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Synthesis of high temperature cholesteric copolysiloxanes and their use as stationary phases for high resolution gas chromatography

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Summary

The synthesis of side-chain liquid crystalline copolysiloxanes containing-cholestery14-(10-undecen-1-yloxy)biphenyl-4'-carboxylate and 4-biphenyl 4-allyloxybenzoate mesogenic side groups is present. Differential scanning calorimetry, optical polarizing microscopy measurements reveal wide temperature range of cholesteric phase for all copolysiloxanes. The cholesteric temperature range depends upon the monomer feeding ratio. The copolysiloxanes containing higher percentage of cholesteryl 4-(10-undecen-1-yloxy)biphenyl-4'-carboxylate side group reveal wider temperature range of cholesteric phase. The synthesized copolysiloxanes were used as stationary phase in gas chromatography capillary columns. They show very unique chiral resolution properties for various kinds of enantiomers, i.e., linalool, menthol and menthone.

Introduction

Thermotropic side-chain liquid crystalline polysiloxanes were first synthesized by Finkelmann and Rehage. Since then, nematic, smectic and cholesteric liquid crystalline polymers, and elastomeric liquid crystalline networks containing polysiloxane backbone have been synthesized. Some of the synthetic works summarized above have been already reviewed(1,2). Interest in the polysiloxane backbone for the preparation of side-chain liquid crystalline polymers (LCPs), comes from the low glass transition temperature and high thermostability exhibited by this class of polymers.

Recently, high temperature mesomorphic polysiloxane "solvents" have demonstrated excellent potential as stationary phases in gas chromatography (GC) because of their superior properties with regard to chromatographic efficiency and thermal stability(3-17). Unlike conventional stationary phases that provide separation based on solute vapor pressure and/or different solubility arising from specific energetic interactions, liquid crystal stationary phases yield separation based upon differences in solute molecular shape. Although the properties exhibited by many monomeric liquid crystals are good from the point of view of GC requirements, polymeric liquid crystals are attracting growing attention because they offer significant improvements in column efficiency as well as thermal stability over monomeric liquid crystals.

In this work, the synthesis of a series of new cholesteric liquid crystalline polysiloxanes which can be used as GC stationary phase over a wide temperature range is presented. The particular examples refer to side chain liquid crystalline copolysiloxanes containing cholesteryl 4-(10-undecen-1-yloxy)biphenyl-4'-carboxylate and 4-biphenyl 4-allyloxybenzoate side groups. Their selectivity for some racemic compounds is also demonstrated.

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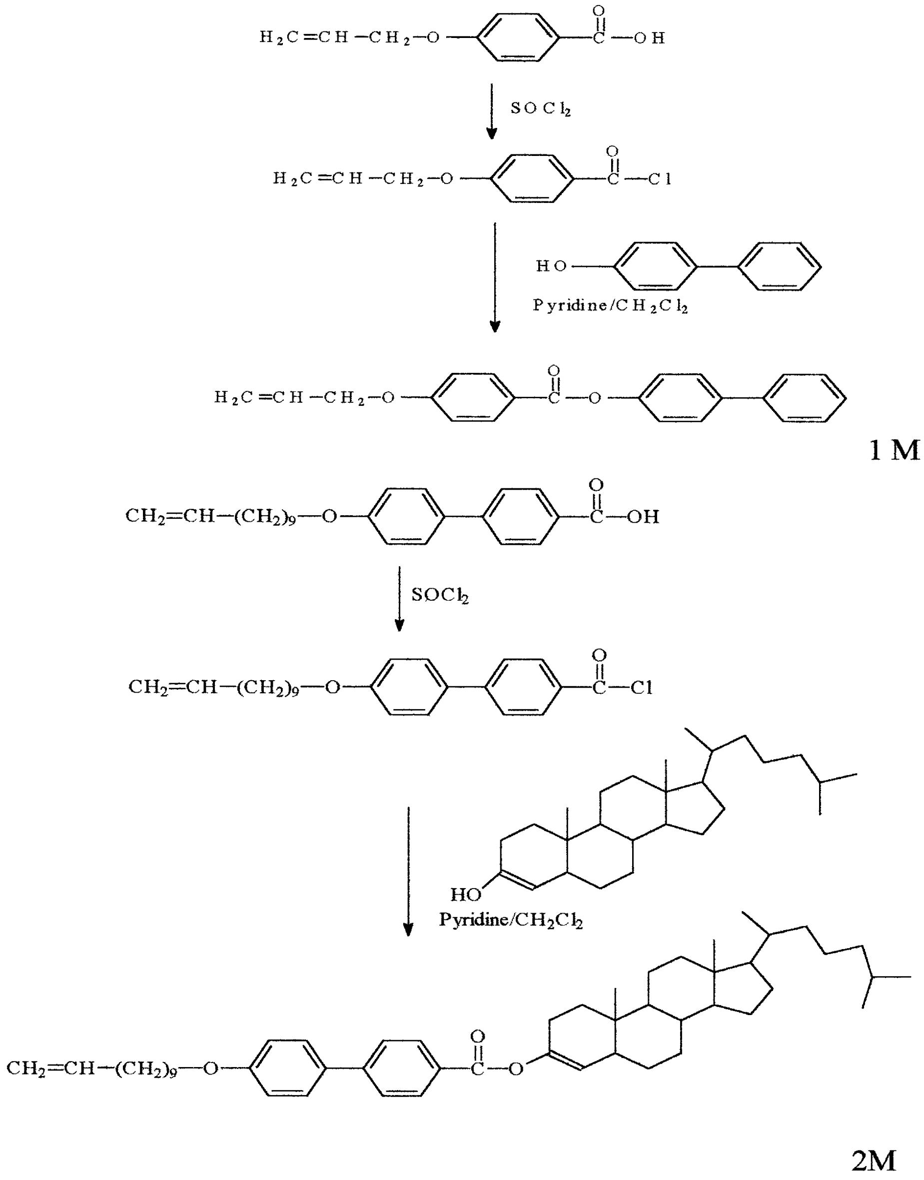
Experimental

Material

Poly(methylhydrogensiloxane)(Mn=2270) and platinum divinyltetramethyl disiloxane catalyst were obtained from United Chemical Technologies Inc., and used as received. 4-Hydroxybiphenyl-4'-carboxylic acid and 4-hydroxy-phenyl-4'-carboxylic acid (from TCI) and all other reagents (from Aldrich) were used as received. Toluene used in the hydrosilylation reaction was first refluxed over sodium and then distilled under nitrogen.

Techniques

The characterization of all polymers was performed by a combination of differential scanning calorimetry (DSC), optical polarizing microscopy and gel permeation chromatography (GPC) according to standard procedures used in our laboratory (17,18).

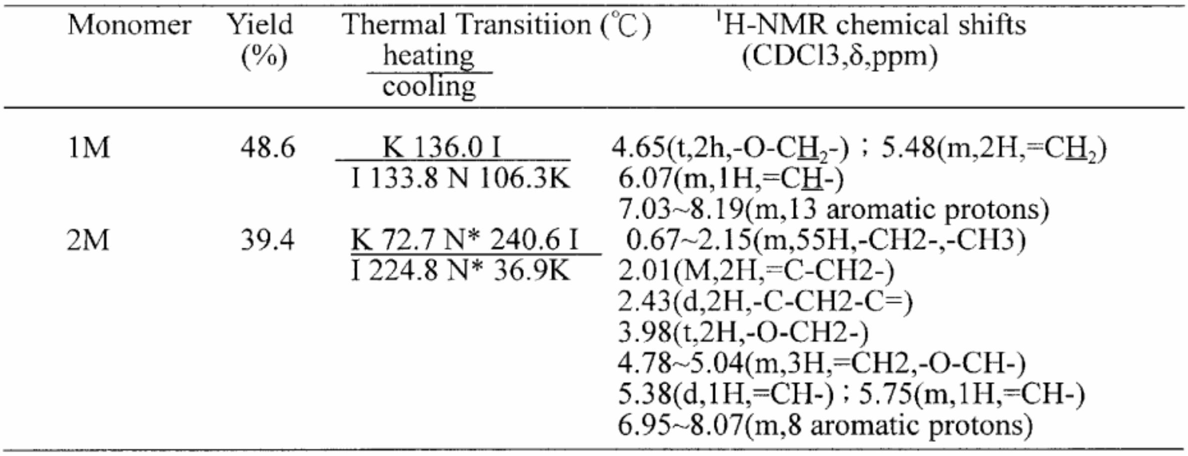


Scheme 1: Synthesis of monomers 1M and 2M

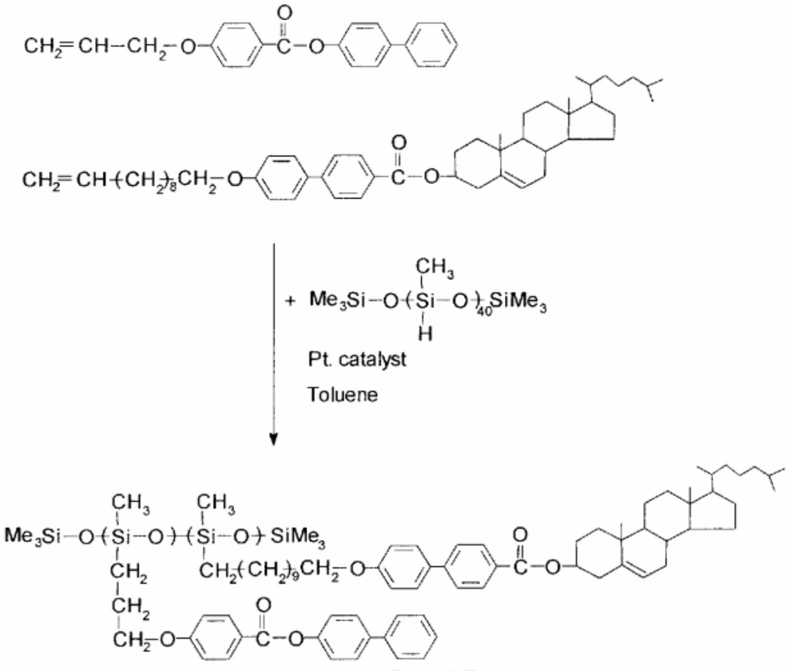
Synthesis of monomers

The synthesis of monomers 4-biphenyl 4-allyloxybenzoate (1M) and cholesteryl 4-(10-undecen -1-yloxy)biphenyl-4-carboxylate (2M) is outlined in Scheme 1. The detailed synthetic procedures for the intermediary compounds and monomers are similar to those reported previously(19). Table 1 reports the yields, thermal transitions and ^{1}H-NMR chemical shifts of both monomers.

Table 1. Yields thermal transitions and ^{1}H-NMR chemical shifts of 1M and 2M.



Monomer	Yield (%)	Thermal Transitiion (℃) heating / cooling	^{1}H-NMR chemical shifts (CDCl3,δ,ppm)
1M	48.6	K 136.0 I I 133.8 N 106.3K	4.65(t,2h,-O-C$\underline{H}_2$-) ; 5.48(m,2H,=C$\underline{H}_2$) 6.07(m,1H,=C$\underline{H}$-) 7.03~8.19(m,13 aromatic protons)
2M	39.4	K 72.7 N* 240.6 I I 224.8 N* 36.9K	0.67~2.15(m,55H,-CH2-,-CH3) 2.01(M,2H,=C-CH2-) 2.43(d,2H,-C-CH2-C=) 3.98(t,2H,-O-CH2-) 4.78~5.04(m,3H,=CH2,-O-CH-) 5.38(d,1H,=CH-) ; 5.75(m,1H,=CH-) 6.95~8.07(m,8 aromatic protons)



1 P ~ 6 P

polymer	1 P	2 P	3 P	4 P	5 P	6 P
monomer feeding ratio 1 M/ 2 M	100/ 0	90/10	80/20	70/30	60/40	50/50

Scheme 2: Synthesis of copolysiloxanes 1P~6P

Synthesis of copolysiloxanes 1P-6P

All copolysiloxanes 1P-6P were synthesized by the hydrosilylation of poly(methyl hydrogen siloxane) with different ratios of both monomers in the presence of a Pt catalyst (Scheme 2). Experiment details concerning their synthesis and purification are identical to those reported previously.

GC Column Fabrication and testing

Deactivated fused silica column, 30m by 0.32mm i.d. (from Restek) was washed with acetone, methylene chloride and water. It was dried at 280°C under a nitrogen flow, and then filled with a solution of 3.125 mg/ml polymer 6P in chloroform, calculated so as to produced a film thickness of ca. 0.25um. One end was then sealed and the other end attached to a vacuum pump, and the entire column was placed in a water bath at 40°C in order to hasten the evaporation of volatile solvent. The stationary phases were crosslinked with dicumyl peroxide. The columns was conditioned at 280°C overnight under a nitrogen flow until a stable baseline was obtained at the maximum sensitivity of the instrument.

Results and Discussion

Table 1 summarizes the thermal transitions of monomers 1M and 2M. Monomer 1M shows a monotropic nematic phase Figure 1A displays the nematic schlieren texture exhibited by 1M. Monomer 2M reveals both nematic and cholesteric phases on both DSC heating and cooling scans. Figure 1B shows the typical cholesteric oily streak texture exhibited by monomer 2M.

Table 2 summarizes the thermal transitions of copolysiloxanes 1P-6P. Polymer 1P reveals an enantiotropic nematic phase while polymers 2P-6P exhibits an enantiotropic cholesteric phase. Figures 2A and 2B present the typical nematic and cholesteric textures exhibited by 1P and 6P respectively.

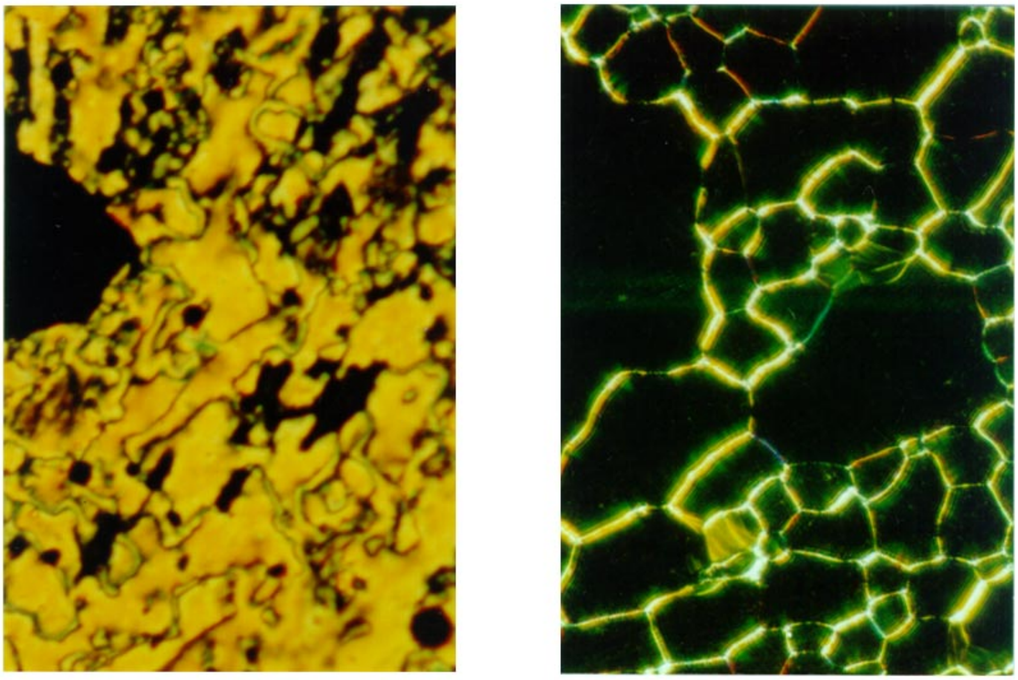
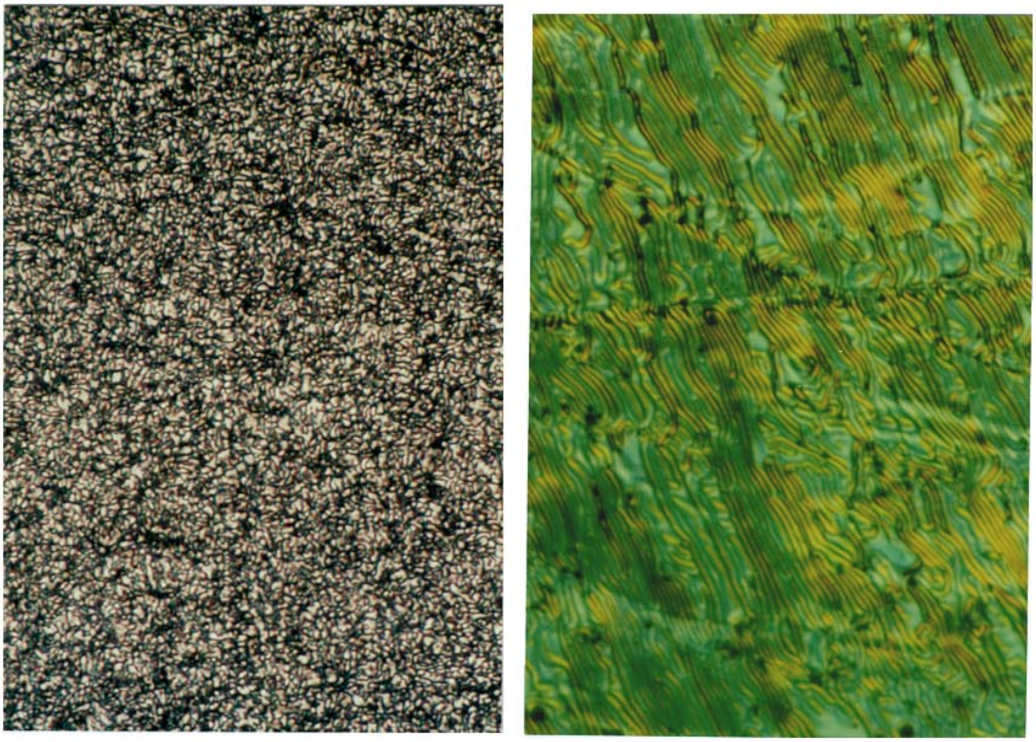

(A) (B)

Figure 1: Typical optical micrographs of monomers
(A) Nematic texture, 133.7℃ (1M) × 200
(B) Cholesteric texture, 189.9℃ (2M) × 200

Table 2. Thermal transitions of copolysiloxanes 1P-6P.

polymer	monomer feeding ratio 1M/2M (mole %)	phase transitions (℃) heating / cooling	temp. breadth of cholesteric phase (degree)
1P	100/0	G 65.9 N 174.5 I I 169.0 N	--
2P	90/10	G 45.7 N* 176.5 I I 173.2 N*	128.8
3P	80/20	G 57.4 N* 212.1 I I 207.6 N*	154.7
4P	70/30	G31.6 N* 213.7 I I 213.0 N*	182.1
5P	60/40	G42.5 N* 227.4 I I 224.2 N*	184.9
6P	50/50	G30.6 N* 253.0 I I 245.5 N*	222.4

G : glassy, N : nematic, I : isotropic



(A) (B)

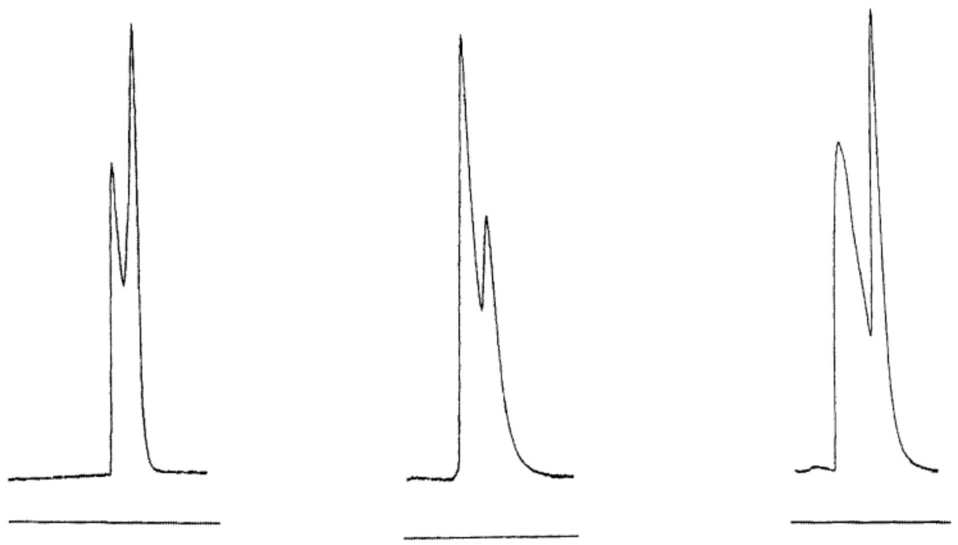
Figure 2: Typical optical micrographs of polymers

(A) Nematic texture,153.2℃ (1P) × 200

(B) Cholesteric texture,132.8℃ (6P) × 200

The mole percentage of cholesteryl 4-(10-undecen-1-yloxy)-biphenyl-4'-carboxylate increases from 10% to 50% and the cholesteric temperature range increases from 128.8 to 222.4 degrees. Therefore, polymer 6p which shows widest temperature range of cholesteric phase, was used as GC stationary phase.

The separation of three kinds of enantiomers, i.e., linalool, menthol and menthone, on polymer 6P capillary column are illustrated in Figures 3A~3C. As can be seen from these figures, three kinds of enantiomers were easily separated by this cholesteric stationary phase. Their separation factors(α) are 1.350, 1.174 and 1.357 for the linalool, menthol, menthone respectively. We believe that the chiral resolution ability is due to the helical supermolecular structure of cholesteric liquid crystalline polymers. As far as we know, this is the first example to demonstrate that cholesteric liquid crystalline polymers have enantioselectivity.



3A 3B 3C

Figure 3: polymer 6P capillary column separation of some enantiomic compounds
(A) Linalool (B) Menthol (C) Menthone

In conclusion, a series of cholesteric liquid crystalline copolysiloxane containing 4-biphenyl 4-allyloxybenzoate and cholesteryl 4-(10-undecen-1-yloxy) biphenyl- 4'-carboxylate side groups, were synthesized and characterized. All of the synthesized copolysiloxanes display very wide temperature ranges of cholesteric phase. The temperature breadth of cholesteric phase depends on the mole percentage of cholesteryl 4-(10-undecen-1-yloxy)biphenyl-4'-carboxylate side group. The copolysiloxane containing highest percentage of cholesteryl 4-(10-undecen-1-yloxy)biphenyl- 4'-carboxylate side group reveals the widest temperature range of cholesteric phase. This copolysiloxane also shows excellent chiral resolution properties for some enantiomers.

Acknowledgement

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