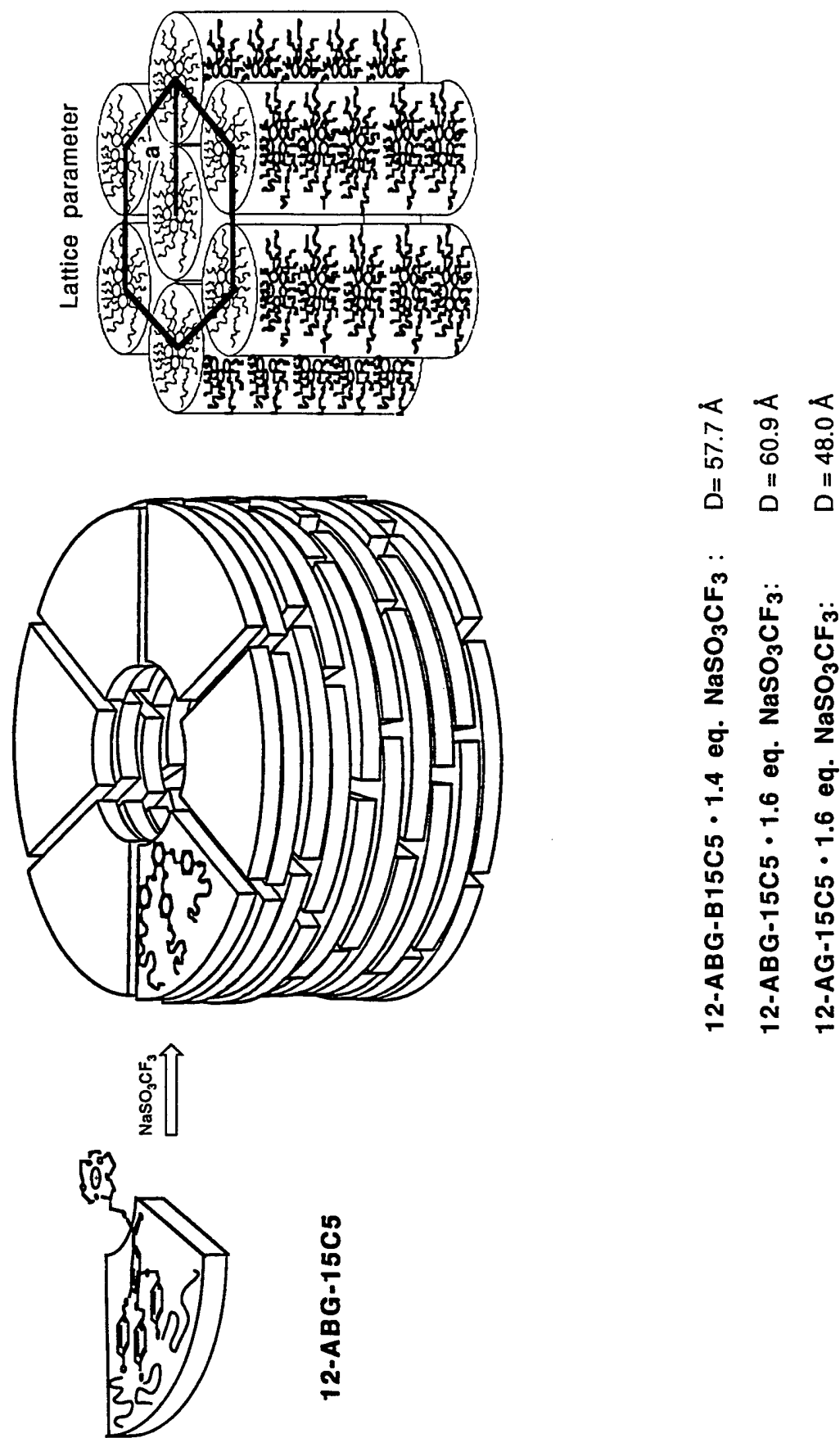
Figure 5: Schematic representation of the self-assembly of tapered building blocks containing crown ethers into the tubular supramolecular architecture which is responsible for the generation of the hexagonal columnar (Φ_h) liquid-crystalline supramolecular assembly. The dimension, D, represents the diameter of the supramolecular column (middle) and is equal to the lattice parameter, a (right).

The shape and size of the brick determines the shape of the construction and also its stability, while the primary role of the cement is to enhance its stability. Co-assembly of these building blocks with other similar structures is controlled both by the nature of their endo- and exo-receptors (10). These self-assembling building blocks demonstrate a very simple system which contains all of the information required for the self-assembly in its components. At the same time the co-assembly of these tapered units demonstrates the concept of self-checking (10). Finally we would like to mention that these self-assembled tubular supramolecular architectures exhibit ionic conductivity which is strongly dependent on the shape of the supramolecular architecture and therefore, can be switched on or off by a phase transition which changes the supramolecular structure from tubular to lamellar or to a disordered isotropic structure (11). Additional examples of self-assembling building blocks from our (12) and from other (13) laboratories were reviewed elsewhere.

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