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Synthesis and characterization of liquid crystalline copolysiloxanes containing azobenzene dyes and 1,3-dioxane based mesogenic side groups

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SUMMARY

The synthesis and characterization of nine side-chain liquid crystalline copolysiloxanes containing trans-5-(n-undecanyl)-2-(4-cyanophenyl)-1,3-dioxane and 4-(alkanyloxyphenylazo)benzonitrile side groups are presented. The azobenzene dye contents in the copolymers range from about 5 to 20 wt.-%. The nature of the mesophase exhibited by the copolysiloxanes depends very much on the dye concentration. Three copolysiloxanes which contain about 5 wt.-% azobenzene dye, display a smectic A phase while the other six copolysiloxanes which contain more then 10 wt.-% azobenzene dye, exhibit a nematic phase. All the obtained copolysiloxanes show a very low glass transition temperature and a very wide temperature range of mesophase.

INTRODUCTION

Side-chain liquid crystalline polymers containing dye side groups were first described by Ringsdorf et al.(1). In the past few years, a number of new liquid crystalline copolymers with photochromic azobenzene-, spiropyrane-, spironaphthoxazine- and flugimide-moieties in side chains were synthesized and used for reversible optical data storage [2-15].

In a previous paper we reported the biphasic side-chain liquid crystalline polysiloxanes containing trans-5-(n-undecanyl)-2-(4-cyanophenyl)-1,3-dioxane side groups (16). The obtained polymers showed a wide temperature range of mesophase and also a high degree of decoupling of the mobility of main chain from that of side chain. We thought they would be suitable for the applications of optical data storage.

The goal of this study is to present the synthesis and characterization of side-chain liquid crystalline copolysiloxanes containing trans-5-(n-undecanyl)-2-(4-cyanophenyl)-1,3-dioxane and 4-(4-alkanyloxyphenylazo) benzonitrile side groups. The effect of azo dye contents on the mesomorphic properties of the obtained coplysiloxanes is discussed.

EXPERIMENTAL

Materials

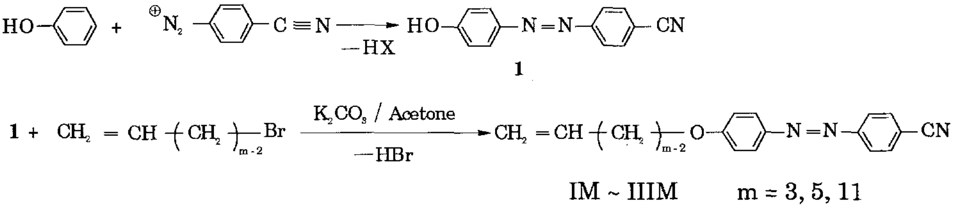
Poly(methylhydrogensiloxane) $(\overline{Mn} = 4500 - 5000)$ (from Petrarch System, Inc.) was used as received. 4-Cyanobenzaldehyde and the other reagents (from Aldrich) were used as received. Toluene used in the hydrosilylation reaction was first refluxed over sodium and then distilled under nitrogen. Dicyclopentadienylplatinum (II) cholride catalyst was synthesized according to a literature procedure (17, 18).

Techniques

Experimental techniques used in the characterization of intermediary compounds and of polymers are identical to those previously reported (19).

Synthesis of monomers

The synthesis of azo dyes is summarized in Scheme 1.



Scheme 1: Synthesis of azobenzene dye monomers IM ~ IIIM.

4-(4-Hydroxyphenylazo) benzonitrile (1)

4-Amino-benzonitrile (11.8 g, 0.1 mol) was dissolved in 50 ml of conc. sulfuric acid and 50 ml of H_2O. For the diazotation sodium nitrite (6.9 g, 0.1 mol) dissolved in 50 ml of H_2O was slowly added at temperature below 5 °C. To the cooled solution, sodium hydroxide (4.6 g, 0.2 mol) and phenol (9.4 g, 0.1 mol), dissolved in 100 ml of H_2O were added and the reaction mixture was stirred for 1 hr at room temperature. The precipitated azo dye was isolated by filtration and washed with H_2O. The residue was dissolved in 200 ml ethanol / H_2O (vol. ratio 1 : 1) and acidified with conc. hydrochloric acid. The precipitate was separated by filtration and vaccum dried. Yield 20 g (90 %) ; mp 202 ~ 204 °C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm) : 7.16 (d, 2H, ArH), 8.02 (m, 6H, ArH) ; 10.26 (s, 1H, –OH) ; UV ($CHCl_3$, nm) $\lambda_{max} = 348$.

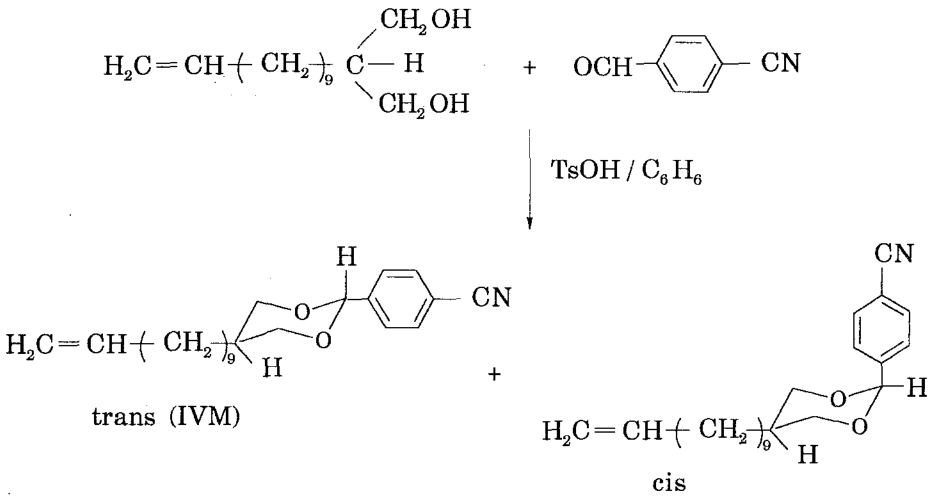
4-(4-Allyloxyphenylazo)benzonitrile (IM)
4-(4-(4-Pentenyloxy)phenyllazo)benzonitrile (IIM)
4-(4-(10-Undecenyloxy)phenyllazo)benzonitrile (IIIM)

All three compounds were synthesized by the same method. An example is presented below.

4-(4-Hydroxyphenylazo)benzonitrile (20 g, 0.09 mol) and potassium carbonate (12.6 g, 0.091 mol) were dissolved in 100 ml of absolute acetone, a pinch of KI was added, and 10-undecenyl chloride was then added dropwise. The reaction mixture was refluxed for 6 days. The precipitated KCl was filtrated off under suction from the warm mixture and the filtrate was evaporated. $CHCl_3$ was added to the crude product and the undissolved material was filtered off. The filtrate was evaporated and the product was recrystallized from ethanol to yield 10.1 g (30 %). The characterization of three monomers are reported in Tables I and II.

trans-2-(4-Cyanophenyl)-5-(10-undecenyl)1,3-dioxane (IVM)

trans-2-(4-Cyanophenyl)-5-(10-undecenyl)-1,3-dioxane was prepared by the acid catalyzed condensation of 2-(10-undecenyl)-1,3-propandiol and 4-cyanobenzaldehyde (Scheme 2) according to a procedure reported previously (19).



Scheme 2 : Synthesis of trans-2-(4-cyanophenyl)-5-(10-undecenyl)-1,3-dioxane.

Table I. Chemical shifts of ^{1}H - NMR of azobenzene dye.

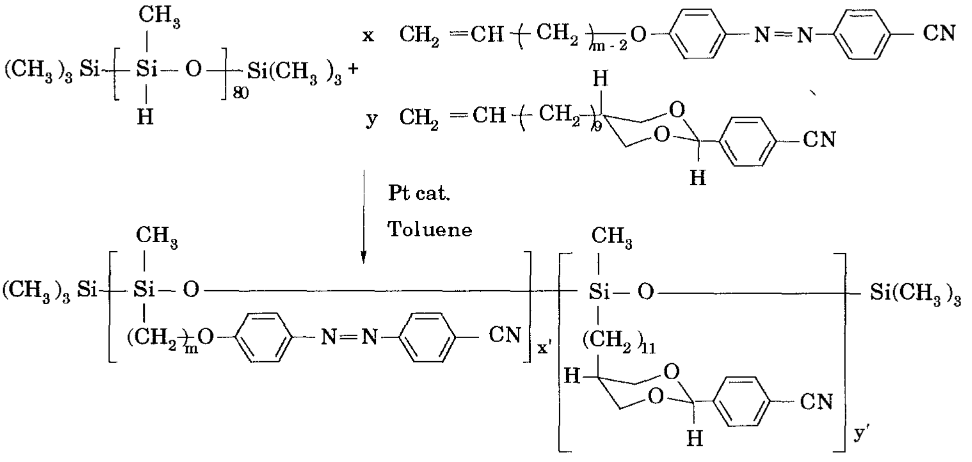
Monomer	100 M Hz ^{1}H - NMR (CDCl$_3$, δ, ppm)
IM	δ = 4.64 (d, 2H, – C$\underline{H}_2$–O–) , 5.39 (dd, 2H, –CH=C$\underline{H}_2$), 6.08 (m, 1H, –C$\underline{H}$=CH$_2$), 7.06 and 7.86 (d, q, 8H, Ar$\underline{H}$)
IIM	δ = 1.86 – 2.31 (m, 4H, =CH–C$\underline{H}_2$–C$\underline{H}_2$–) , 4.13 (t, 2H, – C$\underline{H}_2$–O–), 5.08 (dd, 2H, –CH=C$\underline{H}_2$), 5.80 (m, 1H, –C$\underline{H}$=CH$_2$), 7.04 and 7.85 (d, q, 8H, Ar$\underline{H}$)
IIIM	δ = 1.31 – 2.01 (m, 16H, –(C$\underline{H}_2$)$_8$–CH$_2$–O–), 4.05 (t, 2H, – C$\underline{H}_2$–O–), 4.98 (dd, 2H, –CH=C$\underline{H}_2$), 5.78 (m, 1H, –C$\underline{H}$=CH$_2$), 6.88 and 7.83 (d, q, 8H, Ar$\underline{H}$)

Table II : Elemental analysis, and UV absorption of azobenzene dye.

Monomer	Formula	Elemental analysis (%)				Yield (%)	UV λ_{max} (nm)
			C	H	N		
IM	$C_{16}H_{13}N_3O$ (263.3)	calc.	72.98	4.98	15.96	42	362
		found	72.91	5.00	15.96		
IIM	$C_{18}H_{17}N_3O$ (291.3)	calc.	74.20	5.88	14.42	45	360
		found	74.19	5.85	14.42		
IIIM	$C_{24}H_{29}N_3O$ (375.5)	cacl.	76.76	7.78	11.20	30	359
		found	76.78	7.73	11.30		

Synthesis of Copolymers

Copolymers were prepared by hydrosilation of the corresponding azo dye and trans-2-(4-cyanophenyl)-5-(10-undecenyl)-1,3-dioxane with poly(hydrogenmethylsiloxane) using dicyclopentadienylplatinum (II) chloride as catalyst in toluene (Scheme 3). A detailed procedure is given as follows. The olefinic mixture (0.5 g, 10 mol % excess versus the Si–H groups) was dissolved in 50 ml of freshly distilled toluene together with the proper amount of poly(hydrogenmethylsiloxane). The reaction mixture was heated to 110 °C under nitrogen, and 50 μl of dicyclopentadienylplatinum (II) chloride catalyst were then injected with a syringe as solution in methylene chloride (1 mg / ml). The reaction mixture was refluxed under nitrogen until both IR and ^{1}H-NMR analyses showed that the hydrosilation reaction was complete. The solution was filtered and the copolymers were seperated by precipitation in methanol, purified by several reprecipitation from THF solution into methanol, and dried under vacuum.



m = 3, 5, 11 ; x / y = 1 / 9, 2 / 8 and 3 / 7

IP ~ IXP

Scheme 3 : Synthesis of side-chain liquid crystalline copolysiloxanes

The copolymer compositions were determined by UV-VIS spectroscopy and elemental analysis. The UV-VIS measurements were carried out on a Hitachi 320 spectrophotometer. $CHCl_3$ (spectroscopic grade, Merck) was used as solvent for all measurements. The area of the absorption band of the dyes was used for the quantitative determination of the copolymer composition. The corresponding dye monomers were used for calibration. For the determination of the copolymer composition by elemental analysis the nitrogen values were used.

RESULTS AND DISCUSSION

The phase transitions and corresponding enthalpy changes for the monomers IM ~ IVM are summarized in Table III. Ammong three dye monomers, monomer IM shows no liquid crystalline phase while monomers

Table III: Phase transitions and corresponding ethalpy changes of azo dye monomers **IM ~ IVM** and 1,3-dioxane based monomer IVM.

monomer	m	Thermal transitions, °C (corresponding enthalpy changes, Kcal / mol)[a]	
		heating	cooling
IM	3	k 155 (8.25) i	i 144 (5.69) k
IIM	5	k 122 (5.36) i	i 118 (0.09) n 102 (4.52) k
IIIM	11	k 100 (8.27) i	i 98 (0.33) n 75 (7.90) k
IVM	–	k 63 (7.93) i	i 51 (6.26) k

[a] k = crystalline , n = nematic , i = isotropic.

IIM and IIIM exhibit a monotropic nematic phase. The 1,3-dioxane based monomer IVM, shows no liquid crystalline phase and has no absorption in the visible range.

Scheme 3 illustrates the synthesis of copolysiloxanes. The 1,3-dioxane based monomer was mixed with dye monomers and the mixture was allowed to undergo hydrosilation reaction with poly(methylhydrogensiloxane) in toluene. The dye content in the mixture is 10, 20 or 30 wt.-%. The copolymer were purified by preparative gel permeation chromatography.

The copolymer compositions were determined by two independent methods, UV-VIS spectroscopy and elemental analysis (EA). Since the 1,3-dioxane based monomer shows no absorption in the visible range, the area of the absorption band of the dyes can be used for the quantitative determination of the copolymer composition. The corresponding dye monomers were used for calibration. The evaluation was conducted under the assumption that no change of the absorption coefficient occurs with polymer fixation. The assumption can be made because the polymer backbone and chromophor are separated by flexible spacer and no change in the position and shape of the absorption band was observed in dilute solution. The results are summarized in Table IV. The dye contents in the copolymers range from 5 wt.-% to 20 wt.-%. The values are smaller than those in the monomer mixtures.

The thermal transitions of the copolysiloxanes IP ~ IXP are also summarized in Table IV. Nine copolymers can be separated into three series, i.e. IP ~ IIIP, IVP ~ VIP and VIIP ~ IXP. The difference among three series of copolymers is due to the length of the flexible alkanyl spacer in the dye moieties. In each series, the difference among three copolymers is on the dye contents. In the first series of polymers copolymer, IP which contains 5 wt.-% azobenzene dye shows an enantiotropic smectic A phase while copolymers IIP and IIIP which contain respectively 10 and 18 wt.-% azobenzene dye, present an enantiotropic nematic phase.

Table IV: Composition and phase behavior of copolymers IP ~ IXP.

		Composition (wt.- % of dye monomer or its monomeric unit)		Thermal transition, °C (corresponding enthalpy charges, Kcal / mru)[b]	
Polymer	m	monomer mixture	copolymer[a]	heating	cooling
IP	3	10	5	g −6 S_A 128 (0.61) i	i 123 (0.59) S_A −14 g
IIP	3	20	10	g −1 n 124 (0.53) i	i 114 (0.55) n −10 g
IIIP	3	30	18	g 7 n 116 (0.48) i	i 109 (0.47) n −4 g
IVP	5	10	4	g −6 S_A 130 (0.65) i	i 125 (0.65) S_A −15 g
VP	5	20	13	g −4 n 136 (0.59) i	i 127 (0.49) n −9 g
VIP	5	30	15	g 4 n 128 (0.28) i	i 126 (0.28) n −4 g
VIIP	11	10	5	g −7 S_A 148 (0.73) i	i 146 (0.65) S_A −8 g
VIIIP	11	20	16	g −4 n 144 (0.51) i	i 134 (0.48) n −9 g
IXP	11	30	21	g 0 n 138 (0.40) i	i 131 (0.41) n −10 g

[a] Average of values determined by UV / VIS and EA measurements.

[b] mru = mole repeating unit, g = glassy , S_A = smectic A, n = nematic, i = isotropic.

The phase assignment was conducted by optical polarizing microscopic observation and X-ray diffraction mesurements. Figure 1 presents the X-ray diffraction diagrams obtained from powder of IP ~ IIIP. Curve A which shows a broad reflection at wide angle (associated with the lateral packing) and a sharp reflection at low angle (associated with the smectic layers), indicates the fromation of smectic A phase. Curves B and C which show respectively only a broad reflection at wide angle, indicate th formation of nematic phase. Figure 2 presents the typical smectic A and nematic textures exhibited respectively by polymers IP and IIP. According to the previous report (19) the homopolysiloxane which containing trans-2-(4-cyanophenyl)-5-(10-undecanyl)-1,3-dioxane side groups, exhibits a smectic A mesophase. The results demonstrate that incorporation of dye moieties in the copolymers is able to change the nature of the mesophase. Furthermore, as the dye content in the copolymers increases the glass transition temperature increases while the isotropization temperature decreases. The second and third series of copolymers, i.e., IVP ~ VIP and VIIP ~ IXP, show very similar mesomorphic behavior with that of first series of copolymers. Copolymers IVP and VIIP which contain about 5 wt.-% azobenzene dye, present an enantiotropic smectic A phase. The other four copolymers which contain more than 10 wt.- % azo-

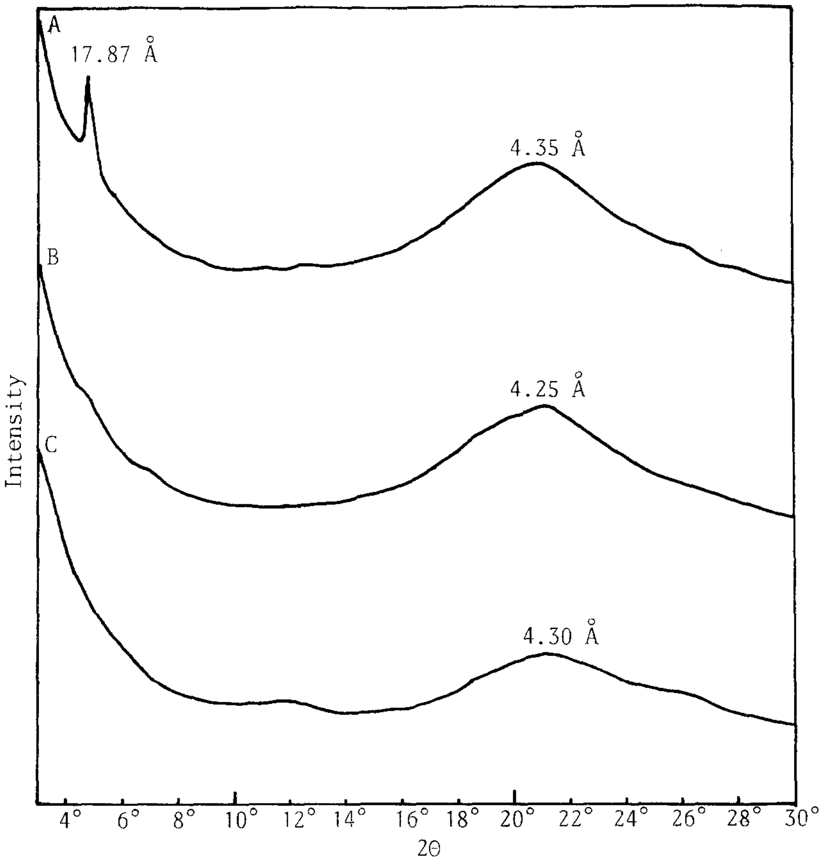


Figure 1 : X-ray diffraction diagrams of : A) IP ; B) IIP ; C) IIIP.

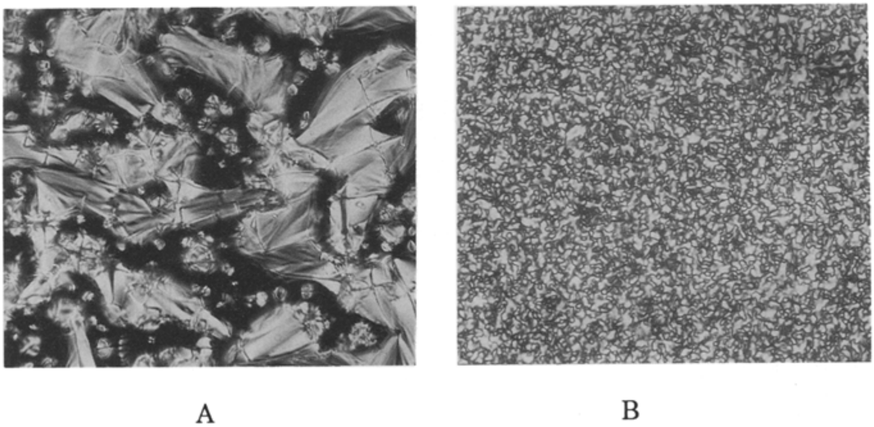


Figure 2 : Optical polarizing micrographs : (A) S_A texture exhibited by IP ; (B) nematic texture exhibited by IIP

benzene dye, present an enantiotropic nematic phase.

In conclusion, the liquid crystalline copolysiloxanes containing up to 20 wt.-% azobenzene were synthesized. The mesomorphic behavior of the copolysiloxanes depends on the dye concentration. All the copolysiloxanes prepared in this study, show a very low glass transition temperature and a very wide temperature range of mesophase. The copolysiloxanes can be used for the preparation of dichroic polymer films and may have the potential applications in the area of information storage.

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REFERENCES

1. H. Ringsdorf and H. W. Schmidt, Makromol. Chem., 185, 1327 (1984).
2. H. Ringsdorf, H. W. Schmidt, G. Baur and R. Kiefer in "Recent Advances in Liquid Crystalline Polymers", L. L. Chapoy Ed., Elsevier Applied Science, London, 253 (1985).
3. C. Noel, Makromol Chem., Macromol Symp., 22, 95 (1988).
4. H. Ringsdorf, H. W. Schmidt, G. Baur, R. Kiefer, and F. Windscheid, Liq. Cryst. 1, 319 (1986).
5. M. Eich, J. H. Wendorff, B. Reck and H. Ringsdorf, Makromol. Chem. Rapid Commun., 8, 59, (1987).
6. M. Eich and J. H. Wendorff, Makromol. Chem. Rapid Commun., 8, 467 (1987).
7. I. Cabrera and V. Krongauz, Macromolecules, 20, 2713 (1987).
8. I. Cabrera and V. Krongauz, Wature, London, 326, 582 (1987).
9. K. Anderle, R. Birenheide, M. Eich and J. H. Wendorff, Makromol. Chem. Rajpid Commun., 10, 477 (1989).
10. S. Yitzchaik, I. Cebrera, F. Buchholtz and V. Krongauz, Macromolecules, 23, 707 (1990).
11. S. Yitzchaik, J. Ratner, F. Buchholtz and V. Krongauz, Liq. Cryst., 8, 677 (1990).
12. T. Ikeda, S. Horiuchi, D. B. Karanjit, S. Kurihara and S. Tazuke, Macromolecules, 23, 36 (1990).
13. T. Ikeda, S. Horiuchi, D. B. Karanjit, S. Kurihara and S. Tazkuke, Macromolecules, 23, 42 (1990).
14. T. Ikeda, S. Kurihara, D. B. Kraranjit and S. Tazuke, Macromolecules, 23, 3938 (1990).
15. I. Cabrera, A. Dittrich and H. Ringsdorf, Angew. Chem. In. Ed. Engl., 30, 76 (1991).
16. C. S. Hsu and V. Percec, Makromol. Chem., Rapid Commun., 8, 331 (1987).
17. M. A. Apfel, H. Finkelmann, G. M. Janini, R. J. Lamb, B. H. Luhmann, A. Price, W. L. Robert, T. J. Shaw and C. H. Smith, Anal. Chem., 57, 651 (1985).
18. M. S. Kharasch and T. A. Ashford, J. Am. Chem. Soc., 58, 1733 (1936).
19. G. H. Hsiue, J. S. Wen and C. S. Hsu, Makromol. Chem., 192, 2243 (1991).

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