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ORIGINAL CONTRIBUTION

Liquid crystalline side chain polymer with a poly (Geraniol-co-MMA) backbone and phenylbenzoate mesogenic group: synthesis and characterization

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Abstract A new side chain liquid crystalline polymers have been synthesized and characterized in which [geraniol-co-MMA] polymer are used as a backbone linked via polymethylene spacer to phenyl benzoate mesogenic group. The polymer exhibits enantiotropic liquid crystallinity with nematic phase and does not exhibit side chain crystallization .A clear difference between the nature of the mesophase is evidenced between [Geraniol-co-MMA] main chain and methacrylate polymers .The LC polymer exhibit glass transition at 40 °C. In a comparative analysis, we discuss the relevance of polymer backbone in the synthesis of side chain liquid crystalline polymers.

Keywords Liquid crystalline polymers · Methyl methacrylate · Mesophase

Introduction

Thermotropic liquid crystalline (LC; elements requiring nonlinear optical characteristics [6] and is piezo-, pyro-, and ferroelectric devices) polymers have become an interesting research topic in the past decade [1, 2] because of scientific applications such as information storage [3–5]. Liquid crystalline polymers were divided into two major classes: (1) polymer containing the mesogenic group in backbone (main chain liquid crystalline polymers, MCLCPs) and (2) polymers with the mesogenic group on the side chains of the polymer (SCLCPs) which are the focus of this study.

Liquid crystalline side chain polymers can be prepared by two general process [7, 8]. The most conventional method is to introduce into a mesomeric molecule a reactive group capable of undergoing addition polymerization. Generally, the polymerizable group is a methacrylate [2], an acrylate [9], or an chloroacrylate [10], which forms a flexible vinyl backbone after radical polymerization. The second possibility starts with "reactive polymers" [2–12], which can be transformed into mesogenic side chain polymers by using suitable reactive mesogenic monomers.

It has been reported that not only the nature and length of the flexible spacer but also the nature of the polymer backbone influence the range of thermal stability of the mesophase [13–15]. In fact, several research groups have mentioned that for the same spacer length and mesogenic unit, the broadest thermal stability of the mesophase is always obtained with the most flexible backbone [15–17]. In the case of polymer backbones, polysiloxanes, polyacrylates, and polymethacrylate backbone have been widely studied. Besides this, other polymers such as polyphosphazenes [16], polyepichlorohydrins [17], poly(phenylene oxide) [18], and polysulfones [19] have been widely used in the synthesis of side chain liquid crystalline polymers. The literature is also enriched by the publications on SCLCPs using polyacetylene [20–22], polyoxetanes [23], and polycarbosilane [24] as backbones. Recently, SCLCPs based on poly (dipropargylamine) [25] and polybutadiene diols [26] backbones have also been reported. The utilization of terpene copolymers as polymer backbone for the synthesis of side chain liquid crystalline polymers is a topic of recent origin from this lab [27, 28]. The terpene copolymers exhibit low T_g values, optical activity, and functionality. These properties can play a vital role in the synthesis of SCLCP, so it was of interest to evaluate these copolymers as backbone for the synthesis of SCLCPs.

The goal of this work was to synthesis and characterize new SCLCP [Geraniol-co-MMA] polymer attached to phenyl benzoate mesogenic group with methylene unit. These SCLCPs show low glass transitions value T_g as compared to their copolymers with enantiotropic mesomorphic behavior.

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Experimental

Materials

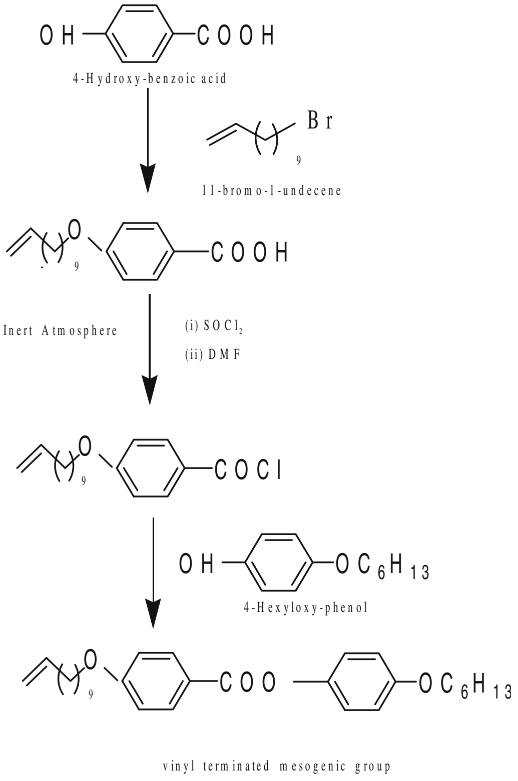
4-hydroxybenzoic acid (Across), 4-hexyloxyphenol (Lancaster), 11-bromo-1-undecene(Lancaster), thionyl chloride (Merck) were used as received. Triethylamine was refluxed over potassium hydroxide and distilled. Azobisisobutyronitrile (AIBN) was recrystallized twice by methanol. Other reagents and solvents were used without further purification.

Instrumental analysis

Thermal transitions were measured with Perkin-Elmer DSC-7 differential scanning calorimeter at heating and cooling rates of 10 °C/min. The anisotropic textures were observed with Censico Optical polarized microscope in conjunction with a Instec HS1 Hot Stage.

Synthesis of monomer and copolymer

The vinyl-terminated mesogen, containing the phenyl benzoate mesogenic core was prepared according to the published literature by and Itoh and Lenz [29]. The scheme is as given below:



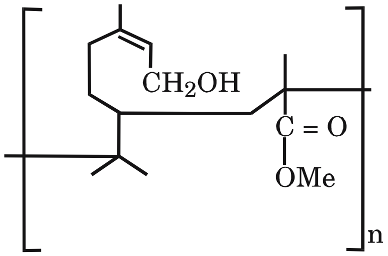
ANAL., Calcd: C, 77.22% H. 9.07%
Found, C, 77.2%; H, 8.09%
Yield, 5.86 g (12.6 mmol, 51%)

Synthesis of copolymer

The synthesis and general characterization of copolymer of Geraniol with MMA have been reported elsewhere [30]. Briefly, a solution containing Geraniol (1.20 mol/l), MMA (2.1 mol/l) and BPO (2.06×10^{-2}) as initiator in xylene were polymerized for 50 min at 80±0.1 °C under inert atmosphere of nitrogen. The copolymer was precipitated in methanol and dried to constant weight. The molecular weight details of the copolymer [30] obtained are as follows:

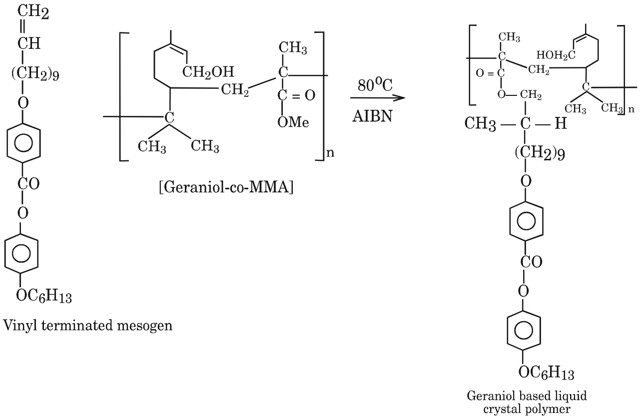
$[\eta]\times10^{-4}$	M_v	M_n	M_w	M_z	MWD
2.84	70,139	10,015	35,007	71,491	3.49

The structure of copolymer of Geraniol with MMA is as follows:



Synthesis of LC polymers

The polymerization was carried out under nitrogen atmosphere using DMF as solvent and BPO as initiator. The concentration of [geraniol-co-MMA] polymer was 6.15 mmol, and the mesogen amount used was 0.160 mmol. The polymerization temperature used for the synthesis was 80 °C. The reaction mixture was heated for 18 h. After the reaction time, the resultant LC polymer solution was precipitated in methanol and vacuum-dried until a constant weight was obtained.



Results and discussion

Characterization of mesogen

Nuclear magnetic resonance (^1H-NMR)

Solvent	^1H chemical shift δ (ppm)
$CDCl_3$	0.92 (t3H, CH_3), 1.32–2.05 (m, 24H, CH2) 3.87–4.04 (t 4H–OCH_2), 5.00 (m, CH_2=) 5.82 (m, 1H=CH), 6.74–7.26 (aromatic protons)

Optical polarized microscopy

The mesogen formed liquid crystalline phases [28]. On cooling from the isotropic state at 81 °C, the mesogen exhibited a nematic droplet texture, followed by Schlieren texture formation at 79.7 °C, then a mosaic texture appeared at 78 °C, and finally a homeotropic texture formed on further cooling (Fig. 1).

Copolymer [Geraniol-co-MMA] characterization

1. Fourier transform infrared spectroscopy [29]

The Fourier transform infrared spectroscopy (FTIR) spectra of the copolymer (Fig. 2) shows bands at 1,750 cm^{-1} for ester group of MMA and at 3,400 cm^{-1} for alcoholic group of geraniol.

2. Nuclear magnetic resonance spectroscopy [30]

The nuclear magnetic resonance (NMR) spectra (Fig. 3) of geraniol a and those of copolymers b show the following peaks:

(a) (1H, OH) Triplet 7–7.7 δ
(3H, CH_3) Singlet 0.9 δ
(2H, CH_2) Triplet 1.2–2.2 δ
(1H, CH) Triplet 1.8–2.2 δ

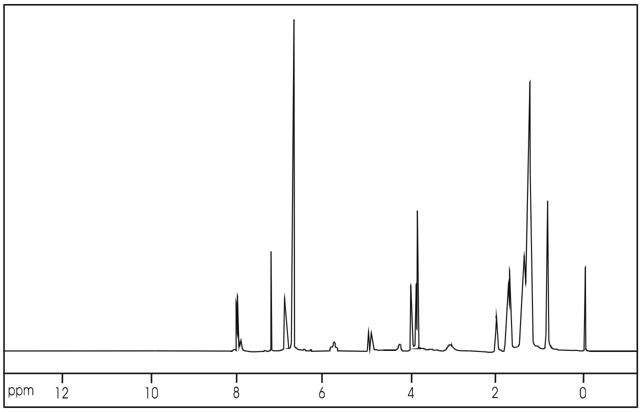


Fig. 1 ^1H-NMR spectrum of mesogen

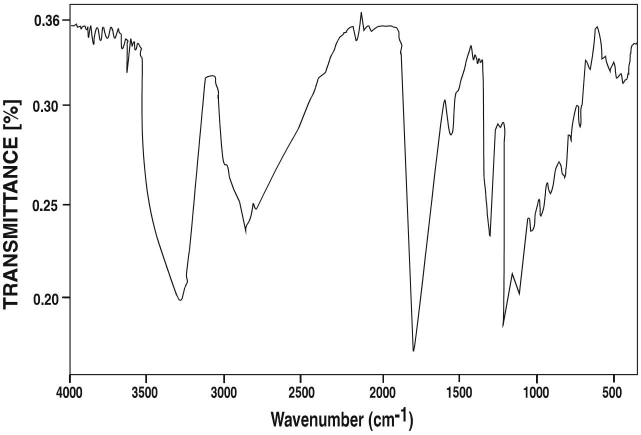


Fig. 2 IR spectrum of the copolymer [geraniol-co-MMA]

(b) (1H, OH) Triplet 7–7.7 δ
(3H, CH_3) Singlet 1.0 δ
(2H, CH_2) Triplet 1.2–2.2 δ
(1H, CH) Triplet 1.8–2.2 δ
(3H, OCH_3) Singlet 3.4–4.0 δ

Copolymer composition and value of reactivity ratios

The relative peak areas of methoxy and alcoholic protons in the NMR spectra of copolymer have been used to calculate the copolymer composition [30]. The reactivity ratio values r_1 (MMA)=0.68 and r_2 (Geraniol)=0.04, respectively, by Kelen–Tüdos method.

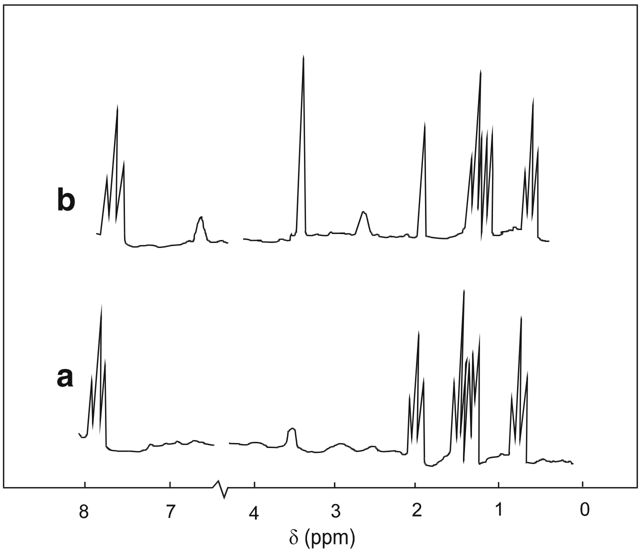


Fig. 3 **a** ^1H-NMR spectrum of geraniol and **b** ^1H-NMR spectrum of geraniol-co-MMA

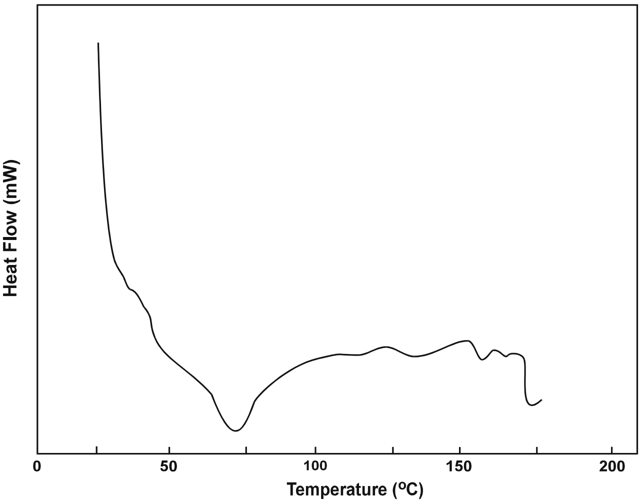


Fig. 4 DSC curve of the copolymer [geraniol-co-MMA]

Thermal property

Differential scanning calorimetry

The differential scanning calorimetry (DSC) curve (Fig. 4) indicates the glass transition temperature (T_g) of Geraniol-co-MMA polymer as 70 °C [30].

LC Polymer characterization

1. FT-IR

The FITR spectra (Fig. 5) of the LC polymer shows bands at 3,334 cm^{-1} due to alcoholic group of geraniol, C–H stretching at 2,985 cm^{-1} due to alkane (–CH_2) units.

2. ^{1}H-NMR

The ^{1}H-NMR spectra (Fig. 6) of LC polymers show the following peaks:

(a) 0.9 δ (t) due to –CH_3 protons
(b) 1.4 δ–2.2 δ (m) due to –CH_2– protons
(c) 3.8 δ–4.1 δ (m) due to –OCH_2 group
(d) 6.8 δ–7.6 δ (m) due to aromatic protons.

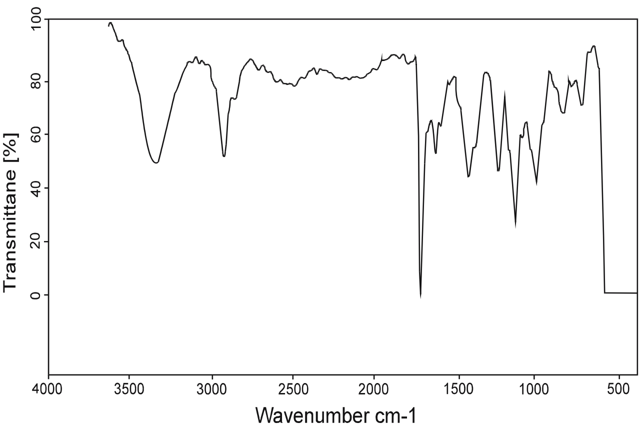


Fig. 5 IR spectrum of the LC polymer

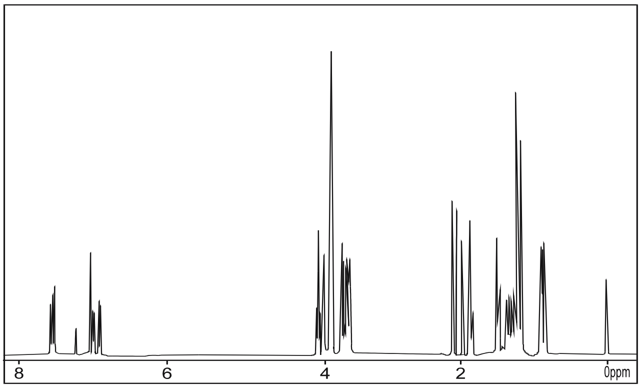


Fig. 6 ^{1}H-NMR spectrum of LC polymer

Evidences in support of proposed chemistry [28]

- The disappearance of multiplets in the range of 5–5.8 δ ppm [due to (m, 2H, CH_2=) and (m, 1H, =CH)] can be noticed in ^{1}H-NMR of the LC polymer.
- The protons of –OCH_2 group at 3.92 ppm of LC polymer appear at higher value of chemical shift than corresponding proton in the copolymer (3.5 ppm).

The ^{1}H-NMR data show that the mesogenic unit is attached to the methyl group of MMA moiety.

3. Thermal and textural analysis

The thermotropic mesomorphism was investigated by a combination of DSC and OPM. The polymer exhibits enantiotropic nematic mesophase and does not undergo side chain crystallization Independent of thermal history and preparation history of the polymer sample, i.e., as precip-

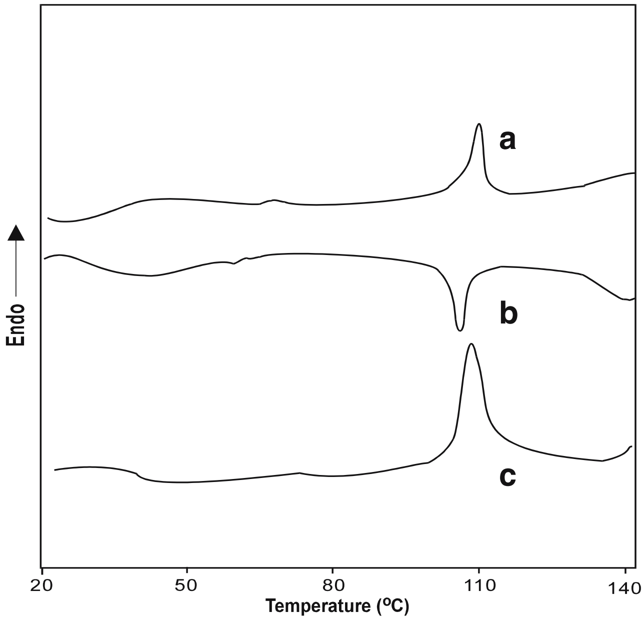


Fig. 7 DSC curve of the polymer on (**a**) I heating, (**b**) cooling, and (**c**) II heating (heating rate 10 °C/min)

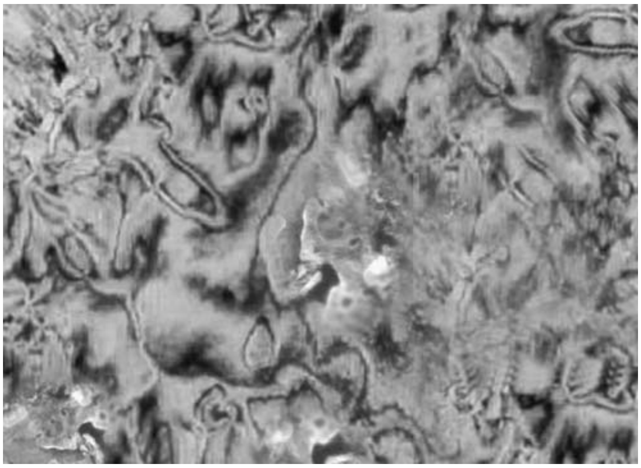


Fig. 8 Polarizing optical micrograph displayed by LC polymer nematic phase

itated from solution and then dried or after several heating and cooling scans in the DSC instrument, the DSC thermograms of these polymers are perfectly reproducible. The polymer exhibits only a glass transition temperature followed by a liquid crystalline mesophase and the isotropization transition. The assignment of the polymer mesophase was made by observing their mesomorphic texture on the hot stage of the optical polarized microscope [12, 31]. The heating and cooling DSC thermograms of the polymer exhibit the same thermal transitions regardless of the thermal history of their previous DSC scan.

Figure 7 represents representative heating and cooling DSC thermograms for the polymer. The polymer exhibits a glass transition step T_g at 42 °C followed by a nematic mesophase which undergoes isotropization at 112 °C. On the optical polarized microscope, the nematic phase displayed a schlieren texture (Fig. 8). The first cooling scan is almost identical to the heating scan, i.e., isotropic to nematic transition at 108 °C and a glass transition temperature T_g at 40 °C were observed. The subsequent heating scans are identical to that presented in Fig. 5 and do not exhibit the melting endotherm, but show glass transition temperature at 40 °C followed by nematic phase which undergoes isotropization at 110 °C.

It has been observed that the nature of the polymer backbone plays an important role in the thermal stability range of the mesophase [13–15]. The enhanced thermal stability of the mesophase and the increased isotropization temperature exhibited by the polymers presenting the flexible backbone can be associated with a high degree of freedom of the side group.

Geraniol is a acyclic monoterpenoid, and the T_g value of its copolymer (with MMA) is 70 °C .It is well documented in the literature that the glass transition temperature exhibited by liquid crystalline methacrylates with identical mesogen is in the range of 47–97 °C. This tendency is expected because poly (MMA) has a T_g value of 105 °C. In the present case, the T_g value shown by the LC polymer is 42 °C, and corresponding transition behaviors are as follows:

$$\frac{g\,42\,n\,112\,I}{i\,108\,n\,40}$$

A detailed comparison of different classes of polymers with same mesogenic group is given as:

Copolymer/LC polymer	Glass transition temperature (T_g)
PMMA	105 °C
PMA	10 °C
LC (PMMA)	47–97 °C
LC(PMA)	25–78 °C
Ger-co-MMA	70 °C
LC [Ger-co-MMA]	40 °C (for 9 spacer groups)

It is well documented that the phase transitions, particularly melting and liquid crystalline transitions, are strongly molecular-weight-dependent up to a certain molecular weight for both main chain [32, 33] and side chain liquid crystalline polymers [34, 35]. The longer spacer offers more freedom for the polymer segments and the mesogenic pendants to act separately. The clear transitions detected by DSC analysis suggest that the [Geraniol-co-MMA] backbone and phenyl benzoate mesogens are well "decoupled" and that the mesogenic pendants can undergo thermal transitions in a relatively independent fashion. The mesogen side chains are, however, not completely decoupled from the polymer main chain as argued by the other scientists [36–38].

It is widely believed that the more flexible the backbone chain, the broader the temperature range of the mesophase stability. The aforementioned results may conclude that not only the mesophase stability but the nature of the mesophase up to a certain extent is also influenced by the type of the polymer backbone taken. The major conclusion from this discussion is that although a more flexible backbone does not effect the type of mesophase formed, it allows a higher degree of freedom to the mesogenic unit.

Although, a quantitative conclusion of this work requires the synthesis of different polymers with varying mesogenic unit and spacers, which will be presented in forthcoming papers.

Conclusions

We have successfully synthesized a new LC polymer with [Geraniol-co-MMA] as a backbone, phenyl benzoate mesogenic group attached to a polymer backbone via polymethylene spacer. A comparison of the thermal and liquid crystalline properties of polymethacrylates and poly [Geraniol-co-MMA] based side chain liquid crystalline polymers containing phenyl benzoate mesogenic group has shown almost similar transition behavior but with different mesophase. The polymer was semi-crystalline but formed a liquid crystalline phases at temperature above T_g. The liquid crystalline polymers are functionally active and showed glass transition temperature at 40 °C.

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