[19]中华人民共和国国家知识产权局

[51]Int. Cl[7]
C07C 69/94
C09K 19/20 C07C 69/92
C09K 19/38 C09K 19/32
C09K 19/34

[12]发明专利申请公开说明书

[21]申请号 99809148.0

[43]公开日 2001年9月5日

[11]公开号 CN 1311768A

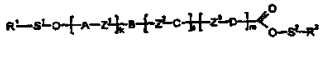
[22]申请日 1999.7.19 [21]申请号 99809148.0
[30]优先权
[32]1998.7.24 [33]CH [31]1564/1998
[86]国际申请 PCT/IB99/01294 1999.7.19
[87]国际公布 WO00/05189 英 2000.2.3
[85]进入国家阶段日期 2001.1.23
[71]申请人 罗利克有限公司
地址 瑞士楚格
[72]发明人 A·欧勒马奇尔 C·博内克
K·施密特
[74]专利代理机构 中国国际贸易促进委员会专利商标事务所
代理人 林柏楠

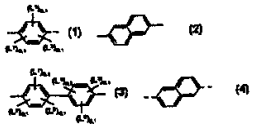
权利要求书10页 说明书40页 附图页数0页

[54]发明名称 可交联的液晶化合物

[57]摘要

式(Ⅰ)表示的化合物,其中A、C和D代表(1)或(2),B代表(3)或(4),其中这些结构中至少一个取代基不是氢,并且至少一个亚苯基环可被1,4-亚苯基环替代,此1,4一亚苯基环上一个或两个不相邻的CH基团已被氮替代;k、l、m是0或1,其中k+l+m必须等于1或2;Z^1、Z^2、Z^3各自独立代表单键、$-CH_2CH_2-$,$-CH_2O-$,$-OCH_2-$,$-COO-$,$-OOC-$,$-CH=CH-COO-$,$-OOC-CH=CH-$,$-(CH_2)_4-$,$-O(CH_2)_3-$、$-O(CH_2)_3O-$或$-C\equiv C-$;R^1、R^2代表可交联的基团,S^1、S^2代表间隔单元。

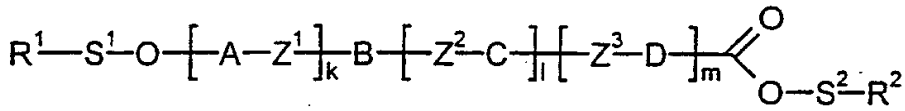




ISSN1008-4274

权 利 要 求 书

1. 通式 I 的一种化合物:



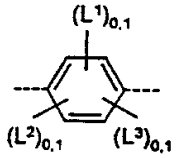
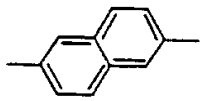
I

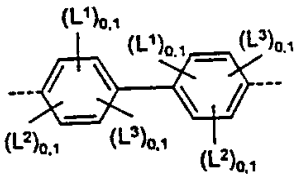
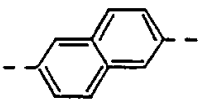
其中

R^1、R^2 各自独立代表可交联的基团;

S^1、S^2 各自独立代表间隔基团;

前提为 R^1-S^1 和 R^2-S^2 不包含任何-O-O-或-N-O-基团;

A、C、和 D 代表  或  ;

B 代表  或  ;

其中 A、B、C 或 D 中至少一个亚苯基环可被 1, 4-亚苯基环替代, 该 1, 4 亚苯基环中一个或两个不相邻的 CH 基团已被氮替代; 并且

L^1, L^2, L^3 各自独立代表氢, C_1-C_{20} 烷基, C_2-C_{20} 烯基, C_1-C_{20} 烷氧基, C_2-C_{20} 烯氧基, C_1-C_{20} 烷氧羰基, 甲酰基, C_1-C_{20} 烷基羰基, C_1-C_{20} 烷基羰氧基或硝基,

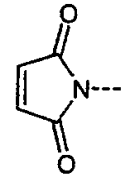
前提为在 A、B、C 或 D 中至少一个亚苯基环上, 上述取代基之一不是氢;

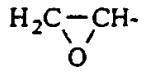
k, l, m 为 0 或 1, 其中 k+l+m 必须等于 1 或 2; 并且

Z^1, Z^2, Z^3 各自独立代表单键、$-CH_2CH_2-$、$-CH_2O-$、$-OCH_2-$、-COO-、-OOC-、-CH=CH-COO-、-OOC-CH=CH-、、$-(CH_2)_4-$、$-O(CH_2)_3-$、$-(CH_2)_3O-$或$-C\equiv C-$。

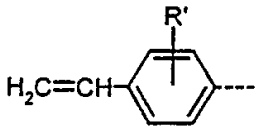
2. 根据权利要求 1 所述的化合物，其中

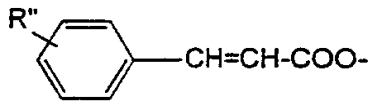
R^1、R^2 各自独立代表 CH_2=CH-、CH_2=CH-COO-、CH_2=C（CH_3）-COO-、CH_2=C（Cl）-COO-、CH_2= C（Ph）-COO-、CH_2=CH-COO-Ph-、CH_2=CH-CO-NH-、CH_2=C（CH_3）-CONH-、CH_2=C（Cl）-CONH-、CH_2=C（Ph）-CONH-、CH_2=C（COOR'）-CH_2-COO-、（R'OOC）-CH_2-C=CH_2-COO-、CH_2=CH-O-、CH_2=CH-OOC-、CH=CH-Ph-、顺式或反式-HOO-CR'=CR'-COO-、硅氧烷，



，


，



或


，

其中（Ph）代表苯基，Ph 代表亚苯基，R'代表低级烷基，R"代表甲基、甲氧基、氰基或卤素。

3. 根据权利要求 1 或 2 所述的化合物，其中

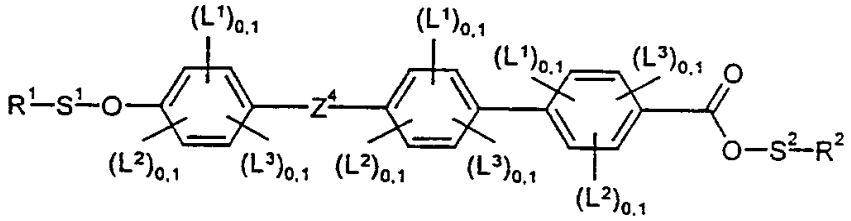
S^1、S^2 各自独立代表间隔单元，例如可任选被氟单取代或多取代的直链或支化亚烷基-（CH_2）$_r$-；或-（（CH_2）$_2$-O）$_r$-；或者可任选被氟单取代或多取代的链-（CH_2）$_r$-Y-（CH_2）$_s$-，其中 Y 是单键或连接官能团。

4. 根据权利要求 3 所述的化合物，其中

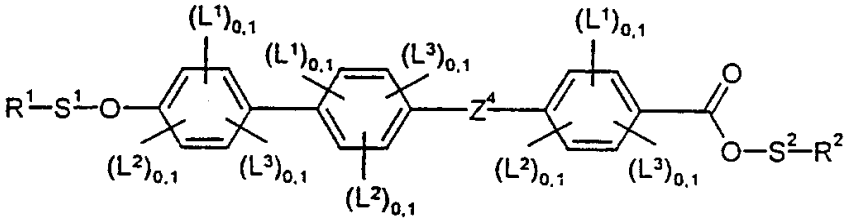
Y 是连接官能团，包含-O-、-COO-、-OOC-、-NR^3-、-NR^3-CO-、-CO-NR^3-、-NR^3-COO-、-OCO-NR^3-、-NR^3-CO-NR^3-、-O-OC-O-、-CH=CH-、-C≡C-，其中 R^3 代表氢或低级烷基，r 和 s 分别是从 0 到 20 的整数，前提是 2 ≤ r+s ≤ 20；或者-（Si[$(CH_3)_2$]O）$_u$-、-O$(CH_2)_t$(Si[$(CH_3)_2$]O)$_u$Si[$(CH_3)_2$]$(CH_2)_t$O-，或

$-NH(CH_2)_t(Si[(CH_3)_2]O)_uSi[(CH_3)_2](CH_2)_tNH-$，其中 t 是从 1 到 12 的整数，而 u 是从 1 到 16 的整数，前提为 $2t+u \leqslant 20$;

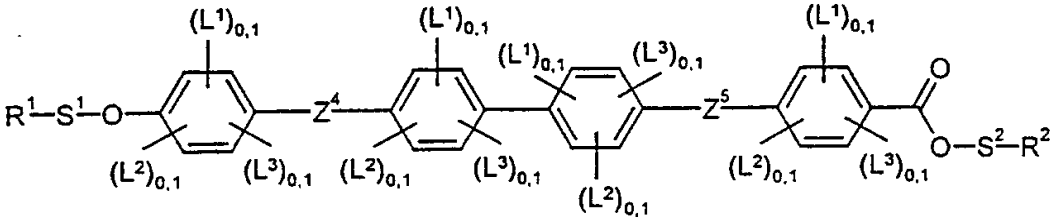
5. 根据前面任一权利要求所述的式 I -A 到 I -G 的化合物，



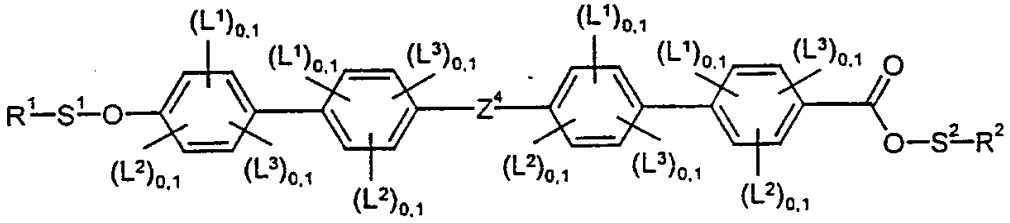
I-A



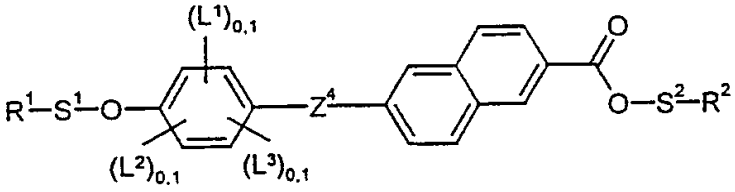
I-B



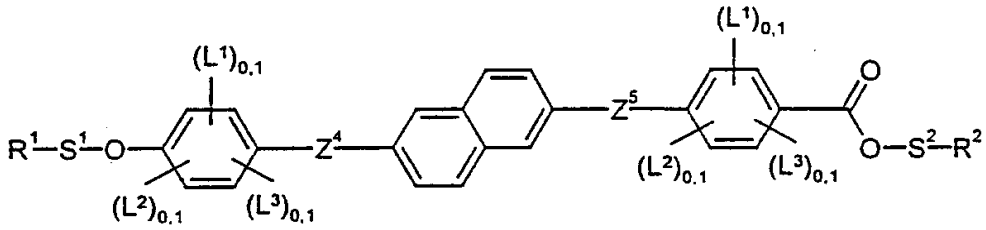
I-C



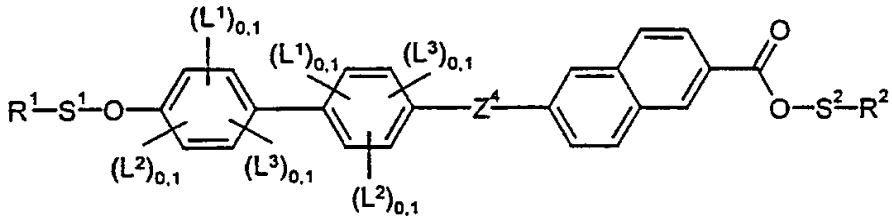
I-D



I-E



I-F



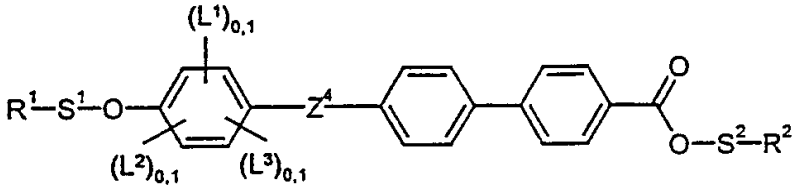
I-G

其中

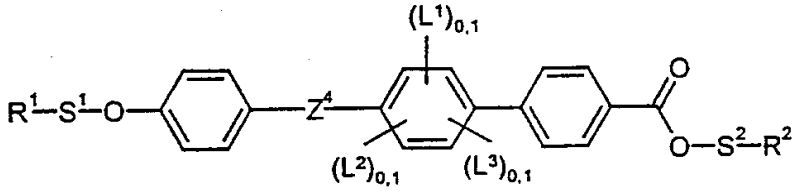
Z^4、Z^5 各自独立代表单键、-C≡C-、-COO-或-CH=CH-COO-；并且

R^1、R^2、S^1、S^2、L^1、L^2和L^3如权利要求 1 中所定义。

6. 根据前面任一权利要求所述的式 I -A-1 和 I -A-2 的化合物，



I-A-1



I-A-2

其中

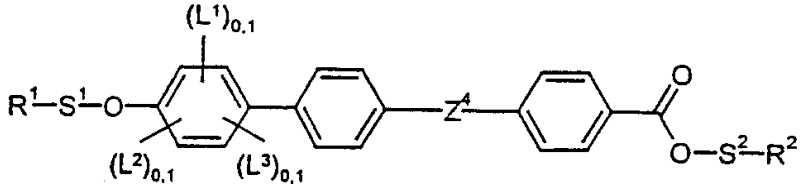
L^1、L^2、L^3 各自独立代表氢、C_1-C_{20} 烷基、C_2-C_{20} 烯基、C_1-C_{20} 烷氧

基或 C_2-C_{20} 烯氧基，其中至少一个取代基必须不是氢；

Z^4 代表-C≡C-、-COO-、-CH=CH-COO-；特别是-COO-或-CH=CH-COO-，更特别是-COO-；并且

R^1、R^2、S^1 和 S^2 如权利要求 1 中所定义。

7. 根据权利要求 1-5 任一项所述的式 I -B-1 化合物，



I-B-1

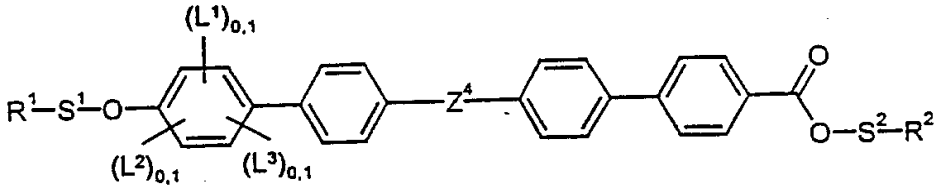
其中

L^1、L^2、L^3 各自独立代表氢、C_1-C_{20} 烷基、C_2-C_{20} 烯基、C_1-C_{20} 烷氧基或 C_2-C_{20} 烯氧基，其中至少一个取代基必须不是氢；

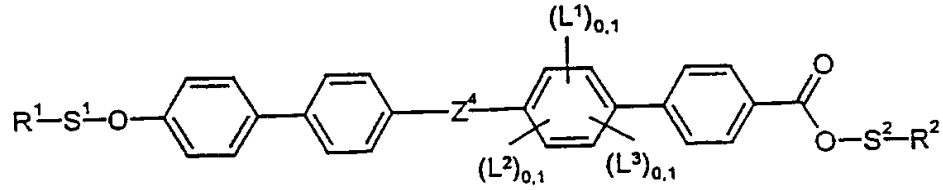
Z^4 代表-C≡C-、-COO-、-CH=CH-COO-；特别是-COO-或-CH=CH-COO-，更特别是-COO-；并且

R^1、R^2、S^1 和 S^2 如权利要求 1 中所定义。

8. 根据权利要求 1-5 任一项所述的式 I -D-1 和 I -D-2 化合物



I-D-1



I-D-2

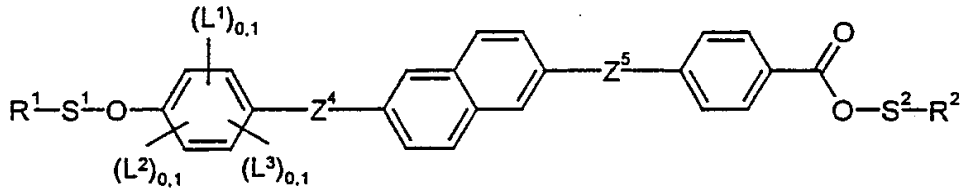
其中

L^1、L^2、L^3 各自独立代表氢、C_1-C_{20} 烷基、C_6-C_{20} 烯基、C_1-C_{20} 烷氧基或 C_2-C_{20} 烯氧基，其中至少一个取代基必须不是氢；

Z^4 代表-C≡C-、-COO-、-CH=CH-COO-；并且

R^1、R^2、S^1 和 S^2 如权利要求 1 中所定义。

9. 根据权利要求 1-5 任一项所述的式 I -F-1 化合物



I-F-1

其中

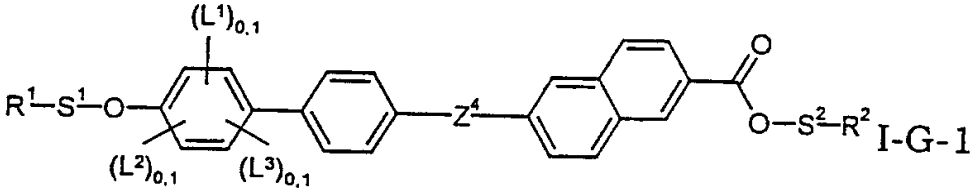
L^1、L^2、L^3 各自独立代表氢、C_1-C_{20} 烷基、C_2-C_{20} 烯基、C_1-C_{20} 烷氧基或 C_2-C_{20} 烯氧基，其中至少一个取代基必须不是氢；

Z^4 代表-C≡C-、-COO-或-CH=CH-COO-；

Z^5 代表单键、-COO-或-CH=CH-COO-；并且

R^1、R^2、S^1 和 S^2 如权利要求 1 中所定义。

10. 根据权利要求 1-5 任一项所述的式 I -G-1 化合物



I-G-1

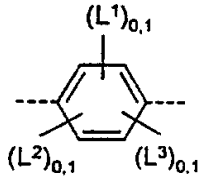
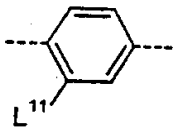
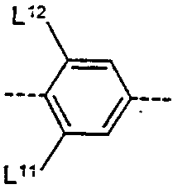
其中

L^1、L^2、L^3 各自独立代表氢、C_1-C_{20} 烷基、C_2-C_{20} 烯基、C_1-C_{20} 烷氧基或 C_2-C_{20} 烯氧基，其中至少一个取代基必须不是氢；

Z^4 代表-C≡C-、-COO-、-CH=CH-COO-；并且

R^1、R^2、S^1 和 S^2 如权利要求 1 中所定义。

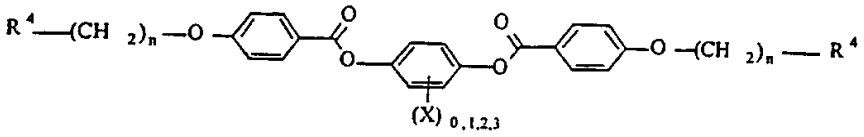
11. 根据权利要求 6-10 中任一项所述的化合物，其中

基团  定义为  或  ，

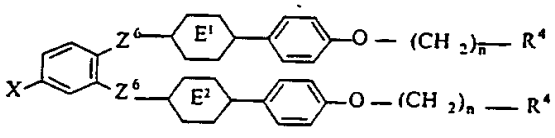
其中 L^{11}、L^{12} 各自独立代表 C_1-C_{20} 烷基、C_2-C_{20} 烯基、C_1-C_{20} 烷氧基或 C_2-C_{20} 烯氧基。

12. 一种可交联的液晶混合物，它包含至少两种组分，其中至少一种是权利要求 1-11 任一项所述的化合物。

13. 根据权利要求 12 所述的可交联液晶混合物，其特征在于除包含根据权利要求 1-11 中的一项或多项所述的一种或多种化合物外，它们还包含下面通式所示的一种或多种化合物

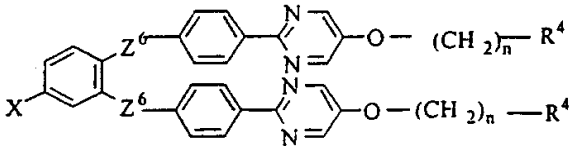


II

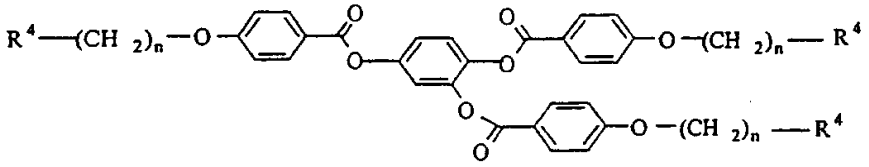


III

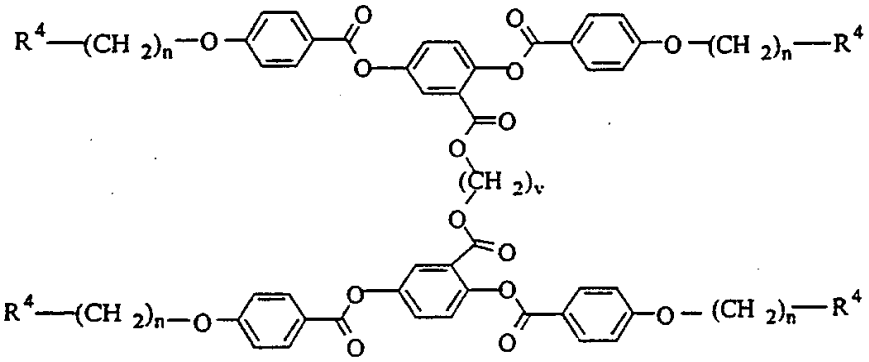
01.01.23



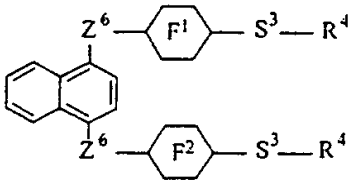
IV



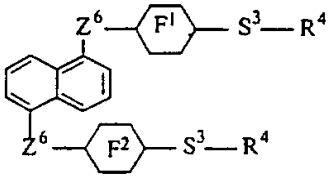
V



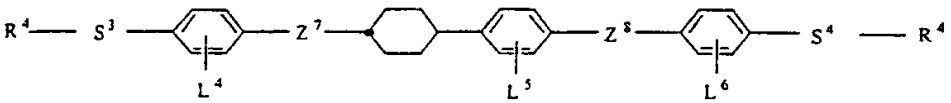
VI



VII



VIII



IX

其中

R^4代表可聚合的基团；

S^3、S^4 各自独立代表-（CH_2）$_n$-或-O（CH_2）$_n$-；

E^1、E^2 各自独立代表1，4-亚苯基、反式1，4-亚环己基、吡啶2，5-二基，嘧啶2，5-二基或反式1，4-亚环己基-1，4-亚苯基；

F^1、F^2 各自独立代表1，4-亚苯基或2-或3-氟-1，4-亚苯基；

L^4、L^5、L^6 各自独立代表氢、C_1-C_{20}烷基、C_2-C_{20}烯基、C_1-C_{20}烷氧基、C_1-C_{20}烷氧羰基、甲酰基、C_1-C_{20}烷基羰基、C_1-C_{20}烷基羰氧基、卤素、氰基或硝基；

每个Z^6 独立代表-COO-、-OOC-、-OCH_2-、-CH_2O-、-O（CH_2）$_3$-、-OOC（CH_2）$_2$-或-COO（CH_2）$_3$-；

Z^7代表单键、-CH_2CH_2-、-CH_2O-、-OCH_2-、-COO-、-OOC-、-（CH_2）$_4$-、-O（CH_2）$_3$-、-（CH_2）$_3$ O -或-C≡C-；

Z^8代表单键、-CH_2CH_2-、-CH_2O-、-OCH_2-、-COO-、-OOC-或-C≡C-；

每个X 独立代表氢、C_1-C_{20}烷基、C_2-C_{20}烯基、C_1-C_{20}烷氧基、C_1-C_{20}烷氧羰基、甲酰基、C_1-C_{20}烷基羰基、C_1-C_{20}烷基羰氧基、氟、氯、溴、氰基或硝基；

每个n各自独立是从2到20的整数；并且

v 是从2到12的整数。

14. 根据权利要求13所述的可交联液晶混合物

其中

R^4代表可聚合的基团，包括 CH_2=CH-、CH_2=CH-O-、CH_2=CH-COO-、CH_2=C（CH_3）-COO-、CH_2=C（Cl）-COO-或  。

15. 一种光学或光电装置，包含根据权利要求1-11中任一项所述的化合物。

16. 一种光学或光电装置，包含根据权利要求12-14中任一项所

述的可交联液晶混合物。

17. 根据权利要求 1-11 中任一项所述的化合物在交联状态下用于光学或光电装置的应用。

18. 根据权利要求 12-14 中任一项所述的可交联液晶混合物用于光学或光电装置的应用。

说　明　书

可交联的液晶化合物

本发明涉及可交联的，特别是光致交联的，二官能度液晶化合物和包含这种化合物的液晶混合物及其在交联状态下作为光学元件的应用。

含有适量光引发剂的光致交联液晶化合物能够在基底上，或者以适当取向层的方式在晶胞内，或者在力场中取向，并且随后能在这种状态下通过适当波长的光辐射而交联。所得到的结构甚至能在高温下保持不变。由此，就可以制得光学元件，例如波导仪、光栅、滤波器和减速器、压电元件及具有非线性光学(NLO)性质的元件等等。这些光学元件可以应用于如频率加倍（SHG）或滤色器等方面。

进一步的性质，例如双折射、折光率、透明度等必须根据应用领域而满足不同的要求。例如，滤光片材料应当兼有高的双折射Δn 和低的散射 n=f（λ）。

可聚合的液晶(即可交联的液晶)除了作为光学元件这种通常的用途外，这类液晶材料还适用于涂覆光数据传输用的玻璃纤维。使用这类材料增加了纤维纵轴上的弹性模量，降低热膨胀系数，并且减少微观变形损失。这样就增加了机械稳定性。此外，可交联的液晶具有各向异性的热导率，能使热量沿一定的方向传递。

可交联的液晶必须具有好的化学和热稳定性，在常用溶剂中好的溶解性以及对电场和电磁辐射的良好稳定性。它们应该在大约 25℃至+100℃，尤其从约 25℃至+80℃的温度范围内有适宜的介晶相。另一重要的方面是各组分之间要有好的溶混性，因为通常以几种组分的混合物形式来使用液晶。

此外，用于光延迟器，偏振干涉滤光片（例如 Solc 滤光片）等时，具有尽可能大的光学各向异性（$\Delta n=|n_e-n_o|$）、且同时具有尽可能短的吸收波长是必要的。由此，就可以通过足够薄的 LCP 膜得到预期的光

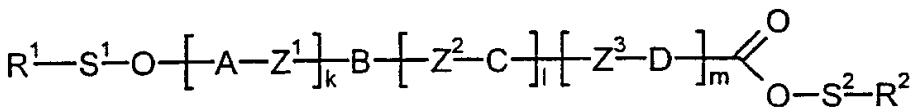
延迟器（LCP 代表‘液晶聚合物’）。同样也可用于胆甾滤光片，因为选择性反射频带宽度与光学各向异性Δn 成比例。

传统的光化学可齐聚或可聚合的液晶通常具有高的熔点和高的澄清点及中等的光学各向异性。首先，高熔点的不利之处是加工过程中在温度刚超过熔点时就会过早地发生自发的热聚合。这种自发聚合会引起畴的形成，导致生成的交联层的光学和热性能严重受损。第二，熔点和澄清点之间小的温差会导致低的有序度，进而引起的低的各向异性程度。可通过制备包括数种组分的复杂混合物来降低熔点，这使得加工可在较低的温度下进行，但可能会有传统的可聚合液晶结晶的危险。例如，在 EP-A-0 331 233 中描述了光化学可齐聚或可聚合的化合物。

因此本发明的目的在于提供可齐聚或可聚合（即可交联）的化合物，其自身或在混合物中同时具有尽可能大的各向异性和尽可能短的吸收波长，尤其是在用于光学元件时。它们还应具有低的熔点和高的澄清点，以便在加工过程中温度刚超过熔点时得到具有尽可能高的有序度及由此引起的光学各向异性程度高的 LCP 膜。进一步，不通过畴而取向和构成化合物也是可能的，并且它们还应在交联状态具有优异的热稳定性和长期稳定性。传统的光化学可齐聚或可聚合的液晶通常只有中等的光学各向异性。

本发明现在提供化合物，它们作为单独组分或作为液晶混合物的组分非常适用于上述应用。

本发明涉及通式 I 的化合物：

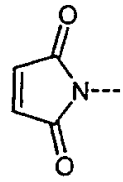


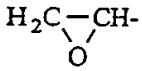
I

其中

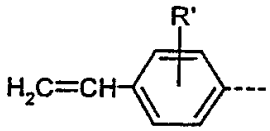
R^1、R^2 各自独立代表可交联的基团，例如 CH_2=CH-、CH_2=CH-COO-、CH_2=C(CH_3)-COO-、CH_2=C(Cl)-COO-、CH_2=C(Ph)-COO-、CH_2=CH-COO-Ph-、CH_2=CH-CO-NH-、CH_2=C (CH_3) -CONH-、CH_2=C (Cl) -CONH-、CH_2=C (Ph)

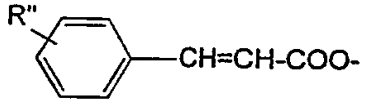
-CONH-、CH_2=C(COOR')-CH_2-COO-、(R'OOC)-CH_2-C=CH_2-COO-、CH_2=CH-O-、CH_2=CH-OOC-、CH=CH-Ph-、顺式或反式-HOO-CR'=CR'-COO-、硅氧烷，



，


，





，

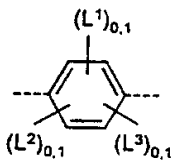
或

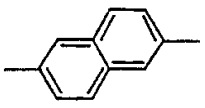
其中（Ph）代表苯基，Ph 代表亚苯基，R'代表低级烷基，R"代表甲基、甲氧基、氰基或卤素；

S^1、S^2 各自独立代表间隔单元，例如可任选被氟单取代或多取代的直链或支化亚烷基-$(CH_2)_r$-；或-$((CH_2)_2$-O$)_r$-；或者可任选被氟单取代或多取代的链-$(CH_2)_r$-Y-$(CH_2)_s$-，其中 Y 是单键或连接官能团，例如 -O-、-COO-、-OOC-、-NR^3-、-NR^3-CO-、-CO-NR^3-、-NR^3-COO-、-OCO-NR^3-、-NR^3-CO-NR^3-、-O-OC-O-、-CH=CH-、-C≡C-，其中 R^3 代表氢或低级烷基，r 和 s 分别是从 0 到 20 的整数，前提是 $2 \leqslant r+s \leqslant 20$；或者-$(Si[(CH_3)_2]O)_u$-、-O$(CH_2)_t(Si[(CH_3)_2]O)_uSi[(CH_3)_2](CH_2)_tO$-，或-NH$(CH_2)_t(Si[(CH_3)_2]O)_uSi[(CH_3)_2](CH_2)_tNH$-，其中 t 是从 1 到 12 的整数，而 u 是从 1 到 16 的整数，前提为 $2t+u \leqslant 20$；

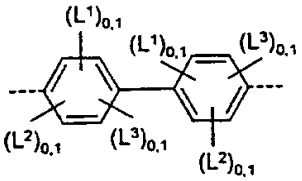
上述的前提是：R^1-S^1 和 R^2-S^2 不含有任何-O-O-或-N-O-基团；

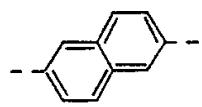
A、C 和 D代表



或

；

B 代表



或

；

其中 A、B、C 或 D 中的至少一个亚苯基环可被 1，4-亚苯基环所替代，该 1,4 - 亚苯基环上的一个或两个不相邻的 CH 基团已被氮替代；并且

L^1，L^2，L^3 各自独立代表氢、C_1-C_{20} 烷基、C_2-C_{20} 烯基、C_1-C_{20} 烷氧基、C_2-C_{20} 烯氧基、C_1-C_{20} 烷氧羰基、甲酰基、C_1-C_{20} 烷基羰基、C_1-C_{20} 烷基羰氧基或硝基，

前提是在 A、B、C 或 D 中至少一个亚苯基环上，上述取代基之一不是氢；

k、l、m 为 0 或 1，其中 k+l+m 必须等于 1 或 2；并且

Z^1、Z^2、Z^3 各自独立代表单键、$-CH_2CH_2-$、$-CH_2O-$、$-OCH_2-$、-COO-、-OOC-、-CH=CH-COO-、-OOC-CH=CH-、$-(CH_2)_4-$、$-O(CH_2)_3-$、$-O(CH_2)_3O-$或-C≡C-。

在本申请的结构式中，虚线（---或------）表示通过单键与相邻元素键接。

必要时，以上用到的术语将在下文中解释。

在本发明上下文中，“卤素”包括氟、氯、溴、碘，尤其是指氟和氯。

在本发明上下文中，“低级烷基”代表含 1-4 个碳原子的直链或支化烷基基团，例如甲基、乙基、丙基、丁基、异丙基、异丁基、叔丁基，但尤其是指甲基、乙基、丙基或丁基。

在本发明上下文中，术语 C_1-C_{20} 烷基、C_1-C_{20} 烷氧基、C_1-C_{20} 烷氧羰基、C_1-C_{20} 烷基羰基、C_1-C_{20} 烷基羰氧基包括含最多 20 个碳原子的直链或支化饱和烃基，例如甲基、乙基、丙基、丁基、戊基、己基、庚基、辛基、壬基、癸基、十一烷基、十二烷基、甲氧基、乙氧基、正丙氧基、异丙氧基、丁氧基、戊氧基、己氧基、庚氧基、辛氧基、壬氧基、癸氧基、十一烷氧基、十二烷氧基、甲氧羰基、乙氧羰基、丙氧羰基、丁氧羰基、戊氧羰基、己氧羰基、辛氧羰基、壬氧羰基、癸氧羰基、十一烷氧羰基、十二烷氧羰基、甲基羰基、乙基羰基、丙基羰基、丁基羰基、戊基羰基、己基羰基、辛基羰基、壬基羰基、癸基羰基、十

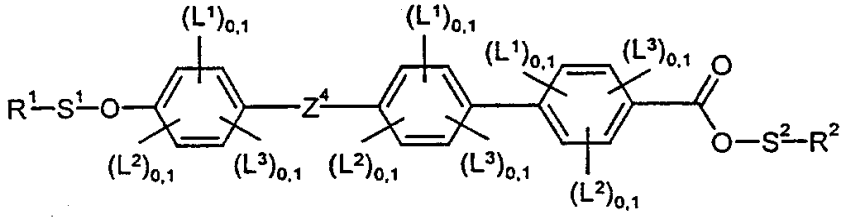
一烷基羰基、十二烷基羰基、甲基羰氧基、乙基羰氧基、丙基羰氧基、丁基羰氧基、戊基羰氧基、己基羰氧基、辛基羰氧基、壬基羰氧基、癸基羰氧基、十一烷基羰氧基、十二烷基羰氧基等。

本发明上下文中，术语 C_2-C_{20} 烯基和 C_2-C_{20} 烯氧基包括含 2-20 个碳原子的烯基，例如 2-烯基、3-烯基、4-烯基；和链端为双键的烯基，例如烯丙基、3-丁烯基、4-戊烯基、5-己烯基、6-庚烯基、7-辛烯基、8-壬烯基、9-癸烯基、10-十一烯基、烯丙氧基、3-丁烯氧基、4-戊烯氧基、5-戊烯氧基、6-庚烯氧基、7-辛烯氧基、8-壬烯氧基、9-癸烯氧基、10-十一烯氧基等。

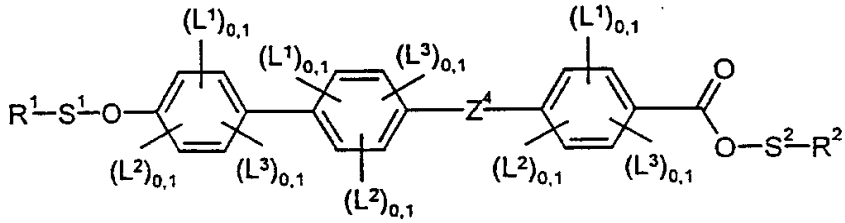
当 L^1、L^2、L^3 中任意一个代表 C_2-C_{20} 烯氧基时，它或者是可聚合的基团，其中带双键的碳原子直接与氧原子相连，即双键在 1-位；或者是 C_3-C_{20} 烯氧基，其中带双键的碳原子不直接和氧原子相连。

上述化合物具有相当高的光学各向异性程度（Δn）。而且，作为适当混合物中的组分，它们会在取向层上引起高的取向能力，这一点非常重要，比如有利于形成好的对比度。

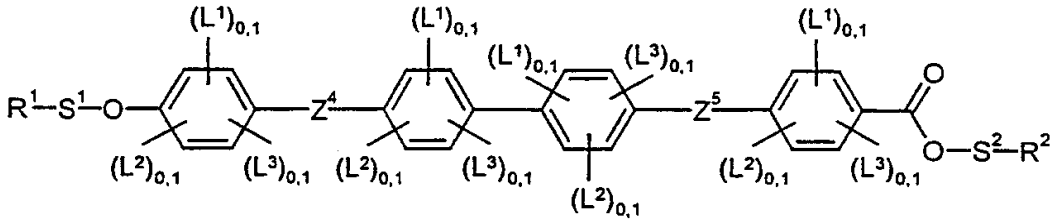
式 I 的优选化合物是式 I -A 到 I -G 的化合物



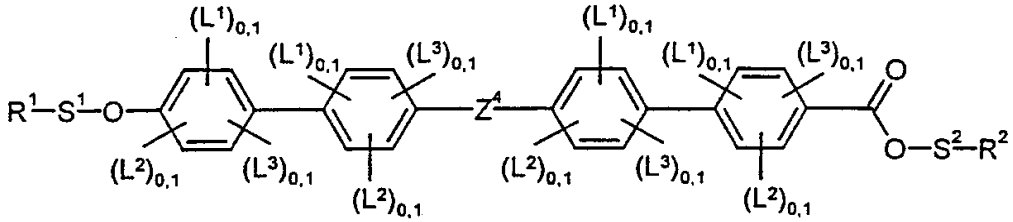
I-A



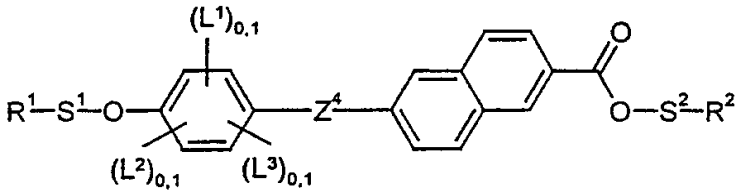
I-B



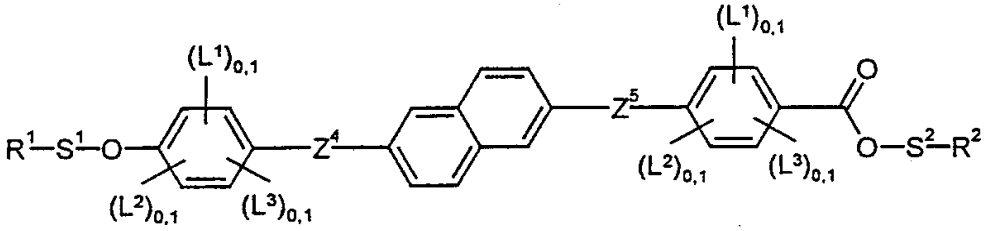
I-C



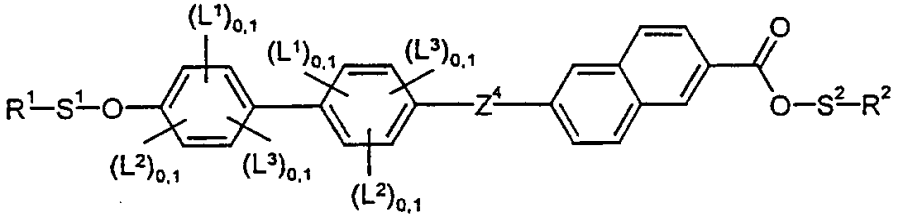
I-D



I-E



I-F



I-G

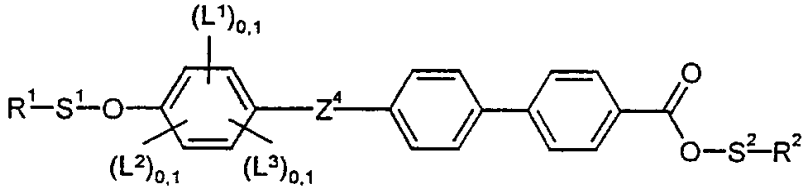
其中

Z^4，Z^5 各自独立代表单键、-C≡C-、-COO-或-CH=CH-COO-；并且

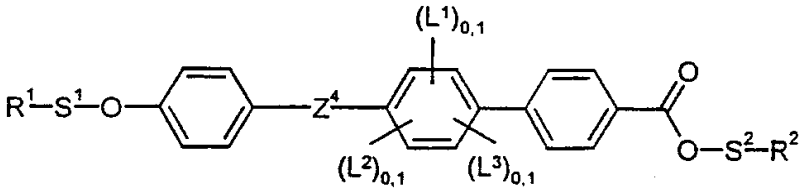
R^1、R^2、S^1、S^2、L^1、L^2和L^3如式 I 所定义。

特别优选式 I -A、I -B、I -D、I -F 和 I -G 的化合物。

式 I -A 的化合物中，特别优选式 I -A-1 和 I -A-2 的化合物



I-A-1



I-A-2

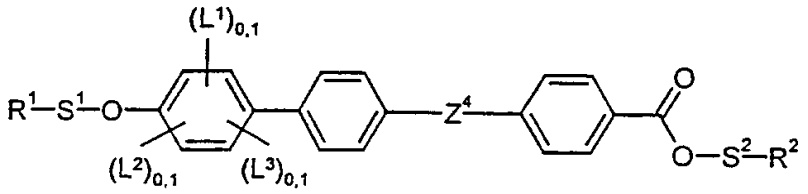
其中

L^1、L^2、L^3 各自独立代表氢、C_1-C_{20}烷基、C_2-C_{20}烯基、C_1-C_{20}烷氧基或C_2-C_{20}烯氧基，其中至少一个取代基必须不是氢；

Z^4代表-C≡C-、-COO-、-CH=CH-COO-，特别是-COO-或-CH=CH-COO-，尤其是指-COO-；并且

R^1、R^2、S^1、S^2如式I中所定义。

式I-B的化合物中，特别优选式I-B-1的化合物

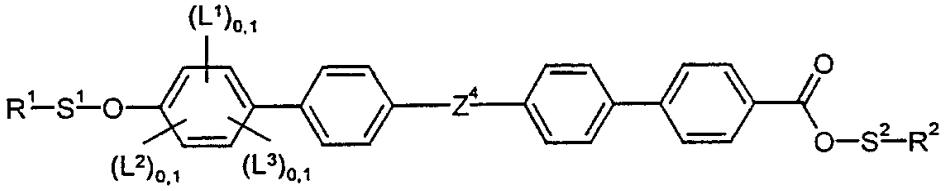


I-B-1

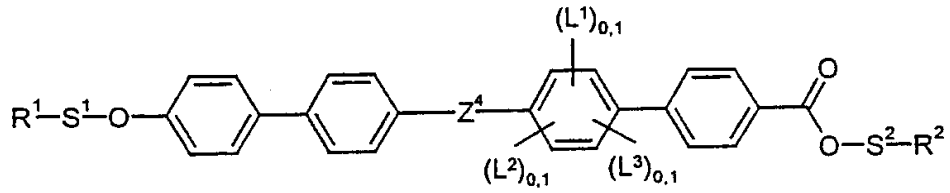
其中

R^1、R^2、S^1、S^2、Z^4、L^1、L^2、L^3 如式I-A-1中所定义。

式I-D的化合物中，特别优选式I-D-1和I-D-2的化合物：



I-D-1

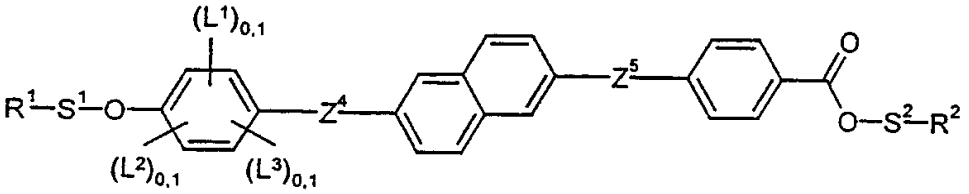


I-D-2

其中

R^1、R^2、Z^4、L^1、L^2、L^3 如式 I -A-1 中所定义。

式 I -F 的化合物中，特别优选式 I -F-1 的化合物



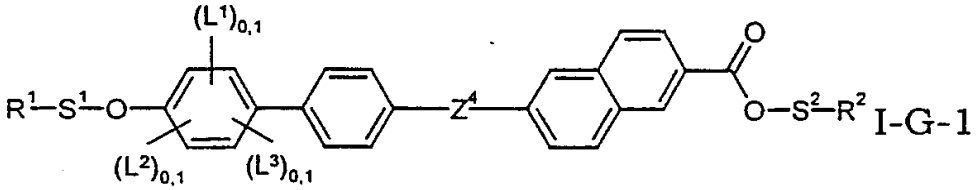
I-F-1

其中

Z^5代表单键、-COO-或-CH=CH-COO-，尤指单键；并且

R^1、R^2、Z^4、L^1、L^2、L^3 如式 I -A-1 中所定义。

式 I -G 的化合物中，特别优选式 I - G-1 化合物



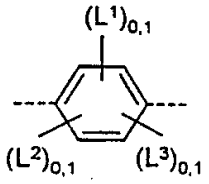
I-G-1

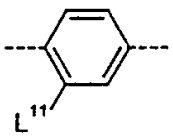
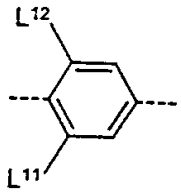
其中

R^1、R^2、Z^4、L^1、L^2、L^3 如式 I -A-1 中所定义。

在式 I -A-1、I -A-2、I -B-1、I -D-1、I -D-2、I -F-1 和 I -G-1

的化合物中更特别优选那些，其中

基团 

定义为  或  ，

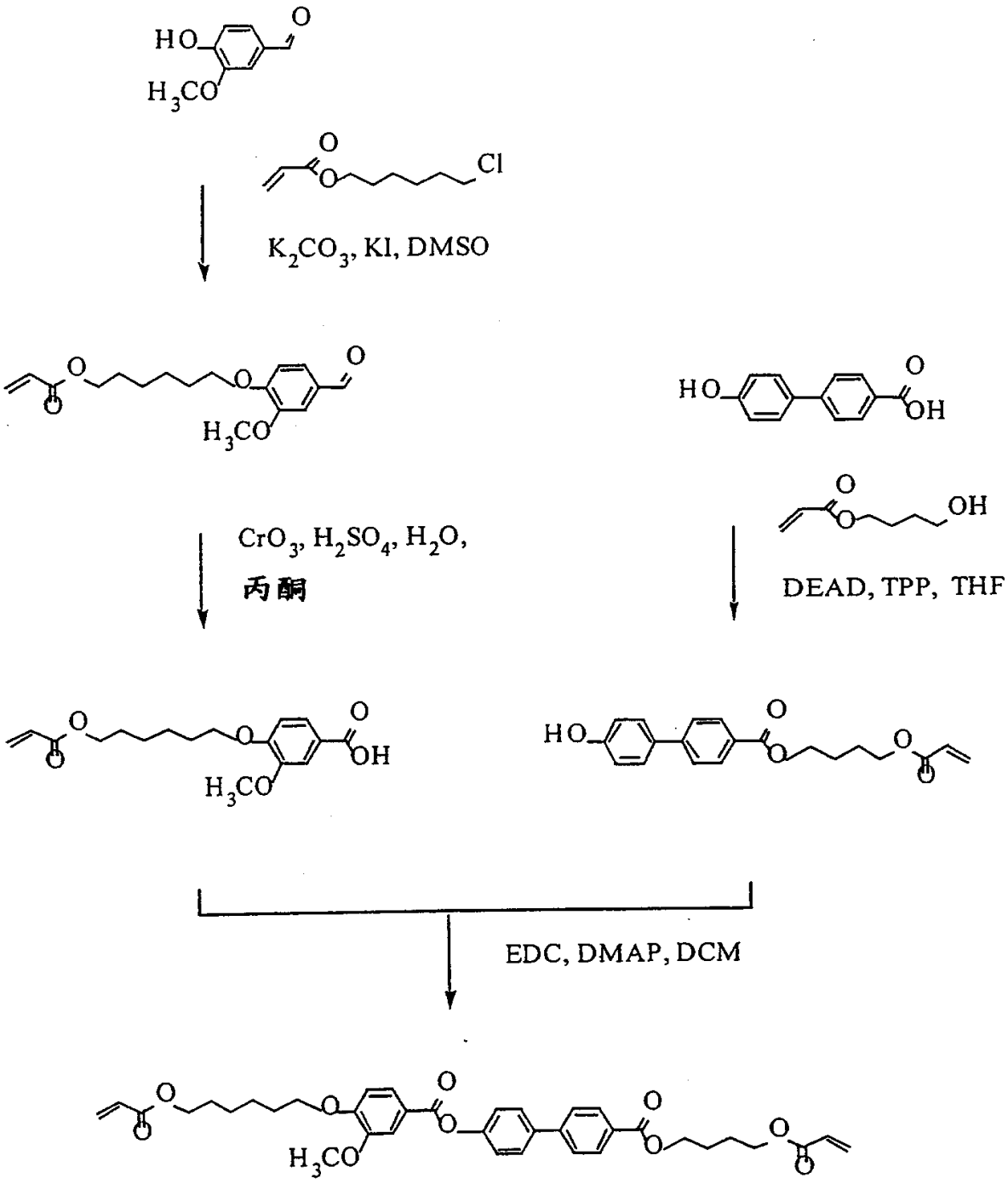
其中 L^{11}、L^{12} 各自独立代表 C_1-C_{20} 烷基、C_2-C_{20} 烯基、C_1-C_{20} 烷氧基或 C_2-C_{20} 烯氧基，特别是 C_1-C_{12} 烷氧基。

根据本发明，易于合成式 I 的化合物。例如可以用本质上类似于下面提到的路线中的方法制备。

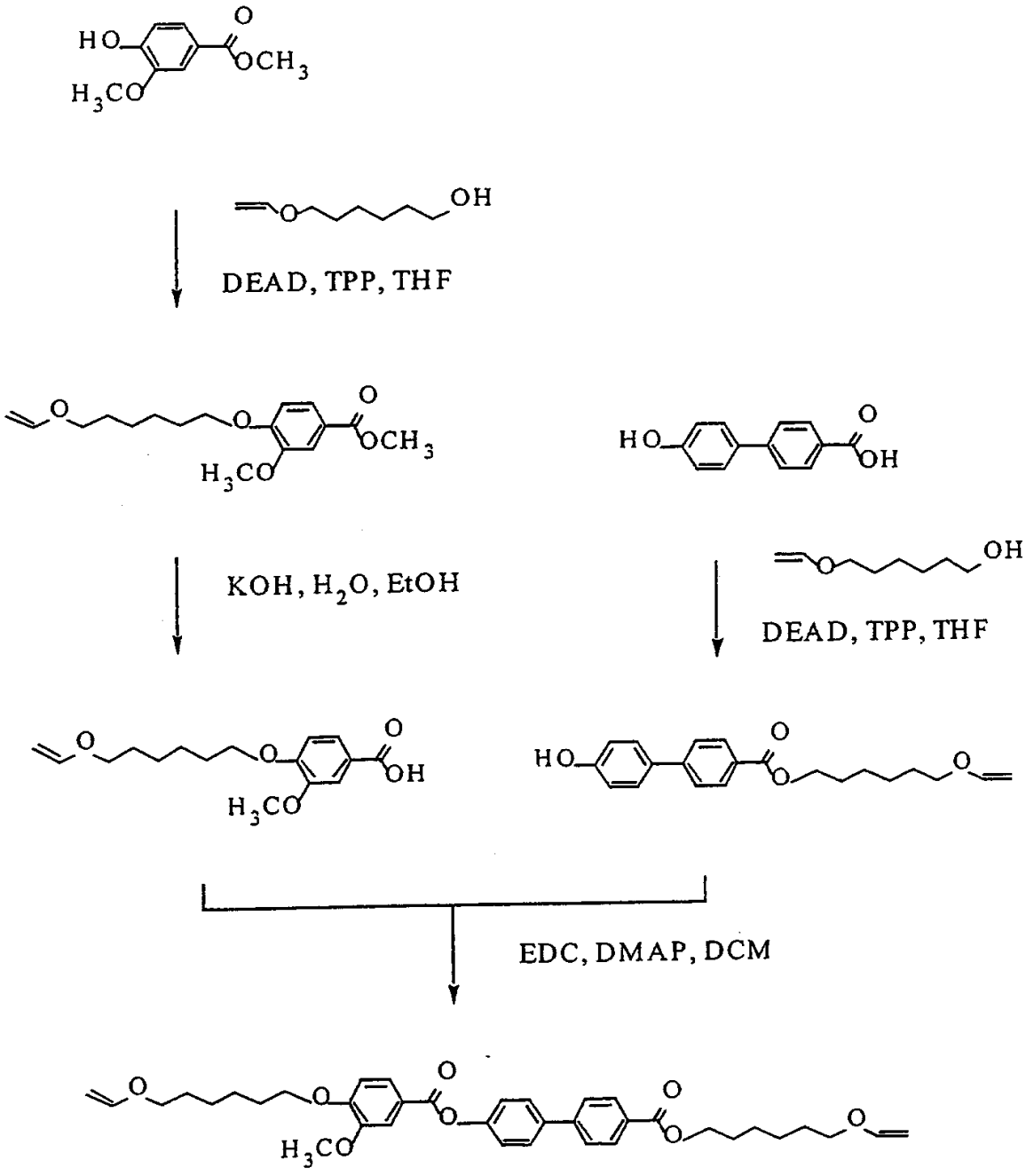
使用以下缩写：

DCM	二氯甲烷
DME	二甲氧基乙烷
DMSO	二甲基亚砜
THF	四氢呋喃
EDC	N-（3-二甲基氨基丙基）-N'-乙基碳二亚胺盐酸化物
DEAD	偶氮二酸二乙基酯（偶氮二羧酸二乙基酯）
DMAP	4-（二甲基氨基）吡啶
TPP	三苯基膦

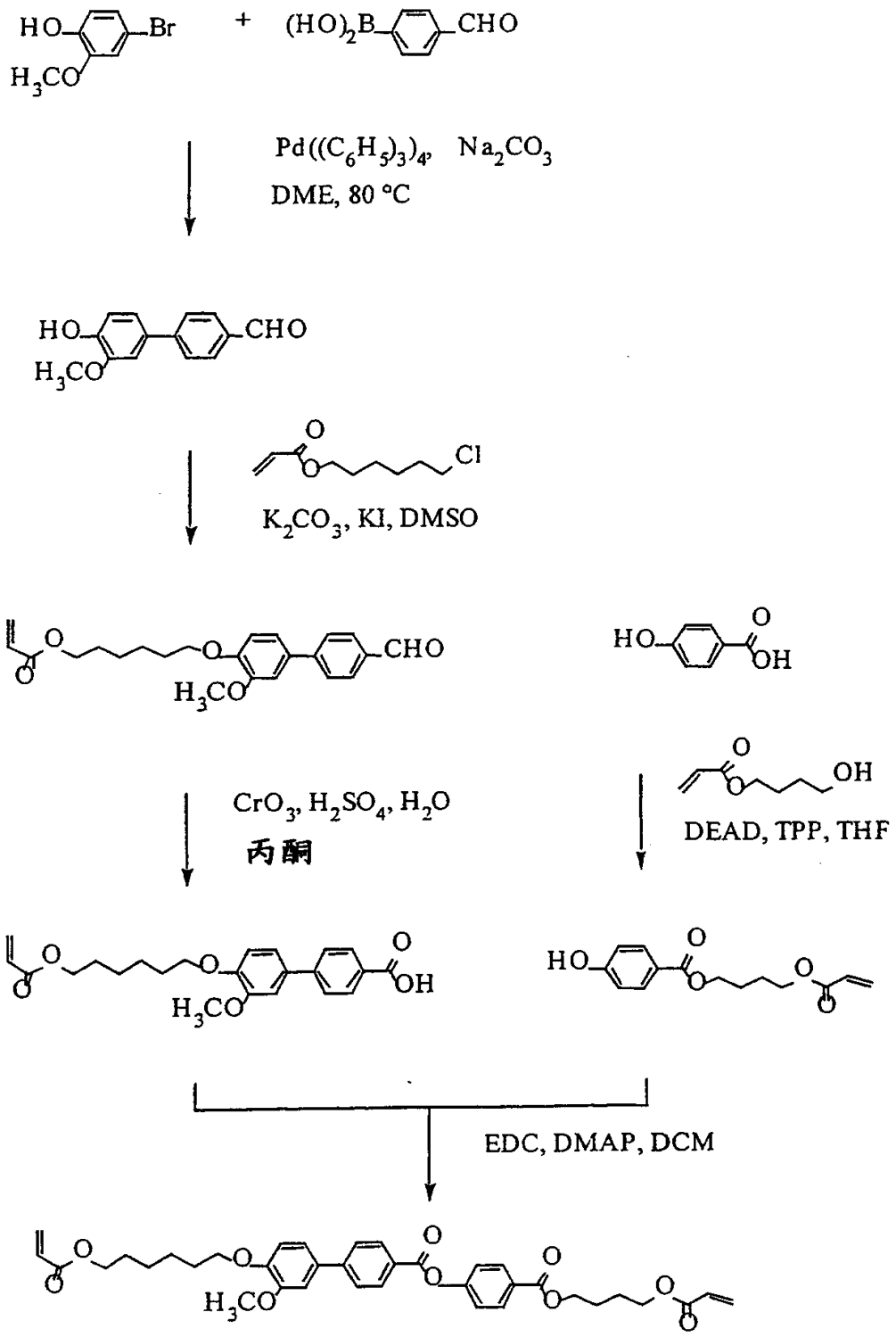
路线 1


HO
O
H3CO
Cl
K2CO3, KI, DMSO
CrO3, H2SO4, H2O,
丙酮
DEAD, TPP, THF
OH
EDC, DMAP, DCM

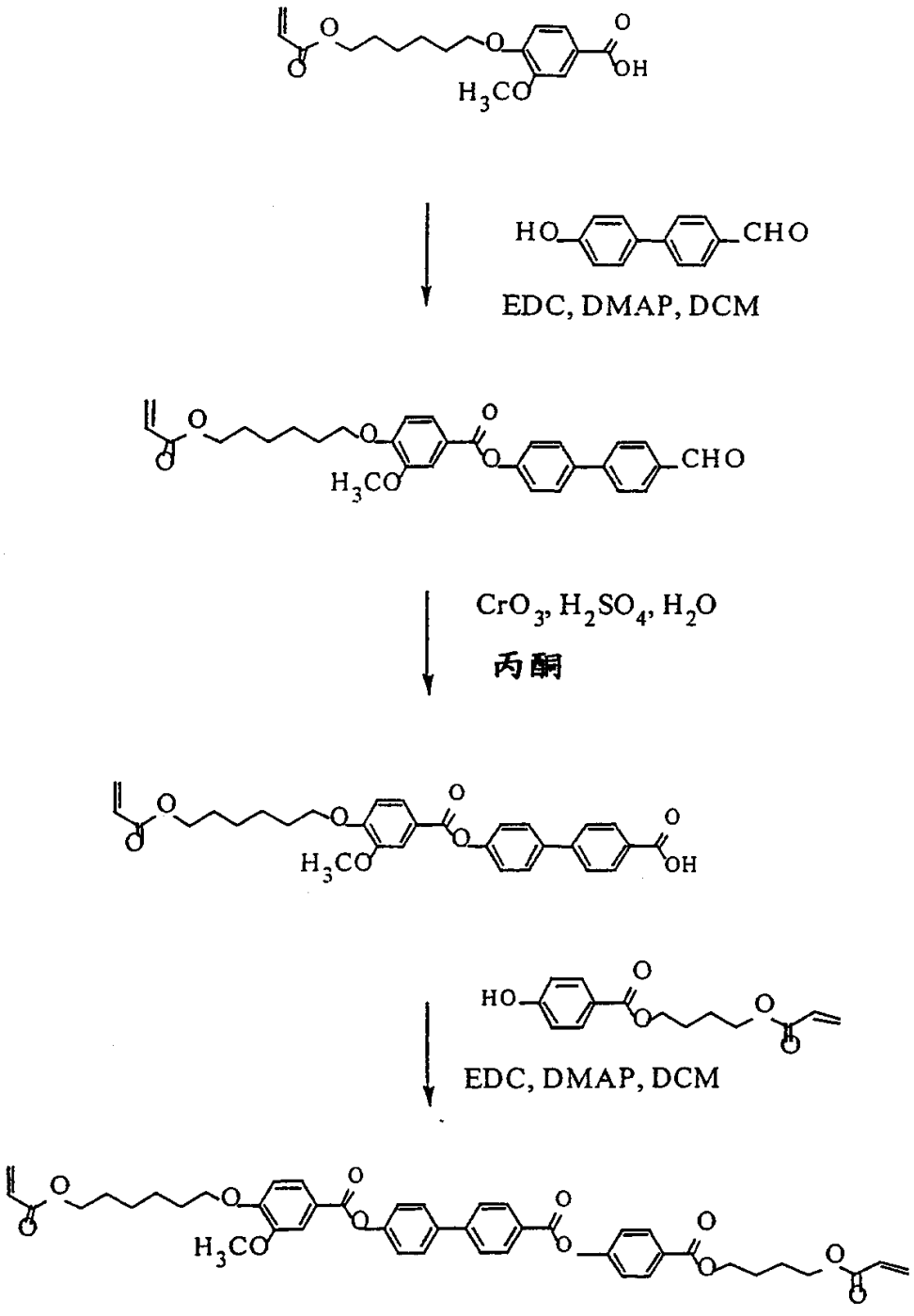
路线 2


HO
O
OCH3
H3CO
OH
DEAD, TPP, THF
O
OCH3
H3CO
HO
O
OH
KOH, H2O, EtOH
OH
DEAD, TPP, THF
O
OH
H3CO
HO
O
O
EDC, DMAP, DCM
O
O
O
O
O
H3CO

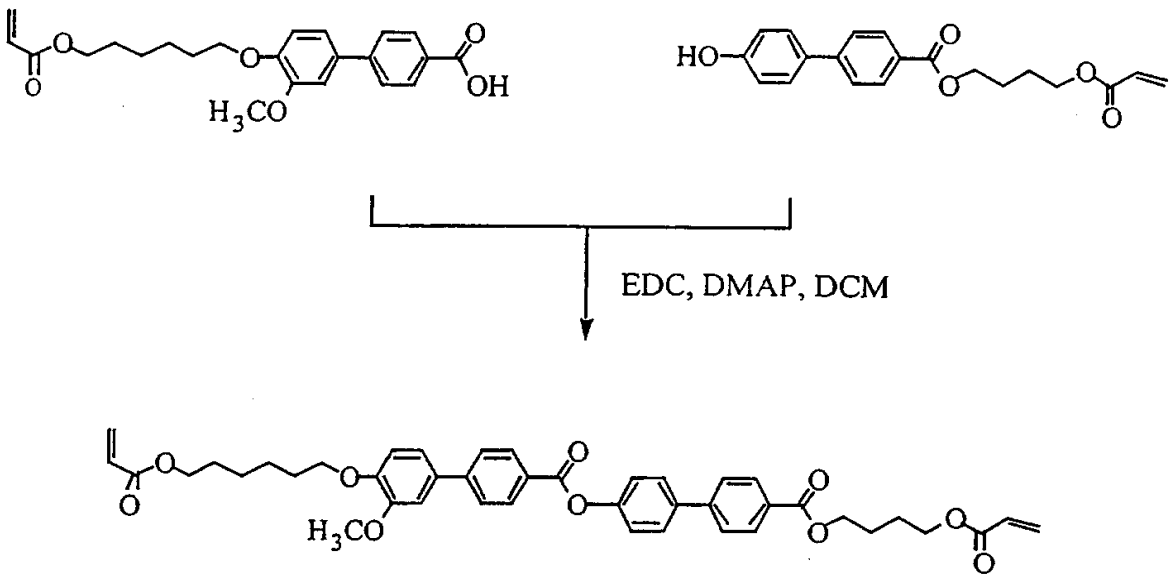
路线 3


HO
Br
H3CO
+
(HO)2B
CHO
Pd((C6H5)3)4, Na2CO3
DME, 80 °C
HO
CHO
H3CO
O
Cl
K2CO3, KI, DMSO
O
CHO
H3CO
HO
O
OH
CrO3, H2SO4, H2O
丙酮
O
OH
DEAD, TPP, THF
O
OH
H3CO
HO
O
O
EDC, DMAP, DCM
O
O
O
O
H3CO

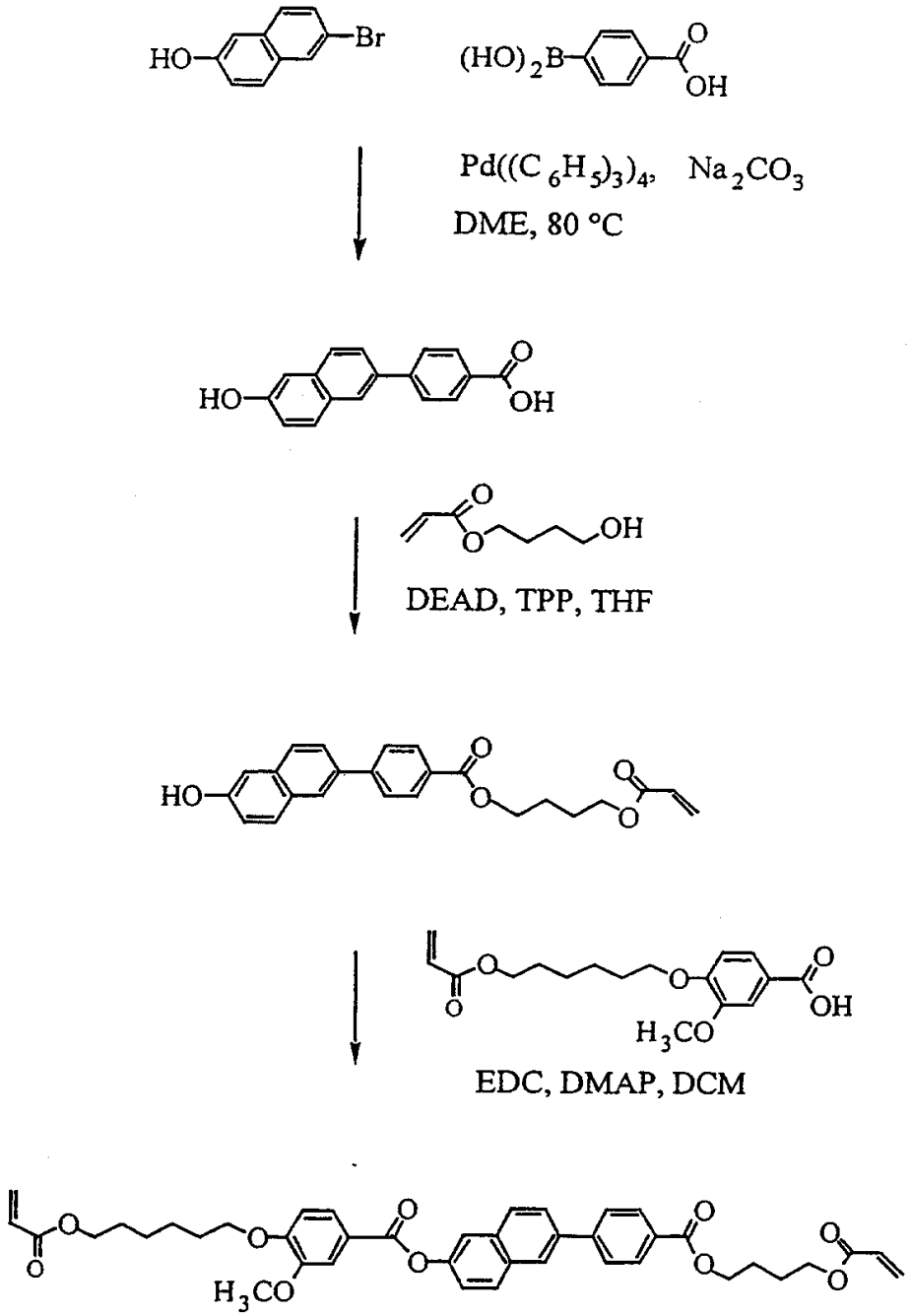
路线 4



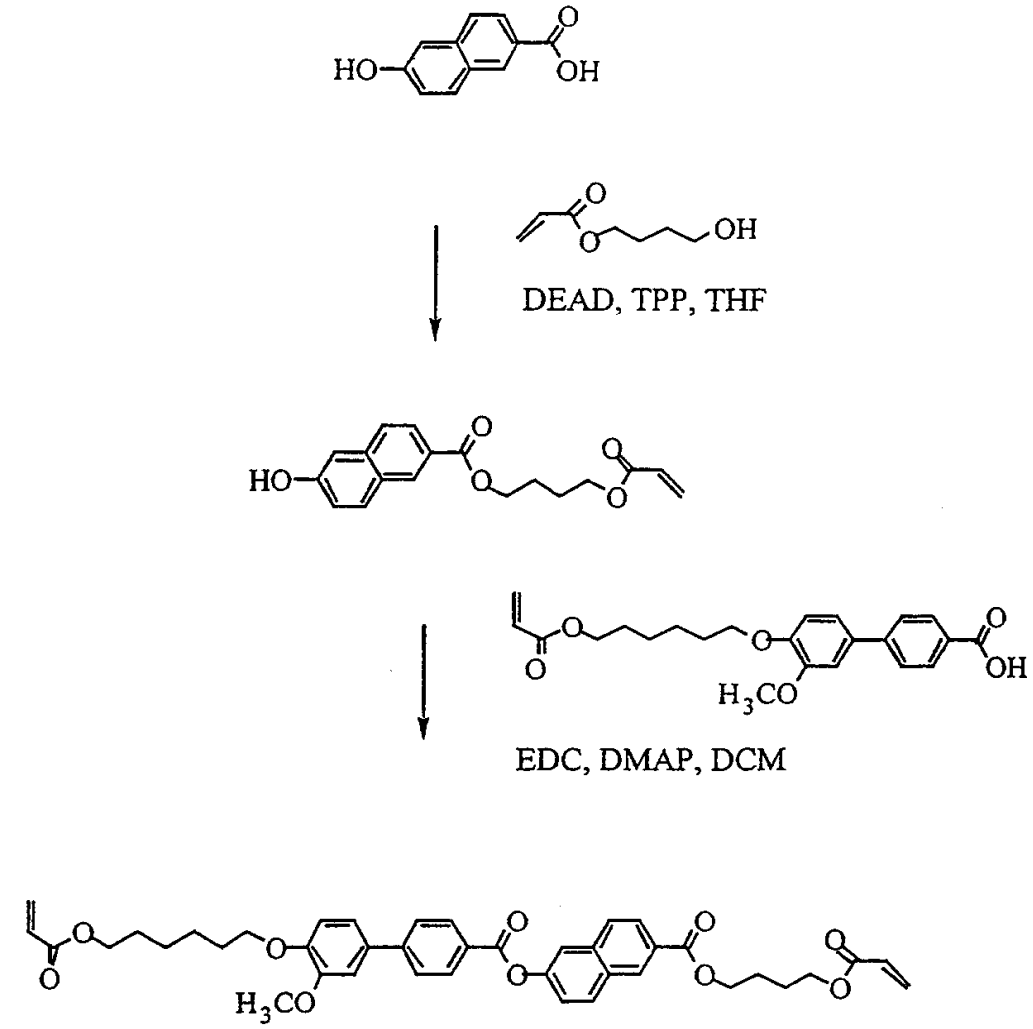
路线 5



路线 6


HO
Br
(HO)2B
O
OH
Pd((C6H5)3)4, Na2CO3
DME, 80 °C
HO
O
OH
OH
DEAD, TPP, THF
HO
O
O
O
O
O
O
OH
H3CO
EDC, DMAP, DCM
O
O
O
O
H3CO
O
O
O
O
O

路线 7

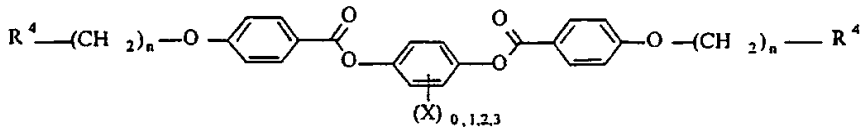


式 I 的化合物可以纯化合物的形式或者以同 I 中其它化合物和（或）其它液晶组分的混合物的形式使用。

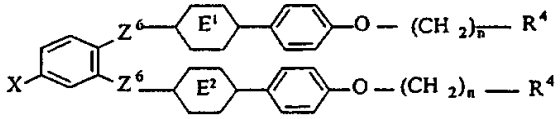
根据本发明，液晶混合物包含至少两种组分，其中至少一种组分是式 I 的化合物。第二种组分和任何其它组分可以是式 I 的其它化合物或者是其它可含有一个或多个可交联基团的已知液晶化合物。该混合物还可包含一种或多种手性组分或各向同性掺杂剂。

根据本发明，由于式 I 化合物具有溶解性好及相互之间混溶性好的优点，式 I 化合物在混合物中的比例可以很高，可达到 99 重量%。

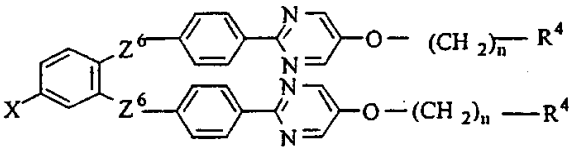
除一种或多种式 I 的化合物外，根据本发明的混合物优选还包含一种或多种以下通式的化合物



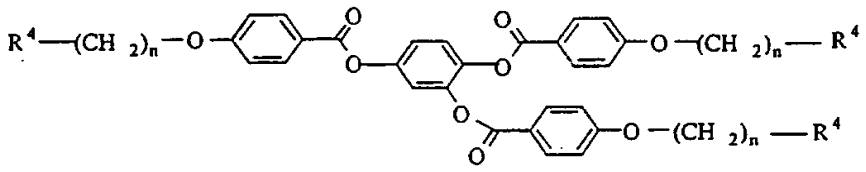
II



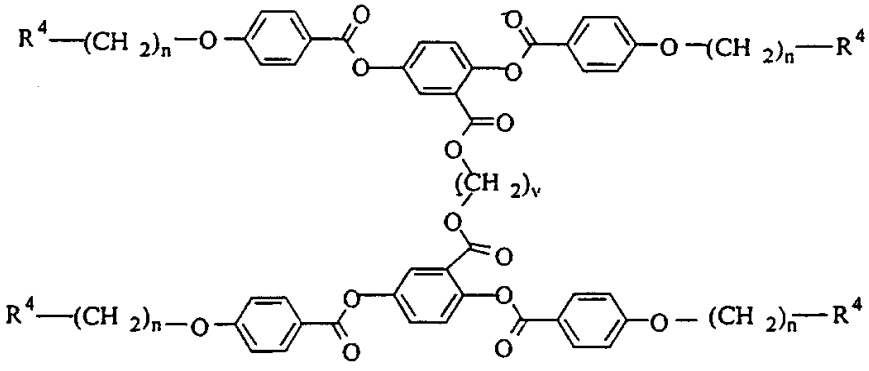
III



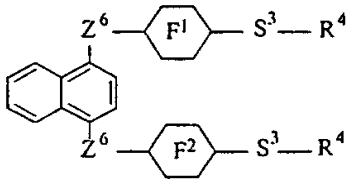
IV



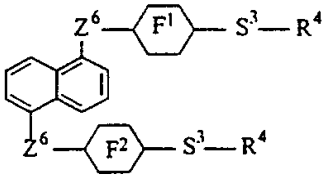
V



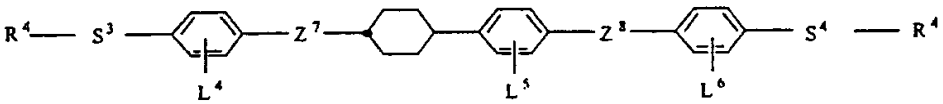
VI



VII

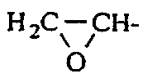


VIII



IX

其中

R^4代表可聚合的基团，例如CH_2=CH-、CH_2=CH-O-、CH_2= CH- COO-、CH_2=C（CH_3）-COO-、CH_2=C（Cl）-COO-或  ；

S^3、S^4 各自独立代表-（CH_2）$_n$-或-O（CH_2）$_n$-；

E^1、E^2 各自独立代表1，4-亚苯基、反式1，4-亚环己基、吡啶2，5-二基，嘧啶2，5-二基或反式1，4-亚环己基-1，4-亚苯基；

F^1、F^2 各自独立代表1，4-亚苯基或2-或3-氟-1，4-亚苯基；

L^4、L^5、L^6 各自独立代表氢、C_1-C_{20}烷基，C_2-C_{20}烯基，C_1-C_{20}烷氧基，C_1-C_{20}烷氧羰基，甲酰基，C_1-C_{20}烷基羰基，C_1-C_{20}烷基羰氧基、卤素、氰基或硝基；

Z^6代表-COO-、-OOC-、-OCH_2-、-CH_2O-、-O（CH_2）$_3$-、-OOC（CH_2）$_2$-或-COO（CH_2）$_3$-；

Z^7代表单键、-CH_2CH_2-、-CH_2O-、-OCH_2-、-COO-、-OOC-、-（CH_2）$_4$-、-O（CH_2）$_3$-、-（CH_2）$_3$ O -、或-C≡C-；

Z^8代表单键、$-CH_2CH_2-$、$-CH_2O-$、$-OCH_2-$、$-COO-$、$-OOC-$或$-C\equiv C-$；

每个 X 独立代表氢、C_1-C_{20}烷基，C_2-C_{20}烯基，C_1-C_{20}烷氧基，C_1-C_{20}烷氧羰基，甲酰基，C_1-C_{20}烷基羰基，C_1-C_{20}烷基羰氧基、氟、氯、溴、氰基或硝基；

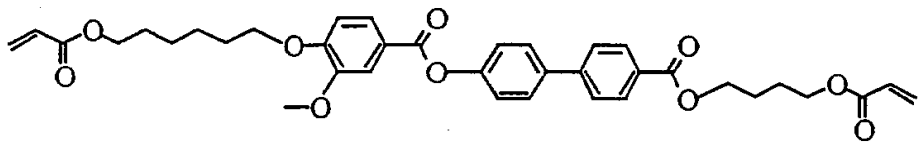
n 是从 2 到 20 的整数；并且

v 是从 2 到 12 的整数。

制备式 I 化合物和包含这些化合物的液晶混合物将在以下实施例中进一步说明。在实施例中，C 代表晶相，N 代表向列相，S 代表近晶相，而 I 代表各向同性相。

实施例 1

4'-[4-（6-丙烯酰氧基己氧基）-3-甲氧基苯甲酸基]联苯基-4-羧酸 4-丙烯酰氧基丁基酯



在 0℃下，将 1.35 克（7 毫摩尔）N-（3-二甲基氨基丙基）-N'-乙基碳二亚胺盐酸化物（EDC）加入到 2.38 克（7 毫摩尔）4'-羟基联苯基-4-羧酸 4-丙烯酰基丁基酯、2.26 克（7 毫摩尔）4-（6-丙烯酰氧基己氧基）-3-甲氧基苯甲酸和 0.86 克（7 毫摩尔）4-二甲基氨基吡啶（DMAP）的 180 毫升二氯甲烷（DCM）溶液中。将该混合物在 0℃搅拌一小时后，在室温下过夜。然后将反应混合物倒入 300 毫升水中，并每次用 150 毫升 DCM 萃取三次。将组合的有机相分别用 200 毫升水洗两次，用硫酸镁干燥，过滤并浓缩。用 300 克硅胶色谱以 7∶3 的环己烷/乙酸乙酯提纯剩余物，并在 0℃20 毫升乙醇中重结晶一次，得到 2.58 克 4'-[4-（6-丙烯酰氧基己氧基）-3-甲氧基苯甲酸基] 联苯基-4-羧酸 4-丙烯酰氧基丁基酯。

熔点（C-S_X）77℃，S_X-N 60℃，澄清点（N-I） 62℃。

用作原料的 4'-羟基联苯基-4-羧酸 4-丙烯酰基丁基酯由以下方法制备:

（a）在 0℃下，将 5.24 克（20 毫摩尔）三苯基膦（TPP）加入到 4.28 克（20 毫摩尔）4'-羟基-4-联苯基羧酸和 2.88 克（29 毫摩尔）丙烯酸 4-羟丁酯的 100 毫升四氢呋喃（THF）溶液中，然后在相同温度下，向其中滴加 3.50 克（20 毫摩尔）偶氮二羧酸二乙酯（DEAD）。混合物在 0℃下搅拌一小时后，在室温下过夜。然后将混合物浓缩，并用硅胶色谱以 2：1 的环己烷/乙酸乙酯提纯剩余物，得到 4.32 克 4'-羟基联苯基-4-羧酸 4-丙烯酰基丁基酯。

用作原料的 4-（6-丙烯酰氧基己氧基）-3-甲氧基苯甲酸由以下方法制备:

(a) 41.45 克 （300 毫摩尔）碳酸钾和 27.4 克（165 毫摩尔）碘化钾加入到 22.8 克（150 毫摩尔）香草醛和 30.7 克（225 毫摩尔）6-氯代己醇的 500 毫升二甲基亚砜（DMSO）溶液中，混合物在氮气保护下于 60℃搅拌过夜。将混合物冷却至室温，倒入 600 毫升水中，并且每次用 150 毫升乙酸乙酯萃取三次。将组合的有机相每次用 200 毫升水洗两次，用硫酸钾干燥后过滤并浓缩。用 400 克硅胶色谱以 1：1 环己烷/乙酸乙酯提纯剩余物，得到 29.95 克 4-（6-己氧基）-3-甲氧基苯甲醛。

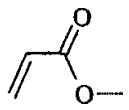
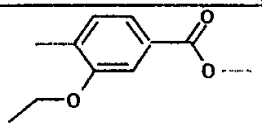
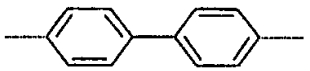
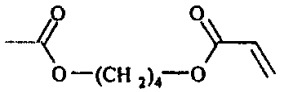
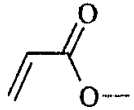
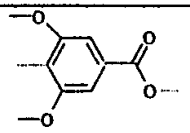
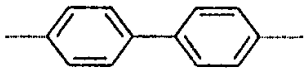
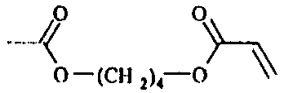
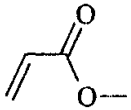
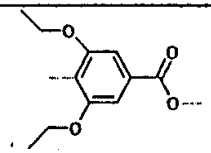
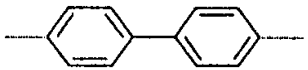
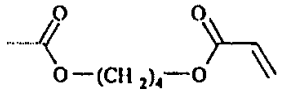
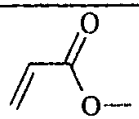
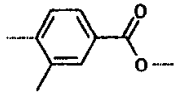
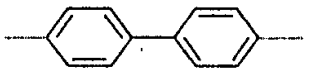
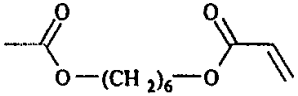
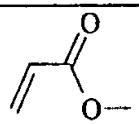
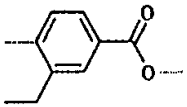
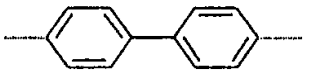
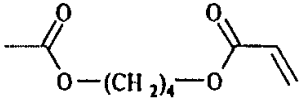
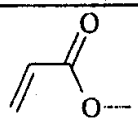
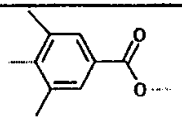
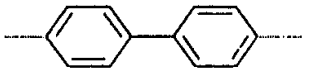
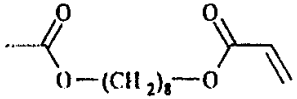
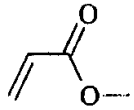
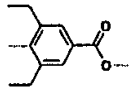
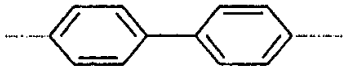
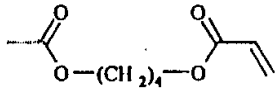
（b）在冰冷却 5℃下，将 97 毫升 Jones 试剂溶液缓慢滴入到 27.3 克（89.1 毫摩尔）4-（6-己氧基）-3-甲氧基苯甲醛的 300 毫升丙酮溶液中。混合物在室温下搅拌 2 小时。一旦不能再检测出原料后，就把反应液倒入至 1 升水和 0.3 升乙酸乙酯中。分相后，水相每次用 150 毫升乙酸乙酯萃取两次。将组合的有机相用 0.5 升水洗涤，用硫酸钾干燥，过滤并浓缩。剩余物用硅胶色谱以 1：1 的环己烷/乙酸乙酯提纯，并用乙酸乙酯/乙醚重结晶一次，得到 16.7 克 4-（6-丙烯酰氧基己氧基）-3-甲氧基苯甲酸。

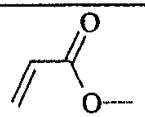
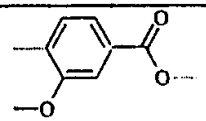
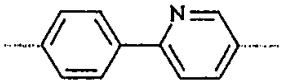
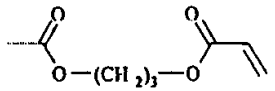
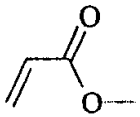
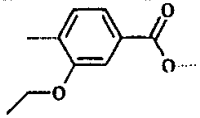
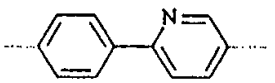
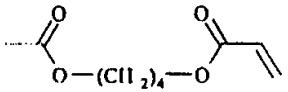
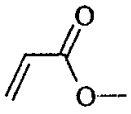
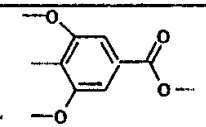
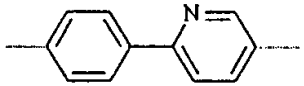
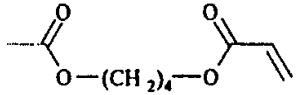
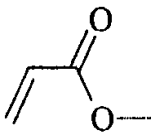
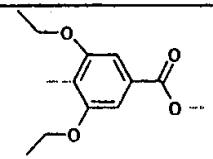
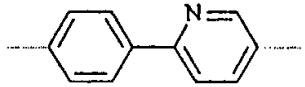
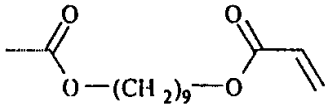
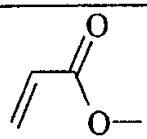
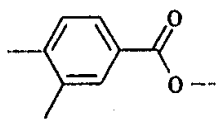
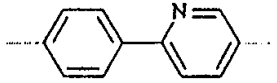
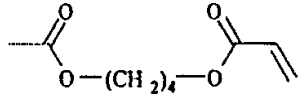
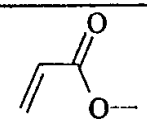
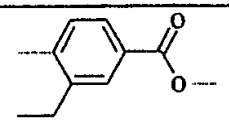
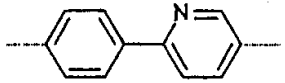
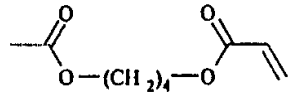
如路线 2 所示，依照本领域熟练技术人员所熟知的反应，使用合适的起始化合物，以乙烯基醚为反应基团，可类似地制备相应的化合

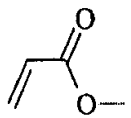
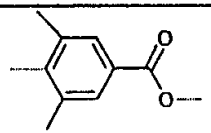
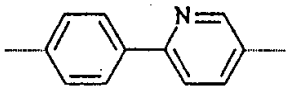
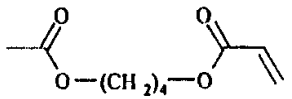
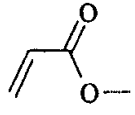
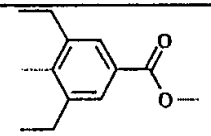
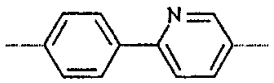
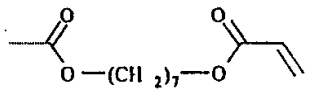
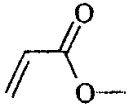
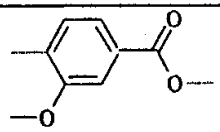
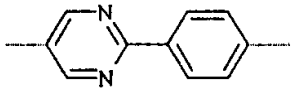
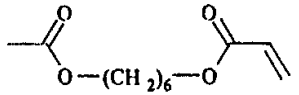
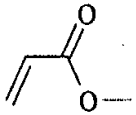
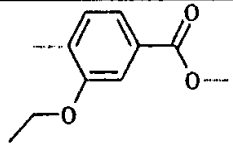
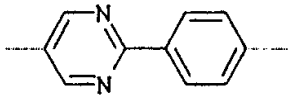
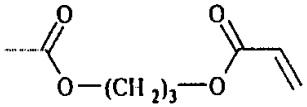
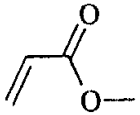
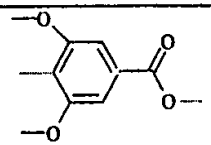
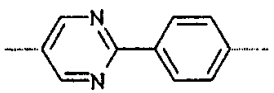
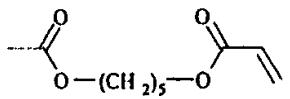
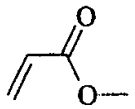
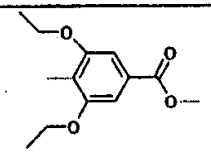
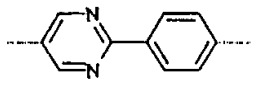
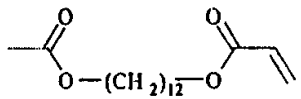
物。具有两个不同的反应基团的液晶也可以按所示的反应路线合成。

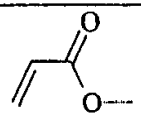
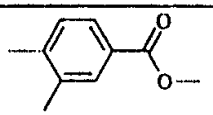
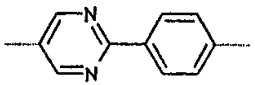
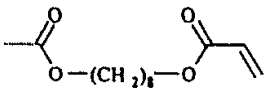
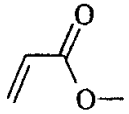
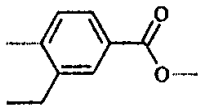
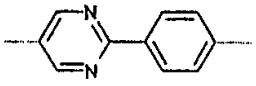
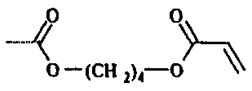
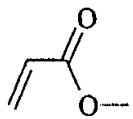
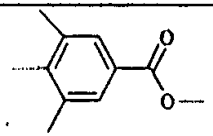
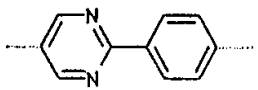
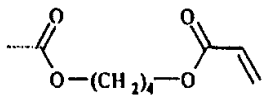
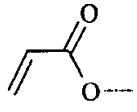
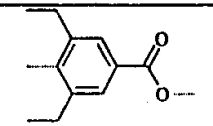
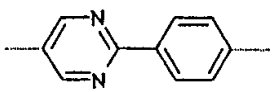
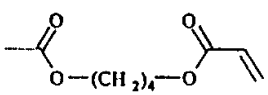
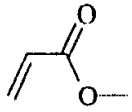
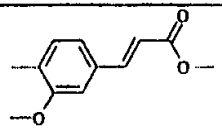
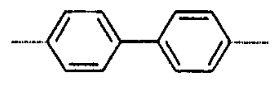
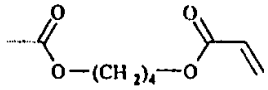
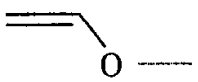
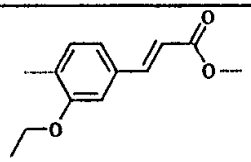
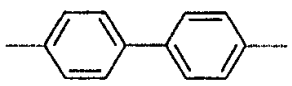
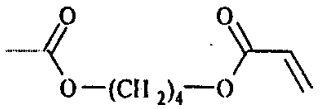
以下化合物可以类似的方式制得:

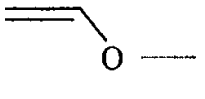
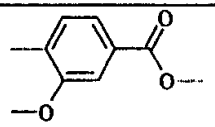
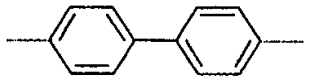
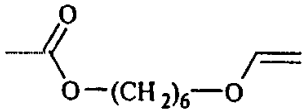
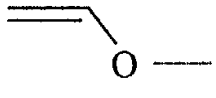
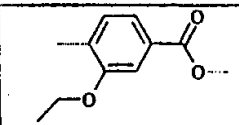
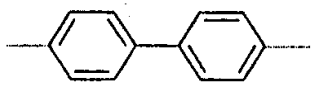
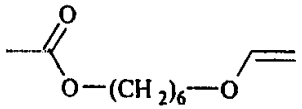
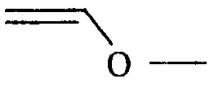
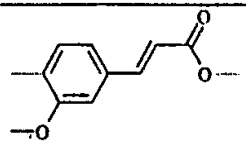
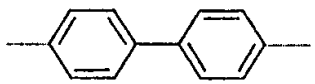
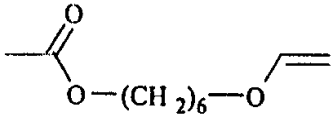
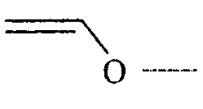
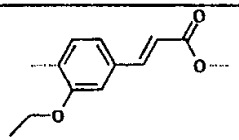
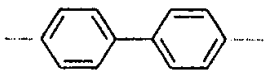
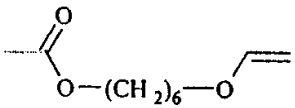
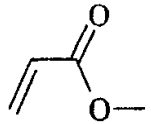
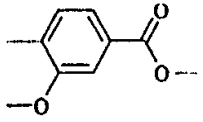
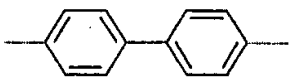
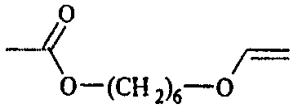
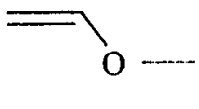
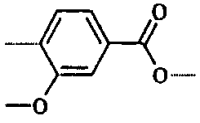
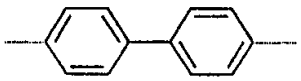
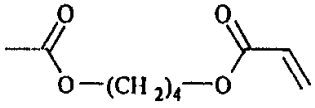
$$R^1-S^1-O-A-Z^1-B-COO-S^2-R^2$$

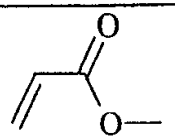
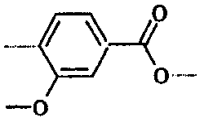
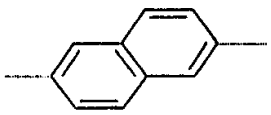
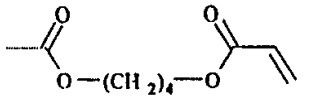
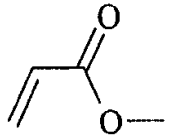
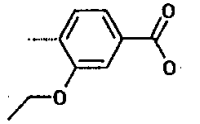
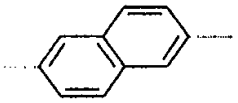
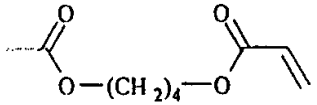
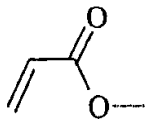
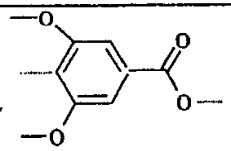
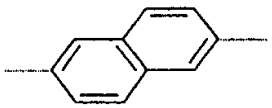
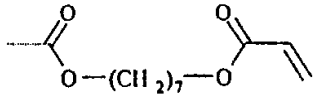
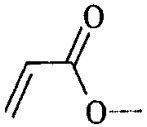
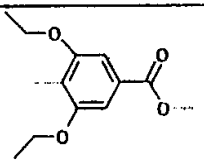
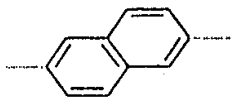
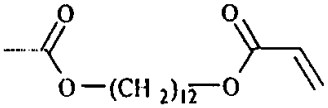
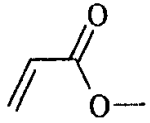
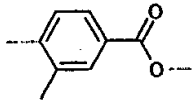
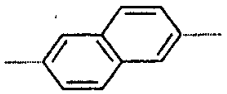
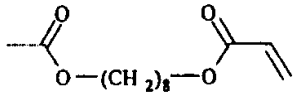
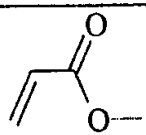
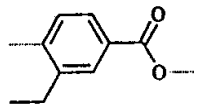
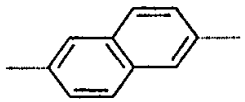
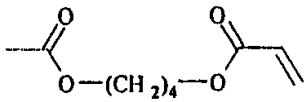
R^1	S^1-O	A-Z^1	B	COO-S^2-R^2	相变
	$(CH_2)_6O$				M.p. (C–I) 79 °C
	$(CH_2)_8O$				
	$(CH_2)_7O$				
	$(CH_2)_6O$				
	$(CH_2)_6O$				
	$(CH_2)_4O$				
	$(CH_2)_6O$				

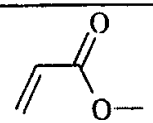
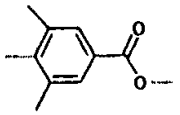
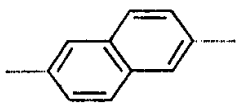
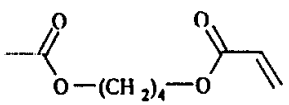
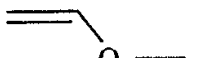
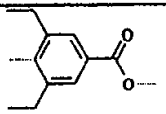
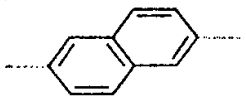
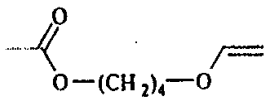
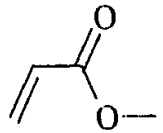
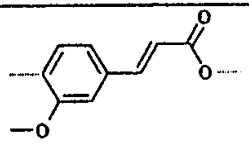
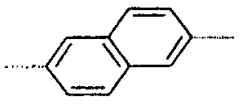
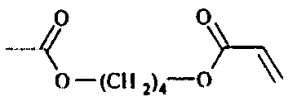
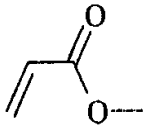
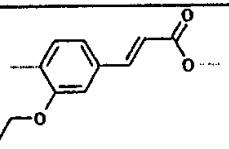
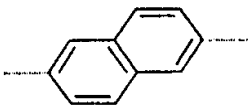
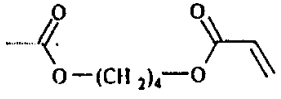
R^1	S^1-O	A-Z^1	B	COO-S^2-R^2	相变
	$(CH_2)_6O$				
	$(CH_2)_9O$				
	$(CH_2)_{10}O$				
	$(CH_2)_6O$				
	$(CH_2)_3O$				
	$(CH_2)_6O$				

R^1	S^1-O	A-Z^1	B	COO-S^2-R^2	相变
	$(CH_2)_{12}O$				
	$(CH_2)_6O$				
	$(CH_2)_7O$				
	$(CH_2)_6O$				
	$(CH_2)_9O$				
	$(CH_2)_6O$				

R^1	S^1-O	A-Z^1	B	COO-S^2-R^2	相变
	$(CH_2)_6O$				
	$(CH_2)_6O$				
	$(CH_2)_6O$				
	$(CH_2)_7O$				
	$(CH_2)_6O$				M.p. (C–N) 95 °C, N–I 102 °C
	$(CH_2)_6O$				

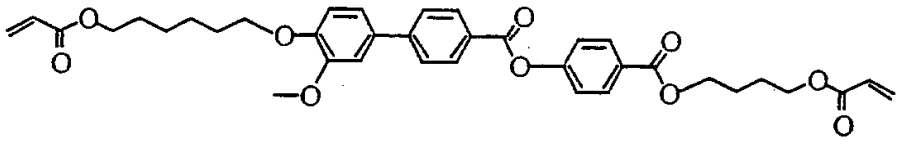
R^1	S^1-O	A-Z^1	B	COO-S^2-R^2	相变
	$(CH_2)_6O$				M.p. (C–S_A) 72 °C, S_A–I 81 °C
	$(CH_2)_6O$				
	$(CH_2)_6O$				
	$(CH_2)_6O$				M.p. (C–S_X) 86 °C, S_X–I 93 °C
	$(CH_2)_6O$				M.p. (C–I) 66 °C
	$(CH_2)_6O$				M.p. (C–S_X) 64 °C, S_X–N 77 °C, N–I 83 °C

R^1	S^1-O	A-Z^1	B	COO-S^2-R^2	相变
	$(CH_2)_6O$				
	$(CH_2)_6O$				
	$(CH_2)_9O$				
	$(CH_2)_6O$				
	$(CH_2)_4O$				
	$(CH_2)_{12}O$				

R^1	S^1-O	A-Z^1	B	COO-S^2-R^2	相变
	$(CH_2)_6O$				
	$(CH_2)_7O$				
	$(CH_2)_6O$				
	$(CH_2)_6O$				

实施例 2

4'-（6-丙烯酰氧基己氧基）-3'-甲氧基联苯基-4-羧酸 4-（4-丙烯酰氧基丁氧基羰基）苯基酯

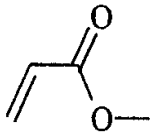
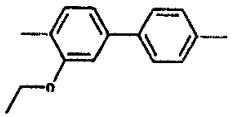
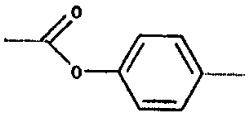
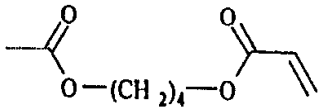
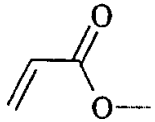
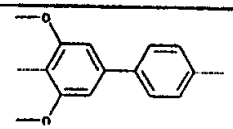
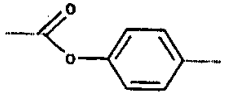
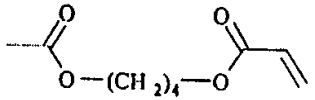
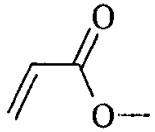
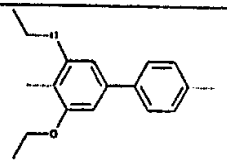
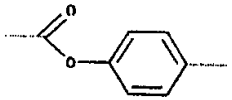
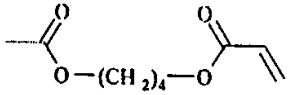
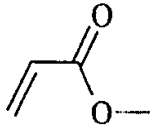
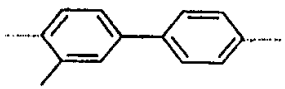
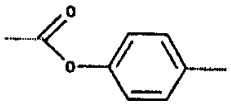
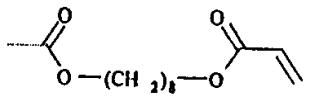
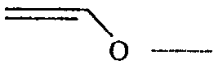
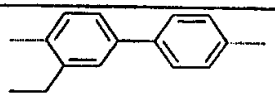
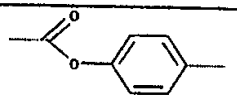
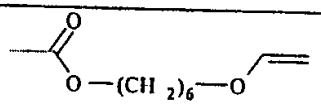
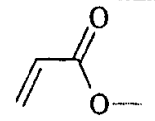
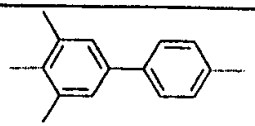
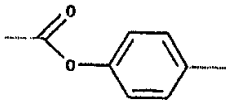
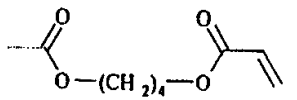
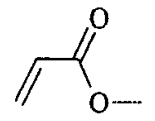
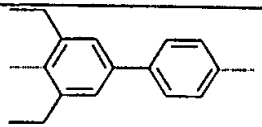
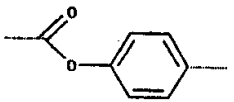
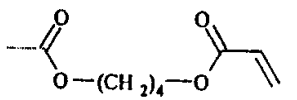


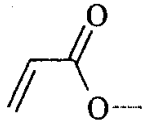
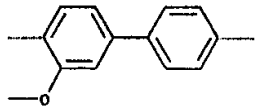
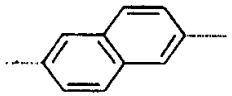
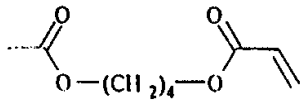
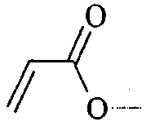
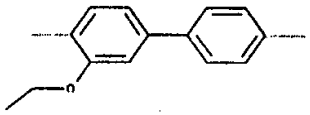
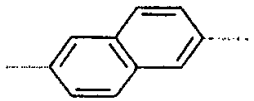
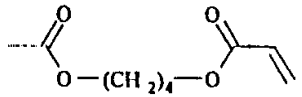
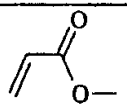
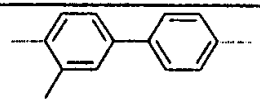
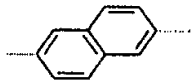
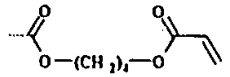
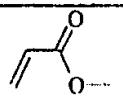
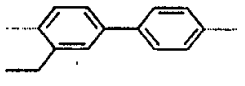
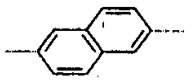
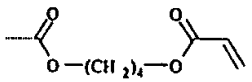
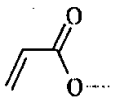
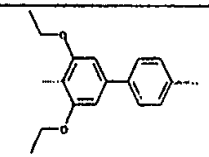
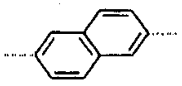
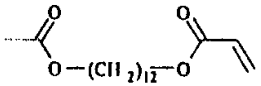
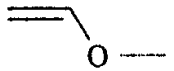
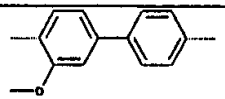
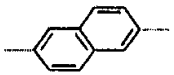
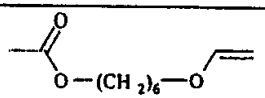
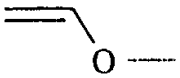
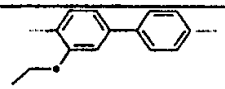
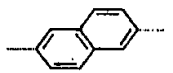
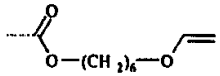
制备方法类似于实施例 1，使用 2.64 克（10 毫摩尔）4-羟基苯甲酸 4-丙烯酰氧基丁基酯，3.99 克（10 毫摩尔）4'-（6-丙烯酰氧基己氧基）-3'-甲氧基联苯基-4-羧酸，0.12 克（1 毫摩尔）DMAP 和 2.11 克（11 毫摩尔）EDC。剩余物用硅胶色谱以环己烷/乙酸乙酯（7：3）提纯，并用乙醇重结晶一次，得到 4'-（6-丙烯酰氧基己氧基）-3'-甲氧基联苯基-4-羧酸 4-（4-丙烯酰氧基丁氧基羰基）苯基酯。

用作原料的 4'-（6-丙烯酰氧基己氧基）-3'-甲氧基联苯基-4-羧酸按照已知的方法制备，这种方法是以钯催化的硼酸偶联 4-溴-2-甲氧基苯酚和 4-甲酰基苯基硼酸，然后用丙烯酸 6-氯己基酯以 Williamson 法醚化酚羟基，再将醛官能团氧化为酸（见路线 3）。

以下化合物可以用类似方法制得:

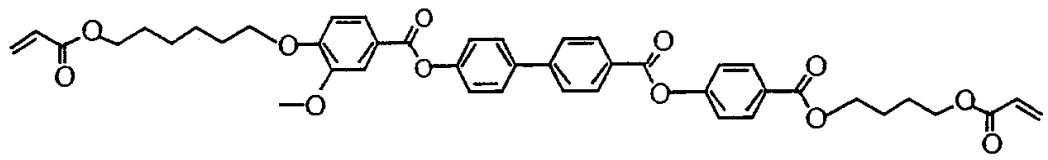
$R^1-S^1-O-B-Z^2-C-COO-S^2-R^2$

R^1	S^1-O	B	Z^2-C	COO-S^2-R^2	相变
	$(CH_2)_6O$				
	$(CH_2)_5O$				
	$(CH_2)_7O$				
	$(CH_2)_6O$				
	$(CH_2)_6O$				
	$(CH_2)_9O$				
	$(CH_2)_3O$				

R^1	S^1-O	B	Z^2-C	COO-S^2-R^2	相变
	$(CH_2)_6O$				
	$(CH_2)_6O$				
	$(CH_2)_8O$				
	$(CH_2)_9O$				
	$(CH_2)_6O$				
	$(CH_2)_6O$				
	$(CH_2)_6O$				

实施例 3

4'-[4-（6-丙烯酰氧基己氧基）-3-甲氧基苯甲酸基]联苯基-4-羧酸 4-（6-丙烯酰氧基己氧基）苯基酯

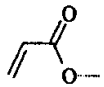
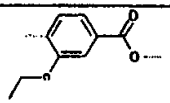
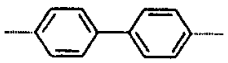
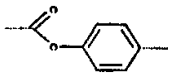
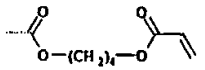
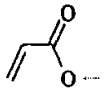
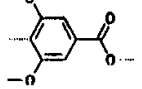
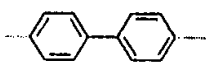
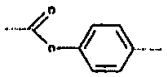
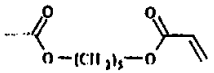
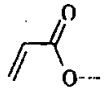
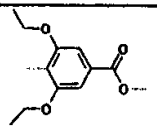
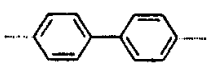
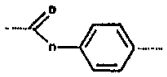
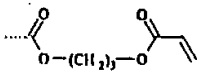
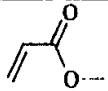
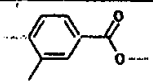
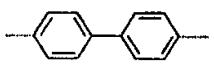
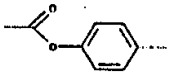
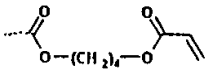
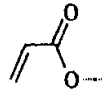
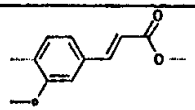
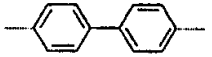
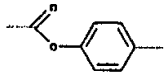
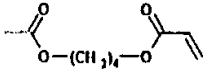
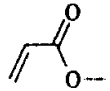
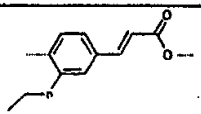
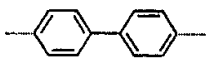
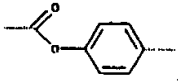
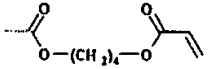
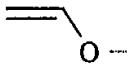
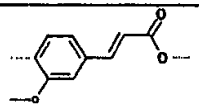
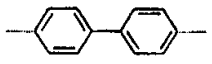
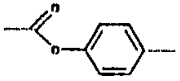
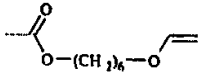


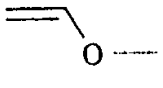
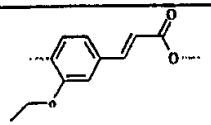
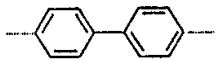
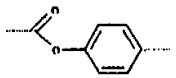
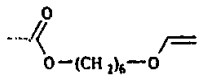
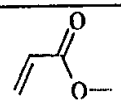
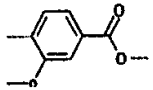
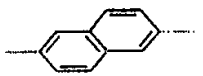
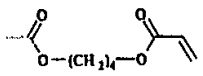
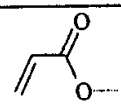
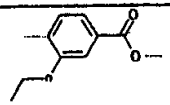
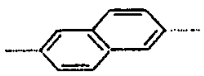
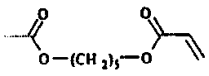
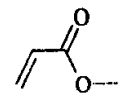
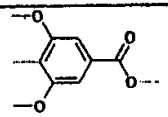
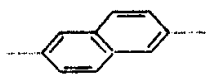
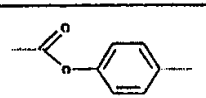
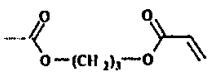
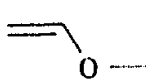
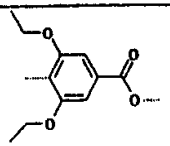
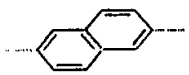
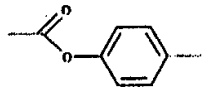
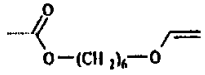
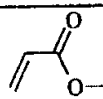
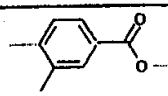
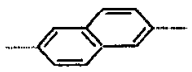
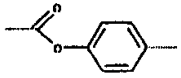
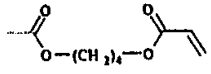
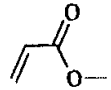
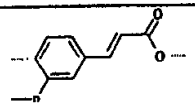
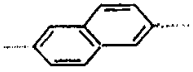
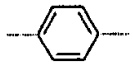
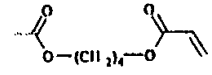
制备方法类似于实施例 1，使用 2.64 克（10 毫摩尔）4-羟基苯甲酸 4-丙烯酰氧基丁基酯，5.19 克（10 毫摩尔）4'-[4-（6-丙烯酰氧基己氧基）-3-甲氧基苯甲酸基]联苯基-4-羧酸，0.12 克（1 毫摩尔）DMAP 和 2.11 克（11 毫摩尔）EDC 制备。剩余物用硅胶色谱以环己烷/乙酸乙酯（7：3）提纯，并用乙醇重结晶一次，得到 4'-[4-（6-丙烯酰氧基己氧基）-3-甲氧基苯甲酸基]联苯基-4-羧酸 4-（6-丙烯酰氧基己氧基）苯基酯。

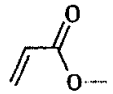
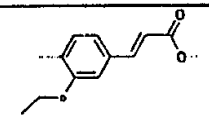
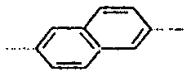
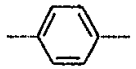
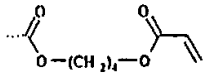
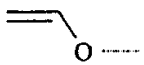
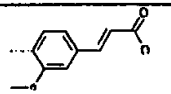
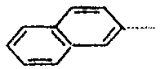
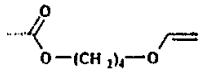
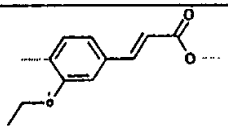
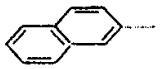
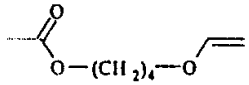
作为原料使用的 4'-[4-（6-丙烯酰氧基己氧基）-3-甲氧基苯甲酸基]联苯基-4-羧酸是依照本领域技术人员所熟知的方法，按路线 4 所示从 4-（6-丙烯酰氧基己氧基）-3-甲氧基苯甲酸制备的。

以下化合物可以用类似方法制得：

$R^1-S^1-O-A-Z^1-B-Z^2-C-COO-S^2-R^2$

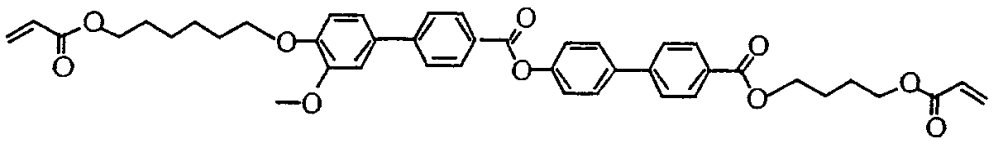
R^1	S^1-O	A-Z^1	B	Z^2-C	COO-S^2-R^2	相变
	$(CH_2)_6O$					
	$(CH_2)_6O$					
	$(CH_2)_6O$					
	$(CH_2)_6O$					
	$(CH_2)_5O$					
	$(CH_2)_8O$					
	$(CH_2)_6O$					

R^1	S^1-O	A-Z^1	B	Z^2-C	COO-S^2-R^2	相变
	$(CH_2)_6O$					
	$(CH_2)_6O$					
	$(CH_2)_6O$					
	$(CH_2)_6O$					
	$(CH_2)_8O$					
	$(CH_2)_7O$					
	$(CH_2)_6O$					

R^1	S^1-O	A-Z^1	B	Z^2-C	COO-S^2-R^2	相变
	$(CH_2)_6O$					
	$(CH_2)_6O$					
	$(CH_2)_6O$					

实施例 4

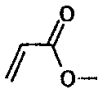
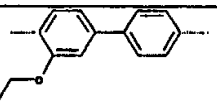
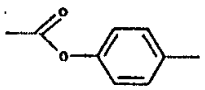
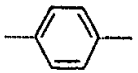
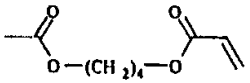
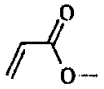
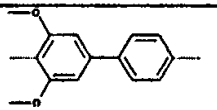
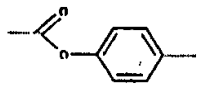
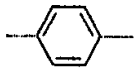
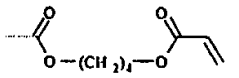
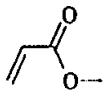
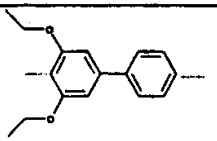
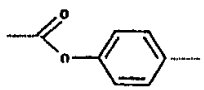
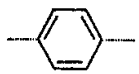
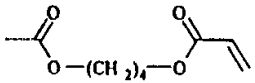
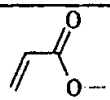
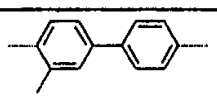
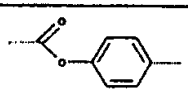
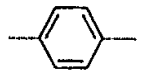
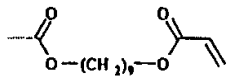
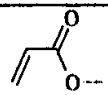
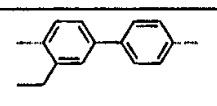
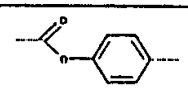
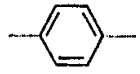
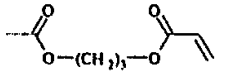
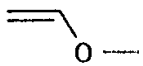
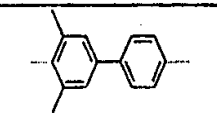
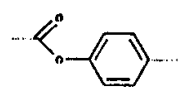
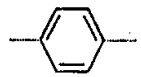
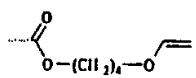
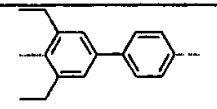
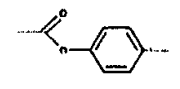
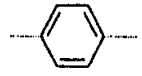
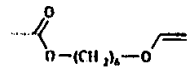
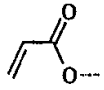
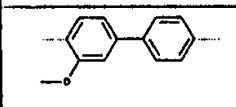
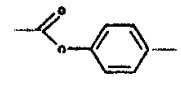
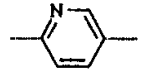
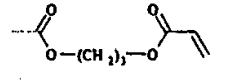
4'-（6-丙烯酰氧基己氧基）-3'-甲氧基联苯基-4-羧酸 4'-（4-丙烯酰氧基丁氧基羰基）联苯基-4-基酯

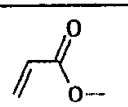
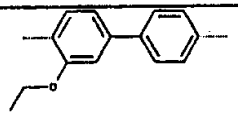
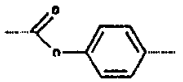
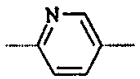
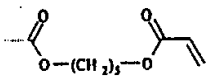
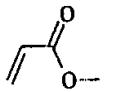
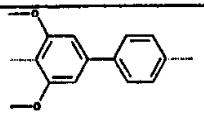
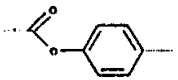
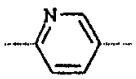
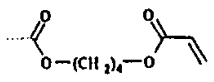
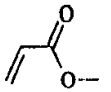
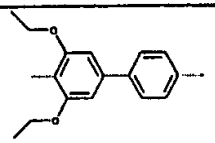
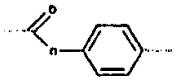
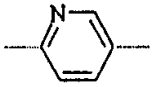
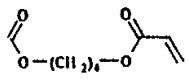
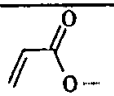
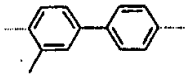
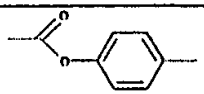
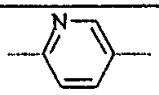
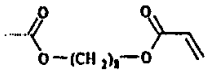
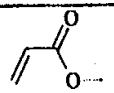
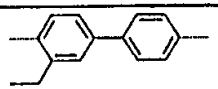
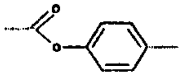
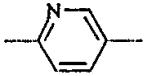
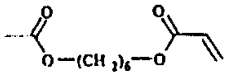
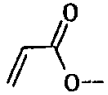
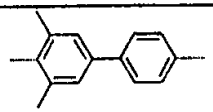
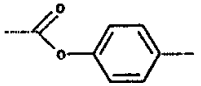
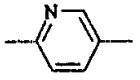
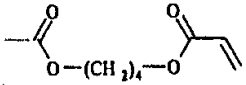
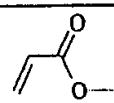
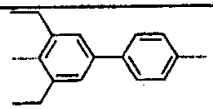
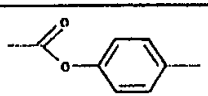
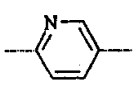
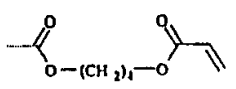
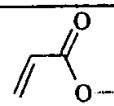
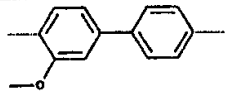
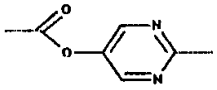
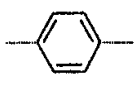
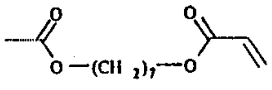


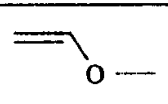
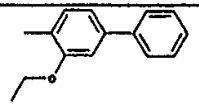
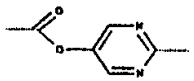
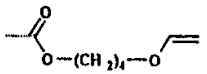
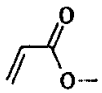
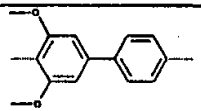
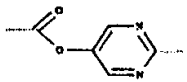
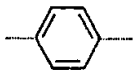
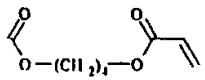
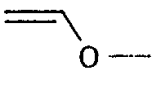
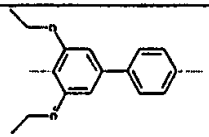
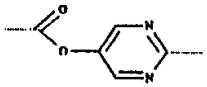
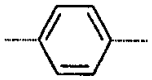
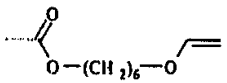
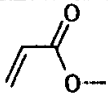
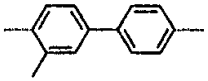
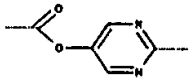
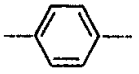
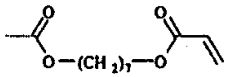
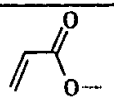
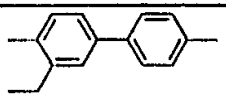
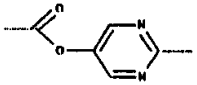
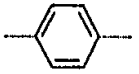
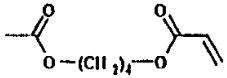
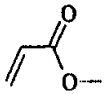
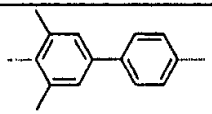
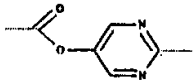
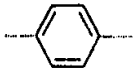
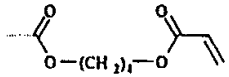
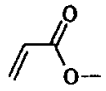
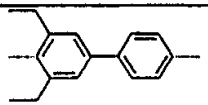
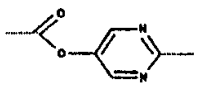
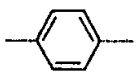
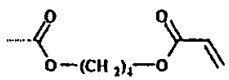
制备方法类似于实施例 1，使用 3.40 克（10 毫摩尔）4'-羟基联苯基-4-羧酸 4-丙烯酰基丁基酯，3.99 克（10 毫摩尔）4'-（6-丙烯酰氧基己氧基）-3'-甲氧基联苯基-4-羧酸，0.12 克（1 毫摩尔）DMAP 和 2.11 克（11 毫摩尔）EDC 制得。剩余物用硅胶色谱以环己烷/乙酸乙酯（7：3）提纯，并用乙醇重结晶一次，得到 4'（6-丙烯酰氧基己氧基）-3'-甲氧基联苯基-4-羧酸 4'-（4-丙烯酰氧基丁氧基羰基）联苯基-4-基酯。

以下化合物可以用类似方法制得:

$R^1-S^1-O-B-Z^2-C-Z^3-D-COO-S^2-R^2$

R^1	S^1-O	B	Z^2-C	Z^3-D	-COO-S^2-R^3	相变
	$(CH_2)_6O$					
	$(CH_2)_5O$					
	$(CH_2)_6O$					
	$(CH_2)_6O$					
	$(CH_2)_{10}O$					
	$(CH_2)_6O$					
	$(CH_2)_5O$					
	$(CH_2)_6O$					

R^1	S^1-O	B	Z^2-C	Z^3-D	-COO-S^2-R^3	相变
	$(CH_2)_6O$					
	$(CH_2)_6O$					
	$(CH_2)_7O$					
	$(CH_2)_6O$					
	$(CH_2)_6O$					
	$(CH_2)_6O$					
	$(CH_2)_6O$					
	$(CH_2)_4O$					

R^1	S^1-O	B	Z^2-C	Z^3-D	-COO-S^2-R^3	相变
	$(CH_2)_6O$					
	$(CH_2)_6O$					
	$(CH_2)_5O$					
	$(CH_2)_6O$					
	$(CH_2)_9O$					
	$(CH_2)_6O$					
	$(CH_2)_3O$					

实施例 5

40 重量%的 4’ -[4-（6-丙烯酰氧基己氧基）-3-甲氧基苯甲酸基]联苯基-4-羧酸 4-丙烯酰氧基丁基酯，40 重量%的 4’-[4-（6-丙烯酰氧基己氧基）-3-乙氧基苯甲酸基]联苯基-4-羧酸 4-丙烯酰氧基丁基酯和 20 重量%4-（6-丙烯酰氧基己氧基）苯甲酸 4-[4-（6-丙烯酰氧基己氧基）苯甲酸基]-2-甲基苯基酯的混合物引入到平行晶胞中。该晶胞的各向异性Δn=0.2。混合物的澄清点 T_C=54.3℃，观察到的 S_A/N 相变温度为 35.3℃。可将该混合物冷却到室温以下。