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## Liquid Crystals

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### Isomorphism within the hexagonal columnar mesophase of molecular and macromolecular self- and co-assembled columns containing tapered groups

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## Isomorphism within the hexagonal columnar mesophase of molecular and macromolecular self- and co-assembled columns containing tapered groups

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The phase behaviour of binary mixtures of self-assembled tapering molecules based on monoesters of oligooxyethylene glycol and 3,4,5-tris[4-(*n*-dodecan-1-yloxy)benzyloxy]benzoic acid, their corresponding polymethacrylates, and of 4'-methyl (benzo-15-crown-5)-3,4,5-tris[4-(*n*-dodecan-1-yloxy)benzyloxy]benzoate within their hexagonal columnar mesophase ( $\Phi_h$ ) is described. The binary blends between molecular tapers co-assemble into a single supramolecular column resulting in isomorphism within their  $\Phi_h$  mesophase over the entire range of composition. The binary blends between polymethacrylates containing tapered side groups co-assemble into a single  $\Phi_h$  phase only when the columns of the parent polymers are of similar diameters. This results in binary mixtures which are isomorphic within the  $\Phi_h$  mesophase over the entire composition range. When the diameters of the columns formed by the parent polymers are dissimilar, isomorphic mixtures are obtained only over a narrow range of composition. Binary mixtures between molecular tapers and macromolecular systems containing tapered side groups co-assemble into a single column to the extent that intercalation of the molecular taper, within the column formed by the macromolecular system containing tapered side groups, is permissible. In all systems increased intra-columnar interactions can be induced by complexation of  $\text{CF}_3\text{SO}_3\text{Li}$  by the oligooxyethylene receptors leading to isomorphism in otherwise non-isomorphic mixtures. Ternary mixtures between molecular tapers with non-specific oligooxyethylene receptors and specific crown ether receptors and  $\text{CF}_3\text{SO}_3\text{Na}$  as the third component are non-isomorphic within their  $\Phi_h$  phase due to preferential complexation of the alkali metal cation by the column of the crown ether containing the molecular taper. This results in two columns of dissimilar diameters, which are isomorphic in the  $\Phi_h$  phase only within a limited range of composition.

### 1. Introduction

Disc-like liquid crystals exhibiting thermotropic columnar mesophases have attracted recently considerable research interest [1]. Several reviews on this field of research have been published [2-4]. It is already accepted, contrary to what had been originally considered, that the presence of a flat rigid polyaromatic core, as for example

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in hexasubstituted triphenylenes [3], is not a necessary requirement for the generation of molecules which exhibit columnar mesophases. Even compounds that can adopt a quasiflat conformation by virtue of their conformational flexibility display columnar mesophases. Several examples of such compounds, like octasubstituted cyclotetra-*tr*atrylene [5], tetra- and hexa-substituted cyclic polyamines [6], hexasubstituted scyllo-inositol (benzene-1,2,3,4,5,6-hexol) [7], hexakis(4-alkylphenoxy)methyl)benzenes and hexakis(4-alkoxyphenyl)benzenes [8] have been reported. In addition, even hexasubstituted cyclotrivenatrylene derivatives [9(a)–(d)] and tungsten-oxo calix[4]arene complexes [9(e)], which have a cone-like and a bowl-like shape, respectively as well as compounds that structurally deviate from a strictly disc-like shape like biforked [10] and phasmidic [11] derivatives, have been shown to form thermotropic columnar mesophases. Diablo compounds, i.e. molecules composed of two disc-like moieties interconnected by a rigid rod through their centres, also exhibit columnar mesophases [12].

Lytropic columnar mesophases are also exhibited by many biological systems. An example is DNA which forms a lyotropic columnar hexagonal mesophase in water [13]. Supramolecular disc-like molecules exhibiting columnar mesophases have been generated via self-assembly of complementary components directed by molecular-recognition [14, 15]. Endo-recognition [14(a)] processes generated by both hydrogen bonding [14] and metal complexation [15] have been used to produce disc-like molecules.

In biological systems, molecular recognition and self-assembly are the two main processes utilized by nature for the generation of supramolecular architectures with remarkable properties. The utilization of these processes exemplified by Tobacco Mosaic Virus (TMV) which is one of the best understood self-assembled biological systems [14(b), (c), 16] TMV consists of a single type of protein molecule (subunit) and a strand of RNA. The protein subunits can form single- or double-layered discs. In the presence of the RNA strand or below a specific pH value (in the absence of RNA), the self-assembled single- or double-layered discs assume a lock-washer shape which is required for the generation of the helical shaped single rod of TMV. The initial driving force for the self-assembly of TMV is therefore provided by exo-recognition by the tapered shape of the protein sub-units, followed by complementary endo-recognition provided by the RNA strand.

The simplicity of this fascinating biological architecture has directed our research towards the development of synthetic approaches to the self-assembly of cylindrical supramolecular architectures by utilizing synthetic analogues which resemble those used by TMV. In the first series of experiments of this topic, we used a combination of exo-recognition generated by the tapered shape of the 3,4,5-tris[4-(*n*-dodecan-1-yloxy)benzyloxy]benzoate group and endo-recognition generated by a benzo-15-crown-5 endo-receptor as a driving force for self-assembly [17]. The complexation of the benzo-15-crown-5 endo-receptor of 4'-methyl(benzo-15-crown-5)-3,4,5-tris[4-(*n*-dodecan-1-yloxy)benzyloxy]benzoate with  $\text{CF}_3\text{SO}_3\text{Na}$  or  $\text{CF}_3\text{SO}_3\text{K}$  destabilizes its crystalline phase and induces its self-assembly into a cylindrical architecture which displays an enantiotropic thermotropic columnar hexagonal  $\Phi_n$  mesophase [17]. In a simpler and more general approach, we have utilized compounds which are derived from 4'-methyl(benzo-15-crown-5)-3,4,5-tris[4-(*n*-dodecan-1-yloxy)benzoate by replacing its selective benzo-15-crown-5 endo-receptor with the non-selective hydroxy-oligooxyethylene group containing from one to four oxyethylene repeat units [18(a)]. The hydroxy terminated oligooxyethylenic endo-receptor functions by a combination

of hydrogen bonding and alkali metal salt complexation, while exo-recognition is provided by the tapered shape to induce the self-assembly into a cylindrical supramolecular architecture which displays a hexagonal columnar ( $\Phi_h$ ) mesophase. The non-selective complexation of metal salts enhances the endo-recognition, and therefore the driving force for self-assembly, as being reflected in the increased  $\Phi_h$ -isotropic ( $\Phi_h-I$ ) transition temperatures of the complexes compared with those of the parent uncomplexed compounds. The corresponding polymethacrylates of the hydroxy terminated compounds allowed, for the first time, a comparison between a 'molecular' and a 'supramolecular' polymer backbone effect to be made [18 (a)]. Both in polymethacrylates containing tapered side groups [18 (a)], as well as in other similar polymer systems [18 (b), (c)], the endo recognition process ('supramolecular' backbone) was replaced by a polymer ('molecular') backbone.

Presently, we are investigating the phase behaviour of binary mixture of various molecular, macromolecular, and supramolecular systems which self-assemble into cylinders displaying a  $\Phi_h$  mesophase. A general discussion on isomorphism in crystalline and liquid crystalline phases of polymers and copolymers is available elsewhere [19]. The goal of this paper is to discuss the isomorphism of binary mixtures of monoesters of oligooxyethylene glycol with 3,4,5-tris[4-(*n*-dodecan-1-yloxy)benzyloxy]benzoic acid, of their corresponding polymethacrylates, and of 4'-methyl(benzo-15-crown-5)-3,4,5-tris[4-(*n*-dodecan-1-yloxy)benzyloxy]benzoate within their  $\Phi_h$  mesophase, using results obtained by a combination of differential scanning calorimetry (DSC) and thermal optical polarized microscopy. The phase behaviour of ternary mixtures with  $CF_3SO_3Li$  or  $CF_3SO_3Na$  as the third component will also be discussed.

## 2. Experimental

### 2.1. Materials

$CF_3SO_3Li$  (97 per cent, Aldrich) was dried under vacuum at 120°C for 24 h and stored in a desiccator.  $CF_3SO_3Na$  was prepared as described previously [17].  $CH_2Cl_2$  was distilled from  $CaH_2$ . Tetrahydrofuran (THF) was distilled from  $LiAlH_4$  under dry nitrogen.

### 2.2. Synthesis of molecular and macromolecular compounds containing tapered groups

Details of the syntheses of the monoesters of oligooxyethylene glycol with 3,4,5-tris[4-(*n*-dodecan-1-yloxy)benzyloxy]benzoic acid, of their corresponding polymethacrylates [18 (a)], and of 4'-methyl(benzo-15-crown-5)-3,4,5-tris[4-(*n*-dodecan-1-yloxy)benzyloxy]benzoate [17] have been reported previously.

### 2.3. Preparation of binary mixtures

Binary mixtures were prepared by weighing the individual components in cleaned and dried glass vials and then adding dry  $CH_2Cl_2$  to give an equal final volume and a homogeneous solution. The solvent was removed under a gentle stream of dry nitrogen, and the vials were placed in a vacuum desiccator at 0.5 mmHg for 12 h.

Ternary mixtures with  $CF_3SO_3Li$  or  $CF_3SO_3Na$  as the third component were prepared in a similar manner, with the exception that  $CH_2Cl_2$  was replaced by dry THF in order to form a homogeneous solution. In this case, after evaporation of the solvent, the vials were evacuated at 0.5 mm Hg for at least 24 h.

### 2.4. Techniques

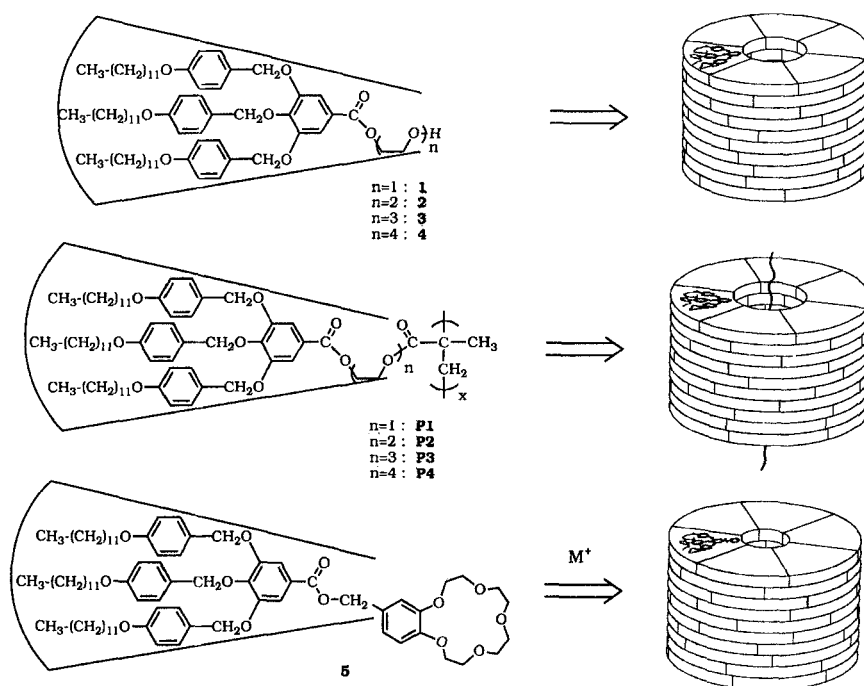
A Perkin–Elmer DSC 4 differential scanning calorimeter equipped with a TADS data station was used to determine the thermal transitions which were taken as the maxima and minima of their endothermic and exothermic peaks. In all cases, heating and cooling rates were  $20^{\circ}\text{C min}^{-1}$ . Second and subsequent heating scans and first and subsequent cooling scans were identical. A Carl-Zeiss optical polarized microscope (magnification  $100\times$ ), equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor, was used to observe the thermal transitions and to analyse the anisotropic textures.

## 3. Results and discussion

To date only very few investigations on the isomorphism of discotic liquid crystals within their columnar mesophase have been reported. One example refers to the isomorphism of binary mixtures of symmetric hexakis(*n*-pentyloxy)triphenylene with asymmetric 3,4,3',4'-tetrakis(*n*-pentyloxy)-3'',4''-bis(*n*-nonyloxy)triphenylene [20]. The binary mixtures of these compounds are isomorphic in their columnar mesophase over the entire range of compositions. Interestingly, the composition dependence of the columnar hexagonal–isotropic transition ( $\Phi_h$ –I) in the phase diagram of these mixtures displays an azeotropic minimum. A second example of isomorphism has been discussed for mixtures of disc-like molecules based on the flexible core of cyclotetrameratrylene [21]. The mixtures resulting from cocyclotetramerization of 3,4-bis(*n*-hexyloxy)benzyl alcohol and bis(*n*-dodecanyloxy)benzyl alcohol are statistical mixtures of six possible isomers of octasubstituted cyclotetrameratrylene. Regardless of composition, all mixtures were found to be isomorphic within their columnar mesophase. Both examples deal with molecular disc-like liquid crystals.

In the present investigation, the formation of the hexagonal columnar mesophase is the result of self-assembly of molecules with tapering shapes and of macromolecules containing tapering side groups via molecular recognition processes.

The chemical structures of all compounds used in the present study are summarized in scheme 1. All low molar mass compounds based on hydroxy terminated oligooxyethylene segments and 3,4,5-tris[4-(*n*-dodecan-1-yloxy)benzyloxy]benzoate moieties (**1–4**) self-assemble into supramolecular cylinders which display enantiotropic hexagonal columnar ( $\Phi_h$ ) mesophases. Their self-assembly is a result of two processes. Exo-recognition, which is provided by their tapered shape and endo-recognition, which results from H-bonding of their –OH terminated oligooxyethylenic segments (scheme 1) [18(a)]. Their polymeric analogues (**P1–P4**) also self-assemble into cylindrical architectures which exhibit an enantiotropic  $\Phi_h$  mesophase. In these compounds, the endo-recognition previously provided by H-bonding is replaced by the covalent attachment of the tapers on to a polymethacrylate backbone [18(a)]. Since this is a covalent interaction, **P1–P4** have higher  $\Phi_h$ –I transition temperatures ( $T_{\Phi_h-I}$ ) than those of **1–4**, respectively. The average column diameters of self-assembled cylinders from **1–4** and **P1–P4** were determined by X-ray scattering experiments and their thermal transitions were determined by DSC (table). The compound 4'-methyl(benzo-15-crown-5)-3,4,5-tris[4-(*n*-dodecan-1-yloxy)benzyloxy] benzoate (**5**) is only crystalline (table). The crown ether moiety can complex alkali metal ions, and thus, functions as an endo-receptor. This interaction leads to the suppression of its crystalline phase and to the generation of an enantiotropic columnar mesophase [17]. Its thermal transitions are also summarized in the table.



Scheme 1. The structures of the monoesters of oligo(oxyethylene glycol) with 3,4,5-tris[4-(*n*-dodecan-1-yloxy)benzyloxy]benzoic acid (**1–4**), of their corresponding polymethacrylates (**P1–P4**), and of 4'-methyl(benzo-15-crown-5)-3,4,5-tris[4-(*n*-dodecan-1-yloxy)benzyloxy]benzoate (**5**).

### 3.1. Binary mixtures of the tapering molecules of monoesters of oligoethylene glycol with 3,4,5-tris[4-(*n*-dodecan-1-yloxy)benzyloxy]benzoic acid

Figure 1 presents the phase behaviour of the binary mixture of **1** and **4**. During both heating and cooling (figure 1(a)) DSC scans,  $T_{\Phi_{n-1}}$  of this binary mixture exhibits an almost linear dependence on composition. The experimental data for  $T_{\Phi_{n-1}}$  from the phase diagram in figure 1(a) can be compared with the data calculated using the Schroeder–van Laar equation [22] which applies to order transitions of ideal binary mixtures

$$F_1 = \left\{ 1 - \frac{\Delta H_1^\circ T_2 (T - T_1)}{\Delta H_2^\circ T_1 (T - T_2)} \right\}^{-1},$$

where  $F_1$  is the mol fraction of component **1**,  $T_1$  and  $\Delta H_1$  are, respectively, the transition temperature and the enthalpy change for pure component **1**,  $T_2$  and  $\Delta H_2$  have the same meaning for component **2**, and  $T$  is the transition temperature corresponding to composition  $F_1$ . An excellent agreement between experimental and calculated  $T_{\Phi_{n-1}}$  values was observed. The enthalpy changes ( $\Delta H$ ) associated with  $T_{1-\Phi_n}$  and  $T_{\Phi_n-C}$  from the cooling scans are presented in figure 1(b) and, within experimental error, the first seems to be independent of composition, while the second displays a positive deviation from ideal values.

The binary mixtures of **2** and **4** (figures 2(a) (b)) and of **3** and **4** (figures 3(a) (b)) display a similar behaviour to the binary mixture of **1** with **4**. In all binary mixtures, the experimentally determined  $T_{\Phi_{n-1}}$  data are in agreement with data calculated using the

## Characterization of compounds 1-5 and P1-P4.

| Compound  | Column diameter/Å | Thermal transitions °C and corresponding enthalpy changes kcal/mru in parentheses                                  |                                |
|-----------|-------------------|--|--------------------------------|
|           |                   | Heating  | Cooling                        |
| <b>1</b>  | 48.4              | C 46(1.8) C 58(4.9) C 71(0.39) $\Phi_h$ 85(0.73) I<br>C 45(1.8) C 48(-1.1) C 56(2.1) C 72(1.2) $\Phi_h$ 84(0.70) I | I 76(0.76) $\Phi_h$ 25(4.2) C  |
| <b>2</b>  | 49.2              | C 66(8.3) $\Phi_h$ 73(0.49) I<br>C 66(8.3) $\Phi_h$ 73(0.45) I   | I 65(0.74) $\Phi_h$ 35(9.5) C  |
| <b>3</b>  | 58.2              | C 56(18.9) $\Phi_h$ 63(0.80) I<br>C 56(13.3) $\Phi_h$ 61(0.92) I   | I 54(0.62) $\Phi_h$ 34(14.7) C |
| <b>4</b>  | 57.4              | C 50(16.4) $\Phi_h$ 59(0.74) I<br>C 49(15.5) $\Phi_h$ 59(0.88) I   | I 52(0.78) $\Phi_h$ 31(15.1) C |
| <b>5</b>  | —                 | C 61(4.81) C 92(18.6) I<br>C 55(2.7) C 91(15.0) I  | I 18(12.4) C                   |
| <b>P1</b> | 52.8              | $\Phi_h$ 127(0.30) I<br>$\Phi_h$ 127(0.30) I   | I 110(0.38) $\Phi_h$           |
| <b>P2</b> | 53.0              | g 36 $\Phi_h$ 116(0.38) I<br>g 37 $\Phi_h$ 116(0.30) I   | I 103(0.38) $\Phi_h$ 29 g      |
| <b>P3</b> | 64.4              | C 48(3.32) $\Phi_h$ 113(0.43) I<br>$\Phi_h$ 112(0.43) I  | I 103(0.45) $\Phi_h$           |
| <b>P4</b> | 61.6              | C 47(3.75) $\Phi_h$ 103(0.50) I<br>$\Phi_h$ 99(0.43) I   | I 87(0.67) $\Phi_h$            |

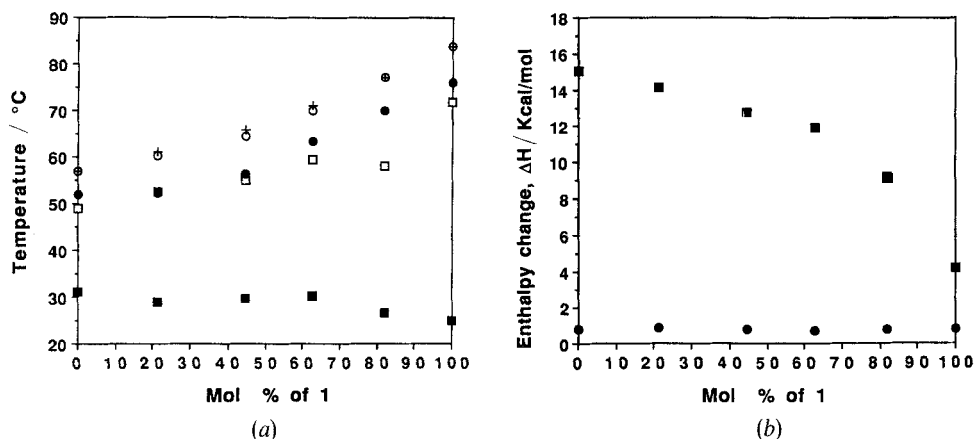


Figure 1. (a) The dependence of phase transition temperatures on composition for the binary mixture of 1 with 4 as determined from a second heating scan ( $\square$ ,  $T_{C-\Phi_h}$ ), ( $\circ$ ,  $T_{\Phi_h-I}$ ); first cooling scan ( $\bullet$ ,  $T_{I-\Phi_h}$ ), ( $\blacksquare$ ,  $T_{\Phi_h-C}$ ); calculated by the Schroeder–van Laar equation for the data corresponding to second heating scans (+). (b) The dependence of  $\Delta H$  associated with the transition temperatures of the binary mixture of 1 with 4 from the first cooling scan ( $\bullet$ ,  $\Delta H_{I-\Phi_h}$ ), ( $\blacksquare$ ,  $\Delta H_{\Phi_h-C}$ ).

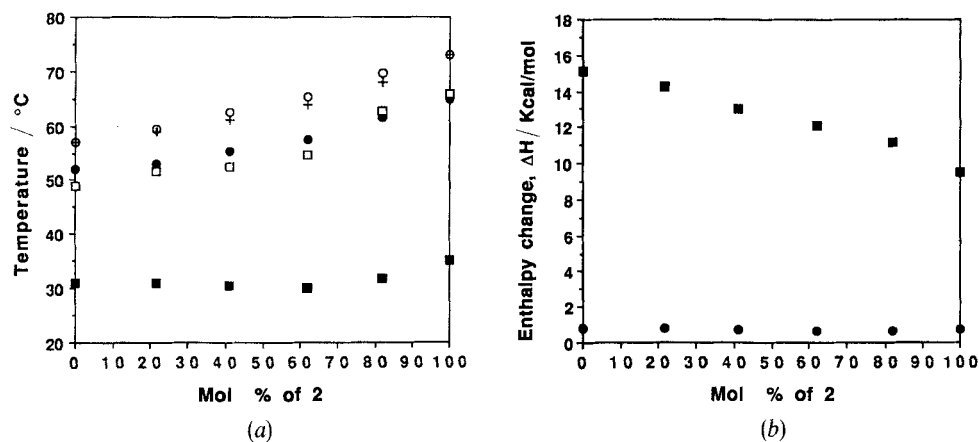


Figure 2. (a) The dependence of phase transition temperatures on composition for the binary mixture of 2 with 4 as determined from a second heating scan ( $\square$ ,  $T_{C-\Phi_h}$ ), ( $\circ$ ,  $T_{\Phi_h-I}$ ); first cooling scan ( $\bullet$ ,  $T_{I-\Phi_h}$ ), ( $\blacksquare$ ,  $T_{\Phi_h-C}$ ); calculated by the Schroeder–van Laar equation for the data corresponding to second heating scans (+). (b) The dependence of  $\Delta H$  associated with the transition temperatures of the binary mixture of 2 with 4 from the first cooling scan ( $\bullet$ ,  $\Delta H_{I-\Phi_h}$ ), ( $\blacksquare$ ,  $\Delta H_{\Phi_h-C}$ ).

Schroeder–van Laar equation. This demonstrates that all binary mixtures of compounds 1–4 are isomorphic within their  $\Phi_h$  mesophase. The isomorphism of these compounds within their  $\Phi_h$  phase is not unexpected, since all of them possess the required features for self-assembly into a single column, i.e. exo-recognition provided by the tapered shape and endo-recognition provided by hydrogen bonding [18(a)]. Both interactions facilitate the intercalation of various mixtures of compounds 1 to 4 into a column of intermediate diameter between those of the parent compounds. A schematic representation of the co-assembly of compounds 1 and 4 within the same



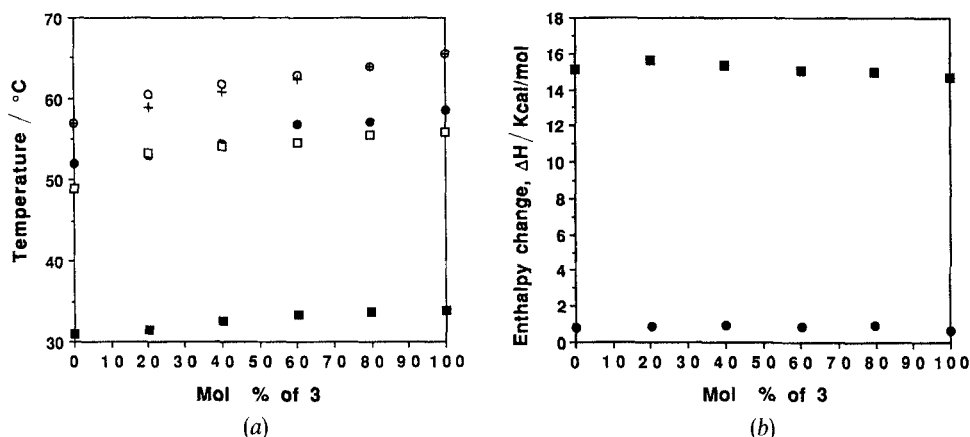
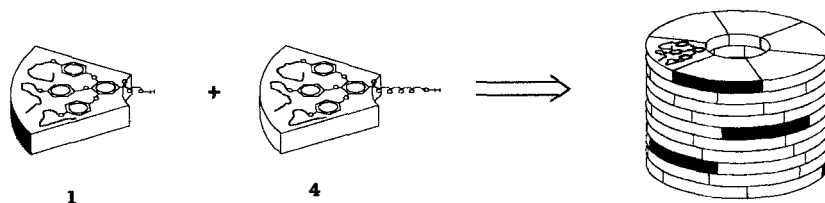


Figure 3. (a) The dependence of phase transition temperatures on composition for the binary mixture of 3 with 4 as determined from a second heating scan (□,  $T_{C-\Phi_h}$ ), (○,  $T_{\Phi_h-I}$ ); first cooling scan (●,  $T_{I-\Phi_h}$ ), (■,  $T_{\Phi_h-C}$ ); calculated by the Schroeder-van Laar equation for the data corresponding to second heating scans (+). (b) The dependence of  $\Delta H$  associated with the transition temperatures of the binary mixture of 3 with 4 from a first cooling scan (●,  $\Delta H_{I-\Phi_h}$ ), (■,  $\Delta H_{\Phi_h-C}$ ).

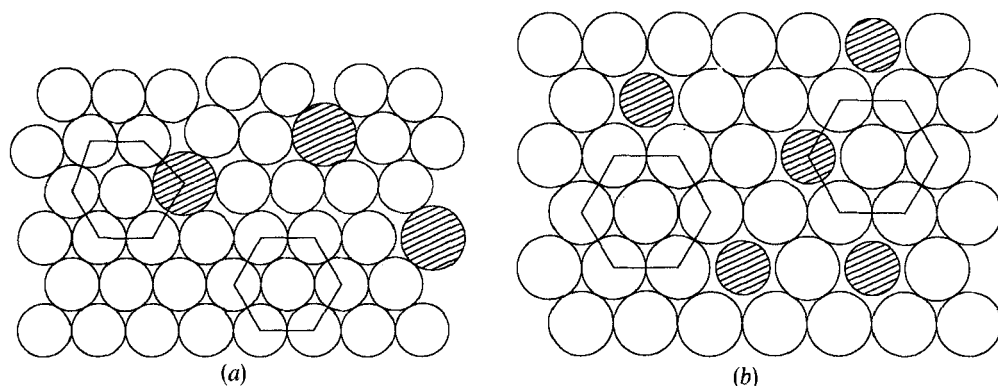


Scheme 2. Schematic representation of the co-assembly of 1 and 4 into the same columnar arrangement.

supramolecular column is shown in scheme 2. Since the only difference between the compounds is the length of their flexible oligoethylene segment, it is expected that this should have very little or no effect at all on their ability to mix in a single column.

### 3.2. Binary mixtures between polymethacrylates containing tapered side groups of monoesters of oligoethylene glycol with 3,4,5-tris[4-(*n*-dodecan-1-yloxy)benzyloxy]benzoic acid

The thermal transitions of the binary mixture of polymers **P1** and **P4** that assemble into columns of dissimilar diameters (see table) are presented in figure 4 (a) (data from second heating scan) and 4 (b) (data from first cooling scan). At low mol per cent compositions in **P1**, the two polymers form mixtures that exhibit a single  $\Phi_h-I$  transition. Above a composition of about 40 mol% of **P1**, the binary mixture displays two  $\Phi_h-I$  transitions which are almost identical to the respective transitions of each individual polymer. This behaviour suggests that, above this composition, the two polymers are non-isomorphic within their  $\Phi_h$  mesophase. While this behaviour is not trivial a possible explanation can be offered if one considers the formation of the  $\Phi_h$  mesophase by these polymers. Although additional experimental support is required, we can assume that the formation of each individual column arises from the self-



Scheme 3. (a) Schematic representation of the columnar hexagonal arrangement resulting from the introduction of a small amount of larger diameter columns into an excess of smaller diameter columns (the resulting distortion is illustrated by the irregular hexagon). (b) Schematic representation of the columnar hexagonal arrangement resulting from the introduction of a small amount of smaller diameter columns into an excess of larger diameter columns (in this case, the arrangement does not become distorted). In both (a) and (b) parts, the circle diameters have been drawn proportional to the ones calculated for **P1** and **P4** from X-ray scattering data.

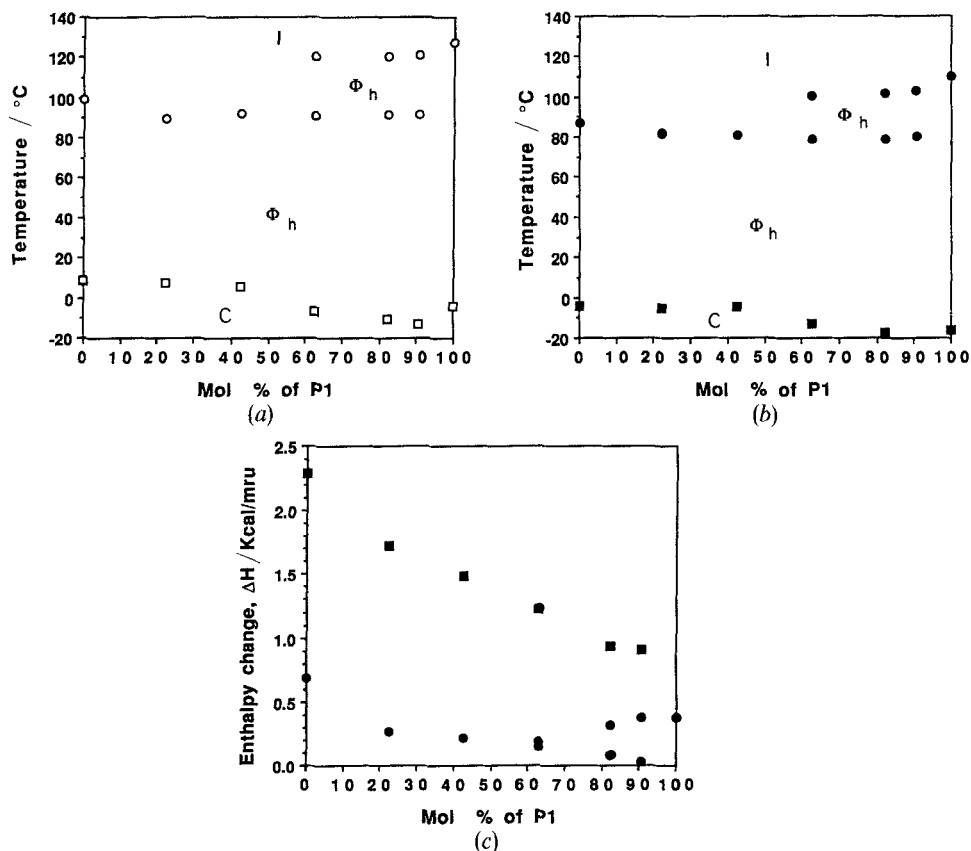


Figure 4. The dependence of phase transition temperatures of composition for the binary mixture of **P1** with **P4**. (a) Second heating scan ( $\square$ ,  $T_{C-\phi_h}$ ), ( $\circ$ ,  $T_{\phi_h-\phi_h}$ ), ( $\circ$ ,  $T_{\phi_h-l}$ ); (b) First cooling scan ( $\bullet$ ,  $T_{l-\phi_h}$ ), ( $\bullet$ ,  $T_{\phi_h-\phi_h}$ ), ( $\blacksquare$ ,  $T_{\phi_h-c}$ ); (c) The dependence of  $\Delta H$  associated with the transition temperatures of the binary mixture of **P1** with **P4** from a first cooling scan ( $\bullet$ ,  $\Delta H_{l-\phi_h}$ ), ( $\bullet$ ,  $\Delta H_{\phi_h-\phi_h}$ ), ( $\blacksquare$ ,  $\Delta H_{\phi_h-c}$ ).

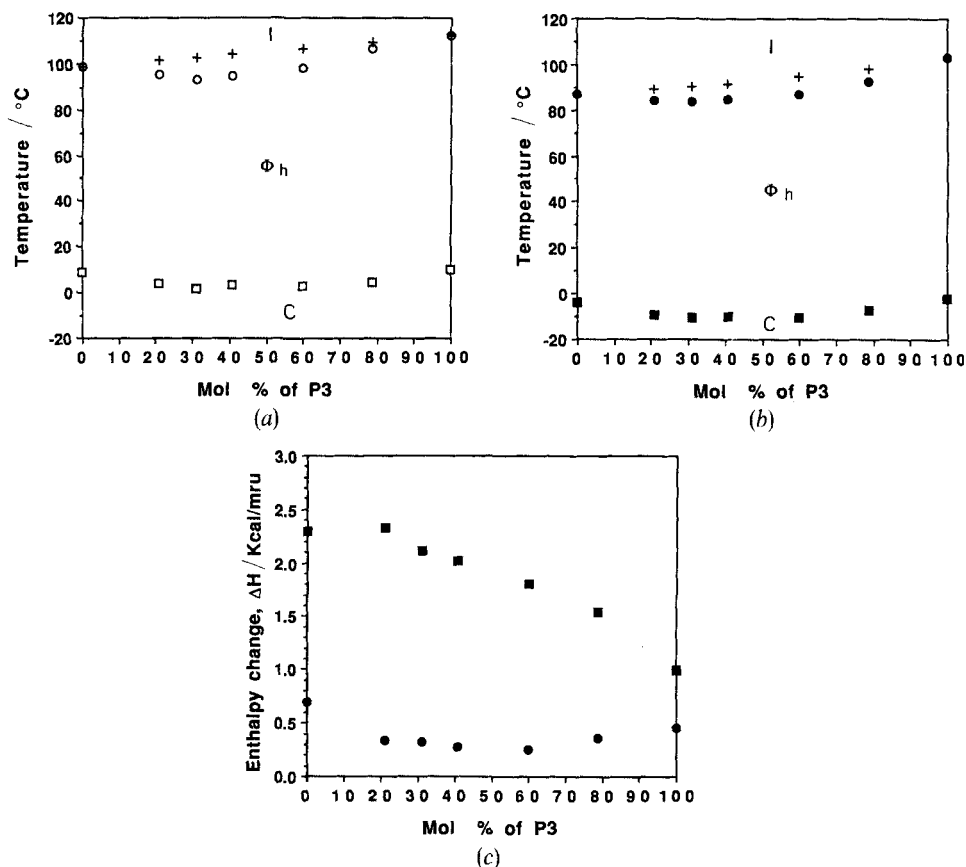


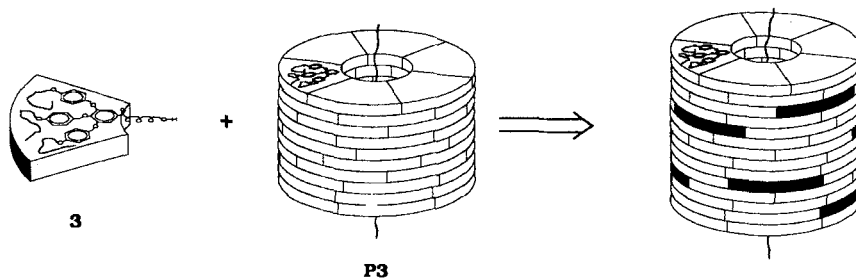
Figure 5. The dependence of phase transition temperatures on composition for the binary mixture of **P3** with **P4**. (a) Second heating scan ( $\square$ ,  $T_{C-\Phi_h}$ ), ( $\circ$ ,  $T_{\Phi_h-\Phi_h}$ ), ( $\circ$ ,  $T_{\Phi_h-I}$ ), (+, calculated by the Schroeder-van Laar equation); (b) First cooling scan ( $\bullet$ ,  $T_{I-\Phi_h}$ ), ( $\blacksquare$ ,  $T_{\Phi_h-C}$ ), (+, calculated by the Schroeder-van Laar equation); (c) The dependence of  $\Delta H$  associated with the transition temperatures of the binary mixture of **P3** with **P4** from a first cooling scan ( $\bullet$ ,  $\Delta H_{I-\Phi_h}$ ), ( $\blacksquare$ ,  $\Delta H_{\Phi_h-C}$ ).

assembly of a single polymer chain, since the possibility of having two polymer chains occupying the inner core of the same column should be both energetically and kinetically unfavourable. Therefore, based on this assumption, columns should be formed from each individual polymer. Consequently, any mixture between polymers **P1** and **P4** should consist of columns of two dissimilar diameters (see table). Scheme 3 represents two extreme situations of binary mixtures **P1** and **P4**. In scheme 3 (a), a small number of larger diameter columns (**P4**) is introduced into the hexagonal arrangement of smaller diameter columns (**P1**). This composition is expected to distort the hexagonal packing as shown by the irregular hexagon drawn in scheme 3. In scheme 3 (b), a small number of smaller diameter columns (**P1**) is introduced into the hexagonal arrangement of larger diameter columns (**P4**). As schematically shown, this composition does not greatly distort the packing in a hexagonal arrangement. Figure 4(c) presents the enthalpy changes associated with the  $T_{I-\Phi_h}$ ,  $T_{\Phi_h-\Phi_h}$  and  $T_{\Phi_h-C}$  transitions obtained from the cooling scans for this binary polymer mixture between **P1** and **P4** as a function of composition.

The thermal transitions of the binary mixture of **P3** and **P4** as a function of mol per cent composition are plotted in figure 5(a) (data from the second heating scan) and figure 5(b) (data from the cooling scan). For all compositions, the two polymers exhibit a single  $\Phi_h$ -I transition on their cooling scans (figure 5(b)). The heating scans of the binary mixtures present a single broad  $\Phi_h$ -I transition, the maximum of which is plotted as a function of mol% composition in **P3** in figure 5(a). The single  $\Phi_h$ -I transition, on both heating and cooling scans, suggests that the two polymers **P3** and **P4**, which form columns with very similar diameters (see table), are isomorphic within the whole range of compositions of their binary mixtures. This is expected, since the introduction of the columns of similar diameter into a hexagonal arrangement should not distort their packing. Figure 5(c) presents the  $\Delta H$  of all transitions, as a function of composition for the binary mixture **P3/P4**, as determined from first cooling scans.

### 3.3. Binary mixture between molecules with tapering shapes and polymethacrylates containing tapering side chains consisting of monoesters of oligoethylene glycol with 3,4,5-tris[4-(*n*-dodecan-1-yloxy)benzyloxy]benzoic acid

The binary mixture of polymer **P3** containing a triethyleneoxide spacer and the hydroxy terminated low molecular weight compound **3**, with the same length of the oligooxyethylene segment, exhibits the phase behaviour presented in figure 6. Up to a composition of about 40 mol% of **3**, a single  $\Phi_h$ -I transition is observed on both heating (figure 6(a)) and cooling (figure 6(b)) scans. This behaviour suggests that the low molecular weight compound **3** becomes intercalated within the column formed by polymer **P3**. Above a composition of about 40 mol%, the excess of **3** that cannot be intercalated within the polymer structure self-assembly, giving rise to a second  $\Phi_h$ -I transition at a lower temperature (figure 6(a), (b)). The previous statement is supported by the fact that this  $\Phi_h$ -I transition remains constant with increasing concentration of **3**. At the same time, the highest temperature  $\Phi_h$ -I transition appears to be constant also above 40 mol% of **3**, suggesting that this value represents the maximum amount of **3** that has been intercalated within the column generated by **P3**. Scheme 4 illustrates the co-assembly of **3** into the column of **P3** via endo-recognition. The enthalpy changes of the  $\Phi_h$ -C and I- $\Phi_h$  transitions determined from the cooling scan are plotted in figure 6(c). The binary mixture between **P2** and **3** behaves in a similar manner as indicated by the data plotted in figure 7(a), (b).



Scheme 4. Schematic representation of the co-assembly of **3** into the column formed by the self-assembly of **P3**.

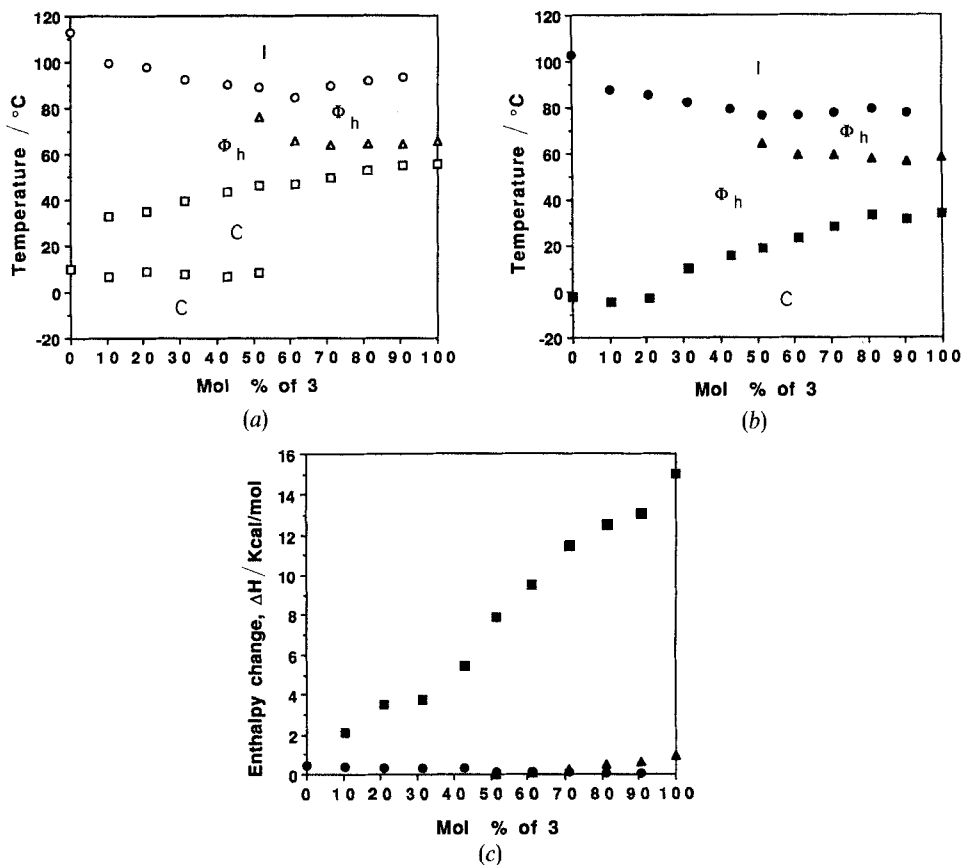


Figure 6. The dependence of phase transition temperatures on composition for the binary mixture of P3 with 3. (a) Second heating scan ( $\square$ ,  $T_{C-C}$ ), ( $\square$ ,  $T_{C-\Phi_h}$ ), ( $\Delta$ ,  $T_{\Phi_h-\Phi_h}$ ), ( $\circ$ ,  $T_{\Phi_h-I}$ ); (b) First cooling scan ( $\bullet$ ,  $T_{I-\Phi_h}$ ), ( $\blacktriangle$ ,  $T_{\Phi_h-\Phi_h}$ ), ( $\blacksquare$ ,  $T_{\Phi_h-C}$ ); (c) The dependence of  $\Delta H$  associated with the transition temperatures of the binary mixture of P3 with 3 from a first cooling scan ( $\bullet$ ,  $\Delta H_{I-\Phi_h}$ ), ( $\blacktriangle$ ,  $\Delta H_{\Phi_h-\Phi_h}$ ), ( $\blacksquare$ ,  $\Delta H_{\Phi_h-C}$ ).

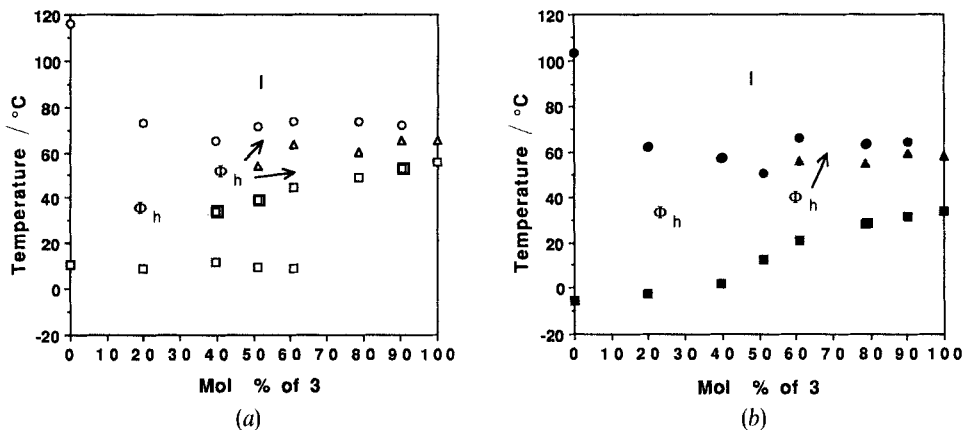


Figure 7. The dependence of phase transition temperatures on composition for the binary mixture of P2 with 3. (a) Second heating scan ( $\square$ ,  $T_{C-C}$ ), ( $\square$ ,  $T_{C-\Phi_h}$ ), ( $\Delta$ ,  $T_{\Phi_h-\Phi_h}$ ), ( $\circ$ ,  $T_{\Phi_h-I}$ ); (b) First cooling scan ( $\bullet$ ,  $T_{I-\Phi_h}$ ), ( $\blacktriangle$ ,  $T_{\Phi_h-\Phi_h}$ ), ( $\blacksquare$ ,  $T_{\Phi_h-C}$ ).

3.4. Ternary mixtures between molecules with tapering shapes and polymethacrylates containing tapering side chains consisting of monoesters of oligoethylene glycol with 3,4,5-tris[4-(*n*-dodecan-yloxy)benzyloxy]benzoic acid and having  $\text{CF}_3\text{SO}_3\text{Li}$  as the third component

The effect of complexation of  $\text{CF}_3\text{SO}_3\text{Li}$  on the phase transitions of a binary mixture containing 10 mol% of **P3** and 90 mol% of **3** is illustrated in figure 8. The uncomplexed mixture of **P3** and **3** exhibits two  $\Phi_{\text{h}}$ -I transitions arising from the columns self-assembled from each individual component (figure 8). The data from the first heating scan are presented in figure 8(a) and resemble the phase behaviour of the pure **3** complexed with  $\text{CF}_3\text{SO}_3\text{Li}$  [18(a)]. This is not unexpected since the binary mixture contains 90 mol% of compound **3**. It also indicates that the ability of **3** to complex  $\text{CF}_3\text{SO}_3\text{Li}$  is much higher than that of **P3**. The complexation ability of the oligooxyethylene group of **3** is higher than that of the corresponding unit of **P3**, most probably due to its higher Lewis base character. Second and subsequent heating scans (figure 8(b)) and first and subsequent cooling scans (figure 8(c)) are different. At low  $\text{CF}_3\text{SO}_3\text{Li}$  concentrations two  $\Phi_{\text{h}}$ -I transitions are observed. The lowest temperature

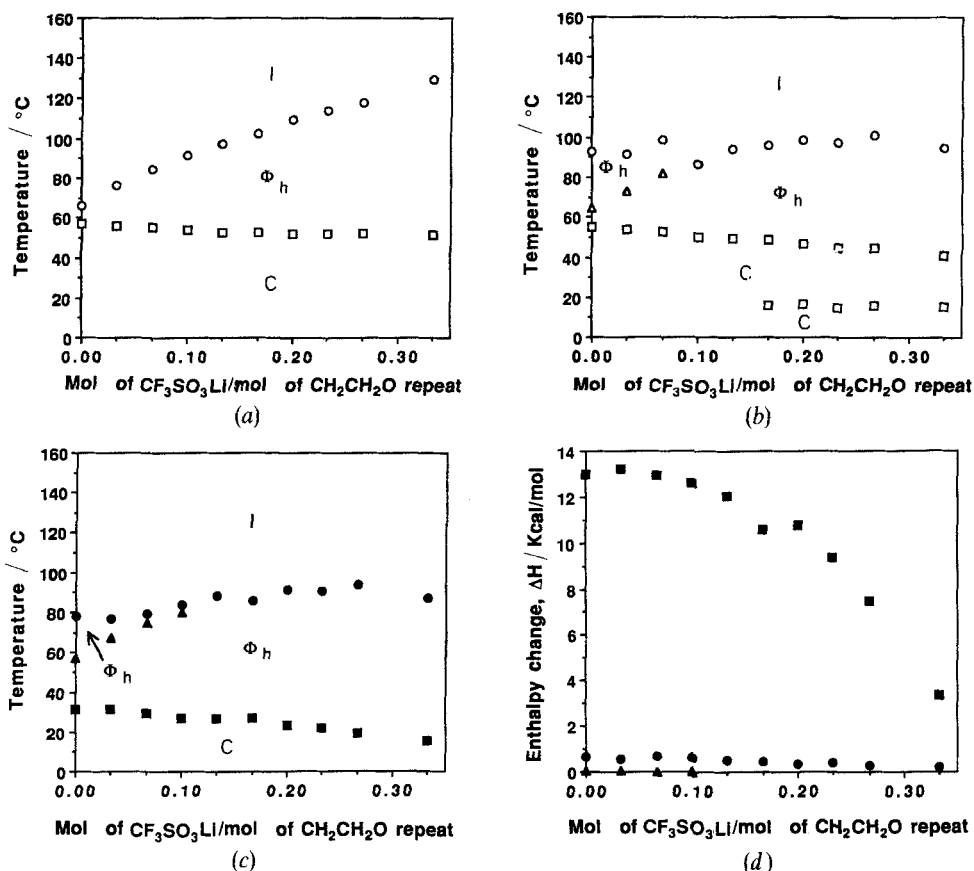


Figure 8. The dependence of phase transition temperatures on the amount of  $\text{CF}_3\text{SO}_3\text{Li}$  in the 10/90 (mol/mol) mixture of **P3** with **3**. (a) First heating scan ( $\square$ ,  $T_{\text{C}-\Phi_{\text{h}}}$ ), ( $\circ$ ,  $T_{\Phi_{\text{h}}-\text{I}}$ ); (b) Second heating scan ( $\square$ ,  $T_{\text{C}-\text{C}}$ ), ( $\square$ ,  $T_{\text{C}-\Phi_{\text{h}}}$ ), ( $\triangle$ ,  $T_{\Phi_{\text{h}}-\Phi_{\text{h}}}$ ), ( $\circ$ ,  $T_{\Phi_{\text{h}}-\text{I}}$ ); (c) First cooling scan ( $\bullet$ ,  $T_{\text{I}-\Phi_{\text{h}}}$ ), ( $\blacktriangle$ ,  $T_{\Phi_{\text{h}}-\Phi_{\text{h}}}$ ), ( $\blacksquare$ ,  $T_{\Phi_{\text{h}}-\text{C}}$ ); (d) The dependence of  $\Delta H$  associated with the phase transitions on the amount of  $\text{CF}_3\text{SO}_3\text{Li}$  in the 10/90 (mol/mol) mixture of **P3** with **3** from a first cooling scan ( $\bullet$ ,  $\Delta H_{\text{I}-\Phi_{\text{h}}}$ ), ( $\blacktriangle$ ,  $\Delta H_{\Phi_{\text{h}}-\Phi_{\text{h}}}$ ), ( $\square$ ,  $\Delta H_{\Phi_{\text{h}}-\text{C}}$ ).

$\Phi_h$  mesophase, attributed to **3**, is affected the most, since its transition temperature clearly increases on increasing the amount of  $\text{CF}_3\text{SO}_3\text{Li}$  (figures 8(b), (c)). At a concentration of 0.1 mol  $\text{CF}_3\text{SO}_3\text{Li}$ /mol of ethyleneoxide repeat unit and above, the two  $\Phi_h$ -I transitions merge into a single one. This transition increases slightly with increase of  $\text{CF}_3\text{SO}_3\text{Li}$  in the mixture and then becomes essentially independent of the amount of  $\text{CF}_3\text{SO}_3\text{Li}$ . This behaviour demonstrates that the introduction of the salt enhances the co-assembly between **P3** and **3** due to complexation. The co-assembly of the tapered **3** into the self-assembled column of **P3** transforms the immiscible mixture of **3** and **P3** into a miscible system. The enthalpy changes ( $\Delta H$ ) of all transitions from the cooling scan of this mixture are plotted in figure 8(d).

### 3.5. Binary mixture between molecules with tapering shapes based on esters of 3,4,5-tris[4-(*n*-dodecan-1-yloxy)benzyloxy]benzoic acid with oligoethylene glycol and 15-crown-5 endo-receptors, and their ternary mixtures with $\text{CF}_3\text{SO}_3\text{Na}$ as the third component

The behaviour of binary mixtures of compounds **2** and **5** was also examined. Compounds **2** and **5** have the same tapered unit but two different endo receptors

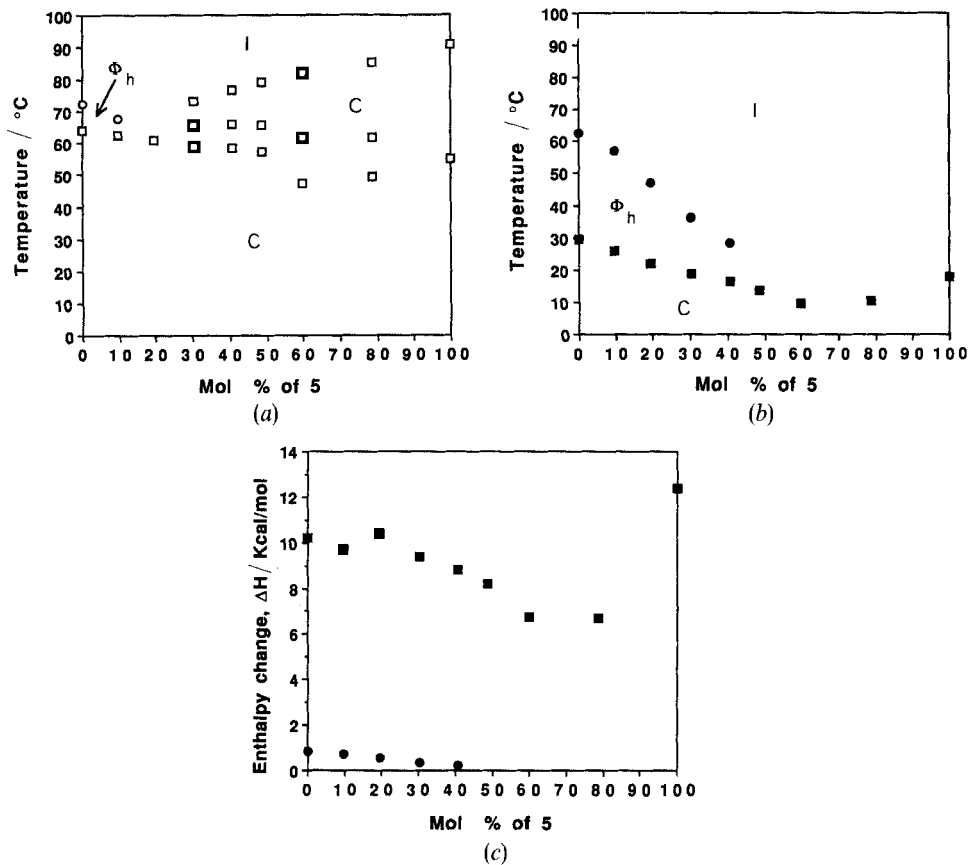


Figure 9. The dependence of phase transition temperatures on composition for the binary mixture of **2** with **5**. (a) Second heating scan ( $\square$ ,  $T_{C-C}$ ), ( $\square$ ,  $T_{C-\Phi_h}$ ), ( $\square$ ,  $T_{C-I}$ ), ( $\circ$ ,  $T_{\Phi_h-I}$ ); (b) First cooling scan ( $\bullet$ ,  $T_{I-\Phi_h}$ ), ( $\blacksquare$ ,  $T_{\Phi_h-C}$ ), ( $\blacksquare$ ,  $T_{I-C}$ ); (c) The dependence of  $\Delta H$  associated with the transition temperatures for the binary mixture of **2** with **5** from a first cooling scan ( $\bullet$ ,  $\Delta H_{I-\Phi_h}$ ), ( $\blacksquare$ ,  $\Delta H_{\Phi_h-C}$ ), ( $\blacksquare$ ,  $\Delta H_{I-C}$ ).

(scheme 1). Compound **2** has a hydroxy terminated diethyleneoxide repeat unit as endo-receptor, while compound **5** has a benzo-15-crown-5 receptor. Compound **2** displays an enantiotropic  $\Phi_h$  mesophase [18 (a)]. In contrast, compound **5** displays a lamellar crystalline phase [17]. The binary mixtures of **2** and **5** exhibit a monotropic  $\Phi_h$  mesophase up to a composition of 40 mol% of **5** (figures 9 (a), (b)). A linear dependence of the I- $\Phi_h$  transition as a function of composition is observed (figure 9 (b)). This suggests that **2** and **5** are isomorphic within the  $\Phi_h$  mesophase. A linear dependence is also observed for the corresponding  $\Delta H_{I-\Phi_h}$  (figure 9 (c)). In their DSC scans, these mixtures exhibit a monotropic  $\Phi_h$  phase and multiple melting transitions which most probably arise from a eutectic mixture (figure 9 (a)). A similar behaviour is observed for the binary mixture of **4** (with a hydroxy terminated tetraethyleneoxide repeat unit segment) and **5** (figures 10 (a), (b), (c)).

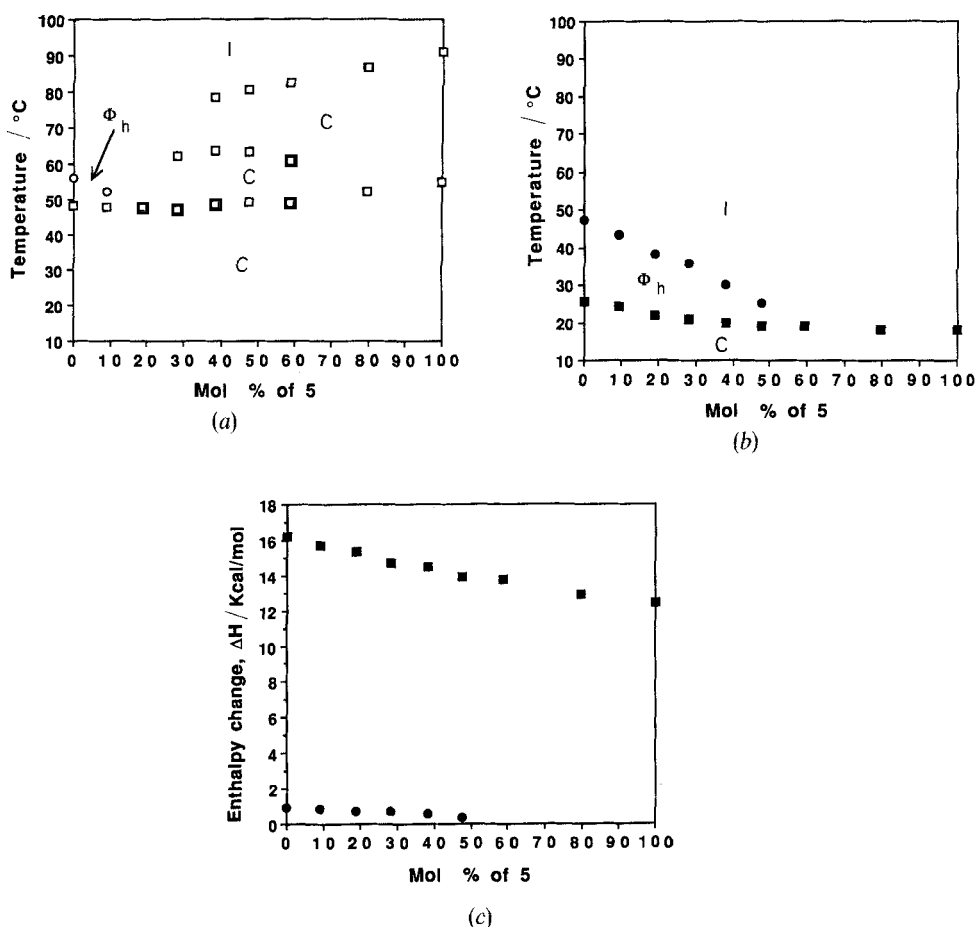


Figure 10. The dependence of phase transition temperatures on composition for the binary mixture of **4** with **5**. (a) Second heating scan ( $\square$ ,  $T_{C-C}$ ), ( $\square$ ,  $T_{C-\Phi_h}$ ), ( $\square$ ,  $T_{C-I}$ ), ( $\circ$ ,  $T_{\Phi_h-I}$ ); (b) First cooling scan ( $\bullet$ ,  $T_{I-\Phi_h}$ ), ( $\blacksquare$ ,  $T_{\Phi_h-C}$ ), ( $\blacksquare$ ,  $T_{I-C}$ ); (c) The dependence of  $\Delta H$  associated with the transition temperatures for the binary mixture of **4** with **5** from a first cooling scan ( $\bullet$ ,  $\Delta H_{I-\Phi_h}$ ), ( $\blacksquare$ ,  $\Delta H_{\Phi_h-C}$ ), ( $\blacksquare$ ,  $\Delta H_{I-C}$ ).



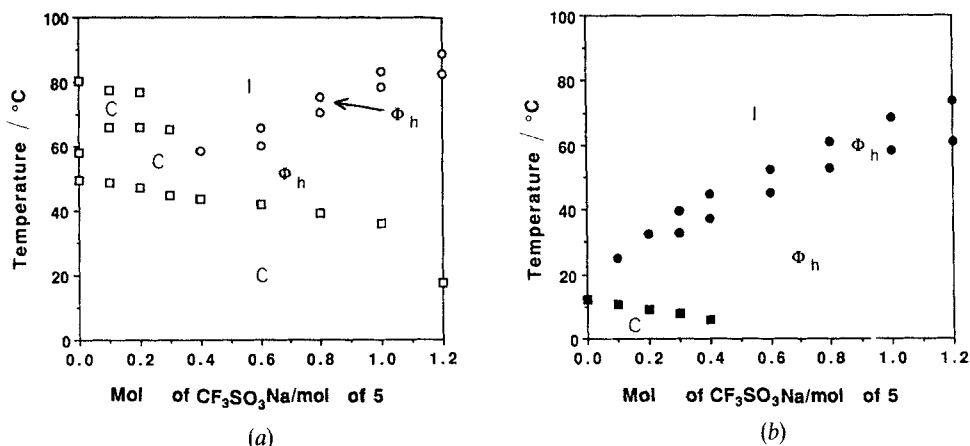


Figure 11. The dependence of phase transition temperatures on the amount of CF<sub>3</sub>SO<sub>3</sub>Na for the 50/50 (mol/mol) mixture of **2** with **5**. (a) Second heating scan (□,  $T_{C-C}$ ), (□,  $T_{C-\Phi_h}$ ), (□,  $T_{C-I}$ ), (○,  $T_{\Phi_h-I}$ ), (○,  $T_{\Phi_h-I}$ ); (b) First cooling scan (●,  $T_{I-\Phi_h}$ ), (●,  $T_{\Phi_h-I}$ ), (■,  $T_{\Phi_h-C}$ ), (■,  $T_{I-C}$ ).

Previous experiments involving the complexation of compound **5** with CF<sub>3</sub>SO<sub>3</sub>Na and CF<sub>3</sub>SO<sub>3</sub>K have shown that the crystalline phase is destabilized upon complexation [17]. In addition, complexation induces its self-assembly into a columnar architecture which generates an enantiotropic Φ<sub>h</sub> mesophase [17]. It was therefore interesting to examine how an equimolar mixture of **5** with **2** behaves upon complexation with CF<sub>3</sub>SO<sub>3</sub>Na. Figures 11(a) and (b) show the phase transition temperatures as a function of the molar content of CF<sub>3</sub>SO<sub>3</sub>Na per mol of **5** obtained from second heating and first cooling DSC scans, respectively. The equimolar mixture of **2** and **5** without CF<sub>3</sub>SO<sub>3</sub>Na is only crystalline. Upon complexation with CF<sub>3</sub>SO<sub>3</sub>Na, a monotropic Φ<sub>h</sub> mesophase is obtained up to 0.2 mol of CF<sub>3</sub>SO<sub>3</sub>Na/mol of **5** (figure 11(b)). Above this value, all mixtures display two distinct Φ<sub>h</sub> mesophases during both heating and cooling scans (figures 11(a),(b)). Although this behaviour is not trivial, it can be explained if one considers the complexing ability of a crown ether in comparison to that of an oligooxyethylene glycol [23]. Since the crown ether is more selective and binds ions much more strongly than the glycol, the phase behaviour of the mixture can be explained by considering the presence of two distinct components. One is the complexed compound **5**, and the other is the mixture of remaining uncomplexed **2** and **5**. Therefore, the single Φ<sub>h</sub> transition present up to a value of 0.2 mol of CF<sub>3</sub>SO<sub>3</sub>Na/mol of **5** arises entirely from the complexed **5**. As the concentration of CF<sub>3</sub>SO<sub>3</sub>Na increases, the relative mol% of **5** in the remaining uncomplexed mixture of **2** and **5** decreases, since free **5** is transformed into complexed **5**. This gives rise to the second Φ<sub>h</sub> mesophase of the mixture of free **5** and **2**, which also increases with the amount of CF<sub>3</sub>SO<sub>3</sub>Na, since the mol% of free **5** decreases at a constant mol% of **2** (the phase behaviour of the mixture of **2** with **5** is presented in figure 9). In addition, the complex between **5** and CF<sub>3</sub>SO<sub>3</sub>Na is very strong and should result in a rigid column. This statement is supported by the fact that complexes of **5** with salt display a glass transition in their DSC scans [17]. The increased rigidity of the column of complexed **5** and the very weak competition of the oligooxyethylene endo-receptor of compound **2**

for  $\text{Na}^+$ , as compared to that of the crown ether receptor of **5**, should prohibit the intercalation of **2** within the column of complexed **5**. This results in the formation of two columns of dissimilar diameters (one consisting of the complex of **5** with  $\text{Na}^+$  and the other consisting of the mixture of **2** and uncomplexed **5**), and consequently, to the observed absence of isomorphism.

#### 4. Conclusions

The present results highlight the effect of structural factors on the isomorphism of self-assembled supramolecular liquid crystals within their hexagonal columnar ( $\Phi_h$ ) mesophases. Our investigation indicates that the primary factors in obtaining isomorphism in binary mixtures is the diameter of the column formed by the self-assembly of the individual compounds, as well as the ability of interaction within the inner core of the columns. Low molecular weight compounds with the same length alkyl tails and segments that can interact in the inner core of the column co-assemble into cylinders which are completely isomorphic within their  $\Phi_h$  phase. In contrast, polymeric compounds are miscible only if their column diameters are approximately the same. When their column diameters are dissimilar, the two polymers are miscible only at low mol% contents of the component forming the smaller diameter column. Mixtures between low molar mass and polymeric components are miscible up to the extent that intercalation of the low molar compound into the polymeric structure is permitted. Mixtures that are immiscible can become miscible by the strength of interaction within the inner core of the columnar architecture. In the present case, this was accomplished by alkali metal salt complexation. Finally, preferential interaction in the inner part of the column of one component in mixtures of low molar mass compounds can induce immiscibility, if the second component can interact only weakly with the first. This was shown by the selective complexation of alkali metal ions by a crown ether moiety compared with the non-selective complexation by an oligoxyethylene glycol moiety. In an unrelated study involving main-chain and side-chain discotic liquid crystalline polymers, the induction of hexagonal columnar mesomorphism and its enhancement, and the induction of compatibility and mesomorphism in an incompatible polymer mixture by electron-donor acceptor interactions were reported [4, 24]. The enhancement of mesomorphism of liquid crystalline polymers through non-covalent interactions was recently reviewed [25].

The present results provide insight in the manipulation of phase transitions in self-assembled liquid crystals displaying columnar hexagonal mesophases. This study is important since it provides complementary information for future research on these supramolecular architectures. As such, one can foresee interest in mesomorphic ionic electrolytes, semiconductor nano-cluster arrays, reactions in spatially confined dipolar solvent media, including polymerization in hexagonal columnar organized phases, etc.

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