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### Geraniol Based Side Chain Liquid Crystalline Polymer: Synthesis and Characterization

Garima Mishra<sup>a</sup>; A. K. Srivastava<sup>a</sup>

<sup>a</sup> Department of Chemistry, H. B. Technological Institute, Kanpur, India

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# Geraniol Based Side Chain Liquid Crystalline Polymer: Synthesis and Characterization

GARIMA MISHRA and A. K. SRIVASTAVA

*Department of Chemistry, H. B. Technological Institute, Kanpur, India*

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Side chain liquid crystalline (SCLC) polysiloxane polymer with a geraniol mesogenic group and polymethylene spacers were prepared, and their properties were compared with those of an equivalent SCLC polymer, SCLCP's, with phenyl benzoate mesogenic group. The phase behavior was studied by differential scanning calorimetry (DSC) and optical polarizing microscopy (OPM). The DSC curve showed a clear melting temperature and isotropization at 72 and 148°C, respectively, with a glass transition at 25°C. The observation of a fan-shaped texture confirms the presence Smectic A phase under an optical polarized microscope.

**Keywords:** LCP; mesophases; polysiloxanes

## 1 Introduction

Side chain liquid crystalline polymers (LCP's) are interesting and useful materials combining the properties of low molecular weight liquid crystals (LC's) such as optical anisotropy, reorientation induced by external stimulations, high mobility, viscous flow, surface-induced orientation etc., and also those of polymers such as mechanical toughness, easy fabrication as solid films and so forth.

Since the flexible spacer concept was established by Finkelmann et al. (1), many side-chain liquid crystalline polymers (SCLCPs) have been synthesized. The intrinsic properties of SCLCPs are of great interest. These are a combination of the properties of monomolecular liquid crystals (their anisotropy and orientation ability) and the properties of macromolecular materials (mainly their good thermal and mechanical stability). Much work in the literature, therefore, focuses on how parameters such as the structure of polymer backbone, nature and length of spacers, and the type of mesogen affect mesomorphic behavior (2–4). Amongst, these the type of mesogen is of prime importance because the high anisotropy of the mesogenic units give rise to polymorphism i.e., to the formation of a number of thermodynamically stable phases between the crystalline and isotropic states (5).

In traditional understanding, the mesogenic group must consist of two or more 1,4-phenylenes directly linked, or through linkages such as ester, oxymethylene or methylene unit. In some cases, the 1,4-cyclohexyl ring or 2,5-disubstituted-1,3 dioxane is also used to replace one of the phenylenes (6). Over the past few years, several reports regarding modifications, and synthesis of new meogens have been reported. These include phenolphthalein as a part of mesogen (7), 1,3,4-thiadiazole ring as mesogen (8), banana shaped mesogen (9), disubstituted ferrocene ester as mesogen (10), [2.2] parafluoroalkyl substituted carbohydrates based mesogen (11), new mesogens with fluoro substituted bent core (12), new smectic C mesogens containing the benzyl, phenylethyl or phenylpropyl moiety (13), new sheet shaped mesogen based on 1,3,5-triazines (14), mesogen with cyclopentanone moiety (15), the list is only illustrative but never be exhaustive.

Although, the literature on low molar mass, liquid crystalline compounds is quite rich (16), most of the research on side-chain liquid crystalline polymers containing rod-like mesogens are based on biphenyl or phenylbenzoate derivatives (17, 18). Moreover, few reports on terphenyl based side chain liquid crystalline polymers are also available (19, 20). The search of the literature reveals that the majority of mesogens have been synthesized using phenylene units in the mesogen but, to the best of our knowledge, the literature on terpene units in mesogen is still scarce (21). However, the use of terpene copolymers as a backbone for the synthesis of side chain liquid crystalline polymers are the recent origin from this lab (22). The goal of this paper

Address correspondence to: A. K. Srivastava, Department of Chemistry, H. B. Technological Institute, Kanpur 208 002, India. E-mail: akspolym@rediffmail.com

is to present the synthesis and characterization of liquid crystalline polysiloxane containing geraniol based mesogen as a new side group.

## 2 Experimental

### 2.1 Materials

4-hydroxybenzoic acid (Across), geraniol (Merck) hydrogen hexachloroplatinate (IV) hydrate ( $\text{H}_2\text{PtCl}_6$ ) (Merck), were used as received. Triethylamine was refluxed over potassium hydroxide and distilled. Other reagents and solvents were used without further purification.

Poly methylhydrogensiloxane (PMS) obtained from Merck PS-122 of  $M_n$  2270 molecular weight was used for the preparation of polymethylsiloxane SCLCP's.

### 2.2 Techniques

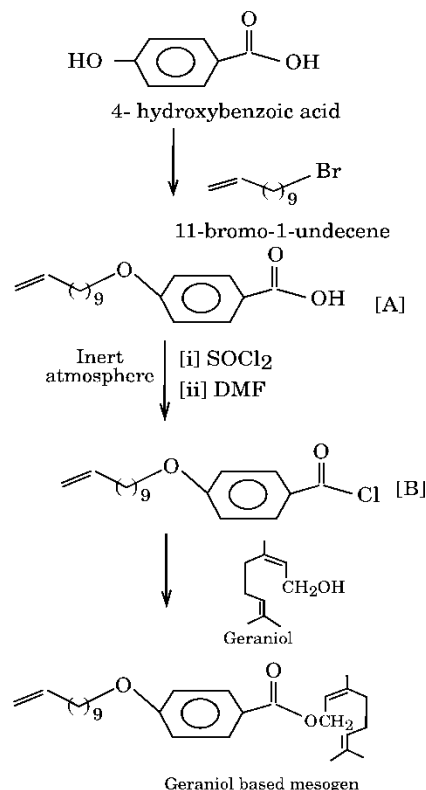
$^1\text{H-NMR}$  spectrum was recorded with a Varian 100HA Jeol LA 400 spectrophotometer using  $\text{CDCl}_3$  as a solvent and tetramethylsilane as an internal reference. The Fourier Transform Infrared (FT-IR) spectrum was recorded with Perkin-Elmer 599B, with KBr pellets. Thermal transitions and thermodynamic parameters were determined by using Perkin-Elmer DSC-7 Differential Scanning Calorimeter. Heating and cooling rates were  $10^\circ\text{C}/\text{min}$ . The anisotropic textures were observed with Censico Optical Polarized Microscope in conjunction with a Instec HS1 Hot Stage.

### 2.3 Synthesis of Monomer and Polymer

Vinyl terminated mesogen was prepared by the Scheme 1. The 4-(10-undecyloxy)benzoic acid [A] was prepared by conventional method. The preparation of geraniol based mesogen is described in Scheme 1.

7 gm (24.13 mmols) of [A] was dissolved in 10 ml of (16.39, 137 mmol) of thionylchloride and 70  $\mu\text{l}$  of dimethylformamide in an inert atmosphere. This solution was stirred overnight, then heated for 2 h in an oil bath with the bath temperature of  $60^\circ\text{C}$ . The excess thionyl chloride, was removed under vacuum and the acid chloride remaining was dissolved in 15 ml of THF. The acid chloride solution was added dropwise to a mixture of 3.83 g (24.9 mmol) of geraniol 3.26 g (32.2 mmol) of triethylamine, and 20 ml of THF, over 30 min. The reaction mixture was stirred for 4 h at room temperature, then heated in a  $60^\circ\text{C}$  oil bath for 1.5 h, after which 50 ml of methylene chloride was added to the mixture, followed by washing 3 times with water. After this product was dried over sodium sulfate, methylene chloride was evaporated, and the crude product was purified by silical-gel column chromatography using a 70:30 ratio mixture of methylene chloride to hexane as the eluent (yellow crystals).

Yield: 5.89 g (13.8 mmols).



Sch. 1. Preparation of geraniol based mesogen.

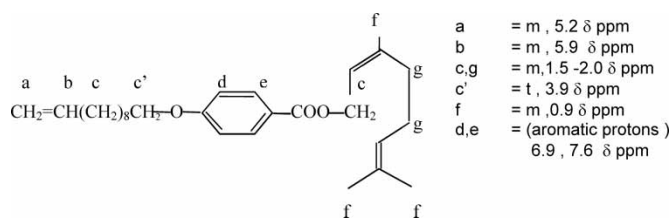
### 2.4 Structural Characterization

#### (i) Fourier Transform Infrared Spectroscopy (FT-IR):

The FT-IR spectra of the monomer shows following band (Figure 1).

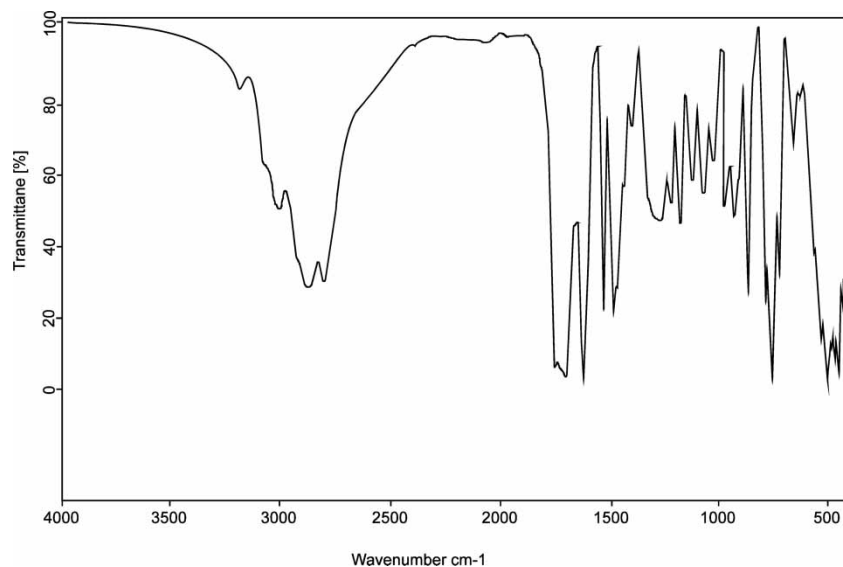
- 2977  $\text{cm}^{-1}$ : alkane C-H stretching
- 3059  $\text{cm}^{-1}$ : aromatic C-H stretching
- 1644  $\text{cm}^{-1}$ : C=C stretching
- 1720  $\text{cm}^{-1}$ : C=O stretching.

#### (ii) Nuclear Magnetic Resonance ( $^1\text{H-NMR}$ ): (Figure 2)



#### (iii) Thermal Analysis:

On cooling from the isotropic state, initially mesogen showed a nematic droplet texture at  $93^\circ\text{C}$ , slowly it gets converted to a schileren texture at  $91^\circ\text{C}$ , then at  $86^\circ\text{C}$ , a mosaic



**Fig. 1.** FT-IR spectrum of the geraniol based monomer.

texture appeared and on further cooling a homeotropic texture gets formed.

K67S86N911

## 2.5 Synthesis of Polysiloxanes

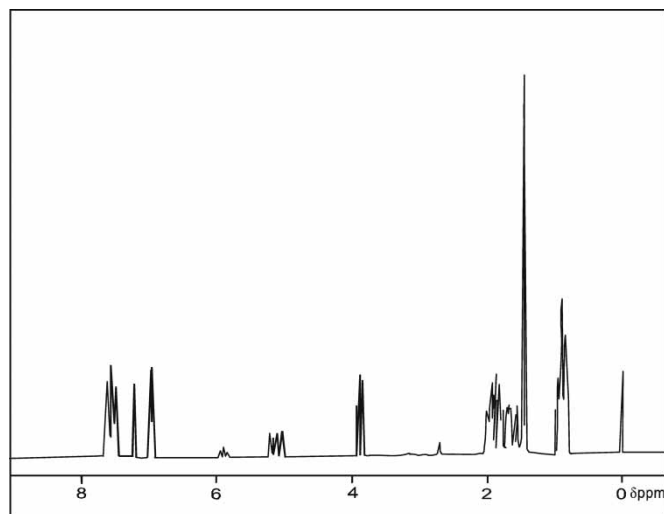
The synthesis of liquid crystalline polysiloxanes is outlined in Scheme 2. A general synthetic hydrosilation reaction (23) procedure is described below.

0.8 g (10 mol% excess vs. the Si-H groups present in polysiloxanes) of the olefinic derivatives was dissolved in 80 ml of dry toluene together with the proper amount of poly(methylhydrogensiloxane). The reaction mixture was heated to 110°C under nitrogen and 100 μg of

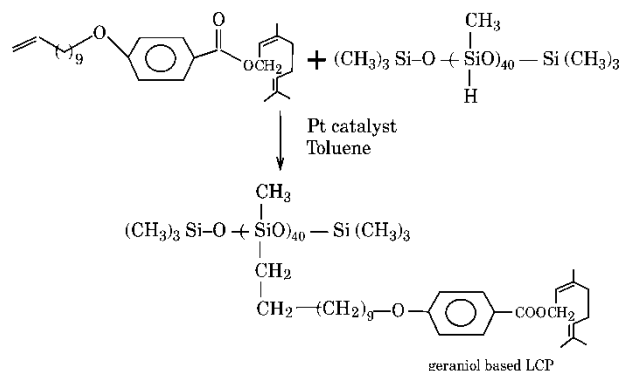
di-cyclopentadienylplatinum (II) chloride catalyst was then injected with a syringe as a solution in methylene chloride. The reaction mixture was refluxed for 24 h. The extent of hydrosilation reaction was monitored by FT-IR analysis (Figure 3) until no or negligible Si-H absorption ( $2160\text{ cm}^{-1}$ ) was detectable by IR spectroscopy on an evaporated film on the reaction mixture. The polymer was washed and precipitated by methanol and dried under vacuum.

## 3 Results and Discussion

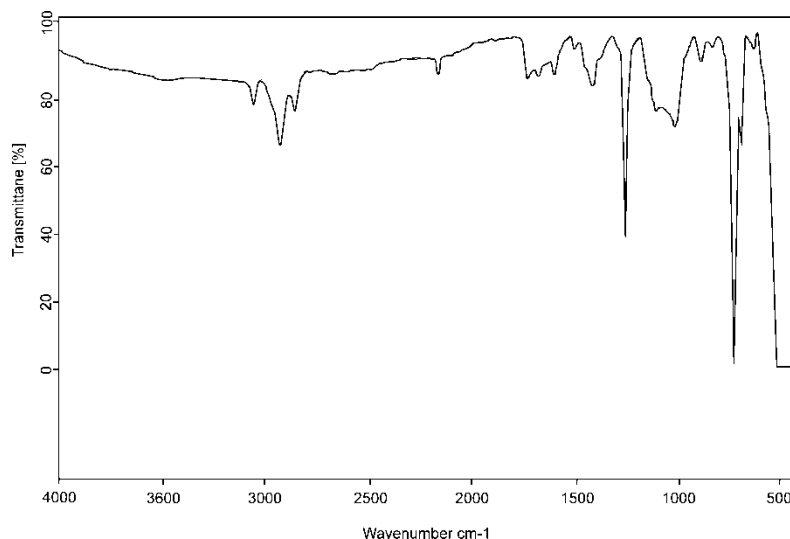
Side Chain Liquid Crystalline Polymers with PMS main chain were prepared by the standard hydrosilation reaction and their structures were confirmed by  $^1\text{H-NMR}$  spectra. Thermotropic mesomorphism was investigated with a combination of DSC and OPM. As expected, the polymer exhibited an enantiotropic mesophase. In the present study, the



**Fig. 2.** FT-IR spectrum of the LC polymer.



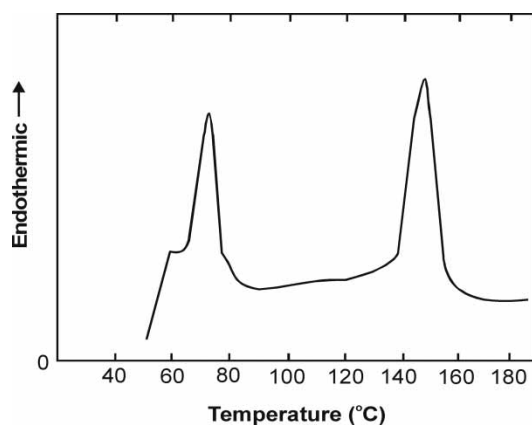
**Sch. 2.** Synthesis of polysiloxane containing geraniol based side group.



**Fig. 3.** FT-IR spectrum of the LC polymer.

geraniol, a acyclic terpenoid, has been introduced for the first time in the mesogen while keeping the spacer group and backbone identical. The polymer showed clear melting and isotropization transition.

The DSC thermogram showed well separated melting and isotropization at 72 and 148°C, respectively (Figure 4). Under an optical polarized microscope, on cooling from the isotropic state, a fan-shaped texture formed at 94°C (Figure 5). This type of textural behavior is typical for smectic A phase (24). In contrast, the biphenyl containing PMS polymers with a spacer length of 3 and 4 underwent side chain crystallization, but the phenyl benzoate containing polymers with identical spacers showed only glass transition by DSC with  $T_g$  values at low temperature, same as the case for geraniol based LCP, it also showed low glass transition value, with clear transitions temperatures. It is widely believed that biphenyl containing PMS polymers, underwent side chain crystallization, but the phenyl benzoate containing polymers



**Fig. 4.** DSC thermogram of the LC polymer for the second heating cycle at 10°C/min.

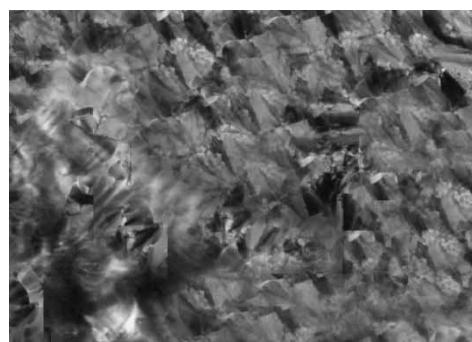
showed only glass transition by DSC with  $T_g$  values at low temperature. Consequently stable mesophases were obtained for the polymers with geraniol based side chains with observable liquid crystalline phases above  $T_m$ , because of longer spacer group the geraniol based PMS polymers, did not underwent side chain crystallization.

The phase transitions showed by geraniol based LC polymer are as follows:



The increased melting and isotropization temperatures is due to the presence of geraniol (a acyclic terpenoid). This result points toward the conclusion that, although a terpene based mesogen does not effect the type of mesophase formed, it does give rise to higher transition temperatures. These results are in good agreement with the literature where phenyl benzoate based units have been used in the mesogen.

The phase transitions showed by phenyl benzoate based LC polysiloxanes (25) with identical spacer is:



**Fig. 5.** Optical polarized micrographs displayed by polymer focal-conic texture of the smectic-A phase.

The result demonstrates that the replacement of phenyl benzoate units by geraniol favors smectic mesomorphism with higher isotropization temperature because the presence of geraniol moiety in mesogen provides higher stability due to hyperconjugation and resonance phenomenon.

A comparison of liquid crystalline polysiloxanes with phenyl benzoate mesogenic group and geraniol based mesogenic group showed that the glass transition temperature  $T_g$  and transition temperatures of geraniol based LC polysiloxanes are higher than that of phenyl benzoate based polysiloxanes.

#### 4 Conclusions

We have synthesized a new LC polymers with geraniol in mesogenic group attached to a polysiloxanes backbone via polymethylene spacer. A comparison with phenyl benzoate based liquid crystalline polysiloxanes showed almost similar mesomorphic behavior with higher isotropization. A focal-conic fan texture typical for smectic-A phase was obtained for the polymers. The geraniol based LCP showed only glass transition temperature by DSC with  $T_g$  value at low temperature.

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