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GEL PERMEATION CHROMATOGRAPHY OF STEREOISOMERS: MODEL COMPOUNDS OF POLY(VINYL CHLORIDE)

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SUMMARY

The possibility of separating stereoisomers of 2,4-dichloropentane and 2,4,6-trichloroheptane by means of gel permeation chromatography on columns packed with S-Gel 832 was investigated using a recycling technique with minimal zone spreading. The results are discussed from the viewpoint of the assumed sizes of the molecules and with respect to a possible interaction of dissolved compounds with the eluent used. The results may not only help to elucidate some aspects of the separation process, but also to find suitable conditions for preparative fractionation of the above compounds employed as models of the PVC chain.

INTRODUCTION

Stereoisomers of 2,4-dichloropentane and 2,4,6-trichloroheptane are employed as model compounds in studying the structure of poly(vinyl chloride)¹⁻³. With 2,4-dichloropentane, the analytical and preparative separation of stereoisomers was carried out by fractional distillation on a high-efficiency column⁴ and by gas chromatography². With 2,4,6-trichloroheptane, the distillation method was unsuccessful⁴, while gas chromatography with a selective stationary phase (Benton 34)^{5,6} yielded pure stereoisomers, which were identified and investigated by IR and NMR spectroscopy^{2,7,8}.

The separation of stereoisomers of 2,4-diphenylpentane and 2,4,6-triphenylheptane (model compounds of polystyrene) by gel permeation chromatography (GPC) with recycling has been described by Lesec *et al.*⁹. Columns packed with Poragel 60 Å and diisopropyl ether as eluent were used in this instance, and the separation was interpreted on the basis of different hydrodynamic volumes of the individual stereoisomers. In another paper by the same group¹⁰, the separation of diastereoisomers of acetal alcohols was compared under similar conditions in diisopropyl ether and tetrahydrofuran (THF). A considerably poorer separation in THF was explained by interactions of the individual diastereoisomers with the eluent.

An interaction of molecules of various polarities with a polar eluent in GPC has been reported by Čoupek *et al.*¹¹ with appropriate model compounds (carboranes). Isomeric carboranes possess an identical rigid molecular structure, but differ greatly in

their dipole moments. In the separation of these compounds in THF, the order of elution followed exactly the decreasing dipole moment. When the chromatographic behaviour of carboranes was investigated in benzene, the separation was much poorer and the order of elution was reversed. This inversion could not be interpreted as unequivocally as the preceding instance, owing to the possibly greater part played by interactions between the solute and the gel.

In this work, we investigated the GPC separation of stereoisomers of 2,4-dichloropentane and 2,4,6-trichloroheptane, using THF as eluent on columns packed with the styrene-divinylbenzene copolymer S-Gel 832.

EXPERIMENTAL

Model compounds

Acetylacetone was used in the synthesis of 2,4-dichloropentane (2,4-DCP)⁴. The stereoisomeric mixture of 2,4-DCP contained 51.3% of the *iso*-form and 48.7% of the *syndio*-form (by analogy with syndiotactic and isotactic polymer chains, the *meso*-form of 2,4-DCP is called the *iso*-form and the *DL*-form is called the *syndio*-form). The mixture was analysed by means of gas chromatography using a packing of 10% of Benton B-34 + 10% of Apiezon L on Celite (60–80 mesh), with an 1800 × 1.9 mm column. Preparative gas chromatography with an F-21 (Perkin-Elmer, Überlingen, G.F.R.) apparatus packed as indicated above permitted the separation of the two stereoisomers of 2,4-DCP. The fraction referred to below as the *iso*-form of 2,4-DCP contained 99.7% of the *iso*-form and 0.3% of the *syndio*-form, while the fraction denoted as the *syndio*-form contained 99.2% of the *syndio*-form and 0.8% of the *iso*-form. Table I shows some of the physical properties of the stereoisomers of 2,4-DCP. The dipole moments of the *iso*- and *syndio*-forms of 2,4-DCP were measured with a Dipolmeter DM 01 apparatus (WTW, Weilheim, G.F.R.) in *n*-hexane and were 4.7 and 4.4 D, respectively.

2,4,6-Trichloroheptane (2,4,6-TCH) was prepared by a multistage synthesis from ethyl acetoacetate⁶. The stereoisomeric mixture contained 26.0% of the *iso*-

TABLE I
PHYSICAL PROPERTIES OF STEREOISOMERS OF 2,4-DICHLOROPENTANE AND 2,4,6-TRICHLOROHEPTANE

Compound	Boiling point (°C/KPa)	n_D^{20} *	Conformation**	Dipole moment (D)	
				calc.	measured
2,4-Dichloropentane					
reaction mixture	142–147/101	1.4409	—	—	—
<i>iso</i> -form	40/1.6	1.4423	TG'	—	4.7
<i>syndio</i> -form	36/1.6	1.4390	TT	—	4.4
2,4,6-Trichloroheptane					
reaction mixture	102.5–104.5/2	1.4699	—	—	—
<i>iso</i> -form	102.5/2	1.4722	TGTG	2.20	—
<i>hetero</i> -form	103.5/2	1.4704	TTTG	2.21	2.68
<i>syndio</i> -form	104.5/2	1.4686	TTTT	4.10	4.07

* For 2,4-DCP *cf.* ref. 12, for 2,4,6-TCH *cf.* ref. 6.

** For 2,4-DCP *cf.* ref. 2, for 2,4,6-TCH *cf.* ref. 3.

form, 51.3% of the *hetero*-form and 22.7% of the *syndio*-form (analysis by gas chromatography, similar to 2,4-DCP). Some physical properties of the stereoisomers are given in Table I.

Methods

The GPC equipment consisted of a membrane pump, a loop injection system of volume 0.350 ml, stainless-steel columns (1200 × 8 mm) packed with the S-Gel 832 (Institute of Macromolecular Chemistry of the Czechoslovak Academy of Sciences, Prague, Czechoslovakia) with an exclusion limit of *ca.* 1000 units of molecular weight, an R 4 differential refractometer (Waters Assoc., Milford, Mass., U.S.A.), and an elution volume-meter with a photoelectric detector and siphon (2.7 ml). The signal from the detector together with the elution volume were recorded with a line recorder. The flow-rate of the eluent (THF) was *ca.* 30 ml/h.

Preliminary analyses of pure stereoisomers of 2,4-DCP were performed by a GPC procedure using a system of five columns. The separation of the mixtures was carried out using the recycling techniques described by Duvdevani *et al.*¹³, which allows minimum zone spreading to be preserved, because the eluate does not pass through the pump before the repeated injection into the system of columns. A simple scheme of the arrangement is shown in Fig. 1. In the first position of the six-port valve A (solid line), the eluent passes from the pump (or from the injection device) through the measuring cell of the detector D into the first system of columns B, and from there through the reference cell of the detector into the second system of columns C. On passing through the columns C, the zone of compounds being separated would leave the separation system. If, however, after all of the compounds under investigation have passed through the detection cell E the six-port valve A is switched over to the second position (denoted by a dashed line), the zone of the compounds being sepa-

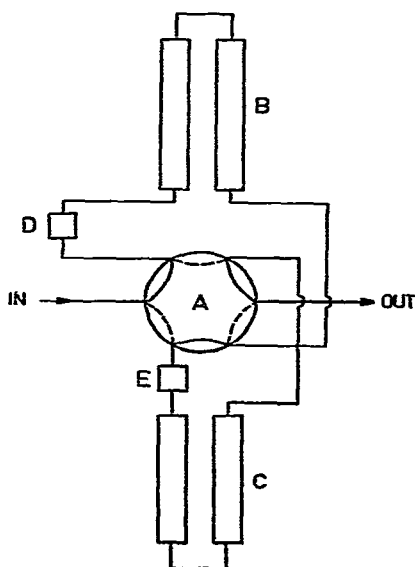


Fig. 1. Scheme of the GPC apparatus adapted for recycling. A, six-port valve; B and C, systems of columns; D and E, measuring and reference cell of detector, respectively.

rated will not leave the system, but will pass through the columns C into the detection cell D and the columns B. This procedure is repeated for a desired number of cycles. The advantages of this system are the minimal zone spreading and the possibility of detection after each passage through the system of columns. In our work, two columns packed with S-Gel 832 were used in either of the systems of columns (B,C).

RESULTS AND DISCUSSION

The analysis of pure stereoisomers of 2,4-DCP by GPC on five columns revealed a small difference in the elution volumes between the *syndio*-form (85.0 counts) and the *iso*-form (83.5 counts). This difference is insufficient for separation and the mixture of stereoisomers was therefore analysed by using the recycling techniques described above. A mixture consisting of 56.6% (w/w) of the *syndio*-form and 43.4% (w/w) of the *iso*-form was used. Fig. 2 shows the separation process, depending on the number of cycles. It can be seen that in order to achieve a baseline separation of both stereoisomers, 16 cycles are necessary, *i.e.*, passage through 32 columns. After these 16 cycles the zone of separated stereoisomers leaves the columns in a volume of 35 ml (the volume injected was 0.35 ml). Further, the quantitative ratio of the two peaks demonstrates that the *iso*-form leaves the columns first, in agreement with the test measurement of the two stereoisomers on the system of five columns. Consequently, in this arrangement the *iso*-form appears to be larger in molecular size than the *syndio*-form. This fact may be due to (a) different sizes of the molecules of the conformational structures TG' or TT of the two stereoisomers, or (b) different interactions with the polar eluent (THF) caused by a difference in the dipole moments of the two stereoisomers.

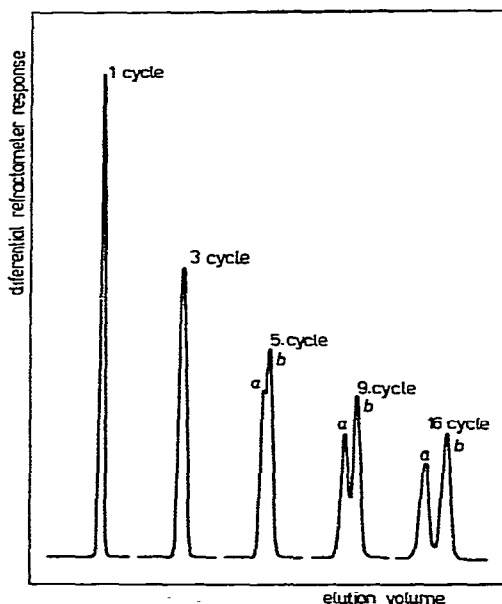


Fig. 2. Separation of stereoisomers of 2,4-dichloropentane: a, *iso*-form; b, *syndio*-form.

In constructing models of the two stereoisomers, the TG' structure of the *iso*-form appears to be bulkier than the *syndio*-form, but the difference in sizes is minimal; moreover, this difference may play a major role only in a non-polar eluent. If a polar solvent (THF in our work) is used in the separation, the influence should probably be assigned to the different interactions of the solvent with the two stereoisomers on the basis of different polarities. The experimental result is in agreement with such an assumption, because the *iso*-form, the dipole moment of which (4.7 D) is higher than that of the *syndio*-form (4.4 D), leaves the column first (Table I).

The separation of stereoisomers of 2,4,6-TCH using the separation system described above was unsuccessful, even with an increased number of cycles (22). A further increase in the number of cycles was useless, because a chromatographic zone is dispersed in a volume of solvent equal to the volume of one system of columns.

The finding that the separation of stereoisomers of 2,4,6-TCH was unsuccessful even with a very efficient system using the recycling techniques may be explained by the unfavourable effect of two counteracting influences, namely the size of the individual stereoisomers and their polarity. While the size increases in the order *syndio*-form (TTTT) < *hetero*-form (TTTG) < *iso*-form (TGTG), the increase in the dipole moments, which may be a measure of the interaction of THF with the dissolved compound, follows the opposite order: *iso*-form (2.20D) < *hetero*-form (2.68 D) < *syndio*-form (4.07 D).

It follows from the above that while in the separation of stereoisomers of 2,4-DCP the use of a polar eluent (THF) has a favourable effect, in the separation of stereoisomers of 2,4,6-TCH it will probably be necessary to employ a less polar eluent, in which the difference in the sizes of molecules of the individual stereoisomers could play a favourable role without the unfavourable effect of solvation.

The search for suitable conditions for a successful analytical or preparative separation of stereoisomers of 2,4,6-TCH is the subject of further study.

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