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Note

Low-temperature side-chain liquid crystalline polysiloxanes used as stationary phases for capillary gas chromatography

YONGHAO JIN, RUONONG FU*, ZHENXI GUAN, JIANSHENG GONG and BAOGUAN LI
Department of Chemical Engineering, Beijing Institute of Technology, P.O. Box 327, Beijing 100081 (China)
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Liquid crystalline stationary phases, which were first introduced in 1963 by Kelker[1], have unique selectivity for chromatographic separations. Although the high selectivity of liquid crystals can be combined with high efficiency by using capillary columns, several factors, such as their low molecular weights, highly crystalline nature and insolubility in common organic solvents, have hindered the application of monomeric liquid crystals in capillary gas chromatography (GC). In recent years, much attention has been paid to the synthesis of liquid crystalline polysiloxanes, which exhibit high column efficiency and low column bleeding, yet provide high selectivity over a wide temperature range in capillary GC[2,3]. Most of these stationary phases are high-temperature liquid crystals, suitable for separating high-boiling complex mixtures such as polycyclic aromatic compounds.

However, the separation of low-boiling isomers, such as xylenes, are also of great importance. In this work, five low-temperature liquid crystalline polysiloxanes were synthesized and coated on capillary columns, and their chromatographic properties were studied.

EXPERIMENTAL

Synthesis of liquid crystalline polysiloxanes

4-Allyloxybenzoyl chloride, which can be easily prepared by reaction of 4-allyloxybenzoic acid with an excess of thionyl chloride, was dissolved in dry pyridine. 4-Substituted phenol was added dropwise to the solution under nitrogen and stirred for several hours at room temperature, then distilled water was added, which caused precipitation. The mixture was neutralized with concentrated hydrochloric acid and filtered and the precipitate obtained was washed with water and saturated aqueous sodium hydrogencarbonate several times. The crude product was recrystallized from suitable solvents. The product obtained was the monomer used for synthesis.

Monomer, polymethylhydrosiloxane and fresh catalyst solution (prepared by adding $H_2PtCl_6 \cdot 6H_20$ to isopropyl alcohol) were added to dry, freshly distilled toluene, with a 10% excess of monomer over a molar ratio of 1:1 based on polymethylhydrosiloxane. The Pt to C=C ratio was in the range 1:10^4 to 1:10^3. The mixture was heated at 50–110°C (depending on the side-chain) and stirred for 24–48 h TABLE Iuntil no Si–H was detectable by IR spectroscopy (2140 cm^{-1}). The resulting

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TABLE I

STRUCTURES OF GROUP R AND PHASE TRANSITION TEMPERATURES OF LIQUID CRYSTALLINE POLYSILOXANES AND THEIR PARENT MONOMERS

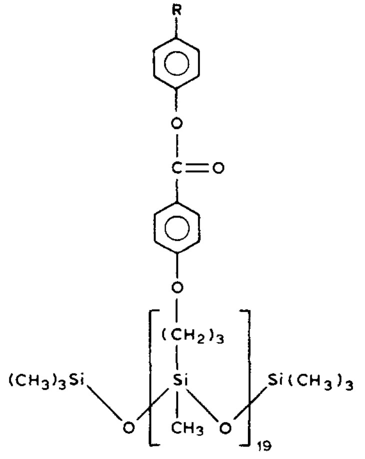
Transition temperatures were measured hot-stage light-polarized microscopy.

Polymer	*R*	*Transition temperature (°C)*[a]	
		Monomer	*Polymer*
PLC-1	$-C_6H_5$	$\mathrm{c}\overset{137}{-}\mathrm{i}$	$\mathrm{c}\overset{60}{-}\mathrm{n}\overset{120}{-}\mathrm{i}$
PLC-2	$-OC_6H_{13}$-*n*	$\mathrm{c}\overset{63}{-}\mathrm{n}\overset{79}{-}\mathrm{i}$	$\mathrm{g}\overset{15}{-}\mathrm{s}\overset{84}{-}\mathrm{i}$
PLC-3	$-OC_7H_{15}$-*n*	$\mathrm{c}\overset{52}{-}\mathrm{n}\overset{73}{-}\mathrm{i}$	$\mathrm{g}\overset{15}{-}\mathrm{s}\overset{83.5}{-}\mathrm{i}$
PLC-4	$-OC_8H_{17}$-*n*	$\mathrm{c}\overset{62}{-}\mathrm{n}\overset{73}{-}\mathrm{i}$	$\mathrm{g}\overset{15}{-}\mathrm{s}\overset{89}{-}\mathrm{i}$
PLC-5	$-O-CO-C_6H_5$	$\mathrm{c}\overset{129}{-}\mathrm{n}\overset{150}{-}\mathrm{i}$	$\mathrm{c}\overset{82}{-}\mathrm{n}\overset{105}{-}\mathrm{i}$

[a] c = Crystalline; g = glassy; n = nematic; s = smectic; i = isotropic.

polymers were purified by filtration or precipitation with methanol. The polymers were collected by centrifugation at 9000 rpm (13 000 *g*) for 25 min and dried in a vacuum oven.

The structures of the polymers are shown. Table I lists the structures of the group R and the phase transition temperatures of the polymers and their parent liquid crystalline monomers.



Column preparation

Fused-silica capillary tubing of 0.22 mm I.D. (Yongnian Optical Fibre Factory) was used. Capillaries were purged with nitrogen at 180°C for 6 h before coating. The liquid crystalline polysiloxanes were dissolved in methylene chloride (35°C) at a concentration of about 2.4 mg/ml, which gave a film thickness of about 0.3 μm using the static coating procedure. The coated columns were evaluated for selectivity and efficiency and were used for the separation of some isomers using an SP-2305 gas chromatograph (Beijing Analytical Instrument Factory) equipped with a capillary split injection system, a flame ionization detector and an integrator.

RESULTS AND DISCUSSION

The column efficiencies of polysiloxane liquid crystals (PLCs) are listed in Table II. The PLC stationary phases provide satisfactory column efficiencies owing to the unique flexibility of the polysiloxane backbone and the concomitant low surface tension, which facilitate the homogeneous coating of the PLC phases on the untreated fused-silica columns.

Fig. 1 illustrates chromatograms for a Grob test mixture on PLC stationary phases. It is obvious that these PLC fused-silica columns have low activity even though the fused-silica tubing was not pretreated.

TABLE II

CHARACTERISTICS OF THE LIQUID CRYSTALLINE CAPILLARY COLUMNS USED

Test compound: *o*-xylene.

Column No.	*Column length (m)*[a]	*Stationary phase*	*T_c*[b] *(°C)*	*Column efficiency (plates/m)*
1	10	PLC-1	110	3600
2	10	PLC-1	103	3780
3	20	PLC-1	94	3300
4	10	PLC-2	97	2850
5	17	PLC-2	80	2900
6	10	PLC-3	80	3100
7	10	PLC-4	85	2060
8	20	PLC-4	99	1800
9	10	PLC-5	86	1850
10	22	PLC-5	85	1850

[a] I.D. = 0.22 mm in each instance.
[b] T_c = column temperature.

APPLICATIONS OF THE COLUMNS

Xylene isomers, especially *p*- and *m*-xylene, have close physical and chemical properties and cannot be separated easily using conventional stationary phases. Fig. 2 shows the separations of xylene isomers on the PLC columns. Five of the PLC stationary phases can separate xylene isomers very successfully in a very short time. Table III lists the $\alpha_{p/m}$ values of the xylene isomers, from which it is clear that the PLC stationary phases have a higher selectivity for xylene isomers than monomeric liquid crystal stationary phases. As PLC-2–PLC-4 have higher selectivities than PLC-1 and PLC-5 (see α value in Table III), it is likely that the former are smectic phases and have a higher order than the nematic PLC-1 and PLC-5.

Fig. 3 depicts plots of α values *versus* column temperature for *p*- and *m*-xylene using the PLC stationary phases. In general the α values decrease as the column temperature increases, but there are some variations, the reason for which is not clear. PLC-5 can separate xylene isomers very successfully below the glass–nematic transition temperature. Although the α values of PLC-5 do not change significantly in the

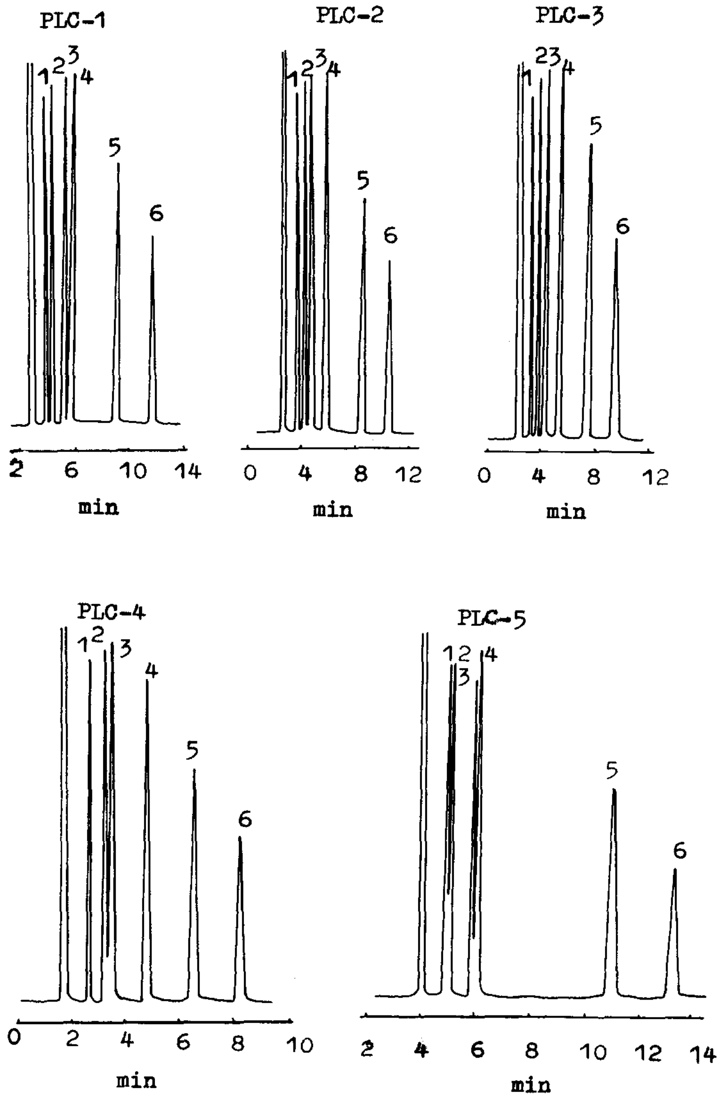


Fig. 1. Chromatograms of Grob test mixture on the PLC stationary phases. Column temperature, 120°C. Peaks: 1 = 2-octanone; 2 = C_{12} hydrocarbon; 3 = 1-octanol; 4 = C_{13} hydrocarbon; 5 = 2,6-dimethylphenol; 6 = 2,4-dimethylaniline.

supercooled state, the column efficiency decreases very rapidly as the column temperature decreases. The transition temperature of PLC-1 and PLC-5 liquid crystals measured in the thin-film state by GC are identical with that observed in the bulk liquid by differential scanning calorimetry. However, this may be not the case generally. PLC-1 and PLC-5 cannot separate xylene isomers in the isotropic form and their $\alpha_{p/m}$ values decrease very quickly when the column temperature increases above the transition temperature T_{n-i} or T_{s-i} (n = nematic, s = smectic, i = isotropic). Of great

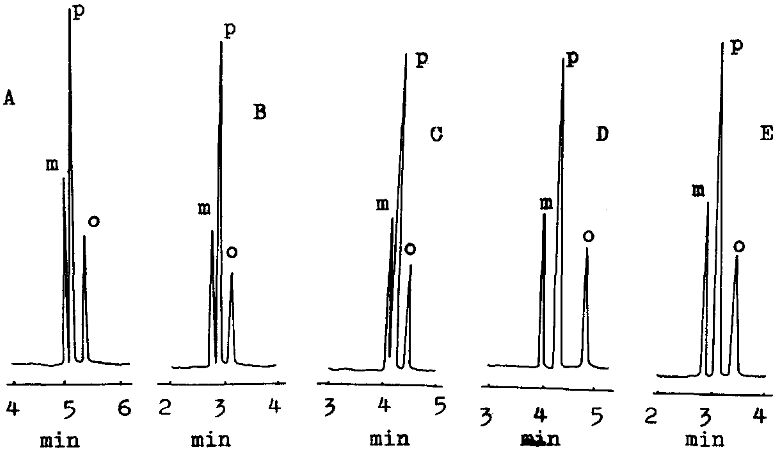


Fig. 2. Chromatograms of xylene isomers on the PLC stationary phases. (A) Column 3 (Table II), $T_c = 102°C$; (B) column 4, $T_c = 97°C$; (C) column 10, $T_c = 85°C$; (D) column 6, $T_c = 80°C$; (E) column 8, $T_c = 90°C$.

interest is the fact that the separations of xylene isomers are clearly preserved with the isotropic forms of PLC-2–PLC-4 stationary phases. Some residual ordering above T_{s-i} seems to exist, although it is not detected by other means. The nature of the substrate on which the liquid crystals are coated can affect the transition temperature substantially. Further studies are needed to determine if the substrate is the only or the main reason why the transition temperature is altered and if residual ordering above T_{n-i} or T_{s-i} exists in the bulk liquid state.

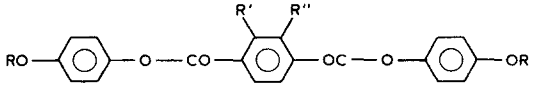
TABLE III

COMPARISON OF $\alpha_{p/m}$ VALUES FOR XYLENE ISOMERS ON CAPILLARY COLUMNS COATED WITH VARIOUS LIQUID CRYSTALLINE PHASES

Stationary phase	$\alpha_{p/m}$	*Stationary phase*[a]	$\alpha_{p/m}$
PLC-1	1.16	DBrPBAmB	1.04
PLC-2	1.18	BrPBAmB	1.08
PLC-3	1.16	BrPBHxB	1.06
PLC-4	1.21	BrPBOB	1.06
PLC-5	1.16		

[a] Taken from the literature[4,5].

The general formula of the compound is



$RO-C_6H_4-O-CO-C_6H_2(R')(R'')-OC-O-C_6H_4-OR$

where for

DBrPBAmB, R = C_5H_{11}, R′ = Br, R″ = Br; for BrPBAmB, R = C_5H_{11}, R′ = Br, R″ = H; for BrPBHxB, R = C_6H_{13}, R′ = Br, R″ = H; for BrPBOB, R = C_8H_{17}, R′ = Br, R″ = H.

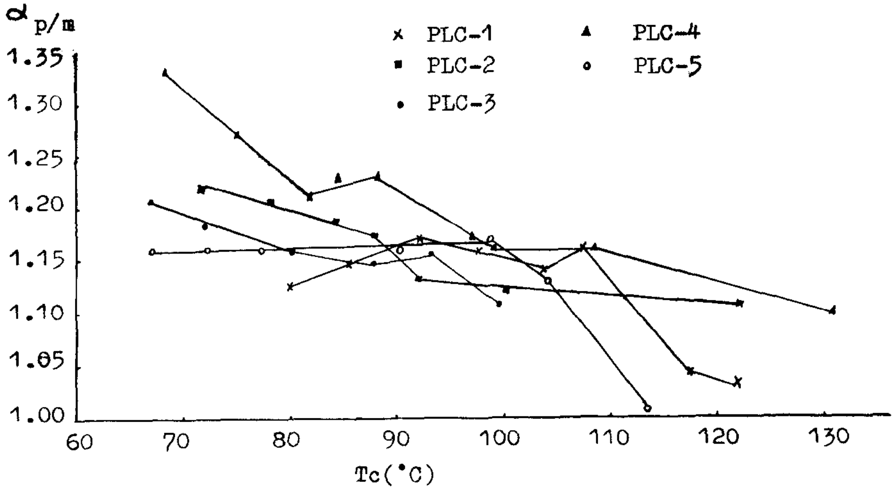


Fig. 3. Plots of α values against column temperature for *p*- and *m*-xylene with the PLC stationary phases: X, PLC-1; ■, PLC-2; ●, PLC-3; ▲, PLC-4; ○, PLC-5.

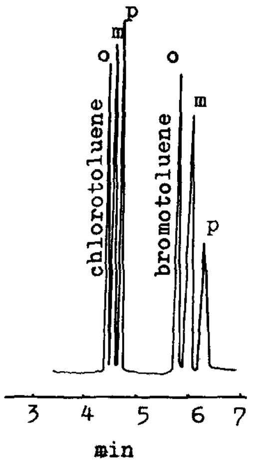


Fig. 4. Chromatogram of chloro- and bromotoluene isomers on PLC-1 stationary phase. Column 3 (Table II), $T_c = 109$°C.

TABLE IV

COMPARISON OF α VALUES OF TDA ISOMERS ON PLC COLUMN AND SE-54 COLUMN

T_c(°C)	PLC-1 (column 3)		SE-54	
	$\alpha_{3,4/2,3}$	$\alpha_{2,4/2,6}$	$\alpha_{2,3/3,4}$	$\alpha_{2,6/2,4}$
120.0	1.07	1.10	1.01	1.02
130.0	1.06	1.08	1.01	1.02
140.0	1.05	1.07	1.02	1.01
150.0	1.04	1.06	1.02	1.02
160.0	1.04	1.06	1.01	1.01

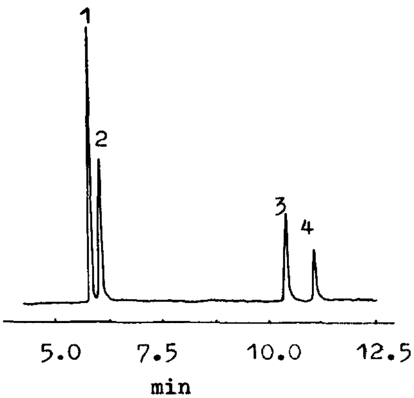


Fig. 5. Chromatogram of TDA isomers on PLC-1 stationary phase. Column 3 (Table II), T_c = 140°C. Peaks: 1 = 2,3-TDA; 2 = 3,4-TDA; 3 = 2,6-TDA; 4 = 2,4-TDA.

To illustrate the practical utility of the PLCs, examples are given of the separations of other low-boiling isomers, such as chlorotoluene and bromotoluene isomers (Fig. 4).

We also separated toluenediamines (TDAs) with a PLC-1 column and compared the results with those obtained on an SE-54 column. 2,3- and 3,4-TDA and 2,4- and 2,6-TDA were separated perfectly on the PLC column, but were not separated on the SE-54 column. Table IV gives the α values of the TDA isomers on these two columns. The retention time of 3,4-TDA is shorter than that of 2,3-TDA on the SE-54 column, but the order is reversed on the PLC column. 2,4-TDA and 2,6-TDA gave the same result. This effect occurs because the separation mechanism on PLC stationary phases is based mainly on differences in the solute molecular geometries (principally the length-to-breadth ratio), and that on SE-54 is based on differences in the polarities and boiling points of the solute. Fig. 5 shows a chromatogram of TDA isomers on PLC-1 phase.

CONCLUSION

Low-temperature side-chain liquid crystalline polysiloxanes can be easily coated on capillary columns to give high column efficiencies and high selectivities for the separation of low-boiling isomers.

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