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SYNTHESIS AND PHASE BEHAVIOR OF AZO DYE CONTAINING LIQUID CRYSTALLINE POLYORGANOSILOXANE

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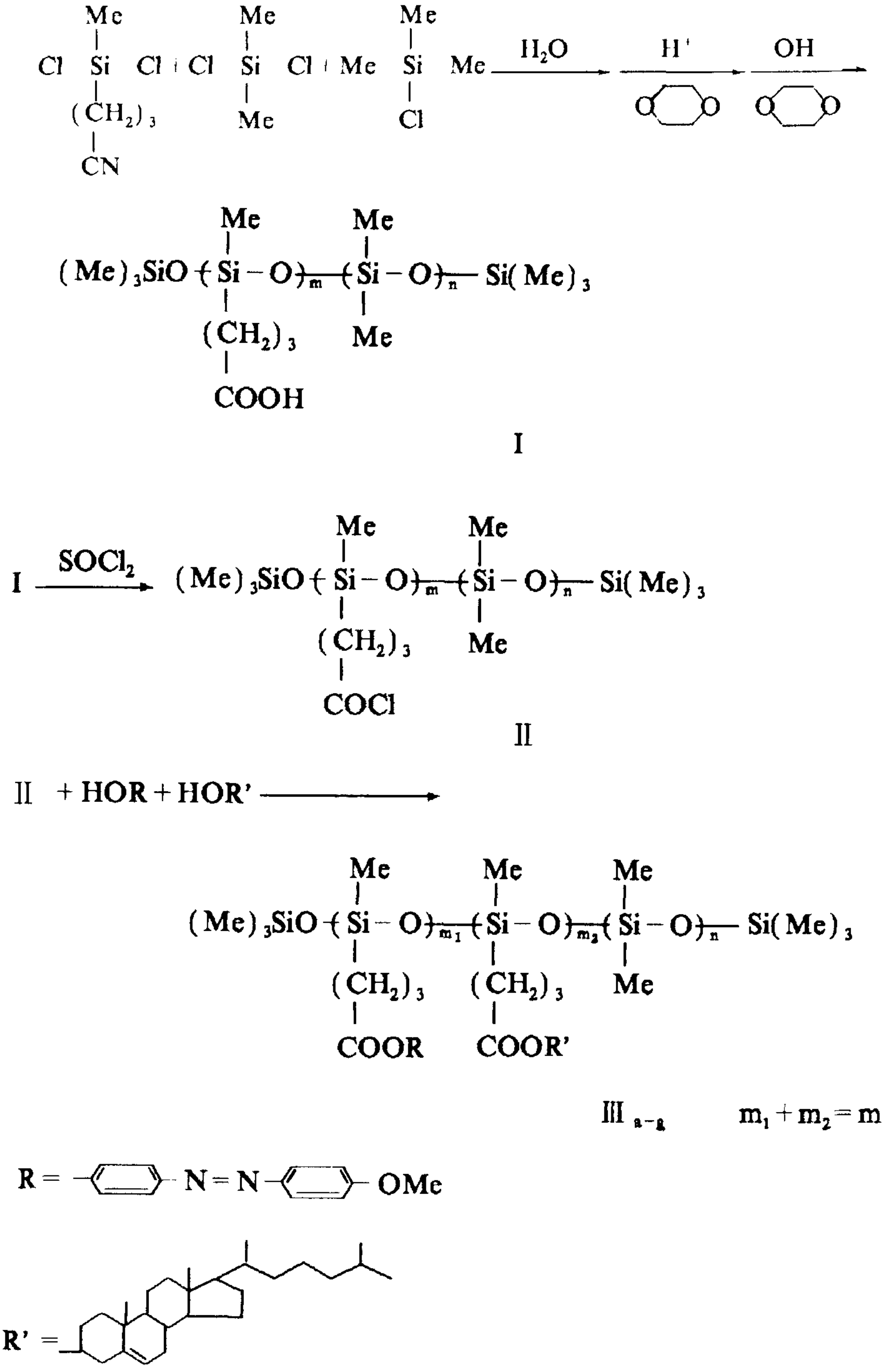
ABSTRACT

A series of liquid crystalline polyorganosiloxanes containing both azo dye and cholesteryl groups were synthesized by reacting poly[3-chloroformylpropyl)methylsiloxane-*co*-dimethylsiloxane] with both cholesterol and 4-(4′-methoxyphenylazo)phenol. The yields were between 73 and 81%. Most of these new polyorganosiloxanes are colored solid products. Their chemical structures were confirmed by IR, ^{1}H NMR, and elemental analysis. Their phase behaviors were also investigated by using differential scanning calorimetry (DSC) and polarizing microscopy. The results show that all these polyorganosiloxanes exhibit liquid crystalline behavior at various temperatures and at any azo dye content. As a result of the orientation of both mesogenic azo dye and cholesteryl groups, smectic phases were formed beginning around 0°C, and cholesteric phases appeared above 60°C.

INTRODUCTION

Dyes containing liquid crystalline polymers might open interesting application possibilities in the field of display technology. It was reported that by the copolymerization of a mesogenic group containing monomer and a dye containing monomer, a new type of colored polymeric liquid crystal with a high, temperature-independent dye content had been prepared [1–6].

We describe here the synthesis and phase behavior of polyorganosiloxanes containing both an azo dye and a cholesteryl side group. These polyorganosiloxanes were prepared by reacting poly[(3-chloroformylpropyl)methylsiloxane-*co*-dimethylsiloxane] with mesogenic 4-(4′-methoxyphenylazo)phenol and cholesterol. The synthetic scheme and structures of these liquid crystalline polyorganosiloxanes are as follows:



EXPERIMENTAL

Materials

All reagents were redistilled before use. Dimethyldichlorosilane, bp 70°C. Trimethylchlorosilane, bp 57-59°C. (3-Cyanopropyl)methyldichlorosilane was prepared according to Ref. 7, bp 120°C/17 mmHg.

Techniques

A Varian EM-360L NMR spectrometer, a Shimadzu IR-440 spectrophotometer, and a Carlo Erba 1106 elementary analyzer were used to determine the chemical structures. Measurement of number-average molecular weight ($\overline{M}_n$) was made on a Knauer Vapor Pressure Osmometer, using acetone as solvent. The thermal behavior of polymers was investigated with a Shimadzu DT-40 differential scanning calorimeter (DSC). The scan speed of the heating runs was 10 K/min. Investigations of the liquid crystalline textures of the polymers were carried out with the Olympus BH-Z polarizing microscope.

Preparation of Polyorganosiloxanes

Poly[(3-carboxypropyl)methylsiloxane-*co*-dimethylsiloxane] (I) [8, 9]: A mixture of (3-cyanopropyl)methyldichlorosilane (127.5 g, 0.70 mol), dimethyldichlorosilane (90.3 g, 0.70 mol), and trimethylchlorosilane (7.6 g, 0.07 mol) was dropped into 1000 mL water with stirring, and stirring was continued for 3 hours at room temperature. The water layer was removed, 150 mL sulfuric acid (50%) and 150 mL dioxane were added to the oily liquid, which was then refluxed with stirring for 20 hours, and the reaction mixture was poured into cold water (1000 mL) and gave a white precipitate. The precipitate was washed three times with water. Dioxane (150 mL) and 150 mL of 4 N sodium hydroxide solution were added to the precipitate, and refluxing with stirring was continued for 20 hours. The reaction mixture was neutralized with 2 N hydrochloric acid to precipitate the product, which was washed with cold water and dried at 90°C *in vacuo*: 110.8 g of (I) was obtained. Yield: 66.8%.

IR(KBr): 1710 ($>$C=O) and 2700-3300 $\mathrm{cm^{-1}}$ (—OH). ^{1}H NMR (DMSO-d^6): $\delta = 0.2$ (s, $>\mathrm{Si{-}C\underline{H}_3}$); 0.7 (t, $>\mathrm{Si{-}C\underline{H}_2{-}}$); 1.6 (m, $>\mathrm{Si{-}CH_2{-}C\underline{H}_2{-}}$); 2.3 (t, $>\mathrm{Si{-}CH_2{-}CH_2{-}C\underline{H}_2{-}}$); 9.0-10.5 ppm (s, $\mathrm{-COO\underline{H}}$).

Analysis. Found (%): C, 40.16; H, 7.51; Si, 22.18; N, 0. Calculated for (I): $m/n = 3.38$; $\overline{M}_n$ (VPO, in acetone): 3680.

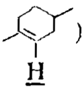
Poly[(3-chloroformylpropyl)methylsiloxane-*co*-dimethylsiloxane] (II): Thionyl chloride (58 mL, 0.82 mol) was added to a solution of (I) (17.5 g, 4.75×10^{-3} mol) in anhydrous dioxane (50 mL), and the mixture was refluxed with stirring for 2 hours. The reaction mixture was heated below 130°C *in vacuo* to remove the excess thionyl chloride and dioxane, and (II) was obtained as a viscous and bright yellow oily intermediate.

Polymethylsiloxane containing both pendant azo dye and cholesteryl group ($\mathrm{III_d}$): The polyorganosiloxane intermediate (II) (2.76 g, 6.78×10^{-4} mol) was dissolved in 10 mL anhydrous dioxane. To this solution, cholesterol (2.71 g, 7×10^{-3} mol) in 10 mL anhydrous dioxane was added. The mixture was refluxed with stirring for 2 hours, and then 4-(4′-methoxyphenylazo)phenol (1.60 g, 7 × 10^{-3} mol) in 10 mL anhydrous dioxane was added, and refluxing with stirring was continued for 6 hours. Dioxane was removed by distillation *in vacuo*. The residue was dissolved in ethyl acetate (10 mL). Cold ethanol was added dropwise to the solution to give a brown precipitate. This process was repeated three times to purify the product, which was then dried at 90°C *in vacuo*: 4.78 g polyorganosiloxane (III_d) was obtained. Yield: 73%.

Polyorganosiloxanes ($III_{a\text{-}c,\ e\text{-}g}$) were synthesized similarly. Different contents of azo dye groups (m_1/m %) were made by varying the ratio of 4-(4′-methoxyphenylazo)phenol to cholesterol. Elementary analyses data of $III_{a\text{-}g}$ are listed in Table 1.

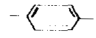
III_a : Yield : 81% .

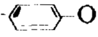
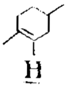
IR(KBr): 1736 (>C=O) and 2868 cm^{-1} (−CH(CH_3)$_2$)

^{1}H NMR(CCl_4): δ=0.1 (s, >Si−C$\underline{H}_3$); 5.4 ppm (m, )

$\overline{M}$n (VPO, in acetone): 11540.

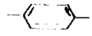
III_b : Yield : 77%.

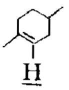
IR (KBr): 1734(>C=O); 1594, 1504(C=C) and 1259 cm^{-1}(−−O−C).

^{1}H NMR(CCl_4): δ=0.1(s, >Si−C$\underline{H}_3$); 3.9(s, −−OC$\underline{H}_3$); 5.4ppm(m, ).

$\overline{M}$n (VPO, in acetone): 10800.

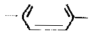
III_c : Yield : 81%.

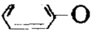
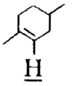
IR (KBr): 1735(>C=O); 1596, 1500(C=C) and 1260 cm^{-1}(−−O−C).

^{1}H NMR(CCl_4): δ=0.1(s, >Si−C$\underline{H}_3$); 3.9(s, −−OC$\underline{H}_3$); 5.4ppm(m, ).

$\overline{M}$n (VPO, in acetone): 10210.

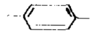
III_d : Yield : 73%.

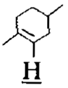
IR (KBr): 1733(>C=O); 1589, 1504(C=C) and 1259 cm^{-1}(−−O−C).

^{1}H NMR(CCl_4): δ=0.1(s, >Si−C$\underline{H}_3$); 3.8(s, −−OC$\underline{H}_3$); 5.3ppm(m, ).

$\overline{M}$n (VPO, in acetone): 9910 .

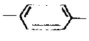
III_e : Yield : 79%.

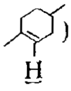
IR (KBr): 1757(>C=O); 1596, 1503(C=C) and 1258 cm^{-1}(−−O−C).

^{1}H NMR(CCl_4): δ=0.1(s, >Si−C$\underline{H}_3$); 3.9(s, −−OC$\underline{H}_3$); 5.4ppm(m, ).

$\overline{M}$n (VPO, in acetone): 9000 .

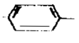
III_f : Yield : 74%.

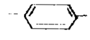
IR (KBr): 1757(>C=O); 1595, 1500(C=C) and 1257 cm^{-1}(−−O−C).

^{1}H NMR(CCl_4): δ=0.1(s, >Si−C$\underline{H}_3$); 3.8(s, −−OC$\underline{H}_3$) and 5.4ppm(m , ).

$\overline{M}$n (VPO, in acetone): 8640 .

III_g : Yield : 75%.

IR (KBr): 1758(>C=O); 1601, 1499(C=C) and 1255 cm^{-1}(−−O−C).

^{1}H NMR(CCl_4): δ=0.1(s, >Si−C$\underline{H}_3$); 3.8 ppm(s, −−OC$\underline{H}_3$)

$\overline{M}$n (VPO, in acetone): 8180 .

TABLE 1. Ratio of HOR to HOR′, Elementary Analysis, and Composition of Polyorganosiloxanes III_{a-g}

Polyorgano-siloxane	HOR/HOR′ (mole ratio)	Elementary analysis, %, calculated (found) C	H	Si	N	Azo dye content, m_1/m, %
III_a	0/1	72.47 (71.52)	10.40 (10.46)	7.16 (7.19)	0.00 (0.00)	0.00
III_b	1/5	70.78 (70.78)	9.84 (9.61)	7.52 (7.59)	0.90 (1.22)	16.7
III_c	1/2	68.89 (68.32)	9.22 (8.89)	7.93 (7.74)	1.90 (1.80)	33.3
III_d	1/1	66.79 (67.33)	8.52 (8.28)	8.38 (9.09)	3.01 (3.57)	50.0
III_e	2/1	64.42 (64.45)	7.74 (8.14)	8.88 (8.04)	4.26 (3.70)	66.7
III_f	5/1	61.78 (61.11)	6.87 (6.77)	9.45 (9.22)	5.66 (4.96)	83.3
III_g	1/0	58.75 (57.38)	5.87 (5.95)	10.10 (10.15)	7.26 (6.40)	100

RESULTS AND DISCUSSION

Poly[(3-carboxypropyl)methylsiloxane-*co*-dimethylsiloxane] (I) was prepared by hydrolysis of linear poly[3-cyanopropyl)methyl-*co*-dimethylsiloxane] which had been made from the cohydrolysis of a mixture of difunctional Me_2SiCl_2, $(NCCH_2CH_2CH_2)MeSiCl_2$, and monofunctional Me_3SiCl organosilicon compounds. By further treatment of (I) with a considerable excess of thionyl chloride, poly[(3-chloroformylpropyl)methylsiloxane-*co*-dimethylsiloxane] (II) was obtained. Esterification of both cholesterol and 4-(4′-methoxyphenylazo)phenol or one of them with (II) leads to the polyorganosiloxanes (III_{a-g}) in 73–81% yields.

The liquid crystalline behavior of the resulting polyorganosiloxanes was studied by polarization microscopy and DSC measurements. The DSC curves of polyorganosiloxane III_a, III_d, and III_g in Fig. 1 and the phase transition temperatures of the polyorganosiloxanes III_{a-g} listed in Table 2 demonstrate that all of these resulting polyorganosiloxanes show liquid crystalline properties. The phase behavior of these polyorganosiloxanes is markedly influenced by their composition and structures.

In addition to the lower glass transition temperatures, polyorganosiloxanes III_{b-f} show smectic and cholesteric phases at various temperatures. As a result of the orientation of both the mesogenic azo dye and the cholesteryl group, smectic phases were formed beginning around 0°C and turned to cholesteric phases at elevated temperatures (>60°C). Figure 2 illustrates that in the cholesteric region, when the azo dye contents are below 50%, the temperature range of the cholesteric phase

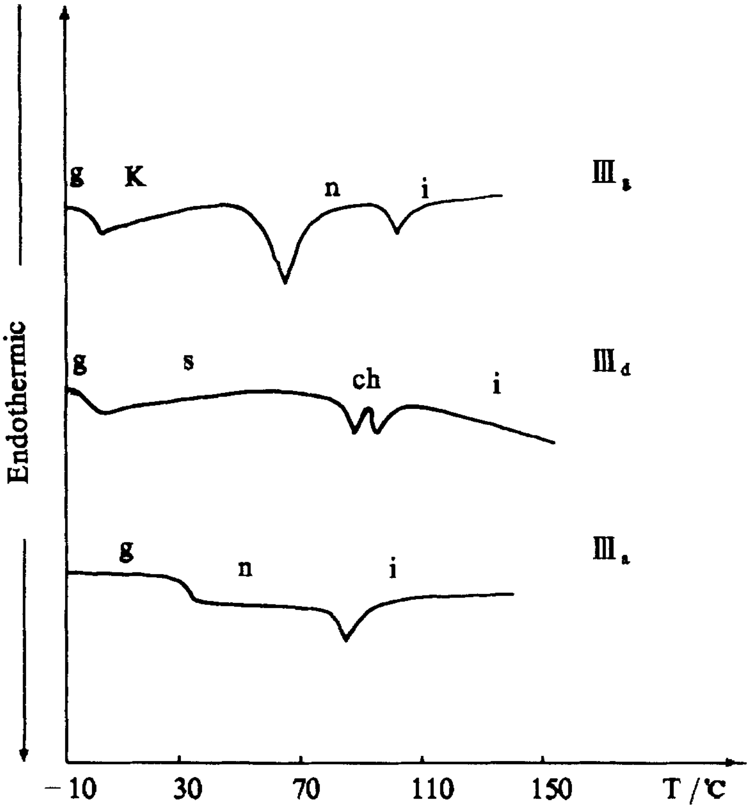


FIG. 1. DSC curves of polyorganosiloxanes III$_a$, III$_d$, and III$_g$ (heating at 10 K/min).

TABLE 2. Composition of Polyorganosiloxanes III$_{a\text{-}g}$ and Their Phase Transition Temperatures

Polyorganosiloxane	Azo dye content, m_1/m, %	Phase transition temperature, °C[a]
III$_a$	0.00	g 33 n 85 i
III$_b$	16.7	g 2 s 60 ch 110 i
III$_c$	33.3	g-1 s 80 ch 96 i
III$_d$	50.0	g-1 s 88 ch 96 i
III$_e$	66.7	g-3 s 85 ch 124 i
III$_f$	83.3	g-2 s 72 ch 165 i
III$_g$	100	g 1 k 66 n 102 i

[a] g = glassy, n = nematic, ch = cholesteric, s = smectic, i = isotropic, k = crystalline.

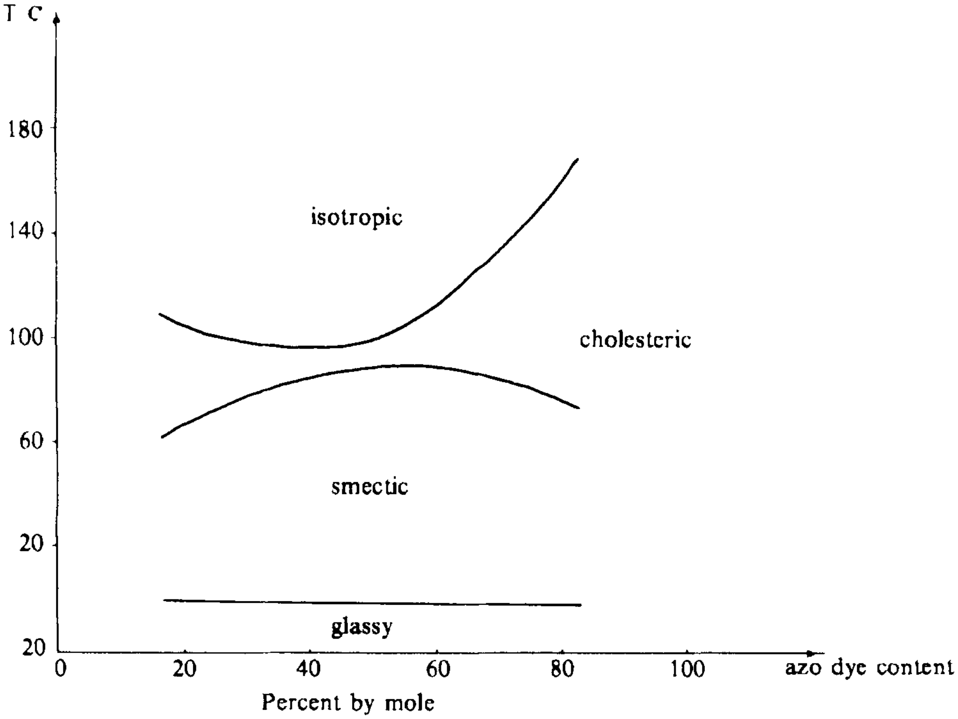


FIG. 2. Phase behavior of the azo dye containing polyorganosiloxanes III_{a-g}.

becomes narrower as the azo dye content increases. On the contrary, the temperature range of the cholesteric phase widens when the azo dye content increases beyond this point. In the latter case, the existence of a pendant cholesteryl group in the polymer structure can be regarded as an optically active material added to the nematic liquid crystals, which may cause the transition of the nematic phase into the cholesteric phase [10, 11].

CONCLUSION

New polyorganosiloxanes were synthesized by reacting poly[(3-chloroformylpropyl)methylsiloxane-*co*-dimethylsiloxane] with the mesogenic azo dye, 4-(4′-methoxyphenylazo)phenol and cholesterol. Their chemical structures were also characterized.

All these colored polyorganosiloxanes show liquid crystalline properties. The phase behavior of these polyorganosiloxanes is markedly influenced by their composition and structures, viz., the mole ratio of the pendant azo dye and the cholesteryl group (expressed by the azo dye content).

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