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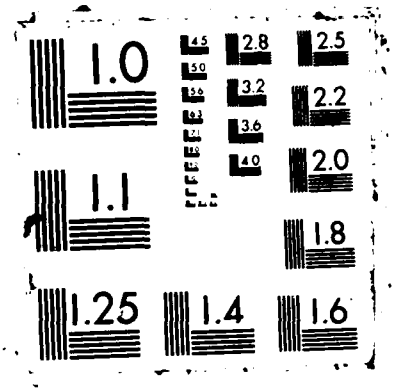
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Liquid Crystalline Copolymers of Monomer-Pairs Containing Mesogenic Units which Exhibit Constitutional Isomerism

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ABSTRACT

The synthesis and characterization of side-chain liquid crystalline copolymers obtained from a monomer pair containing a mesogenic unit which exhibits constitutional isomerism are presented. The particular example described refers to copolymethacrylates obtained from 4-hydroxy-4'-methoxy-α-methylstilbene and 4-methoxy-4'-hydroxy-α-methylstilbene containing six methylenic units presents a nematic mesophase, while the polymer containing eleven methylenic units presents a smectic A or C mesophase. None of these polymers exhibited side-chain crystallization.

Liquid Crystalline Copolymers of Monomer-Pairs Containing Mesogenic Units which Exhibit Constitutional Isomerism

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SUMMARY

The synthesis and characterization of side-chain liquid crystalline copolymers obtained from a monomer pair containing a mesogenic unit which exhibits constitutional isomerism are presented. The particular example described refers to copolymethacrylates obtained from 4-hydroxy-4'-methoxy-α-methylstilbene and 4-methoxy-4'-hydroxy-α-methylstilbene containing six and eleven methylenic units in the spacer. The polymer containing six methylenic units presents a nematic mesophase, while the polymer containing eleven methylenic units presents a smectic A or C mesophase. None of these polymers exhibited side-chain crystallization.

INTRODUCTION

Side-chain liquid crystalline polymers (LCP) containing long spacers and calamitic mesogens undergo side-chain crystallization (1, 2). Copolymerization is most frequently employed to depress the tendency towards crystallization in both main-chain and side-chain LCP (1, 2). Recently, we have developed a novel concept concerning the synthesis of side-chain LC copolymers. It is based on the homopolymerization of a monomer containing a mesogenic unit which undergoes conformational isomerism. Since in both solution or melt the conformational isomers are in a dynamic equilibrium, this homopolymer can be visualized as a "copolymer" obtained from a single monomer. Therefore, the composition of these copolymers is temperature dependent both in solution and in the mesomorphic phase. So far, we were able to supress side-chain crystallization by using trans-2,5-disubstituted-1,3-dioxane (6), 2,5-disubstituted-1,3,2-dioxaborinane (7), and benzyl ether (8) based mesogenic units.

A slightly different approach to the same problem can be designed by using monomers containing mesogenic units which can give rise to constitutional or structural isomerism. This concept has been of interest both to us (3-5) and to Pino's group (9) in connection with main chain LCP.

The goal of this paper is to present our first results on the synthesis and characterization of side-chain LC copolymers of comonomer pairs containing mesogenic units which are constitutional isomers. Because of our previous experience with 4,4'-dihydroxy-α-methylstilbene based main-chain LC polyethers (3-5), this paper will describe the copolymethacrylates obtained from monomers based on 4-hydroxy-4'-methoxy-α-methylstilbene and 4-methoxy-4'-hydroxy-α-methylstilbene containing eleven and six methylenic units in the spacer.

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EXPERIMENTAL

A. Materials

All the reagents were commercially available and were used as received, unless otherwise specified. 4,4'-Dihydroxy-α-methylstilbene (HMS) was synthesized and purified according to a method previously developed in our laboratory (10). Its purity was higher than 99.5% as determined by HPLC. m.p. (DSC, 20°C/min), 185°C. 200 MHz ^{1}H-NMR (DMSO-d_6-TMS, ppm): 2.2 (-CH_3, s), 6.7 (=CH-, s), 6.85 (4 aromatic protons, o to -OH, d), 7.25 (2 aromatic protons, o to α-CH_3, d), 7.4 (2 aromatic protons, o to =CH-, d).

B. Synthesis of Monomers and Polymers

Scheme 1 describes the synthesis of the monomers.

Synthesis of 4(4')-Methoxy-4'(4)-hydroxy-α-methylstilbene (I)

4,4'-Dihydroxy-α-methylstilbene (30g, 0.133 mole) was dissolved in a solution of 12.74g (0.32 mole) of NaOH in 120 ml of water. Dimethyl sulfate (12.5 ml, 0.133 mole) was added dropwice, and the solution was stirred at room temperature overnight. The resulting precipitate was filtered and washed with 10% aqueous NaOH, and then with water. The separated solid was dissolved in boiling water and traces of insoluble 4,4'-dimethoxy-α-methylstilbene were separated by hot filtration. The resulting solution was acidified at room temperature with HCl to precipitate the monomethoxylated product. It was filtered, washed with water, and recrystallized from methanol to yield 14.3g (45%) of white crystals. DSC (20°C/min) shows two overlapped broad melting peaks at 139 and 156.6°C, supporting that the resulting compound consists of a mixture of the two constitutional isomers. HPLC (equipped with UV detector) (5, 10), can not discriminate between the two isomers. The chemical shifts of the 200 MHz ^{1}H-NMR spectrum are presented in Table I.

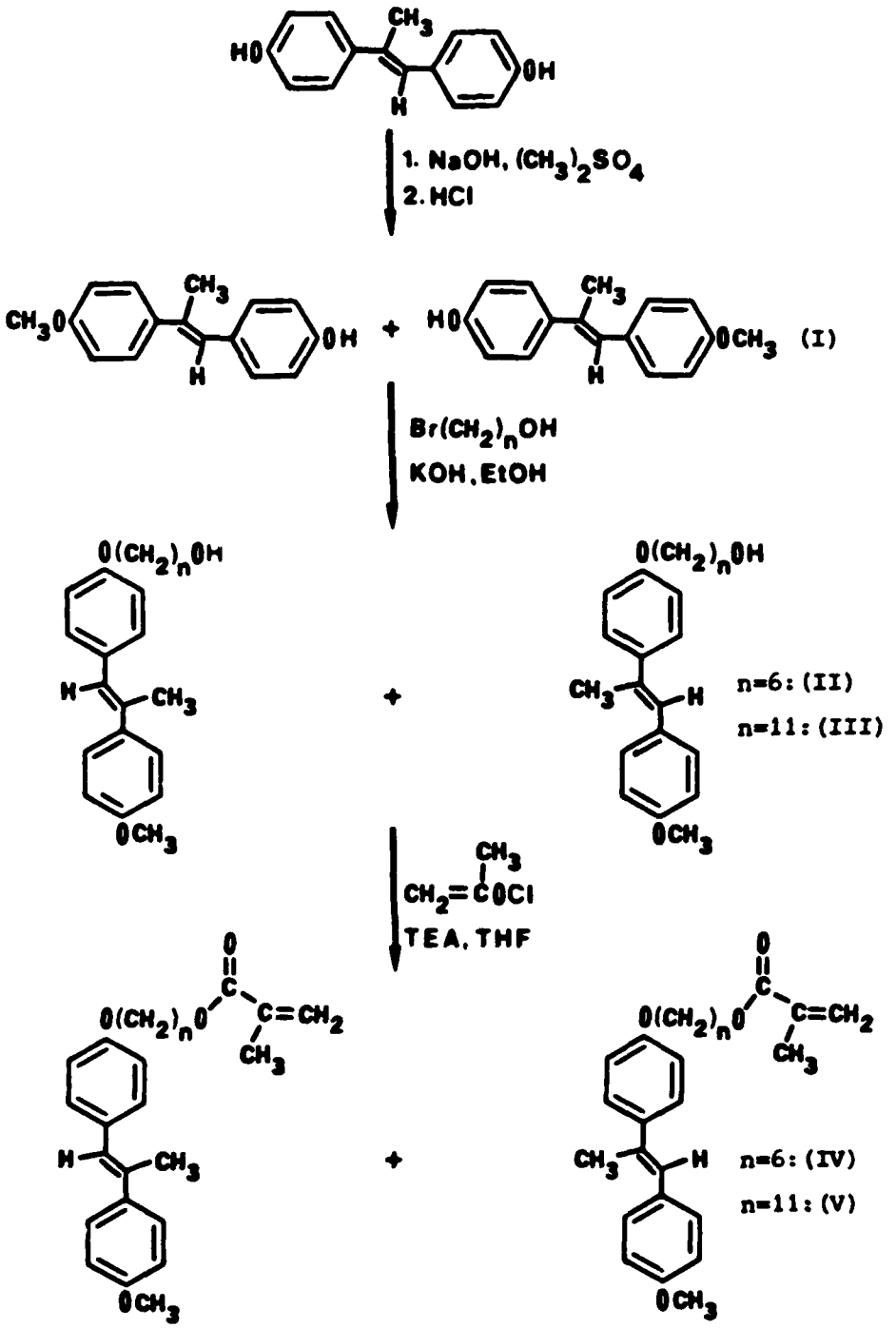
Synthesis of 4(4')-(1-hydroxyhexanyloxy)-4'(4)-methoxy-α-methylstilbene (II) and of 4(4')-(1-hydroxyundecanyloxy)-4'(4)-methoxy-α-methylstilbene (III).

Both compounds were prepared by the etherification of 4(4')-methoxy-4'(4)-hydroxy-α-methylstilbene with 11-bromoundecanol and 6-chlorohexanol respectively , in ethanol at reflux temperature in the presence of KOH as base. An example of this procedure is given below. 4(4')-Methoxy-4'(4)-hydroxy-α-methylstilbene (3g, 0.0125 mole) and KOH (1.05g, 0.0188 mole) were dissolved in 50 ml of 95% ethanol. 11-Bromoundecanol (4.72g, 0.0188 mole) was added and the solution was refluxed for 15 hrs. The reaction mixture was then poured into water and the precipitated product was filtered, washed with dilute solution of aqueous NaOH, water, and recrystallized from methanol to yield 4.65g (90.7%) of white crystals. m.p.=117-119°C. Compound III (61%) has a m.p.=107-109°C. The ^{1}H-NMR chemical shifts for both compounds are presented in Table I.

Synthesis of Methacrylates IV and V

Both monomers were synthesized by the esterification of the corresponding alcohols (II and III) with methacryloyl chloride. An example follows. III (1.5g, 0.0037 mole) was dissolved in 50 ml of dried THF and 1 ml (0.007 mole) of dried triethylamine was added. The obtained solution was cooled to 0°C in an ice-water bath and 0.5 ml (0.005 mole) of methacryloyl chloride were added dropwise. The reaction was allowed to warm up to room temperature and was kept stirring at this temeperature overnight. Finally, it was poured into water, and the precipitated product was filtered, dried, and recrystallized from methanol to yield 1.26g (72%) of white crystals. m.p.= 60-85°C (DSC at 20°C/min). Compound IV (65%) presents on its DSC thermogram (20°C/min), two endothermic transitions at 21.6 and 27.5°C, followed by a

nematic mesophase which undergoes isotropization at 46.6°C.



Scheme 1: Synthesis of Monomers

Radical Polymerization of Monomers

Both monomers were polymerized in dried dioxane by using AIBN as a radical initiator at 60°C for 15 hrs. Polymerizations were carried out in Sch-

lenk tubes under an argon atmosphere after the monomer solutions were degassed. The monomer concentration was 10% (w/V) and the initiator concentration was 1 wt% versus the monomer. After the polymerization time, the reaction mixture was diluted with THF and precipitated into methanol. The filtered polymers were dried under vacuum and then purified by reprecipitation from THF solutions into methanol. The characterization of the resulting polymers is presented in Table II.

Table I: Characterization of Monomers and Intermediary Compounds

Compound	Solvent	200 MHz ^{1}H-NMR (δ, ppm)
I	$(CD_3)_2CO$	2.21 (s, CH_3-C=), 3.11 (s, -OH), 3.80 (s, CH_3O-), 6.73 (s, HC=), 6.84-7.49 (m, 8 aromatic protons)
II	$CDCl_3$	1.30-1.87 (m, 4 -CH_2-), 2.24 (s, CH_3-C=), 3.65 (t, -CH_2OH), 3.82 (s, CH_3O-), 3.97 (t, -CH_2OPh), 6.72 (s, HC=), 6.85-7.47 (m, 8 aromatic protons)
III	$CDCl_3$	1.30-1.79 (m, 9 -CH_2-), 2.24 (s, CH_3-C=), 3.63 (t, -CH_2OH), 3.83 (s, CH_3O-), 3.97 (t, -CH_2OPh), 6.72 (s, HC=), 6.87-7.47 (m, 8 aromatic protons
IV	$CDCl_3$	1.45-1.83 (m, 4 -CH_2-), 1.94 (s, CH_3-C-COO), 2.24 (s, CH_3-C=), 3.81 (s, CH_3O-), 3.96 (t, -CH_2OPh), 4.16 (t, -CH_2OOC-), 5.54 and 6.10 (s, C=CH_2), 6.72 (s, HC=), 6.85-7.46 (m, 8 aromatic protons)
V	$CDCl_3$	1.34 -1.80 (m, 9 -CH_2-), 1.93 (s, CH_3-C-COO), 2.24 (s, CH_3-C=), 3.82 (s, CH_3O-), 3.97 (t, -CH_2OPh), 4.15 (t, -CH_2OOC-), 5.53 and 6.08 (s, C=CH_2), 6.72 (s, HC=), 6.86-7.47 (m, 8 aromatic protons)

C. Techniques

The experimental techniques used in the characterization of monomers and polymers i.e., 200 MHz ^{1}H-NMR spectroscopy, differential scanning calorimetry (DSC), optical polarization microscopy, gel permeation chromatography (GPC), and high pressure liquid chromatography (HPLC) have been previously described (5).

Table II

Radical Polymerization of Monomers and Characterization of the Polymers

Monomer	Conv. (%)	$\bar{M}n \times 10^{-3}$ (GPC)[b]	$\bar{M}w/\bar{M}n$	Thermal Transitions and Thermodynamic Parameters[a]					
				Heating			Cooling		
				Tg	Ti	ΔHi	Ti	ΔHi	Tg
IV	79	15.2	2.17	23	113	0.63	108	0.58	19
V	75	15.6	2.17	12	118	2.16	110	2.18	6

a) Tg and Ti are in °C; ΔHi, in kcal/mru; mru=mole repeat unit.
b) polystyrene standards.

RESULTS AND DISCUSSION

Scheme 1 outlines the synthesis of the two monomers. As we have discussed in the experimental section, the DSC thermograms of the monomethylated 4,4'-dihydroxy-α-methylstilbene have shown two broad overlapped melting

transitions. This result suggests that compound I consists of a mixture containing the two constitutional isomers i.e., 4-methoxy-4'-hydroxy-α-methylstilbene and 4-hydroxy-4'-methoxy-α-methylstilbene. This mixture can be enriched in one of the two isomers by succesive recrystallizations from methanol. The analysis of this mixture by 200 MHz ^{1}H-NMR spectroscopy revealed an almost 50/50 molar ration between the two isomers.

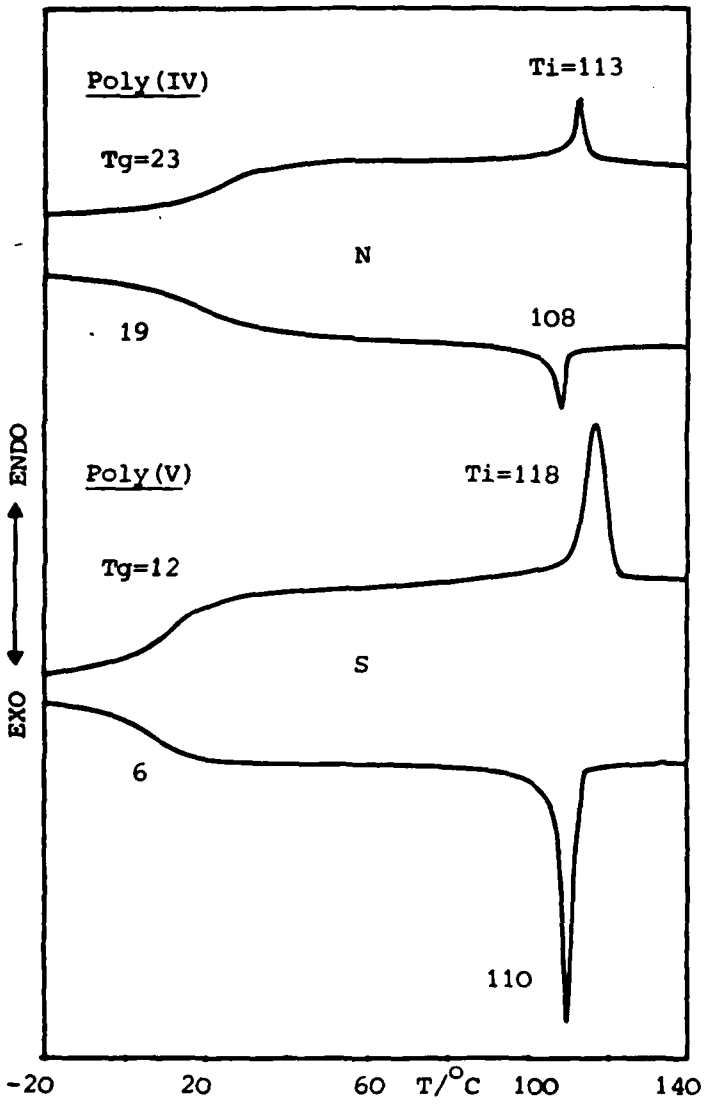
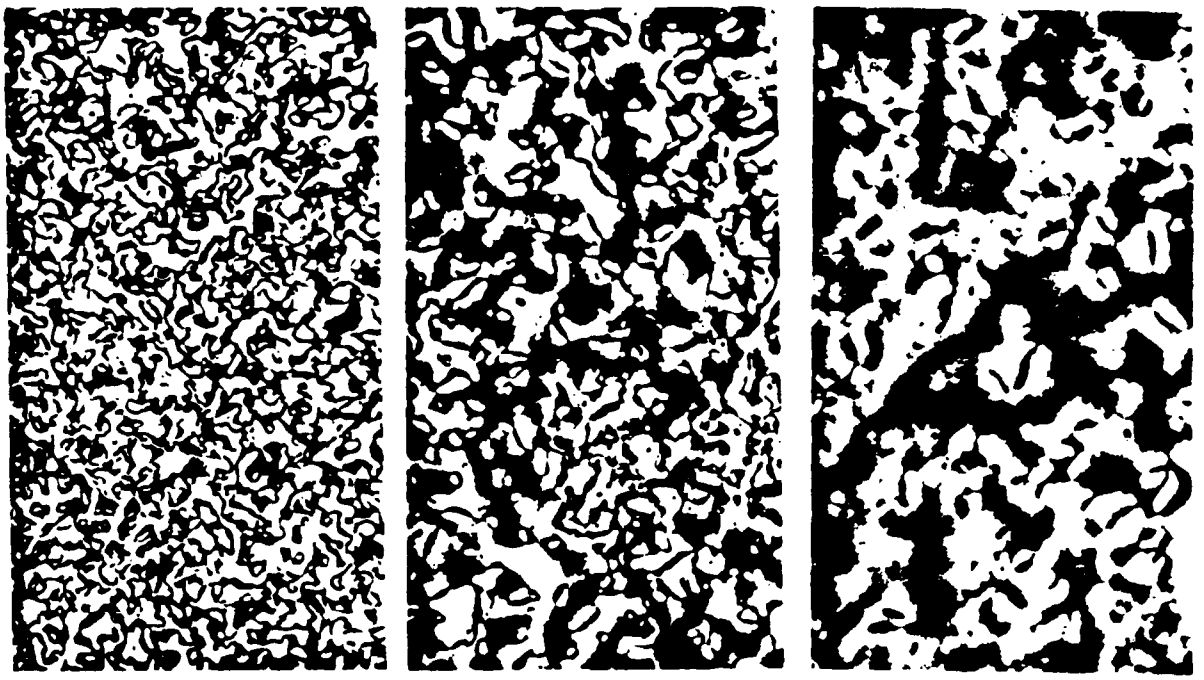


Figure 1: Normalized differential scanning calorimetric thermograms (20°C/min) of: A)Poly(IV), second heating scan; B) Poly (IV), second cooling scan; C) Poly(V), second heating scan; D) Poly(V), second cooling scan.

The DSC thermogram of the monomer IV presents two unidentified endotherms at 21.6 and 27.5°C, followed by a nematic mesophase which undergoes isotropization at 46.6°C. Monomer V presents a broad melting endotherm situated in between 60 and 85°C.

Table II summarizes the radical polymerization of the monomers IV and V and the thermal characterization of the resulting polymers. The number average molecular weights and the polydispersities of the two polymers are quite similar. Therefore, their thermal behavior can be compared in a quantitative way. Typical DSC thermograms for the two polymers are presented in Figure 1. The corresponding tnermal transitions and tneir thermodynamic



A) B) C)

Figure 2: Typical optical polarization micrographs (magnification, 300x) of the nematic texture exhibited by Poly(IV): A) after 5 min. at 112°C; B) after 20 min. at 112°C; C) after 40 min. at 112°C.

Figure 3: Typical optical polarization micrographs (magnification, 300 x) of Poly(V): smectic focal-conic texture obtained after 5 hrs of annealing at 118°C.

parameters are listed in Table II. None of these polymers present side-chain crystallization. This could be the consequence of the fact that once the constitutional isomers are attached as polymeric side-groups they supress the cocrystallization tendency of the side-chains.

Poly(IV) exhibits an enantiotropic nematic mesophase. This assignment is supported by: the low value of the isotropization enthalpy (Table II), its low degree of supercooling (5°C), and the nematic texture observed by optical polarization microscopy (Figure 2).

The isotropization enthalpy of Poly(V) is within the expected values for a smectic mesophase, and at the same time the isotropization transition is suppercooled with 8°C (Fig. 1, Table II). Figure 3 presents the focal-conic texture exhibited by poly(V). This texture is characteristic for a smectic A or C mesophase. No definitive assignment for this mesophase is available at this time.

These preliminary results suggest that at least for the examples described here, the copolymerization of two monomers containing mesogenic units which are constitutional isomers, leads to liquid crystalline copolymers which do not undergo side-chain crystallization. A quantitative understanding of these copolymers requires the synthesis, homopolymerization and copolymerization of the individual isomers. Research on this line is in progress in our laboratory.

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REFERENCES

1. H. Finkelmann and G. Rehage, Adv. Polym. Sci., 60/61, 99(1984)
2. V. P. Shibaev and N. A. Plate, Adv. Polym. Sci., 60/61, 173(1984)
3. T. D. Shaffer and V. Percec, Makromol. Chem., Rapid. Commun., 6, 97(1985)
4. V. Percec and T. D. Shaffer, in "Advances in Polymer Synthesis", B. Culbertson and J. E. McGrath,Eds., Plenum, New York, 1985, p. 133
5. V. Percec and H. Nava, J. Polym. Sci: Part A: Polym. Chem., 25, 405(1987)
6. C. S. Hsu, J. M. Rodriguez-Parada and V. Percec, J. Polym. Sci: Part A: Polym. Chem., in press
7. B. Hahn and V. Percec, Macromolecules, submitted
8. C. S. Hsu and V. Percec, J. Polym. Sci: Part A: Polym. Chem., in press
9. R. Deschenaux, P. Neuenschwander and P. Pino, Helv. Chim. Acta., 69 1349(1986)
10. V. Percec, H. Nava and H. Jonsson, J. Polym. Sci: Part A: Polym. Chem., in press

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