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Synthesis of side chain liquid crystalline poly(vinyl ether)s containing 2,2′-dimethyl-4-methoxy-4′-[undecanyloxy-4-benzoyl]ester biphenyl side group

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Summary

The synthesis and characterization of 2,2'-dimethyl-4-methoxy-[(11-vinyloxy)undecanyloxy-4-bezoyl]ester biphenyl (7), its cationic polymerization to side chain liquid crystalline polymers with relative number average degrees of polymerization (DP) of 2, 8 and 19 are presented. The mesogenic vinyl ether monomer displays an inverse monotropic nematic phase. The oligomers with DP=2 and DP= 8 display an enantiotropic nematic, while the polymer with DP=19 exhibits an inverse monotropic smectic A and an enantiotropic nematic phases. All the liquid crystalline polymers display only liquid crystalline phases and do not undergo side chain crystallization even though eleven methylenic units are used as the flexible spacer.

Introduction

Thermotropic side chain liquid crystalline polymers (SCLCP) consist of rigid mesogenic units connected via a sufficiently flexible spacer group to a polymer backbone.[1,2] The spacer group must be of sufficient length to allow decoupling of the motions of the side chain and the randomly coiled main chain, enabling the mesogens to exist in an anisotropic liquid crystalline state. It is known that the nature of mesophases depends on the nature of their polymer backbone, the nature of mesogenic group and the length of the flexible spacer group. Therefore it is, in principle, possible to adjust the properties of a liquid crystalline polymer to that required for a given application by structural modifications of polymer components. Also, the ability to control the polymer molecular weight represents another important parameter required to manuplate the phase transitions of side chain liquid crystalline polymers.[3] Recently, synthetic procedures for a convenient synthesis of mesogenic vinyl ether monomers and for their living cationic polymerization have been elaborated. particularly, the initiating system $CF_3SO_3H/(CH_3)_2$ can be used to polymerize mesogenic vinyl ethers since it tolerates a variety of functional groups.[4,5]

The goal of this paper is to report the synthesis of novel side chain liquid crystalline poly(vinyl ether)s containing 2,2'-dimethyl-4-methoxy-4'-[undecanyloxy-4-benzoyl]ester biphenyl side group and the mesomorphic phase behavior of the synthesized monomer and the resulting polymers.

Experimental

Materials

4-Chloro-3-methylphenol (99%, Aldrich), nickel(II) chloride (anhydrous, 98%, Aldrich), 11-bromo-1-undecanol (98%, Aldrich), n-butyl vinyl ether (98%, Aldrich), triphenyl phosphine (99%, Aldrich), 1,10-phenanthroline (anhydrous, 99%, Lancaster) and palladium(II)diacetate (from Aldrich) were used as received. $(CH_3)_2S$ (anhydrous,

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99%, Aldrich) was refluxed and then distilled over sodium metal under argon. CF_3SO_3H (98%, Aldrich) was distilled under vacuum.

Techniques

^1H-NMR spectra were recorded from $CDCl_3$ solution on a Bruker AC 250 spectrometer operating at 250 MHz proton frequency. TMS was used as internal standard. Infrared (IR) spectra were recorded on a Nicolet FX 6160 FT IR spectrophotometer. A Perkin Elmer DSC-7 differential scanning calorimeter, equipped with a 1020 thermal analysis controller was used to determine the thermal transitions which were reported as the maxima and minima of their endothermic or exothermic peaks, respectively. In all cases, heating and cooling rates were 10 °C/min unless otherwise specified. A Nikon Optiphot 2-pol optical polarized microscope (magnification: 100x) equipped with a Mettler FP 82 hot stage and a Mettler FP 90 central processor was used to observe the thermal transitions and to analyze the anisotropic textures.[6,7] Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) with a Waters R401 instrument equipped with US HR5E-500-H22 column and a Millenum data station. The measurements were made at 40 °C using the UV detector with THF as solvent (1ml/min) and a calibration plot constructed with polystyrene standards was used to determine the molecular weights and molecular weight distributions. Microanalysis was performed with a Perkin Elmer 240 elemental analyzer.

Synthesis of monomer

The synthesis of 2,2'-dimethyl-4-methoxy-4'-[(11-vinyloxy)undecanyloxy-4-benzoyl]ester biphenyl (7) and its cationic polymerization are outlined in Scheme 1.

4-Chloro-3-methylphenyl acetate (1).

1 was synthesized according to the procedure described in a previous publication.[8]

2,2'-Dimethyl-4,4'-dihydroxy biphenyl (2)

DMAc (30 ml) was added to a mixture of nickel chloride (0.1 g, 1.1 mmol), triphenyl phosphine (1.5 g, 56 mmol), Zn powder (2.1 g, 32 mmol) and 2,2'-bipyridine (0.4 g, 2.8 mmol). The mixture was heated to 60 °C, 4-chloro-3-methylphenyl acetate (4.0 g, 22 mmol) was added, and the reaction mixture was then stirred at 70 °C for 7 h. The mixture was filtered, poured into a solution of 10% aqueous NaOH, stirred overnight at 25 °C, washed with ethyl ether, and acidified with conc. HCl. The mixture was extracted with methylene chloride, and the methylene chloride solution was dried over magnesium sulfate, and the solvent was removed in a rotary evaporator. The crude product was recrystallized a mixture of methylene chloride and n-hexane (10:1) to yield 1.1 g (23 %) of white crystals.

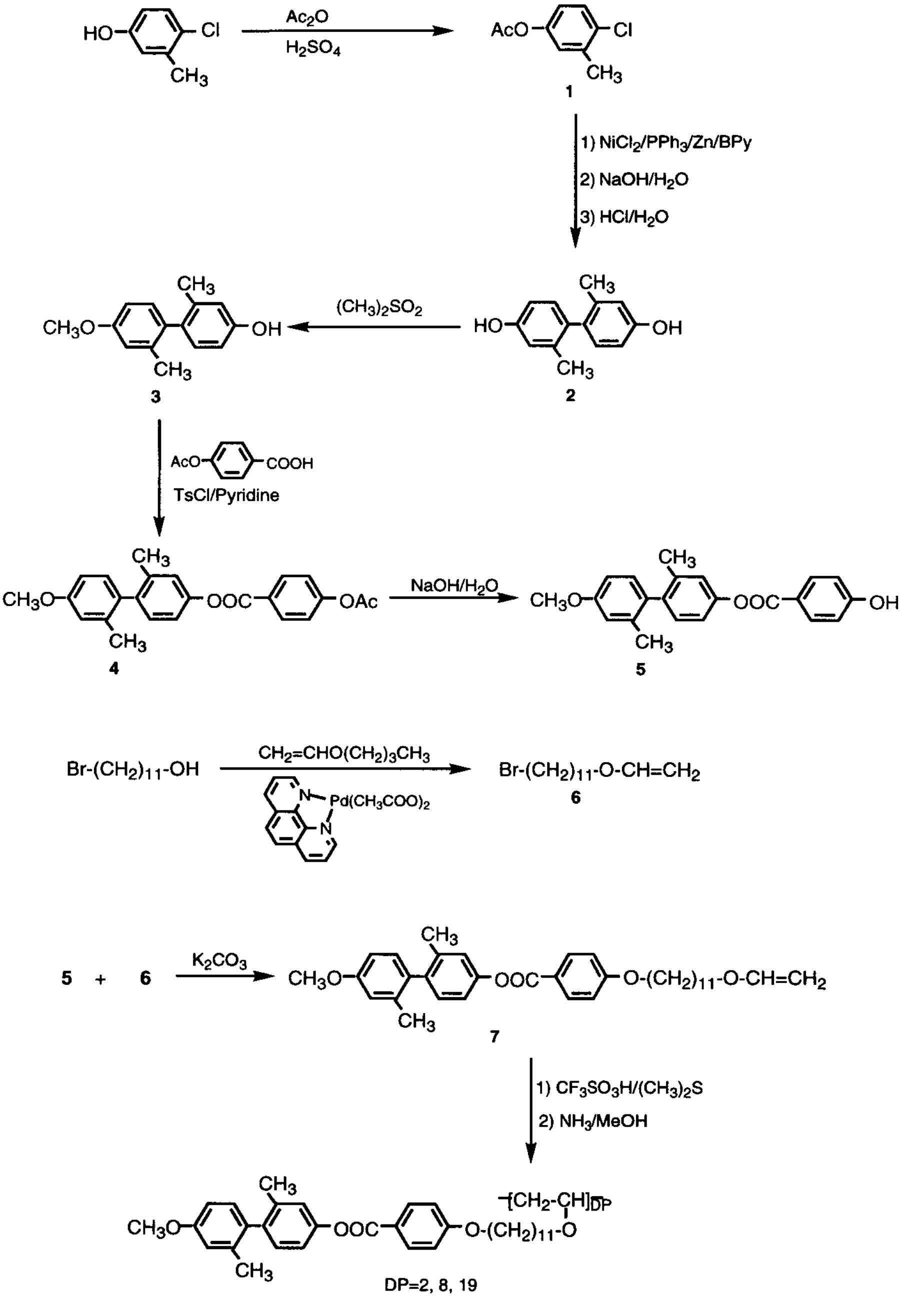
mp; 152 °C (lit.[8] mp 154 °C). ^1H-NMR ($CDCl_3$, TMS, δ, ppm); 2.00 (s, 6H, $C\underline{H}_3$-phenyl), 6.73 (m, 4 Ar-H, o to hydroxy), 6.98 (m, 2 Ar-H, o to phenyl).

2,2'-Dimethyl-4-methoxy-4'-hydroxy biphenyl (3)

2,2'-dimethyl-4,4'-dihydroxy biphenyl (3g, 14 mmol) was dissolved in a solution of KOH (0.8 g, 14 mmol) in a mixture of H_2O-methanol (1:1, 60 ml). Dimethyl sulfate (1.76g, 14 mmol) was then added and the solution was stirred at room temperature for 2h. The resulting mixture was extracted with methylene chloride and the methylene chloride solution was then washed with 10% aqueous NaOH solution and then water. The solvent was removed in a rotary evaporator and the resulting oily residue was purified by column chromatography on a silica gel using methylene chloride as eluent to yield 1.0g (32 %) of a colorless liquid.

^1H-NMR ($CDCl_3$, TMS, δ, ppm); 2.03 (s, 6H, $C\underline{H}_3$-phenyl), 3.84 (s, 3H, $C\underline{H}_3O$), 6.74 (m, 4 Ar-H, o to CH_3O and o to hydroxy), 6.95 (m, 2 Ar-H, o to phenyl).

2,2'-Dimethyl-4-methoxy-4'-(4-acetoxybenzoyl)ester biphenyl (4)



Scheme 1; Synthesis of the monomer and poly(vinyl ether)s

To a solution of 4-acetoxybenzoic acid (1.8 g, 9.9 mmol) in dry pyridine (5 ml), a solution of p-toluenesulfonyl chloride (3.8 g, 20 mmol) in 10 ml of dry pyridine was added dropwise in an ice bath. A solution of **3** (1.5 g, 6.6 mmol) in 15 ml of dry pyridine was added to a resulting mixture and the mixture was then refluxed for 2h under nitrogen. The resulting solution was poured into methylene chloride. The methylene chloride solution was washed with 1N aqueous HCl and then aqueous $NaHCO_3$, and dried over magnesium sulfate. The solvent was removed in a rotary evaporator and the crude product was then purified by column chromatography (silica gel, methylene chloride) to yield 1.0 g (37%) of a colorless liquid.

^{1}H-NMR ($CDCl_3$, TMS, δ, ppm) 1.98 (s, 6H, $C\underline{H}_3$-phenyl), 2.45 (s, 3 H, $C\underline{H}_3COO$), 3.85 (s, 3 H, $C\underline{H}_3O$), 6.86 (m, 2 Ar-H, m to CH_3-), 7.17 (m, 4 Ar-H, o to phenyl-COO and o to CH_3O), 7.30 (d, 2 Ar-H, o to acetoxy, J=8.1 Hz), 8.28 (d, 2 Ar-H, m to acetoxy, J=8.3 Hz).

2,2'-Dimethyl-4-methoxy-4'-(4-hydroxybenzoyl)ester biphenyl (5)

3 (1.0 g, 2.5 mmol) was added to a solution of methanol and saturated aqueous $NaHCO_3$ (10:1, 150 ml), and the resulting mixture was stirred at 30 °C for 2h. The resulting transparent solution was extracted with methylene chloride. The methylene chloride solution was washed with 1N aqueous HCl, dried over magnesium sulfate and then removed in a rotary evaporator. The resulting precipitate was recrystallized from methanol to yield 0.6 g (67%) of a white solid.

mp; 185-187 °C: ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm); 2.07 (s, 6H, $C\underline{H}_3$-phenyl), 3.85 (s, 3 H, $C\underline{H}_3O$), 6.82 (m, 2 Ar-H, m to CH_3-), 6.96 (d, 2 Ar-H, o to hydroxy, J=8.7 Hz), 7.12 (m, 4 Ar-H, o to phenyl-COO and o to CH_3O), 8.16 (d, 2 Ar-H, m to hydroxy, J=8.7 Hz).

11-Bromoundecanyl vinyl ether (6)

6 was synthesized according to the procedure described in a previous publication.[9]

2,2'-Dimethyl-4-methoxy-4'-[(11-vinyloxy)undecanyloxy-4-benzoyl]ester biphenyl (7)

Potassium carbonate (1.0 g, 0.29 mmol) was added to a solution of **5** (0.1 g, 0.28 mmol) and 11-bromoundecanyl vinyl ether (80 mg, 0.29 mmol) in acetone (90 ml). After being refluxed for 12 h, the reaction mixture was poured into water and then extracted with methylene chloride. The methylene chloride solution was dried over magnesium sulfate and the solvent was removed in a rotary evaporator. The crude product was purified by column chromatography [silica gel, n-hexane-ethyl acetate (10:1) eluent] to yield 80 mg (53%) of a white solid, which was further purified by recrystallization from methanol.

mp; 63.0 °C (DSC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm); 1.32-1.86 (m, 18 H, $-(CH_2)_9-$), 2.07 (s, 6H, $C\underline{H}_3$-phenyl), 3.68 (t, 2 H, $CH_2=CHOC\underline{H}_2$-, J=6.5 Hz), 3.85 (s, 3 H, $C\underline{H}_3O$), 3.98 (d of d, 1 H, $C\underline{H}_2=CHO$- trans, J_1=5.0 Hz, J_2=1.8 Hz), 4.05 (t, 2 H, phenyl-$OC\underline{H}_2$-, J=6.5 Hz), 4.20 (d of d, 1 H, $C\underline{H}_2=CHO$- cis, J_1=12.5 Hz, J_2=1.8 Hz), 6.46 (q, 1 H, $CH_2=C\underline{H}O$-, J=6.8 Hz), 6.82 (m, 2 Ar-H, m to CH_3-), 6.96-7.17 (m, 6 Ar-H, o to undecanyloxy, o to phenyl-COO and o to CH_3O), 8.16 (d, 2 Ar-H, m to hydroxy, J=8.8 Hz). IR (KBr); 847, 1071, 1163, 1255, 1314, 1485, 1611, 1742 cm^{-1}. Elemental Analysis for $C_{33}H_{40}O_5$: Calc. C, 76.71; H, 7.80. Found C, 77.17; H, 8.32 %.

Cationic polymerizations

Polymerization were carried out in a two-neck round bottom flask equipped with teflon stopcock and rubber septum under argon atmosphere at -10 °C for 3h. All glassware was dried overnight at 120 °C. The monomer was further dried under vacuum in the polymerization flask. After the flask was filled with argon, freshly distilled dry methylene chloride was added through a syringe and the solution was cooled to -10 °C. Freshly distilled dimethyl sulfide and CF_3SO_3H were then added consecutively through a syringe. The monomer concentration was about 0.2 M and the dimethyl sulfide concentration was 10 times larger than that of the CF_3SO_3H. The polymer molecular weight was controlled by the monomer to initiator ($[M]_o/[I]_o$) ratio. After quenching the polymerization with ammoniacal methanol, the reaction mixture was precipitated into methanol. The resulting polymers were purified by precipitation from methylene chloride solution into methanol and were collected by filtration. The filtered polymers were dried and reprecipitated from methylene chloride solution into methanol until GPC curve showed no traces of unreacted monomer.

Results and discussion

The synthesis of mesogenic vinyl ether monomer is outlined in Scheme 1. The most important step in this reaction scheme is Ni(0)-catalyzed homocoupling reaction of chlorobenzene derivative to produce 2,2'-dimethyl-4-,4'-dihydroxy biphenyl (**2**). The Ni(0) catalyst was generated in situ from $NiCl_2$, PPh_3, Zn and 2,2'-bipyridine in DMAc as reported previously.[8] The synthesis of **6** followed the procedure described previously for the preparation of related monomers.[9] The mesogenic monomer **7** was obtained from etherification reaction of **5** and **6** in the presence of potassium carbonate.

The phase transition temperature and the nature of the mesophase of **7** were determined by differential scanning calorimetry (DSC) and thermal optical polarized microscopy as summarized in Table 1. As can be seen in this table, **7** exhibits a crystalline melting to isotropic transition at 63.0 °C in the first heating scan. In the second heating scan, however, it uncovers a crystalline melting at 16.7 °C followed by a nematic liquid crystalline phase which undergoes isotropization at 62.6 °C. In the cooling scan, **7** displays only a crystalline phase from 14.2 °C. Therefore, the nematic mesophase exhibited by **7** is an unusual inverse monotropic liquid crystalline phase.[10,11]

The cationic polymerization of **7** was performed with a $CF_3SO_3H/(CH_3)_2S$ initiating system in methylene chloride at -10 °C. Although particular efforts were not made to demonstrate the living nature of this polymerization, side chain liquid crystalline poly(vinyl ether)s with relative degrees of polymerization to polystyrene standards of 2, 8 and 19 were easily prepared (Table 1).

Table 1. Characterization of the monomer and the poly(vinyl ether)s (g=glassy phase, n=nematic phase, s_A=smectic A phase, k=crystalline phases, i=isotropic phase). Data on first line are from first heating and cooling scans. Data on second line are from second heating scan.

compound	DP		Mn	Mw/Mn	phase transitions (°C) and corresponding enthalpy changes (J/g)	
	calc.	exp. (GPC)			heating	cooling
monomer					k 63.0 (78.9) i k 16.7 (1.8) n 62.6 (0.08) i	i 14.2 (1.7) k
oligomer (1)	2	2	970	1.09	g -20.1 n 29.2 (1.5) i g -19.6 n 29.0 (1.4) i	i 27.3 (1.5) n -23.1 g
oligomer (2)	8	8	4670	1.03	g -3.8 n 38.6 (1.2) i g -4.3 n 38.4 (0.9) i	i 34.8 (1.3) n -8.4 g
polymer (3)	30	19	10400	1.94	g 8.9 s_A 32.5 (0.1) n 61.3 (1.8) i g 8.2 s_A 32.0 (0.1) n 60.6 (1.9) i	i 57.9 (1.7) n 6.2 g

DSC traces of the second heating scans which are identical to the first heating scans, and of the first cooling scans are presented in Figure 1. The thermal transitions collected from DSC and the nature of the mesophase characterized by thermal optical microscopy are summarized in Table 1. The oligomers with DP=2 and DP=8 exhibit a

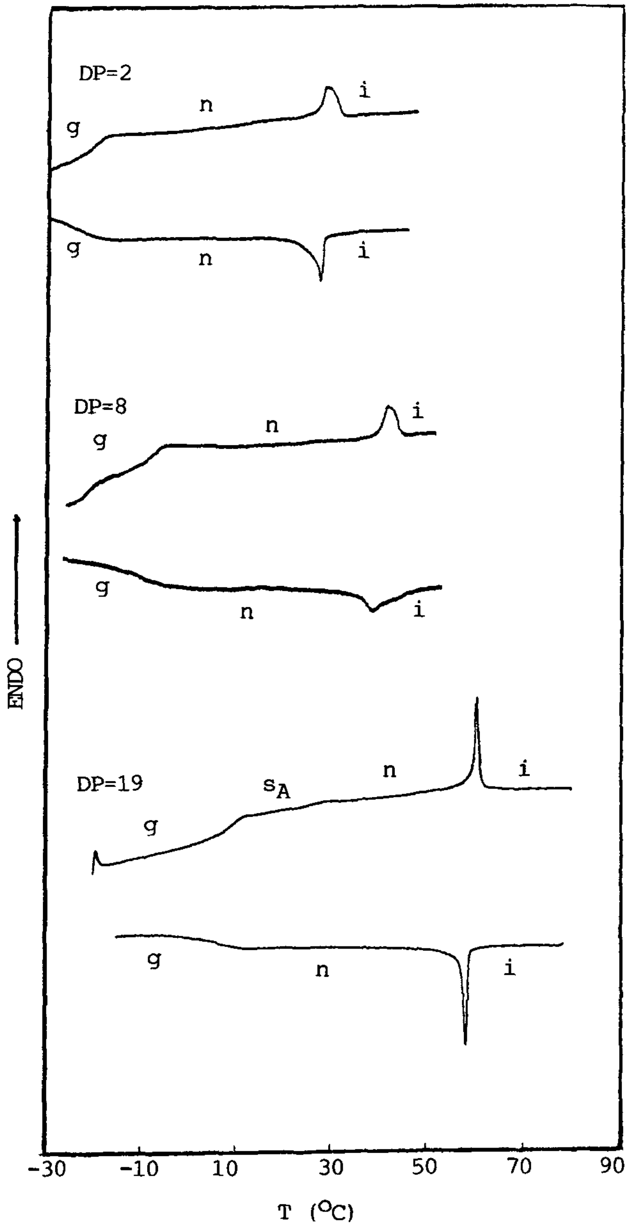


Figure 1; DSC traces (10 °C/min) recorded during the second heating scan and first cooling scan of the polymers with DP=2, 8 and 19.

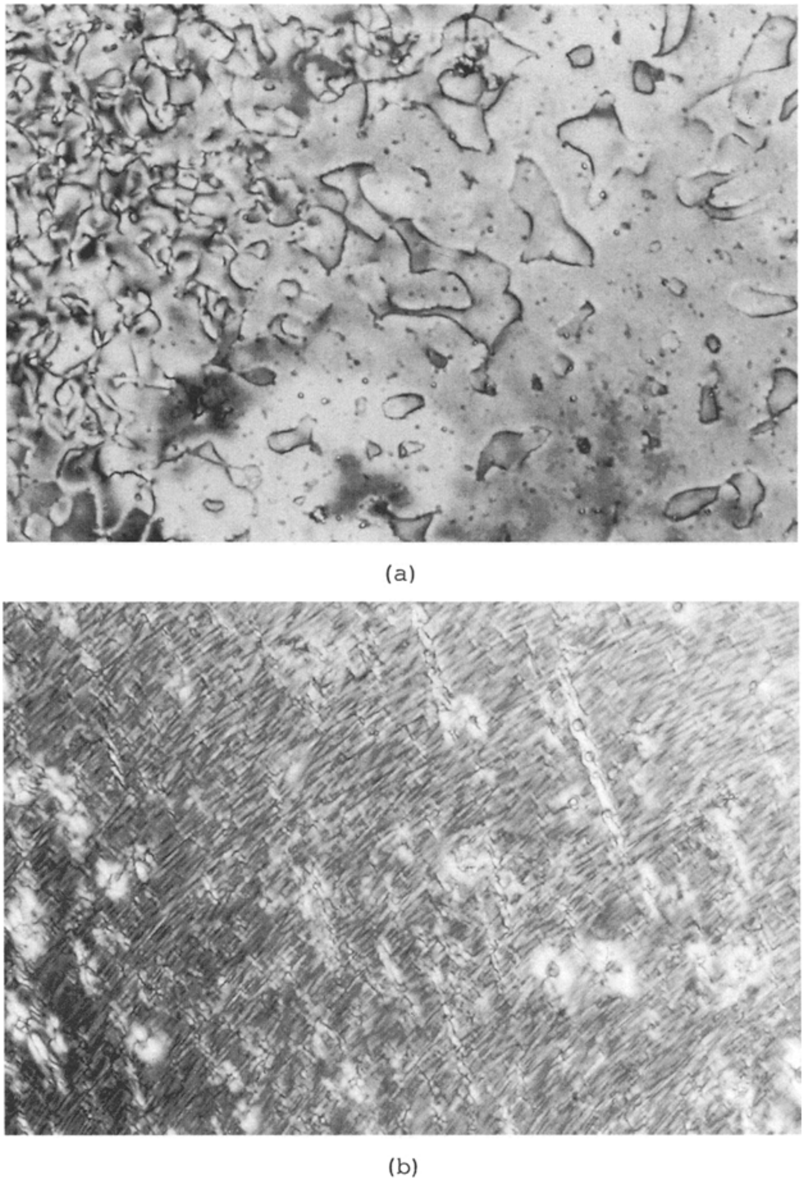


Figure 2; Representative optical polarized micrographs (100 X) of the texture exhibited by; (a) the nematic mesophase of the polymer with DP=19 at 61 °C on the cooling scan; (b) the s_A mesophase of the polymer with DP=19 at 28 °C on the second heating scan.

glass transition (Tg) and an enantiotropic nematic phase. With increasing the degree of polymerization from 2 to 8, the glass transition temperature increases from -19.6 °C to -4.3 °C, while the nematic to isotropic transition temperature from 29.0 °C to 38.4 °C in the case of second heating. The results are rewarding because side chain liquid crystalline polymers can show a nematic mesophase even at room temperature without side chain crystallization.

On the other hand, the polymer with DP=19 presents a glass transition at 8.2 °C, followed by a s_A mesophase which turns into a nematic phase at 32.0 °C and then, the nematic phase undergoes isotropization at 60.6 °C on the second heating. On cooling, however, the polymer presents the isotropic-nematic transition at 57.9 °C and the nematic phase turns directly into glassy state at 6.2 °C. Upon quenching from the isotropic phase to -30 °C, subsequent heating scans are always reproducible. Therefore, the s_A phase exhibited by the polymer is also an inverse monotropic mesophase which is unusual case in side chain liquid crystal polymer systems. The first example of an inverse monotropic mesophase was reported by Percec et. al.[11] On the optical polarized microscope, the nematic mesophase of the polymer exhibits a marble texture while the s_A mesophase a stripped texture as shown in Figure 2. The formation of a second mesophase at higher polymer molecular weight as is the case of the s_A mesophase from this example agrees well with previous results available in the literature.[3] Such a dependence on polymer molecular weight can be explained by thermodynamic scheme predicted by theory.[12]

In conclusion, the monomer and the polymer with DP=19 based on 2,2'-dimethyl-4-methoxy-4'-(undecanyloxy-4-benzoyl)ester biphenyl exhibit an unusual inverse monotropic mesophase. All the liquid crystalline poly(vinyl ether)s display only liquid crystalline phases and do not undergo side chain crystallization even though eleven methylenic units are used as the flexible spacer. This can be explained by the presence of dimethyl side groups in the mesogen which is attributed to hindrance of crystal packing of side mesogenic groups. In the case of most liquid crystalline poly(vinyl ether)s containing flexible spacers based on 11 methylenic units, they undergo side chain crystallization.[3,4,9] Also, the results described in this paper demonstrate that a higher molecular weight is leading to the formation of a more stable mesophase.

Acknowledgment

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References

1. McArdle, C. B. *Side Chain Liquid Crystal Polymers* ; Chapman and Hall: New York, 1989
2. Collyer, A. A. *Liquid Crystal Polymer;* Elsevier Applied Science: London and New York, 1992
3. Percec, V.; Tomazos, D. *Adv. Mater.* 1992, **4**, 548
4. Percec, V.; Lee, M. *Macromolecules* 1991, **24**, 2780
5. Percec, V.; Gomez, A. D. S.; Lee, M. *J. Polym. Sci.; Part A; Polym. Chem.*1992, **29**, 1615
6. Demus, D.; Richter, L. *Textures of Liquid Crystals;* Verlag Chemie, Weinheim, 1978
7. Gray, G. W.; Goodby, J. W. *Smectic Liquid Crystals. Textures and Structures;* Leonard Hill, Glasgow, 1984
8. Percec, V.; Zhao, M.; Bae, J.-Y.; Hill, D. H. *Macromolecules,* 1996, **29**, 3727
9. Percec, V.; Zheng, Q.; Lee, M. *J. Mater. Chem.* 1991, **1**, 1015
10. Martellcci, S.; Chester, A. N. *Phase transitions in Liquid Crystals*; Plenum Press, New York, 1992
11. Percec, V.; Tomazos, D.; Feiring, A. E. *Polymer* 1991, **32**, 1897
12. Percec, V.; Keller, A. *Macromolecules* 1990, **23**, 4347