行政院國家科學委員會補助專題研究計畫成果報告

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※ 液晶材料研究 ※

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本研究的目的探討 4-烷氧基-4'-苯醯氧基二苯乙烯衍生物其取代基變化時對液晶相的影響。合成最主要系列有五：系列一爲 4-alkyloxy-4'-(4"-alkyloxy benzoyloxy) Stilbene，C_n-p-C_k，主要以二苯乙烯和 4-氧-4'-苯羧酸核心結構之下，改變尾端碳鏈的長短，其中 n=8，k=8,9,10 和 12，液晶相爲 K— N— Sc— K，溫度範圍 105℃－228℃，且層相的溫度範圍佔全部的三分之二到四分之三，可見得核心結構所形成側作用力(side interaction)對整個液晶相的形成影響很大。系列二爲 4-alkyloxy-4'-(3"-alkyloxy benzoyloxy) Stilbene，C_n-m-C_k，其中 n=8 和 12，k=8,9,10 和 12，與系列一比較，主要差異在核心的 3-氧-4'-苯羧酸，因爲尾鏈接在苯環的間位上，造成尾鏈偏離分子主軸，進而擾動鄰近分子的排列，故當 n=8，k=8,9,10 和 12；n=12，k=8 時，液晶相爲單向〈monotropic〉Sc，n=12，k=9,10 和 12 時，液晶相爲雙向〈enantiotropic〉Sc。除此之外，比較苯乙烯砒碇衍生物和 m-CnOBA 的混液晶，在由氫鍵轉變爲 C— O 單鍵時，因爲作用力增強，距離縮短，因此反鐵電性液晶相消失。系列三爲 S-(-)-4-alkyloxy-4'-(4"-(2-methylbutyloxy) benzoyloxy) Stilbene，Cn-p-MBOB*，n=1,8,9,10,12和14，此系列主要是將接在系列一中4-氧-4'-苯羧酸的尾端基改爲 S-(—)-2-甲基丁基，因爲多了旋光基，液晶相的溫度範圍稍微減小爲 216℃— 105℃，液晶相變成了旋光相 N*和 Sc*，而且，N*和 Sc*的溫度範圍比約 1:1，這可能是旋光基擾亂了鄰近分子的排列，擴大向列相的溫度範圍。系列四爲 S-(-)-4-alkyloxy-4'-(4"-(2-methylbutyloxy carbonyl) benzoyloxy) Stilbene，Cn-p-MBT*，與系列三的差異在改變 4-氧-4'-苯羧酸爲對苯二羧醯，改變後的液晶相溫度範圍幾乎一致，但由於酯基的偶極矩大於醚基的偶極矩，故分子的側作用力加強，連同層相的溫度範圍也擴大，其次由於羰基加入，液晶相的序列爲 I－BPⅢ－BPⅡ－BP－Ⅰ－N*－TGB_A－S_A-Sc*-Si*-K，藍相的生成，通常是在分子的扭轉力較大的情況下出現，但在向列相範圍縮小的情形下，仍舊出現藍相。還有 TGB_A 相的生成，應該是在分子的扭轉力和傾向生成層相的作用力，在達到某一平衡時出現，在偏光顯微鏡下，觀察到的紋理圖爲 TGB 相的 filament 結構。系列五爲 s-(+)-4-alkyloxy-4'-(4"-(1-methyl-heptyloxy carbonyl) benzoyloxy) Stilbene，Cn-p-MHT*，將 2-甲基丁基改爲 1-甲基庚基後，首先發現因碳鏈變長，因此向列相消失，液晶相有 S_A、S_{X1}、S_{X2}、S_{X3}、S_{X4}、S_{X5}、S_{X6}、S_{X7}和 S_{X8}，根據 Goodby 等人的研究，在尾端基爲 1-甲基庚基時，通常易生成反鐵電和亞鐵電性液晶，而 Cn-p-MHT*中的 S_X 相中有幾個紋理圖上的疑點，是否就是反鐵電和亞鐵電性液晶，爲我們有興趣的地方。

Five series of mesogenic 4-alkyloxy-4'-benzoyloxy stilbene derivatives were synthesized. Series 1, 4-alkyloxy-4'-(4"-alkyloxy benzoyloxy) stilbene homologues (C_n-p-C_k, where n=8, k=8,9,10 and 12) exhibited enantiotropic nematic (N) and smectic C (S_C) phases in a temperature range of 105 to 228℃. Lateral interactions between the cores played an important role for the S_C phases spaned two thirds or three quarters of the mesophase temperature ranges.

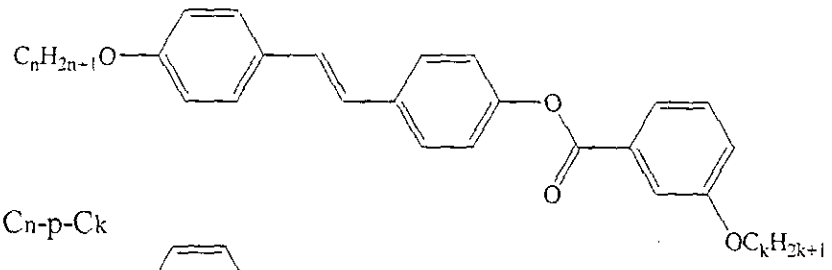
Series 2, 4-alkyloxy-4'-(3"-alkyloxy benzoyloxy) stilbene homologues(C_n-m-C_k), exhibited monotropic Sc phases for n=8 and k=8,9,10 and 12, monotropic Sc phase for n=12 and k=8, and enantiotropic Sc phases for n=12 and k=9,10 and 12. The temperature ranges of mesophases were less than 10℃, it was attributed to the bending of the molecular skeleton because of the attachment of alkyloxy group at the meta-position.

Series 3, S-(−)-4-alkyloxy-4'-(4"-(2-methylbutyloxy) benzoyloxy) stilbene homologues, (C_n-p-MBOB), n=1,8,9,10,12 and 14, exhibited N* and Sc*. The transition temperatures were slightly lower than those of series 1. The ratios of temperature ranges of N* and Sc* were about 1. These variations were attributed to the structural effect of the chiral unit.

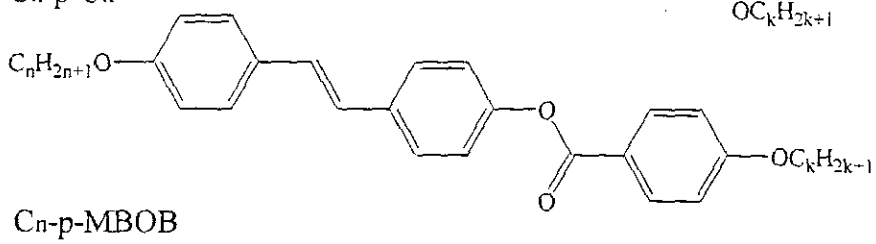
Series 4, S-(−)-4-alkyloxy-4'-(4"-(2-methylbutyloxy carbonyl) benzoyloxy) stilbene homologues (C_n-p-MBT), n=1,2,3,4,5,6,7,8,9,10,12,14 and 16, i.e., the 2-methylbutyloxy group of series 3 was changed to 2-methylbutyloxy carbonyl group. The increment of lateral interaction between molecules due to the extra carbonyl group resulted in wider smectic phase temperature ranges and higher clearing point. More importantly, frustrating phases were observed; I−BP Ⅲ−BP Ⅱ−BP Ⅰ−N*−TGB_A−S_A−Sc*−S_I*−K.

Series 5, S-(−)-4-alkyloxy-4'-(4"-(1-methylheptyloxy carbonyl) benzoyloxy) stilbene homologues, (C_n-p-MHT), n=4,5,6,7,8,9,10 and 12, i.e., the 2-methylbutyloxy group of series 4 was changed to 1-methylheptyloxy group. The enantiotropic phases observed were I− S_A− S_{X1}− S_{X2}− S_{X3}− S_{X4}− K. The blue phase, chiral nematic and TGB_A of series 4 were not observed. This variation was attributed to the stabilization of smectic layers due to the longer terminal chain.

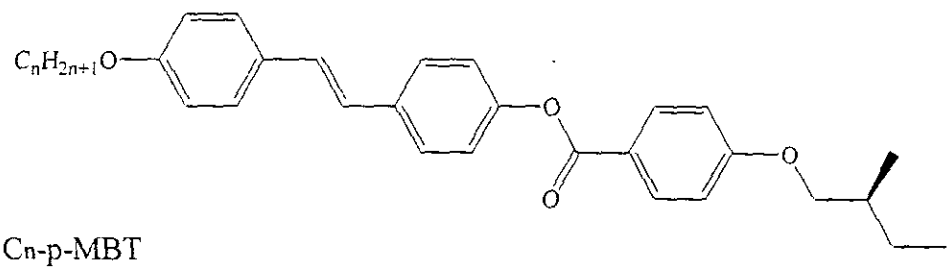
Cn-m-Ck



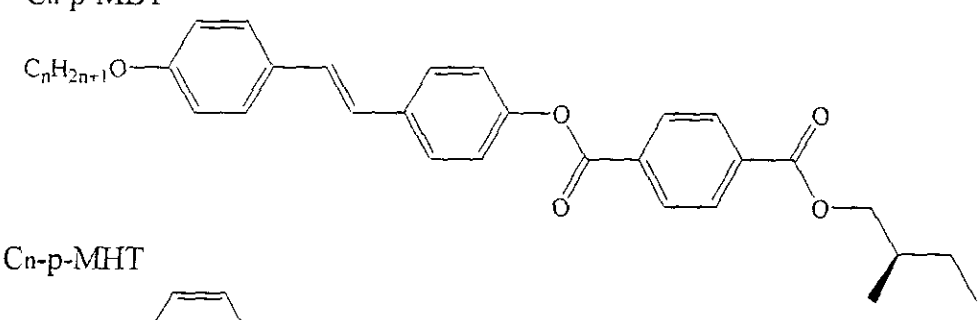
Cn-p-Ck



Cn-p-MBOB



Cn-p-MBT



Cn-p-MHT