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Side-Chain Liquid Crystalline Polymers with [α-terpineol-co-MMA] Main Chain: Synthesis and Characterization of Polymers with Phenyl Benzoate Mesogenic Group

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Summary

Side chain liquid crystalline (SCLC) [α-terpineol-co-MMA] polymers with a phenyl benzoate mesogenic group with polymethylene spacers have been synthesized and characterized in which the spacer length is taken 9 methylene units. The thermal behavior and liquid crystallinity of the polymer has been characterized using Differential Scanning Calorimetry (DSC) and Polarized Optical Microscopy (POM) techniques. The DSC curve of the LCpolymer shows glass transition at 52°C followed by nematic phase which undergoes isotropization at 120°C without undergoing side chain crystallization. Under optical polarized microscope the appearance of characteristic schlieren texture confirms the presence of nematic phase.

Introduction

In the past few years the side chain liquid crystalline polymers have aroused considerable attention in electro-optical devices, optical data storage systems[1],non-linear optics[2-4], ferroelectric switching[5] and so forth[6,7].

The systematic synthesis of liquid crystalline side chain polymers has become accessible by applying the "flexible spacer concept" originally proposed by Finkelmann et al.[8], which certifies that the flexible spacer decouples the mesogenic side groups from the polymer backbone and renders the mesogenic unit into an order. Following this concept, a variety of backbone polymers including polyacrylates[9], polymethyl-acrylates [10], polychloroacrylate [11], and polysiloxanes [12-14], have been synthesized.

The nature of the backbone chain affects the stability range of the mesophase. Percec[15] has concluded that the more flexible the backbone chain, the broader the temperature range of mesophase stability and the nature of the least ordered phase is governed mainly by the length of the spacer unit.

The widely studied polymer backbones are polysiloxane, polyacrylate and polymethacrylates, besides this other polymers backbone such as polyphosphazenes [16-17], poly epichlorohydrins [18], poly(phenylene oxide)[19] and polysulfones.[20] have also been examined for the synthesis of side chain liquid crystalline polymers

(SCLCP's) Polysiloxane backbones is particularly favoured because of its low glass transition temperature T_g, which can permit the formation of a mobile mesophase at room temperature. Several brief publications have pointed out that not only the nature and length of the flexible spacer, but also the nature of the polymer backbone influences the range of thermal stability of the mesophase[21-25]. In fact, it has been mentioned by several research groups that for the same spacer length and mesogenic unit, the broadest thermal stability of the mesophase is always obtained with the most flexible backbone [21-25].

A search of literature reveals that LCP’s have been prepared either by varying mesogenic group or polymer backbone. The use of terpene copolymers(with vinyl monomers) as a backbone is still in its infancy with few examples[26] of such polymers being documented in the literature. The flexibility of terpene co-polymers can play a vital role in the synthesis of SCLCP, so it was of interest to evaluate these copolymers as backbone for SCLCP's.

Recently we have reported the synthesis of copolymers[27-34] of terpene such as limonene [a monocyclic terpenoid], with vinyl monomers, as well as their possible use in the synthesis of side chain liquid crystal polymers [26]. The terpene copolymers are of great use due to their specific properties such as low T_g, optical activity and functionality. This encouraged us to extend our investigations to other terpenes also.

This article presents the synthesis and characterization of side chain liquid crystal polymers with [α-terpeniol–co-MMA] backbone and phenyl benzoate mesogenic group. A comparison has also been made with liquid crystalline polymers of poly-acrylates and methacrylates. It has been observed that LCpolymers with [α-terpeniol–co-MMA] backbone show liquid crystalline behaviour with nematic mesophase above its glass transition temperature i.e. 52°C and isotropization at 120°C.

Experimental

Materials

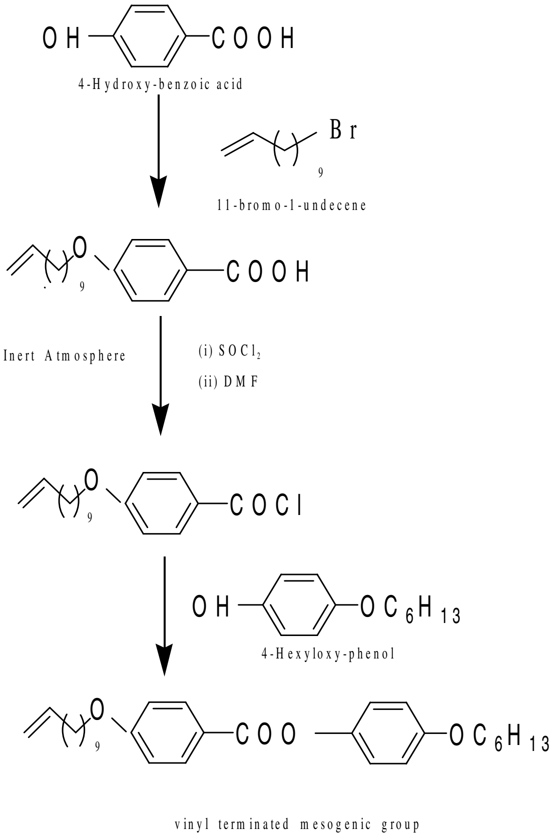
4-hydroxybenzoic acid (Across), 4-hexyloxyphenol (Lancaster), 11-bromo-1-undecene(Lancaster), thionyl chloride (Merck) were used as received. Triethylamine was refluxed over potassium hydroxide and distilled. 2-2 'azobisisobutyronitrile (AIBN) was recrystallized twice by methanol. Other reagents and solvents were used without further purification.

Instrumental Analysis:

^{1}H-NMR spectra were recorded with a Varian 100 HA Jeol LA 400 spectrophotometer using $CDCl_3$ as a solvent and tetramethylsilane as an internal reference. The Fourier Transform Infrared (FT-IR) spectra were recorded with Perkin-Elmer 599 B, with KBr pellets. 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 conjuction with a Instec HS1 Hot Stage.

Synthesis of monomer and co-polymer:

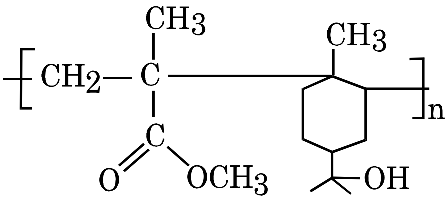
The vinyl-terminated mesogen, containing the phenylbenzoate mesogenic core was prepared according to the published literature by Itoh and Lenz[35].



ANAL., Calcd: C, 77.22% H. 9.07%
Found, C, 77.27%; H, 8.09%
Yield: 5.86 g (12.5 mmol, 59%)

Nuclear Magnetic Resonance (^{1}H-NMR):(fig. 1)

Solvent	*^{1}H Chemical Shift, δ, ppm*
CDCl3	0.92 (t, 3H, CH_3), 1.32-2.05 (m, 24H, CH_2)
	3.87-4.04 (t, 4H, CH_2O), 5.00 (m, 2H, CH_2=)
	5.82 (m, 1H, =CH), 6.74-8.16 (aromatic protons)

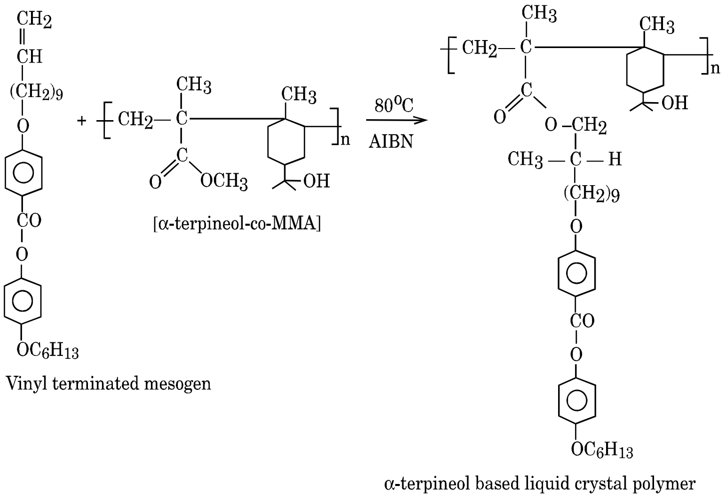


[α-terpeniol-co-MMA]

The synthesis and general characterization of co-polymer of α-terpineol with MMA has been reported elsewhere[36]. The radical copolymerization of α-terpineol with methyl-methacrylate was carried out in xylene at 80 ± 0.1°C for 50 minutes in the presence of azobisisobutyronitrile (AIBN) under inert atmosphere of nitrogen.

Synthesis of LC Polymers:

The polymerization was carried out in DMF at 80 ± 0.1°C for 18 hrs., using 5.82 mmol of $[\alpha\text{-terpineol-co-MMA}]_{\text{baseM}}$ polymer, 0.160 mmol of mesogenic compound and 0.121 mmol of AIBN. The polymer was precipitated in methanol and vacuum dried until a constant weight was obtained.



Scheme 1. Synthesis of α-terpineol based liquid crystal polymer

Results and discussion

^{1}H-Nuclear Magnetic Resonance (^{1}H-NMR) of LC Polymer

The ^{1}H-NMR spectra (Fig.5) of the LC polymer shows following peaks:

a) (1H, OH) singlet at 7.2 δ ppm,
b) (3H, CH_3) triplet at 0.93 δ ppm,
c) ($-CH_2$ units) multiplet at 1.4 - 1.7 δ ppm,
d) aromatic protons multiplet at 6.3 - 7.8 δ ppm

The ^{1}H-NMR spectra of LC polymer (fig. 2) shows disappearance of multiplet in range of 5.0 to 5.8 δ ppm due to (2H, $CH_2=$ & 1H, $=CH$), which is clearly visible in the ^{1}H- NMR spectrum of mesogen(fig. 1). The sharp peak at 3.8 δ ppm due to $-OCH_3$ group of [α-terpineol-co-MMA] shifted down field and show peak of $-OCH_2$ at 4.2 δ ppm in ^{1}H-NMR spectra of LC polymer(fig 2).

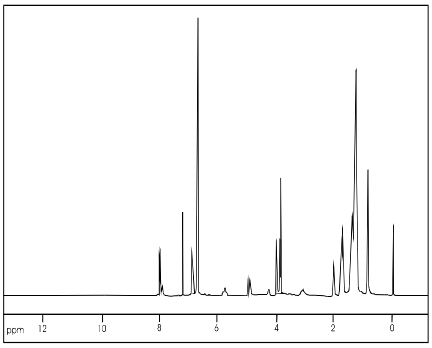


Fig.1

Figure 1. ^{1}H-NMR spectrum of mesogen.

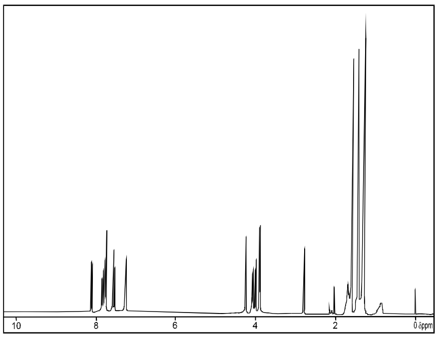


Fig.2

Figure 2. ^{1}H-NMR spectrum of the LC polymer.

Thermal and texture analysis:

The phase behaviour of the [α-terpineol-co-MMA] LC polymer was determined by means of Differential Scanning Calorimetry (DSC) & Optical polarized microscopy (OPM). The phase transition were reversible and did not change on repeated heating and cooling cycles. The phase transition temperatures determined by DSC were consistent with OPM observation results.

Liquid-crystalline phases are normally birefringent and show periodic structures or other textures under cross polarizers. The colour in these images is caused by a spatial periodicity of the order of the wave- length of light and interference of the transmitted polarized light. Typical textures include nematic, smectic etc. caused by discontinuities in the orientation.

In general the polymer backbone, rigidity of mesogenic unit and the length of flexible spacer cast the major effect on the phase behaviour of side chain liquid crystal polymers. The polysiloxanes polymer backbones account for the majority of side chain liquid crystal polymers (SCLCP's) because they show mesomorphic properties at moderate temperatures. The flexible spacer plays a vital role in this because it decouples, to some extent, the ordering tendencies of the mesogenic unit from those of the backbones to adopt random coil conformations. Its presence endows upon the polymer a unique duality of properties.

The thermotropic mesomorphism of the polymer was investigated by a combination of Differential Scanning Calorimetry (DSC) and polarized optical microscopy (POM). The phase transition temperatures are relevant thermodynamic parameters were determined by DSC measurements and the liquid crystalline behaviour was elucidated by polarizing microscopy. The polymer was previously heated to the temperature higher than the isotropization point in order to channel any effect of the former thermal history on the phase transitions.

In order to check the reproducibility of phase transitions heating and cooling scans were performed. Figure 3 shows the DSC thermogram of the LC polymer during the first cooling and the second heating scans. The thermogram recorded in the first cooling scan of polymer displays a broad exothermic peak associated with the i-n transition at 122°C. The second heating scan displays the glass transition step at 52°C followed by n-i transition at 120°C, however the cooling curve does not give very clear information on the T_g of the polymer, the endothermic baseline shift in the heating curve indicates that its glass transition occurs at 52°C.

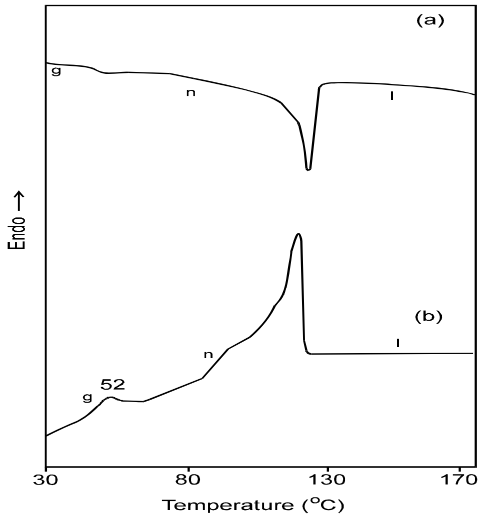


Figure 3. DSC thermograms of mesomorphic poly (α-terpineol-co-MMA) (a) first cooling and (b) second heating scans at a scan rate of 10°C/min.

The longer spacer offers more freedom for the polymer segments and the mesogenic pendants to act separately. The clear transitions detected by DSC analysis suggests that the [α-terpineol-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[37].

Figure 4 shows the OPM microphotographs of mesomorphic texture of LC polymer when the polymer is cooled from its isotropic state, small optically anisotropic entities emerges from the dark background of the isotropic liquid. The fine texture grow to large monodomain and clearly visible as schlieren textures of nematic phase.

A comparison[38] of liquid crystalline polyacrylates with the corresponding polymethacrylates showed that the glass transition temperature of the polyacryaltes (T_g 25–78°C) are lower than those of the polymethacrylate series (T_g 47–97°C). This

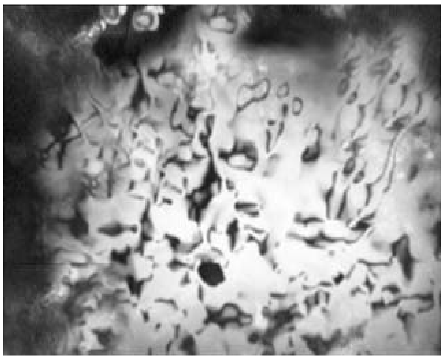


Figure 4. Mesomorphic textures observed on cooling at 80°C from their isotropic states. Polarizing optical micrograph displayed by LC polymer, nematic phase.

tendency is expected, because poly(methyl methacrylate)(PMMA) has a T_g value of 105°C, while poly (methyl acrylate)(PMA) has T_g value of 10°C. It is generally assumed that the glass transition temperature (T_g) of liquid crystalline polyacrylates are higher than PMA, where as the T_g value of the corresponding polymethacrylate are lower than PMMA. In the present case the glass transition temperature T_g of the LCpolymer is 52°C, which is quite low, as the T_g of the terpenes polymers' [39-40] are also low (35°C to <100°C).

A comparison has also been made with polyacrylate and polymethacrylate liquid crystalline polymers with 6 spacer units and phenyl benzoate mesogenic group since no data was available for 9 spacer unit for analogous mesogenic group. The phase transitions of liquid crystalline polyacrylate[38]are (g 20 s 130°C i) while for the analogous mesogenic group the phase transitions of liquid crystalline polymethacrylates[38,10] are:

g 47s 115°C i

In the present study, instead of polymethacrylate poly [α-terpineol-co-MMA] has been taken as a backbone. The phase transition observed for these liquid crystalline polymers are in very much agreement to that of polymethacrylate, these polymers show schlieren textures for nematic phase under hot stage polarized light microscopy. The phase transitions shown by [α-terpineol-co-MMA] LC polymers are:

g 52 n 120°C i

It has been observed that the glass transition temperature of liquid crystalline polyacrylates and methacrylates are less than their corresponding homopolymer. In the present article where the [α-terpineol-co-MMA] has been taken as a backbone, the glass transition temperature T_g shown by liquid crystalline polymer is 52°C. This tendency is expected, because poly [α-terpineol-co-MMA] has T_g value of 80°C. These results point towards that the nature of the polymer backbone has a profound effect on mesomorphism of liquid crystal polymers.

It is widely believed that the polymer backbone has a major effect on the liquid crystalline behavior. The above mentioned data is in very much agreement with that. Besides their phase behavior these polymers also show functionality. The general prediction that the introduction of a spacer leads to the formation of liquid crystalline phases with the properties of low molecular weight liquid crystals is also verified. On the other hand the complete decoupling model in which the liquid crystalline behavior is governed only by the mesogenic group and the glass transition temperature only by the main chain, need modification.

Conclusions

A new LC polymer with [α-terpineol-co-MMA] backbone and phenyl benzoate mesogenic group attached to backbone, via polymethylene spacers has been synthesized and characterized. A comparison of the thermal and liquid crystalline properties of polymethacrylates and poly [α-terpineol-co-MMA]based side chain liquid crystlalline polymers containing phenyl benzoate mesogenic group has shown almost similar transition behaviour with a different mesopahse.

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