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SYNTHESIS AND POLYMERIZATION OF REACTIVE CHIRAL LIQUID CRYSTALS BEARING A TETRAFLUOROPHENYLENE IN CORE STRUCTURE

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ABSTRACT

A new reactive fluorinated liquid crystal (1) was synthesized. The thermal behavior was studied by polarizing microscopy and DSC. The monomeric mesogen was polymerized to afford a novel fluorinated side-chain polysiloxane which exhibits liquid crystallinity. The nonfluorinated mesogen and polysiloxane were also synthesized for comparison. The results show that the displacement of phenylene by tetrafluorophenylene causes mesogen to exhibit preferentially nematic mesophase rather than cholesteric or smectic one, and the large polarization in main core section leads mesogen to show the higher smectic mesophase.

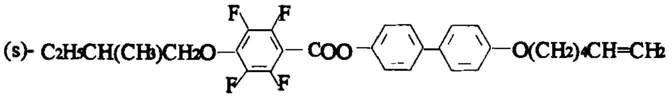
INTRODUCTION

Liquid crystalline side-chain polymers have been the subject of much attention due to their potential application in electro-optical devices [1 -7].

Liquid crystalline side-chain polysiloxane which has been investigated extensively, is one of the main liquid crystalline polymers [2 - 7]. The fluorine atom has been used for a long time as a substituent in place of hydrogen on the aromatic ring of rod-like mesogen [8, 9]. Varying the position and number of substitutions allows one to modify the range of mesomorphism as well as other physical properties in low molecular weight mesogen. However. the incorporation of a fluorinated aromatic ring into mesogen moiety of liquid crystalline side-chain polymers has not been exploited so far. Hence, we try to synthesize fluorinated polysiloxanes. In this paper, two types of reactive chiral liquid crystals one of which contains a tetrafluorophenylene in core structure is noted and their polymeric liquid crystals were obtained by polysilylation. The fluorinated liquid crystal is expected to possess low viscosity and good compatibility which are very important for liquid crystalline polymers in practice.

SYNTHESIS

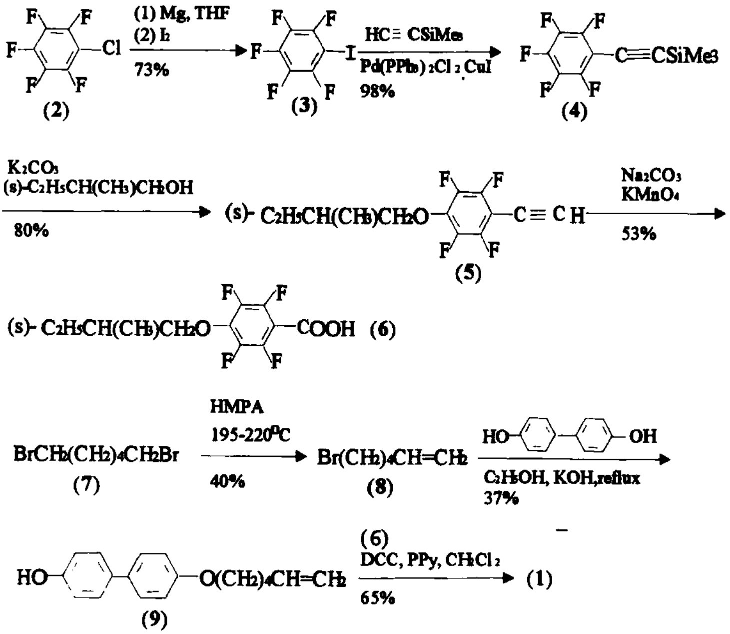
The liquid crystal studied in this paper bears a tetrafluorophenylene, a chiral alkoxy and a polymerizable vinyl moiety pictured as follows:



(1)

The incorporation of a tetrafluorophenylene into mesogen is relatively difficult. Often, introduction of fluorine into aromatic ring involves a series of procedure — nitration, reduction, diazonation and substitution. We get around these long steps by employing chloropentafluorobenzene as starting reagent, a much readily available fluoride reagent. The synthesis route is given in Scheme 1.

Halogen exchange from chloropentafluorobenzene to iodopentafluorobenzene was completed via Grinard reagent.



SCHEME 1

Iodopentafluorobenzene 3 reacted with trimethylsilylacetylene catalyzed by bis(triphenylphosphine)palladium dichloride and copper(I) iodide in triethylamine to afford 1-pentafluorophenyl-2-trimethylsilylacetylene(4) [10]. Nucleophilic substitution of pentafluorophenyltrimethylsilylacetylene 4 by (s)-2-methyl-butan-1-ol yielded p-((s)-2-methyl-butoxy)tetrafluorophenylacetylene(5) which was, in turn, oxidized readily by $KMnO_4$ in basic dioxane to give the chiral acid 6.

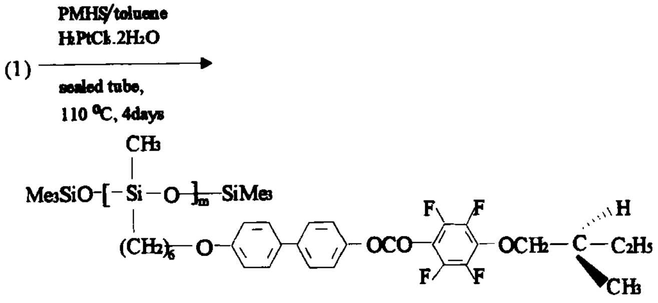
ω-Bromoalkene-1 used in this study was prepared by standard method reported [11]. 6-Bromohexene-1 8 reacted with 4,4'-biphenol to give biphenol 9. Biphenol 9 condensed with chiral acid 6 using dicyclohexylcabodiimide(DCC) as dehydrating reagent and catalytic

4-pyrrolidinopyridine(PPY) monomeric liquid crystal 1. Intermediates 3 and 8 were distilled to give pure products. The other compounds were purified by flash chromatography on silica gel columns. The procedure to synthesize chiral liquid crystalline polysiloxane 10 is illustrated in Scheme 2.

Polymerization was carried out in dried toluene in sealed tube at 110°C for 4 days according to the classical hydrosilylation reaction between the monomer 9 and polymethyltydrosiloxane(PMHS) in the presence of catalytic $H_2PtCl_6.2H_20$. The desired polymer was purified by dissolving the polymer in CH_2Cl_2 and precipitating it with methanol repeatedly until the unreacted precursor was removed(monitored by TLC). For comparison, nonfluorinated mesogen (14) and polysiloxane(15) were also prepared as shown in Scheme 3. All the compounds were examined by NMR, IR, MS and elemental analysis and gave good results.

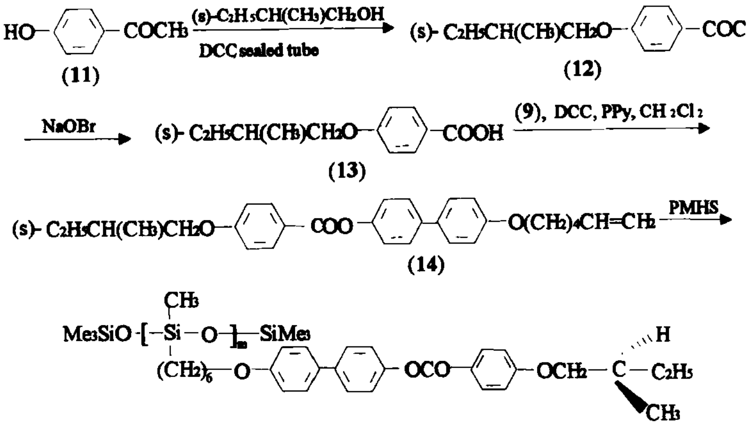
RESULTS AND DISCUSSION

Fluorinated monomer 1 whose characteristic texture was confirmed by polarizing optical microscopy (POM) exhibits nematic and cholesteric mesophase. The mesophase ranges on DSC are in good accordance with those on stage-heat set monitored by POM as shown in Table 1. For investigating the effect of tetrafluorophenylene instead of phenylene on mesomorphic property, we also synthesized the nonfluorinated mesogen as structure 14. Mesogen 14 only shows cholesteric mesophase, the melting point and the clearing one are 139.8°C and 176°C, respectively. However, the transition temperatures of the corresponding fluorinated mesogen 1 are 79.6 and 131.2°C. These results reveal that fluorinated phenylene in mesogen core structure reduces both melting point and clearing point more than 40°C, and depresses cholesteric mesophase because fluorinated mesogen 1 shows only relatively narrow cholesteric range and rather wide nematic range.



Polysiloxane(10)

SCHEME 2



Polysiloxane (15)

SCHEME 3

TABLE 1

Transition temperature(^{o}C) of mesogens and polysiloxanes

mesogen	polysiloxane	transition temperature* (corresponding enthalpy change, J/g)
1		$C \underset{66.8(24.56)}{\overset{79.6(27.51)^{**}}{\rightleftarrows}} Ch \underset{72.4(0.19)}{\overset{87.5}{\rightleftarrows}} N \underset{128.8(0.60)}{\overset{131.2(0.56)}{\rightleftarrows}} I$
14		$C \underset{123.0(62.39)}{\overset{139.8(60.5)}{\rightleftarrows}} Ch \underset{172.1(1.53)}{\overset{176.0(1.50)}{\rightleftarrows}} I$
	10	$C \underset{108.5(6.46)}{\overset{111.6(7.98)}{\rightleftarrows}} S_A \underset{156.7(0.92)}{\overset{164.1(0.78)}{\rightleftarrows}} I$
	15	$C \underset{150.0(7.63)}{\overset{157.0(5.11)}{\rightleftarrows}} S_A \underset{189.0(0.60)}{\overset{192.0(0.61)}{\rightleftarrows}} I$

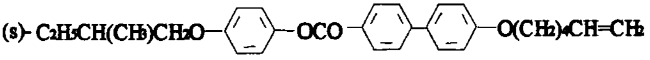
* C, crystal; S_A, smectic; Ch, cholesteric; N, namestic; I, isotropic phase. The temperatures shown are the peak values on DSC with heating and cooling rates at 3°C and -3°C, respectively.

** The value contains the enthalpy from crystal phase to Ch and Ch to N phase.

Fluorinated polymer 10 shows S_A phase over wide temperature range from 111.6 to 164.1°C. The transition temperature rises to higher temperature than that of the corresponding vinyl monomer. The polymer only exhibits S_A because polymer structure does not allow mesogenic moiety to arrange freely.

The nonfluorinated mesogen 14 and polysiloxane 15 shows the same rule. Polymerization results in the improvement of the melting point from 139.8 to 157°C and the clearing point from 176.0 to around 192°C. The texture feature of polysiloxane 15 on polarizing microscopy is fan-focused structure of S_A mesophase.

Hsu et al. [12] reported mesogen 16 as shown below which have the same molecular structure as compound 14 except for the direction of central ester linkage. Mesogen 16 actually is a isomer of 14 which has reverse ester bond comparing to compound 16. However, the mesophases of them are quite different.



(16)

Mesogen 16 where the carbonyl function of ester is conjugated with biphenylene shows smectic A and monotropic B phase. In contrast, mesogen 14 with reverse ester bond attached the terminal aromatic ring bearing chiral alkyl exhibits Ch mesophase. The mesomorphic difference of mesogen 14 and 16 confirms again the fact that the direction of central linkage effects mesomorphism considerably.

CONCLUSION

Incorporation of fluorine into aromatic core of mesogen decreases phase transition temperature. Polymerization of mesogen raises both melting point and clearing point.

ACKNOWLEDGMENTS

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