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HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY OF AROMATIC COMPOUNDS ON POLYCHLORAL

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SUMMARY

Chloral was polymerized by the lithium alkoxide of cholesterol and the polymer obtained was used as a packing material for high-performance liquid chromatography. Various types of aromatic compounds were chromatographed on the polychloral column mostly with methanol as carrier solvent, and correlations between the relative retention times of the solutes and their ^{13}C nuclear magnetic resonance chemical shifts were found. Three isomers of xylene were separated with this column at lower temperatures with a methanol–water mixture as carrier.

INTRODUCTION

Chloral can be polymerized to an isotactic, helical polymer with anionic initiators such as lithium alkoxides[1–4]. The polychloral obtained is insoluble in all solvents and can be successfully used as a column packing material for liquid chromatography. In a previous paper[5] we reported that polychloral, initiated by the lithium alkoxide of cholesterol, is capable of partially resolving isotactic polymers of *R*-(+)- and *S*-(−)-α-methylbenzyl methacrylates. We suggested that the resolution resulted from the specific interaction between the optically active polychoral helix of one screw-sense and the two poly(α-methylbenzyl methacrylate)s.

In this work, various types of aromatic compounds were chromatographed on polychloral and correlations between the relative retention times of these solutes and their ^{13}C nuclear magnetic resonance (NMR) chemical shifts were found.

EXPERIMENTAL

Chloral was purified by refluxing over phosphorus pentoxide for 1 day followed by fractional distillation in a nitrogen atmosphere[6,7].

The polymerization of chloral was carried out with the lithium alkoxide of cholesterol at 0°C in hexane according to a method previously described[1,2,5]. The mole percentage (mol %) of the initiator used relative to chloral was 0.2. The polymer plug obtained was grated and the powder stabilized by successive treatments with 10% hydrochloric acid in methanol and a 0.5 *M* solution of phosphorus pentachloride in carbon tetrachloride[8,9]. The polymer was then extracted with acetone for 3 days in a Soxhlet apparatus and dried at 0.1 mmHg. The polychloral particles of diameter 44–105 μm were prepared by grinding the stabilized polymer powder in a small ball-mill and subsequent sifting through a sieve. The particles were suspended in a carrier solvent and packed into a stainless-steel column (50 × 0.72 cm) with the pressure increased to 100 kg/cm^2.

A JASCO Tri Rotar-II liquid chromatograph was used with either a JASCO UV-254-II UV detector operating at 254 nm or with a Shodex RI SE-11 refractive index (RI) detector. The temperature of the column was controlled by jacketing the column and pumping water or ethanol through the jacket from a thermostat bath. The samples were injected as 1–5-μl aliquots from 1–5% solutions in the carrier solvent. The number of theoretical plates for the column was determined from the benzene peak except for the experiment with toluene carrier where pentane was used for the determination.

The ^{13}C NMR spectra were measured on a JEOL JNM FX-100 Fourier transform NMR spectrometer at room temperature and at 25 MHz. Tetramethylsilane was used as an internal standard. The ^{13}C chemical shifts of polycyclic aromatic hydrocarbons and of substituted benzenes were determined in 2 and 5% (w/v) solutions, respectively, in [^{2}H]chloroform; the spectra of dihydroxybenzenes were measured in [^{2}H]methanol.

RESULTS AND DISCUSSION

A mixture of several aromatic hydrocarbons was chromatographed on polychloral prepared with the lithium alkoxide of cholesterol in hexane. Table I shows the relative retention times of these hydrocarbons with toluene, hexane and methanol as carrier solvents. When the polychloral was used with toluene, short retention times and poor separations resulted. Some improvements were achieved with hexane but, with methanol as the carrier, the retention times were even longer and good separation was obtained. Fig. 1 shows the chromatograms obtained with methanol as a carrier at different temperatures. The resolution was improved with an increase in the temperature and complete separation was observed at 50 and 60°C.

Vogl and Hatada[10] measured the ^{1}H NMR line-widths of aromatic solvents including toluene and xylenes in a polychloral matrix and found that the line-broadening of the signal of the entrapped solvent molecule was greater for the aromatic protons than for those of the aliphatic substituents. They suggested a charge-transfer-type interaction between the aromatic ring and the trichloromethyl group as the latter has an electron-withdrawing ability. The higher affinity of toluene for polychloral may cause "squeezing-out" of the solute molecules from the polychloral stationary phase and thus result in poor resolution. However, when methanol is used as carrier, elution of the aromatic solute molecules is delayed and separation is improved because of the decreased affinity of the methanol carrier for the polychloral.

A correlation between ^{13}C NMR chemical shifts of polycyclic aromatic hydrocarbons and their relative retention times in high-performance liquid chromatogra-

TABLE I

RELATIVE RETENTION TIMES OF SEVERAL AROMATIC HYDROCARBONS ON POLYCHLORAL AT 24°C

Column: Polychloral (44–105 μm) in a 50 × 0.72 cm I.D. stainless-steel column; flow-rate, 1.0 ml/min.; pressure, 20–50 kg/cm^2 depending on the mobile phase.

Hydrocarbon	*Mobile phase**				
	Toluene (2640)	*Hexane (3067)*	*Methanol (2300)*		
			24°C	*50°C*	*60°C*
Benzene	1.00	1.00	1.00	1.00	1.00
Toluene	–	1.02	1.14	–	–
p-Xylene	1.01	1.04	1.54	1.34	1.28
Naphthalene	1.02	1.14	1.39	1.35	1.33
Biphenyl	–	1.13	1.76	1.73	1.64
Phenanthrene	1.03	1.42	2.41	2.38	2.27
Anthracene	1.04	1.49	3.58	2.97	2.74
Pyrene	1.05	1.62	4.05	3.61	3.47
1,3,5-Triphenylbenzene	–	1.43	8.95	7.46	6.52

* Values in parentheses represent the number of theoretical plates determined at 24°C.

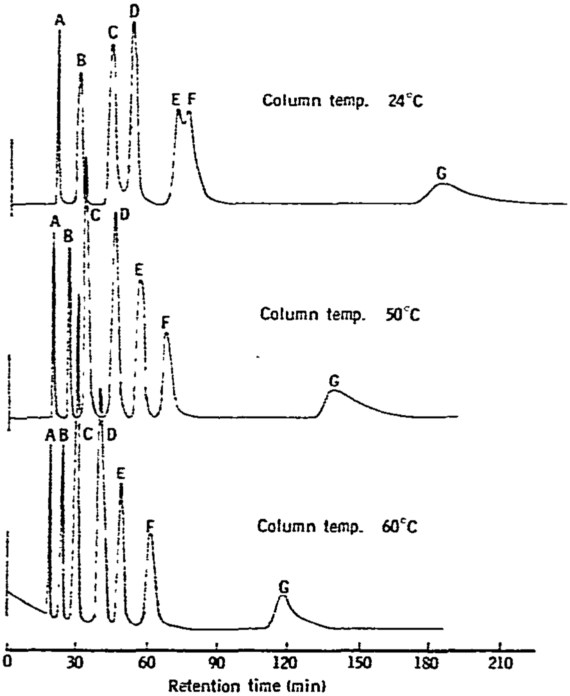


Fig. 1. HPLC separation of aromatic hydrocarbons on polychloral at different temperatures with methanol as carrier. Peaks: A = benzene; B = naphthalene; C = biphenyl; D = phenanthrene; E = anthracene; F = pyrene; G = 1,3,5-triphenylbenzene. Column, polychloral (44–105 μm) in a 50 × 0.72 cm I.D. stainless-steel column; flow-rate, 1.0 ml/min; pressure, 50 kg/cm^2.

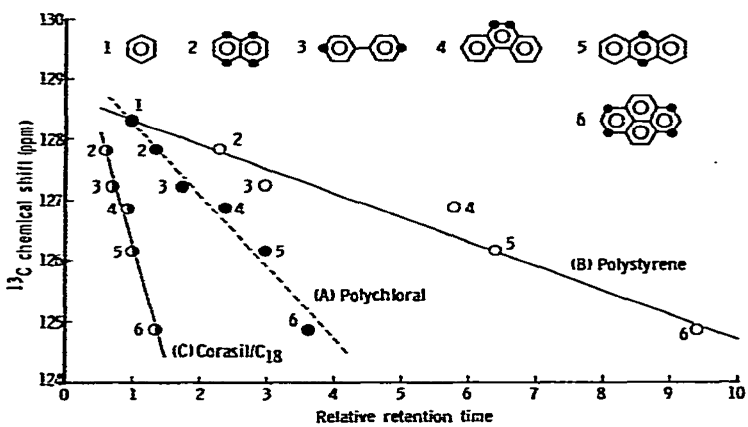
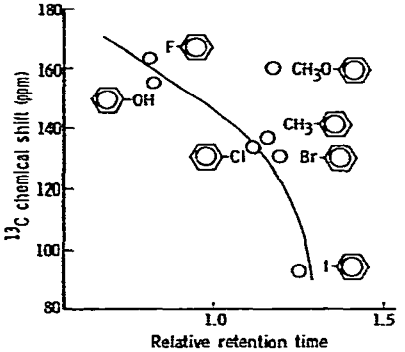


Fig. 2. Correlation between ^{13}C chemical shifts of aromatic hydrocarbons and their relative retention times in HPLC on (A) polychloral (44–105 μm) in a 50 × 0.72 cm I.D. stainless-steel column; solvent, methanol; flow-rate, 1.0 ml/min; pressure, 50 kg/cm^2; temperature, 50°C; number of theoretical plates, 2300; (B) polystyrene gel (7 μm) in a 25 × 0.72 cm I.D. stainless-steel column; solvent, methanol; flow-rate, 1.0 ml/min; temperature, 21°C; number of theoretical plates, 4800; (C) Corasil/C$_{18}$ (37–50 μm) in a 105 × 0.22 cm I.D. stainless-steel column; solvent, methanol–water (3:1); flow-rate, 0.5 ml/min; pressure, 650 p.s.i.; temperature, 25°C (data for Corasil/C$_{18}$ taken from ref. 13).

phy (HPLC) on polychloral was found and is shown in Fig. 2. The ^{13}C chemical shift values are for those carbon atoms at which the frontier electron density is highest[11,12]. The points marked in the structural formulae in Fig. 2 indicate the position of the highest density of the frontier electrons. The ^{13}C chemical shift for the aromatic-ring carbons is considered to be controlled mainly by the π-electron density and shows an upfield shift when the density on the carbon atom increases. The results in Fig. 2 indicate that the frontier electrons of these hydrocarbons play an orienting or guiding role in the retention process and that the charge-transfer-type interaction between the aromatic hydrocarbons and polychloral takes place at the position of the highest frontier-electron density. Linear relationships between the ^{13}C NMR chemical shifts and the relative retention times were also observed in HPLC on polystyrene gel with methanol as carrier or on Corasil/C$_{18}$ with methanol–water (3:1) as carrier (Fig. 2). The separation may be caused by π-electron interactions with the polystyrene gel and by Van der Waals interactions with the Corasil/C$_{18}$–methanol–water system. All the results mentioned here indicate that the frontier electrons play an important role in the retention processes for aromatic hydrocarbons.

1,3,5-Triphenylbenzene had a very long retention time, as shown in Table I and Fig. 1, and *p*-diphenylbenzene was not eluted from the column. The significance of these phenomena is not clear at present. Perhaps the terminal phenyl rings of these compounds geometrically fit the neighbouring trichloromethyl groups of polychloral with the molecules being tightly adsorbed on the polychloral surface.

In Fig. 3 are plotted the ^{13}C chemical shift values for the substituted carbon (*ipso*-carbon) atoms of various monosubstituted benzenes against their relative retention times. The retention times increase as the chemical shift values of the *ipso*-carbons shift upfield, *i.e.* as the electron densities of the carbons increase. In disubstituted benzenes similar correlations were observed between the average chemical-



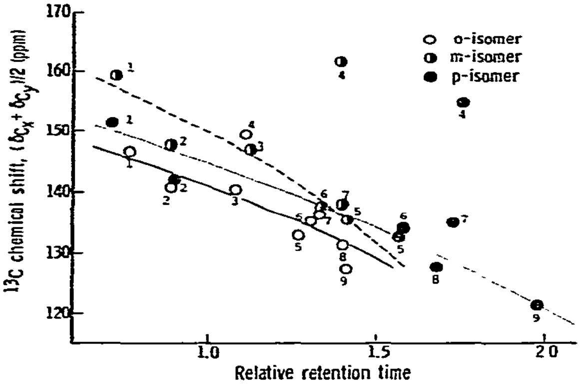
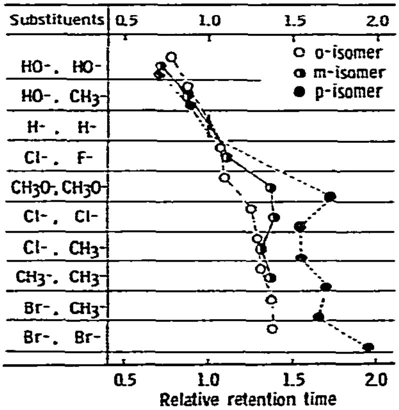


Fig. 3. Correlation between ^{13}C chemical shifts of *ipso*-carbons in monosubstituted benzenes and their relative retention times in HPLC on polychloral at 24°C with methanol as carrier.

Fig. 4. Correlation between the average chemical shift of substituted carbons in disubstituted benzenes and their relative retention times in HPLC on polychloral at 24°C with methanol as carrier. Compounds: 1 = dihydroxybenzene; 2 = hydroxymethylbenzene; 3 = chlorofluorobenzene; 4 = dimethoxybenzene; 5 = dichlorobenzene; 6 = chloromethylbenzene; 7 = dimethylbenzene; 8 = bromomethylbenzene; 9 = dibromobenzene.



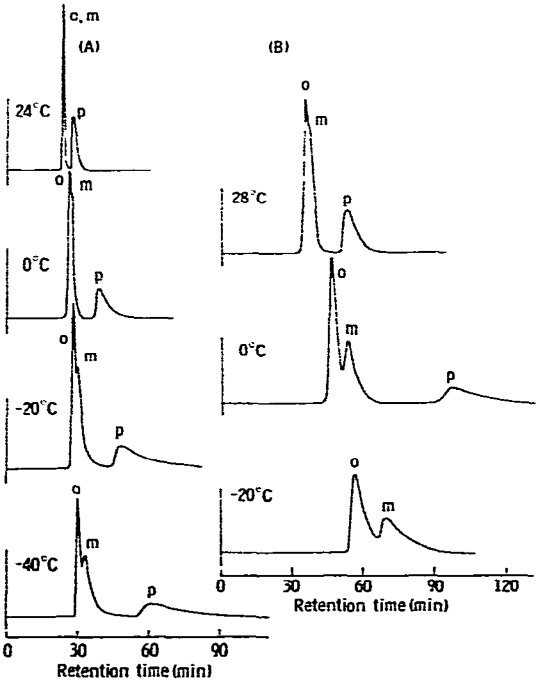


Fig. 5. Relative retention times of disubstituted benzenes in HPLC separation on polychloral at 24°C with methanol as carrier.

Fig. 6. HPLC separation of xylene isomers on polychloral at various temperatures with (A) methanol and (B) methanol-water (9:1) as a carrier solvent. Column, polychloral (44–105 μm) in a 50 × 0.72 cm I.D. stainless-steel column; flow-rate, 1.0 ml/min; pressure, 30–80 kg/cm^2 depending on the temperature and the mobile phase.

shift values of the two *ipso*-carbon atoms and their relative retention times, as shown in Fig. 4. These results indicate that the π-electron densities at the *ipso*-carbons are of significance in the retention process. However, the effect of interactions between the dipole of the substituent–*ipso*-carbon bond in the solute and the dipole of a trichloromethyl group in the polychloral matrix cannot be ruled out, since changes in the ^{13}C chemical shift values could be attributed to the difference in the electronegativities of the substituents. The deviation of the plots for methoxy-substituted benzenes from the curves may suggest an additional interaction between the lone-pair electrons of the oxygen atom and the polychloral. On the other hand, the plots for the hydroxy-substituted benzenes fit the curves, owing to the strong affinity of the solute for methanol. This would compensate for the interaction between the electron pair of the oxygen atom and the polychloral.

Fig. 5 shows the relative retention times of various disubstituted benzenes on polychloral. The order of elution was *o*-, *m*- and *p*-isomers for most of the disubstituted benzenes. The ^{1}H NMR line-broadening of the phenyl proton signal of xylenes in the polychloral matrix increased in the order of *o*- and *p*-isomers, indicating a stronger interaction of *p*-xylene with polychloral than that of *o*-xylene[10]. The two *ipso*-carbons are further apart from each other in *p*- than in *o*-isomers. Therefore the *p*-isomer interacts with more adsorption sites on the polychloral matrix than the *o*-isomer. This may be one of the reasons for the elution order of the three isomers, but it is not completely understood at present. For dihydroxybenzenes and hydroxytoluene the elution order was reversed. In these hydroxy-substituted benzenes the interaction between the solute and solvent overcomes the solute–polymer interaction and the order of elution is controlled predominantly by the solvent–solute interaction.

It was difficult to separate the three positional isomers of xylene by liquid chromatography. Fig. 6 shows the chromatographic separation of xylenes using polychloral and methanol or a methanol–water (9:1) mixture. The bands of *o*- and *m*-xylenes overlapped notably when xylenes were chromatographed at room temperature; however the separation improved when the temperature was lowered. Addition of water to the solvent methanol also improved the separation because it decreased the affinity of the carrier for the polychloral matrix. A fairly good chromatographic separation was achieved at −20°C by using a methanol–water mixture as a carrier.

REFERENCES

1 O. Vogl, *U.S. Pat.*, 3,454,527 (1969).
2 O. Vogl, H. C. Miller and W. H. Sharkey, *Macromolecules*, 5 (1972) 658.
3 P. Kubisa, L. S. Corley, T. Kondo, M. Jacovic and O. Vogl, *Polym. Eng. Sci.*, 21 (1981) 829.
4 G. Wasai, T. Iwata, K. Hirano, M. Kuragano, T. Saegusa and J. Furukawa, *Kogyo Kagaku Zasshi*, 67 (1964) 1920.
5 K. Hatada, S. Shimizu, H. Yuki, W. Harris and O. Vogl, *Polym. Bull.*, 4 (1981) 179.
6 P. Kubisa and O. Vogl, *Macromol. Synth.*, 6 (1977) 49.
7 L. S. Corley and O. Vogl, *Polymer*, 20 (1979) 1535.
8 L. S. Corley and O. Vogl, *Makromol. Chem.*, 181 (1980) 2111.
9 L. S. Corley and O. Vogl, *J. Macromol. Sci., Chem.*, A14(7) (1980) 1105.
10 O. Vogl and K. Hatada, *J. Polym. Sci., Polym. Lett. Ed.*, 13 (1975) 603.
11 K. Fukui, T. Yonezawa and H. Shingu, *J. Chem. Phys.*, 20 (1952) 722.
12 K. Fukui, T. Yonezawa, C. Nagata and H. Shingu, *J. Chem. Phys.*, 22 (1954) 1433.
13 C. G. Vaughan, B. B. Wheals and M. J. Whitehouse, *J. Chromatogr.*, 78 (1973) 203.