

## Dehydrochlorinated Adduct of $\beta$ -Cyclodextrin and Poly(vinylidene Chloride)

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### ABSTRACT

In the fractionation of the dehydrochlorinated product of polymerization of  $\beta$ -cyclodextrin ( $\beta$ -CD) and vinylidene chloride ( $\beta$ -CD·DH PVDC) by ultrafiltration, high molecular weight products (MW 37,000) and oligomeric ones (MW 2900) were separated. The high molecular weight compounds contain about 27 weight % of  $\beta$ -CD, which corresponds to nine  $\beta$ -CD molecules per DH PVDC chain. The  $\beta$ -CD content in the oligomeric products is about 40 weight %, so about 1  $\beta$ -CD molecule is bonded to 1 oligomer chain. The monocrystal fraction containing 95%  $\beta$ -CD has been obtained additionally by precipitation fractionation. By means of gel chromatography it was established that the precipitation fractionation of  $\beta$ -CD·DH PVDC is accompanied by dissociation leading to free  $\beta$ -CD separation. The total product separates 28 weight %, while the monocrystal fraction 83 weight % of  $\beta$ -CD. The dissociation indicates the nonchemical character of  $\beta$ -CD·DH PVDC. On the basis of  $^{13}\text{C}$ -NMR spectra, the nonchemical bonding of  $\beta$ -CD to the polymer [ $\beta$ -CD·P/VDC + AC] for at least half the cyclic molecules has been established. The convergence of chemical shift values in the  $^{13}\text{C}$ -NMR spectra of some products investigated and that of model  $\beta$ -CD, as

well as the ability of some fractions to form adducts with fluorobenzene, is evidence for the retention of the  $\beta$ -CD cyclic structure in the reaction products. The occurrence of dissociation on treating  $\beta$ -CD·PVDC with solvents (DMF, cyclohexanone, water) and of acid hydrolysis of  $\beta$ -CD·DH PVDC confirms the practically normal structure of the PVDC chain in the adduct with  $\beta$ -CD. The presence of carboxylic groups in the chain reveals some structural anomalies of the chain. On comparing this with x-ray diffraction studies it can be assumed that some parts of the chain have the head-to-head structure. The likelihood of dependence of formation of topological bonds on the size of substituents in the chain has been considered on the basis of studies of molecular models.

## INTRODUCTION

Recently publications [ 1-4 ] have dealt with the polymeric (or oligomeric) adducts of  $\beta$ -cyclodextrin ( $\beta$ -CD). Some of these  $\beta$ -CD adducts, like that of poly(vinylidene chloride) ( $\beta$ -CD·PVDC) or that of vinylidene chloride-allyl chloride copolymer ( $\beta$ -CD·P(VDC + AC)) constitute stable systems, and when hot water acts on them, they can be considered as the topological structures of polyrotaxane type [ 4 ]. The polymeric adducts are water-insoluble, like the majority of the low molecular ones [ 5 ], but unlike the low molecular weight adducts they neither dissociate nor dissolve even in hot water.

Unexpectedly, the product of  $\beta$ -CD·PVDC dehydrochlorination ( $\beta$ -CD·DH PVDC), which is suspected to be a real polyrotaxane, appeared to be very well soluble in water [ 1, 4 ]. The present paper deals with further investigations of  $\beta$ -CD·CH PVDC the aim of which is to obtain some information concerning its structure, homogeneity, and stability of the polymer- $\beta$ -CD molecule linkage as well as the identification of nonchemical bonds in the products studied. Investigations on  $\beta$ -CD·DH PVDC were mainly carried out by the dehydrochlorination of the product of  $\beta$ -CD and vinylidene chloride adduct radiation polymerization.

## EXPERIMENTAL

### Materials

$\beta$ -Cyclodextrin was obtained from Corn Products Company and was once crystallized;  $[\alpha]_D^{25} = +162^\circ$  (1, H<sub>2</sub>O).

Vinylidene chloride (Koch-Light) and allyl chloride (Merck) were distilled freshly before use. Other substances were analytical grade and were freshly distilled or recrystallized.

### Equipment

IR spectra were obtained on a Specord 71 IR instrument.

Specific rotation measurements were performed on a Perkin-Elmer 141 polarimeter.

$^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra were obtained on Varian  $\times 100$  and CFT-20 instruments, respectively.

The source of irradiation was a Gammator M-34-3.

Molecular weight determinations were performed by vapor pressure osmometry (Hewlett-Packard 302B osmometer), by membrane osmometry (membrane: Selectron AC-61), and by gel chromatography (Pharmacia Fine Chemicals, Uppsala).

### Preparation and Characterization of Products

Polymerization of Vinylidene Chloride and  $\beta$ -Cyclodextrin Adduct ( $\beta\text{-CD}\cdot\text{VDC}$ ). The adduct  $\beta\text{-CD}\cdot\text{VDC}$  was prepared according to Cramer's experiments on adducts with other organic compounds [6, 7]  $\beta\text{-CD}$  (100 g) was dissolved in 2500 ml distilled water. The solution was boiled for 30 min, so that the gaseous products absorbed by the dextrin molecules could be evacuated, then it was cooled to room temperature. VDC (75 ml) was added, and the solution was mixed vigorously for 30 min, after which it was allowed to stand for 12 hr. All operations were carried out under nitrogen atmosphere. The precipitate formed was filtered off and washed with 150 ml of ice water. It was put into a 300 ml flask and dried with  $\text{P}_2\text{O}_5$  under nitrogen atmosphere and in the presence of VDC vapors for 12 hr. The dried adduct in the powder form was put into glass ampoules. It was cooled to  $-70^\circ\text{C}$ , then evacuated three times and flushed with nitrogen. After sealing, the ampoule was irradiated with  $\gamma$ -rays at a dose of 5 Mr. The yield of product was 82 g. The elemental composition found was: C, 41.60%; H, 6.00%; O, 41.96%; Cl, 10.48%.

A 1-g portion of  $\beta\text{-CD}\cdot\text{PVDC}$  was boiled with a cyclohexanone-water mixture (10 ml + 100 ml). From the separated organic phase the traces of a solid substance were precipitated with an excess of methyl alcohol. Its IR spectrum was similar to that of PVDC obtained without  $\beta\text{-CD}$ .

A 1-g portion of  $\beta\text{-CD}\cdot\text{PVDC}$  was heated with 10 ml DMF at  $70^\circ\text{C}$  for 48 hr. Undissolved sediment was washed with DMF and an excess

of water. After vacuum drying, 0.095 g of a powdery substance containing 31.15% C, 3.08% H, 7.47% O, and 58.20% Cl was obtained. Its IR spectrum contained bands at 1044, 1071, 1360 and 1410  $\text{cm}^{-1}$ .

Polymerization of the  $\beta$ -Cyclodextrin Adduct with a Mixture of Vinylidene Chloride and Allyl Chloride.

The adduct of monomer mixture was prepared by stirring 10 g of vinylidene chloride and allyl chloride (1:2 mole ratio) with a solution of 15 g  $\beta$ -CD in 375 ml water. The same method was used as in the case of vinylidene chloride only. The dry product of irradiation shows  $[\alpha]_{\text{D}}^{25} = +112.5^{\circ}$  (1, DMF). The product (14.6 g) was extracted with water in a Soxhlet apparatus at 75-77°C for 30 hr and washed free of copolymer with 250 ml dioxane for 48 hr; 0.014 g of the substance dissolved in dioxane. A substance (4.96 g) insoluble in water but practically entirely soluble in DMF and DMSO was obtained [ $\beta$ -CD·P(VDC + AC)]. Its elemental composition was: C, 41.55%; H, 6.15%; O, 43.35%; Cl, 8.05%. It showed  $[\alpha]_{\text{D}}^{25} = +117.5$  (1, DMF), while for free  $\beta$ -CD,  $[\alpha]_{\text{D}}^{25} = +136^{\circ}$  (1, DMF). The  $^{13}\text{C}$ -NMR spectra of  $\beta$ -CD·P(VDC + AC) and  $\beta$ -CD as a standard for comparison were made in DMSO solution.

Dehydrochlorination of  $\beta$ -CD·PVDC. A 60-g portion of  $\beta$ -CD·PVDC was boiled with 60 g NaOH dissolved in 2400 ml ethyl alcohol for 1 hr. The reaction product (45 g) was filtered off and washed off with an excess of alcohol. Next it was dissolved in 900 ml distilled water (almost entirely soluble). The solution was purified by centrifuging. On addition of five times the volume of methyl alcohol, a dark substance precipitated. The precipitate obtained (25 g) was dissolved in 1000 ml water and treated with fluorobenzene in order to remove the remains of free  $\beta$ -CD. The substance precipitated with fluorobenzene was filtered off, and the filtrate was evaporated to dryness. A yield of 6 g  $\beta$ -CD·CH PVDC was obtained after drying over  $\text{P}_2\text{O}_5$ . The elemental composition was: C, 46.03%; Cl, 1.20%; H, 5.84%; ash, 3.25%.

Typical bands in the IR (KBr) were found at 3400 (very broad), 2930, 2200-2030, 1720 (weak), 1630, 1450-1200, 1160, 1080, 1030, 1000, 950, and 860  $\text{cm}^{-1}$ . The same product can be obtained by dehydrochlorination at the room temperature.

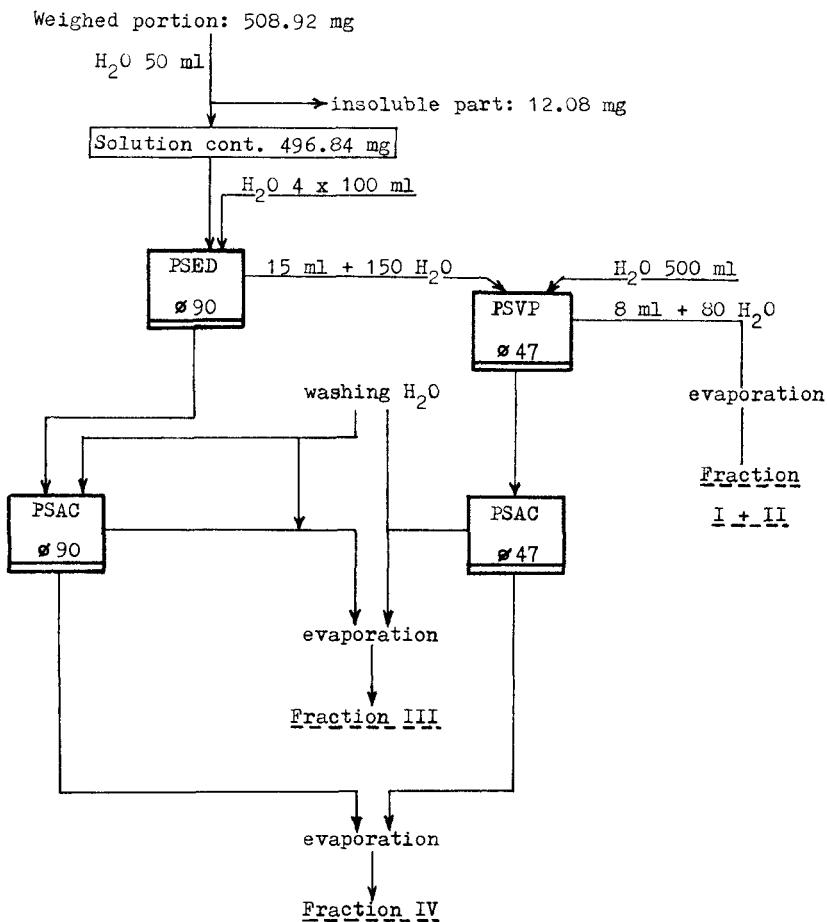
The  $^1\text{H}$ -NMR spectrum (in DMSO +  $\text{D}_2\text{O}$ ) in the range 8.5-4.5 ppm shows  $\delta = 7.82 - 7.43$  (m, 1.77 H, arom.); 4.84 (s, 1 H, CH) ppm. A sample of 0.05 g  $\beta$ -CD·CH PVDC was mixed with 0.005 g diphenyl sulfoxide as internal quantitative standard. NMR results correspond to 45 weight %  $\beta$ -CD content in the sample.

A 1% aqueous solution of  $\beta$ -CD·DH PVDC was passed through a cation exchanger containing -COOH groups (Amberlit IRC-50) shows pH = 2.4.

The hydrolysis of 0.5 g  $\beta$ -CD·DH PVDC with HCl [8] at 45°C leads to the formation of 0.02 g insoluble precipitate.

### Fractionation of $\beta$ -CD·DH PVDC

$\beta$ -CD·DH PVDC was subjected to fractionation according to Scheme 1 by means of ultrafiltration on four Pellican membranes system (Millipore type PSVP, nominal retention limit 1,000,000; PSJM, nominal



Scheme 1.

retention limit, 100,000; PSED, nominal retention limit, 25,000; PSAC, nominal retention limit, 1000. The PSAC membrane was used to remove some low molecular weight impurities, especially sodium chloride. The membranes used had diameters of 47 mm and 90 mm with corresponding Millipore pressure filters: the first one, of 47 mm diameter, 85 ml volume, was equipped with magnetic stirrer and the second one, 90 mm diameter, 600 ml volume, was stirred by vibration. The pressure in the filters (1.6 - 2.5 atm) was maintained by compressed nitrogen. Redistilled water was used for dissolving and washing off the samples.

Before being introduced to the filter, the solutions were filtered through weighed straining membranes (pores 1.2 or 0.8 nm), and when filtering was difficult, spun glass prefilters (AP-25, Millipore) were used. The membranes and prefilters used for clarification were dried and weighed for determination of amount of suspended material. The thick end over the membrane solutions was always clarified before being introduced to the next filter. The filtrates containing water which was used for washing off the unfilterable parts were concentrated in the next stage of ultrafiltration. The final filtrates were thickened by evaporation at reduced pressure. The concentrated solutions were transferred by means of a syringe from above the membranes to measuring flasks. The membranes and the filter chamber were washed with several small portions of water until color disappeared. All portions of water were collected and concentrated, then added to the flask with the main portion of solution. The solutions were evaporated and dried to constant weight for calculating the mass of fractions. The succeeding stages of ultrafiltration lasted for several days each. The solutions over membranes were completed with water until the filtrate became almost colorless. The fractionation results are shown in Table 1.

The typical IR (KBr) absorption bands are as follows.

Fraction I + II: 3400 (very broad), 2930, 2200 - 2030, 1720 (weak), 1630, 1450-1200, 1160, 1080, 1030, 1000, 950 and 860  $\text{cm}^{-1}$ .

Fraction III: 3400 (very broad), 2930, 2200 - 2030, 1720 (weak), 1630, 1450 - 1200, 1160, 1080, 1030, 1000, 950 and 860  $\text{cm}^{-1}$ .

$^1\text{H-NMR}$  in the range 8.5 - 4.5 ppm shows the following bands.

Fraction I + II (0.074 g) + benzoic acid (0.0075 g) as internal quantitative standard dissolved in  $\text{DMSO} + \text{D}_2\text{O}$ ,  $\delta = 7.97 - 7.67$  (m, 2.3 H, arom.) and 4.84 (s, 1 H, CH). Results obtained correspond to the content of 27 weight %  $\beta$ -CD in fraction I + II.

Fraction III (0.06 g) + benzoic acid (0.006 g) dissolved in  $\text{DMSO} + \text{D}_2\text{O}$ ,  $\delta = 7.97 - 7.67$  (m, 1.6 H, arom.) and 4.84 (s, 1 H, CH) which corresponds to 39.2 weight % of  $\beta$ -CD in fraction III.

$\beta$ -CD-DH PVDC and fractions obtained were investigated chromatographically by employing two columns: the first had diameter 25 mm, 450 mm long, packing CL Sepharose 6B gel, eluent 0.3% water solution of NaCl; the second had diameter 12 mm, 700 mm long; packing, Sephadex G-10 gel; eluent, water.

TABLE 1. Fractionation According to Scheme 1<sup>a</sup>

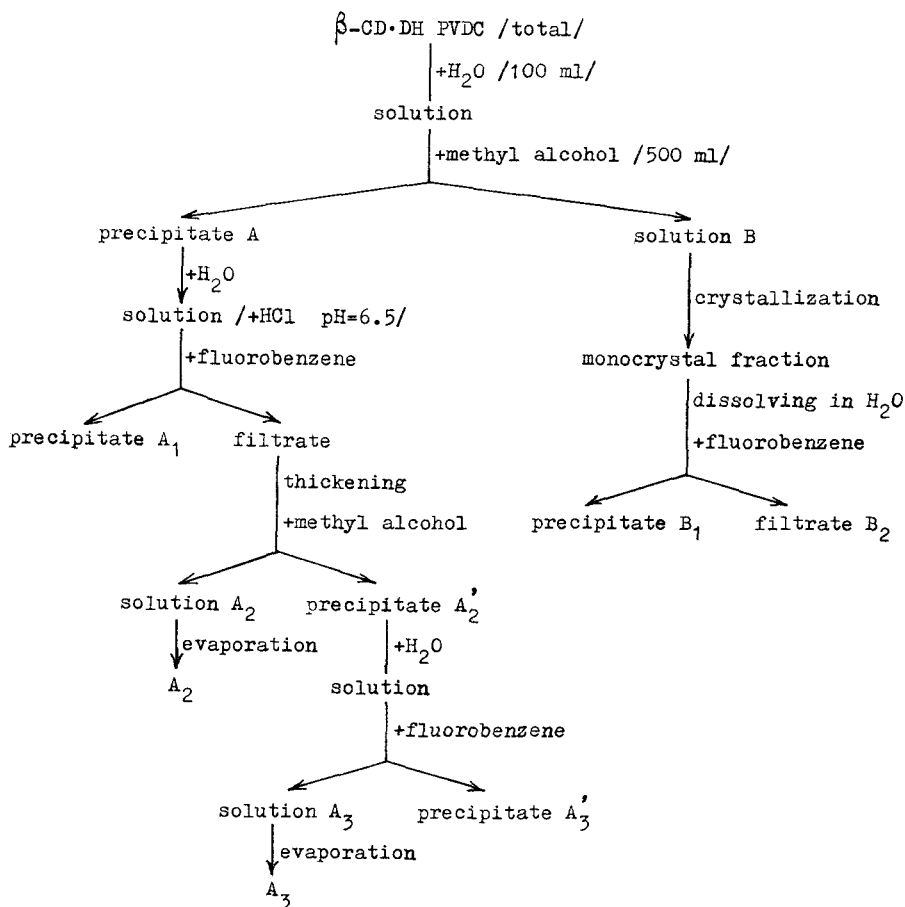
Fraction	Weight of fraction (mg)	% of fraction	$\bar{M}_n$
I + II	192.13	38.67	37,080 (Membrane osmometry)
III	196.42	39.15	2,900 (Vapor pressure)
IV	83.74	16.85	
Suspension filtered off	1.29	0.25	

<sup>a</sup>Starting amount: 496.84 mg of soluble product, (after rejecting 12.08 mg of insoluble part).

#### Fractionation of $\beta$ -CD·DH PVDC According to Scheme 2

Adduct  $\beta$ -CD·PVDC was prepared as described above. The irradiated product (48 g) was boiled for 1 hr with water (2500 ml) in order to wash out free  $\beta$ -CD. After washing, 12 g of solid remained. A 7-g sample of this solid was dehydrochlorinated as described above. There were 7.1 g of total raw dehydrochlorination product obtained after washing with ethyl alcohol. This product was fractionated according to Scheme 2.

It was dissolved in 100 ml water and freed from traces of undissolved solid by centrifuging. After treating the solution with 500 ml of methyl alcohol, precipitate A (2.7 g) and dissolved fraction B were obtained. A 1.5-g portion of fraction A was dissolved in 75 ml water, neutralized with 5% HCl to pH 6.5, and shaken with fluorobenzene. The precipitate A<sub>1</sub> was formed. Its weight after centrifuging, washing with water, and drying in vacuum over P<sub>2</sub>O<sub>5</sub> was 0.35 g. The solution which remained after centrifuging was evaporated to 15 ml and treated with 50 ml methyl alcohol. Two other fractions were obtained: A<sub>2</sub> left in the solution, and precipitated A<sub>2</sub>' (0.7 g after drying). A<sub>2</sub>' (0.35 g) was separated by evaporation of solvents to dryness. A<sub>2</sub>' was dissolved in 35 ml of water (pH 6.5) and shaken with fluorobenzene. Two new fractions formed: A<sub>3</sub> in the solution and precipitate A<sub>3</sub>' (0.5 g). The weight of A<sub>3</sub> after evaporation of solvents and drying was 0.2 g. Fraction B, after remaining in solution for several days



Scheme 2.

(in some cases several weeks) crystallizes in monocrystalline form. The precipitate obtained was washed with methyl alcohol and dried (1.5 g).

All fractions separated absorbed IR in the "fingerprint" range of  $\beta$ -CD. The characteristic absorption at  $2030 - 2200 \text{ cm}^{-1}$  was observed in total product and in fractions A, A<sub>1</sub> (very weak), A<sub>2</sub>, A<sub>2</sub>', and A<sub>3</sub>'. A weak absorption at  $1720 \text{ cm}^{-1}$  characterized fractions A, A<sub>1</sub>, A<sub>2</sub>', A<sub>3</sub>, and A<sub>3</sub>'.

The fractions obtained were investigated chromatographically by means of column 12 mm in diameter, 700 mm long, with Sephadex



G-10 gel packing. Distilled water was used as eluent. All fractions except A<sub>3</sub>' were soluble in water. Fraction A<sub>3</sub>' (150 mg) was dissolved in alkali (3.5 ml 0.1 N NaOH + 6.5 ml H<sub>2</sub>O) and partitioned in a 1000 mm of 25 mm diameter with Sephadex G-10 gel packing in order to separate off the excess alkali. Then the molecular weight of the fraction was determined ( $M = 1820$ ). The <sup>13</sup>C-NMR spectrum of fraction A<sub>3</sub>' was obtained in a solution of 2.5 ml 5% NaOD in D<sub>2</sub>O. Chemical shifts and other data are collected in Table 2. The spectrum of β-CD was used for a basis of comparison.

### Characteristics of Fraction B

Fraction B showed  $[\alpha]_D^{20} = +154^\circ$  (1, H<sub>2</sub>O).

The IR spectrum (KBr pellet) was identical with that of β-CD.

When 50 ml of 2% aqueous solution of fraction B was shaken with 5 ml fluorobenzene, precipitate B<sub>1</sub> and a solution containing unprecipitable B<sub>2</sub> were obtained. The precipitate B<sub>1</sub> was dissolved again in hot water and the solution was subjected to evaporation of solvent (water with fluorobenzene) to dryness. The weight of B<sub>1</sub> after drying was 0.86 g. B<sub>2</sub> after evaporation of water and drying weighed 0.09 g.

The IR spectrum (KBr pellet) of B<sub>1</sub> is identical with that of β-CD.

The IR spectrum (KBr pellet) of B<sub>2</sub> showed bands at 3400 (very broad), 2930, 1720 (weak), 1630, 1450 - 1200, 1160, 1030, 1000, 950, and 860 cm<sup>-1</sup>.

## RESULTS AND DISCUSSION

β-CD·DH PVDC is a dark-brown substance. Its IR spectrum shows evidence of a great amount of β-CD; in the "fingerprint" range, the spectrum of β-CD·DH PVDC contains all characteristic absorption bands corresponding to that of pure β-CD. The basic polymer (dehydrochlorinated PVDC) in the total product β-CD·DH PVDC is shown in the absorption at 2200 - 2030 cm<sup>-1</sup> which is typical of triple bonds formed as a result of the PVDC chain dehydrochlorination. The unsaturated character of the basic polymer which most probably contains conjugated system of multiple bonds is indicated by the presence in products on the basis of UV absorption.

TABLE 2. NMR Spectra

Substance and measurement conditions	Chemical shifts of $\beta$ -CD carbon atoms (ppm) <sup>a</sup>						Intensities of peaks related to that of C <sub>6</sub>					
	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>1</sub> /C <sub>6</sub>	C <sub>2</sub> /C <sub>6</sub>	C <sub>3</sub> /C <sub>6</sub>	C <sub>4</sub> /C <sub>6</sub>	C <sub>5</sub> /C <sub>6</sub>	
$\beta$ -CD 10% solution in DMSO-d <sub>6</sub> (standard: TMS)	101.46	71.84	72.59	81.12	71.63	59.61	1.15	1.87	1.51	1.16	1.86	
$\beta$ -CD·P(VDC + AC) 10% solution in DMSO-d <sub>6</sub> (standard: TMS)	101.58	71.97	72.67	81.19	71.71	59.66	1.25	2	1.66	1.25	2	
0.188 g $\beta$ -CD dissolved in 2.5 ml 5% NaOD (standard: DMSO-d <sub>6</sub> )	65.02	35.28	36.19	43.88	33.97	22.39	1.16	1.86	1.54	1.16	1.86 <sup>b</sup>	
0.188 g fraction A <sub>3</sub> ' dissolved in 2.5 ml 5% NaOD (standard: DMSO-d <sub>6</sub> )	65.09	35.34	36.24	43.96	34.12	22.57						

<sup>a</sup>Chemical shifts were attached to corresponding glucofuranose carbons.

<sup>b</sup>Relative intensities  $\times 0.93$  (correction for C<sub>6</sub> intensity decrease in relation to free  $\beta$ -CD).

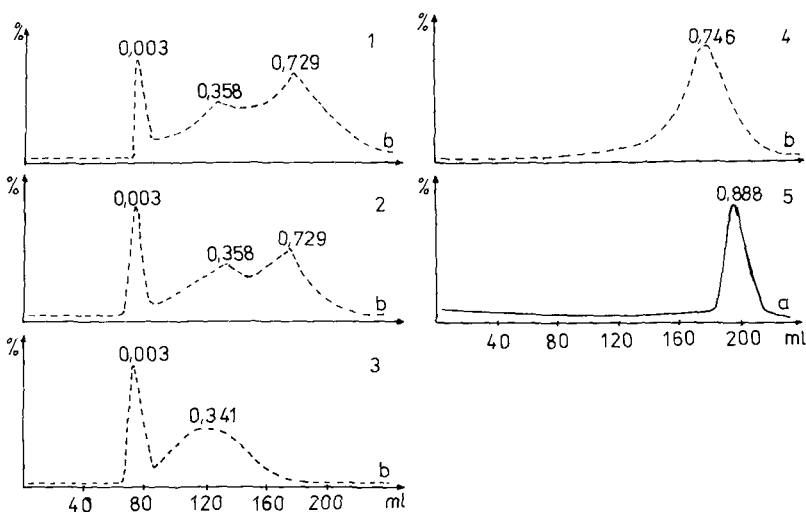


FIG. 1. Elution graphs (a determined according to RI, b according to UV) of fractions obtained from CL6B column according to scheme 1: (1) total  $\beta$ -CD·DH PVDC; (2) I + II + III; (3) I + II; (4) III; (5)  $\beta$ -CD. Numbers at tops of the bands are the values  $K_{av}$ .

### Polydispersity of $\beta$ -CD·DH PVDC

Gel chromatography was used to evaluate  $\beta$ -CD·DH PVDC and separate fractions by degree of homogeneity. On the basis of the preliminary investigations two chromatography columns were chosen, with gel packing of CL Sepharose 6B (CL6B) and with Sephadex G-10 (G10). The CL6B column was used to characterize the polymer molecular weight distribution in a relatively broad molecular weight range from 1135 for pure  $\beta$ -CD ( $K_{av} = 0.888$ ) to over 40,000 for higher fractions of  $\beta$ -CD·DH PVDC ( $K_{av} = 0.003$ ). The G10 column made possible the identification of low molecular weight fractions and free,  $\beta$ CD ( $K_{av} = 0.46$ ). According to gel chromatography (CL6B) the character of  $\beta$ -CD·DH PVDC is polydisperse, and its molecular weight distribution is described by the chromatogram (Fig. 1). A considerable amount of the product is characterized by the partition coefficient  $K_{av} = 0.729$ , which corresponds to molecular weight about 3000 (vapor pressure osmometry). However, the fraction

characterized by  $K_{av} = 0.003$ , which corresponds to the molecular weight higher than 40,000 ( $\bar{M}_n = 37,000$  for the mixture of fractions  $K_{av} = 0.003$  and  $K_{av} = 0.358$ ) is also present in the product. Because of the lack of information concerning the size and the shape of molecules even approximate calculation of molecular weight of fractions was not feasible. In the case of globular proteins,  $K_{av} = 0.4$  would correspond to molecular weight 300,000; for dextrans, to about 120,000; and for acetylated gelatin, about 30,000. But on the basis of these data it could be suspected that the molecular weight of  $\beta$ -CD·DH PVDC was relatively high.

In order to separate the fractions and determine directly their molecular weights,  $\beta$ -CD·DH PVDC was subjected to an ultrafiltration with the use of four types of Pellican membranes characterized by nominal retention limits: 1,000,000 (PSVP), 100,000 (PSJM), 25,000 (PSED), and 1000 (PSAC). Effects of the separation were chromatographically tested. The quantitative data of the ultrafiltration are collected in Table 1. Of the product 78 weight % (fraction unfilterable through PSAC) is characterized by  $\bar{M}_n = 8000$ /membrane osmometry). The distribution of polymer molecular weight is shown in diagram 2 of Fig. 1. Further ultrafiltrations (Scheme 1) allowed us to separate two other parts. One of them contained fractions I and II ( $K_{av} = 0.003$  and 0.341); the second contained fraction III  $K_{av} = 0.746$  (Fig. 1, diagrams 3 and 4). Fractions I and II could not be separated by means of ultrafiltration because of their unfilterability through any of membranes used. Fraction I + II is characterized by  $\bar{M}_n = 37,000$  (membrane osmometry) and fraction III by  $\bar{M}_n = 2900$  (vapor pressure osmometry). According to the value of the gel partition coefficient ( $K_{av} = 0.003$ ), the molecular weight of fraction I was suspected to be considerably higher than 37,000. Fractions I, II, and III cannot be separated on column G10, because their partition coefficients do not differ. Instead, elution graphs of fractions I, II, and III obtained from this column demonstrated a lack of free  $\beta$ -CD unbonded to the basic polymer or oligomer. Free  $\beta$ -CD gave a broad elution graph (G10 column) with  $K_{av,max} = 0.46$ . As can be seen in the elution graphs, the separated fractions (I + II) and III have sharp maxima at  $K_{av} = 0.036$  (Fig. 2, diagrams 1 and 2) which indicate a lack of contamination of the fraction with free  $\beta$ -CD. As chemical composition is concerned, fractions I + II and III are similar. Both products contain approximately the same amount of  $\beta$ -CD molecules (30 - 40 weight %,  $^1\text{H-NMR}$ ). This means that  $\beta$ -CD molecules do not form any end groups but are distributed along the

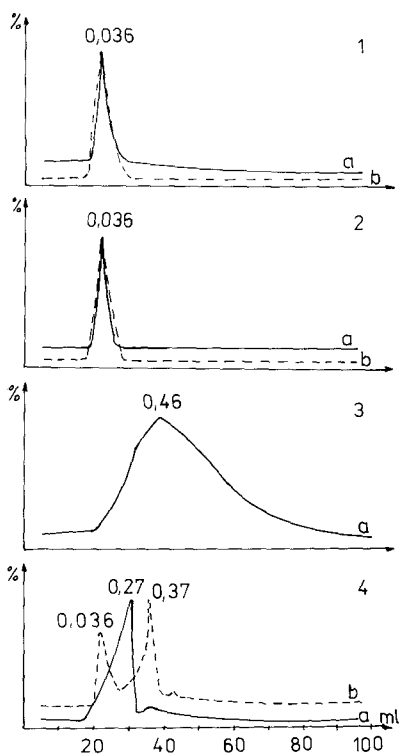


FIG. 2. Elution graphs (a determined according to RI, b according to UV) from G-10 column: (1) fraction I + II (scheme 1); (2) fraction III (scheme 1); (3)  $\beta$ -CD; (4)  $\beta$ -CD·DH PVDC radically obtained. Numbers at tops of the bands are the values of  $K_{av}$ .

polymer chain. There are about 9  $\beta$ -CD molecules per polymer chain in fraction I + II, while the fraction III is an oligomer mixture in which approximately 1  $\beta$ -CD molecule occurs per chain.

It is worthwhile noticing that, contrary to the radiation polymerization,  $\beta$ -CD·DH PVDC obtained from  $\beta$ -CD·PVDC synthesized by free-radical initiated, solvent polymerization of  $\beta$ -CD·VDC [4] contains only a small amount of fractions characterized by molecular weight 2900 or even higher (Fig. 2, diagram 4). Its main constituent is the fraction characterized by  $K_{av} = 0.27$ , which indicates a molecular weight between that of  $\beta$ -CD and fraction III of the radiation product.

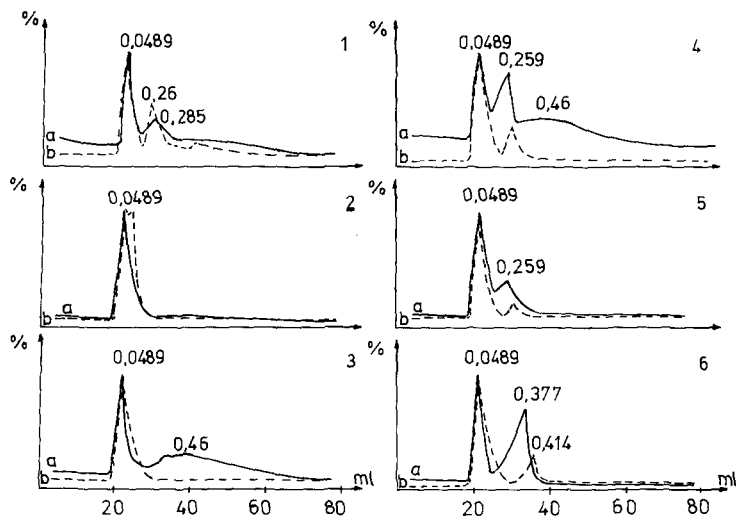


FIG. 3. Elution graphs (a determined according to RI, b according to UV) of fractions from G-10 column according to Scheme 2: (1) total  $\beta$ -CD·DH PVDC; (2) fraction A; (3) fraction A<sub>1</sub>; (4) fraction A<sub>2</sub>; (5) fraction A<sub>3</sub>; (6) fraction A<sub>3</sub>'. Numbers at tops of the bands are the values of  $K_{av}$ .

So, the polymerization of  $\beta$ -CD·VDC in solvent leads mainly to formation of oligomeric products.

The adduct of  $\beta$ -CD·DH PVDC obtained by radiation, discussed above, was purified from substrates by precipitation with methyl alcohol from aqueous solution and by linking free  $\beta$ -CD in an adduct with fluoro-benzene. Interesting information concerning the character of bonds between the polymer chain and cyclic molecules was obtained from investigation of product devoid of free  $\beta$ -CD which was removed before dehydrochlorination by washing off with hot water. After fractionation according to Scheme 2 it can be stated the following: According to elution graph G10 (Fig. 3, diagram 1) the total product of dehydrochlorination contains no free  $\beta$ -CD or only small amounts of it (all fractions determined by absorbed UV). The total product consists essentially of two fractions characterized by  $K_{av} = 0.0489$  and  $0.285$ , the first of which corresponds approximately to that described above under fractions I-III. After precipitation of total product with methyl alcohol from aqueous solution, product A contained only higher fraction ( $K_{av} = 0.0489$ , Fig. 3, diagram 2) and traces of free  $\beta$ -CD ( $K_{av \max} = 0.46$ ).

Quite large amounts of  $\beta$ -CD form in further fractionation (Scheme 2) by means of fluorobenzene. As a result of treating with fluorobenzene, fractions  $A_1$  and  $A_2$  were formed. The first of these contains 63% free  $\beta$ -CD, while the second contains 55% (Fig. 3, diagrams 3 and 4). The complementary parts of A (fractions  $A_3$  and  $A_3'$ ) contain practically no free  $\beta$ -CD. Considering the weights of separate fractions it can be calculated from elution graphs that as a result of the total product fractionation according to Scheme 2, 28 weight % of free  $\beta$ -CD was formed. This is significant fact because free  $\beta$ -CD was created in the nonchemical process of precipitation with methyl alcohol and fluorobenzene. Therefore, in the total product and in fraction A,  $\beta$ -CD was linked to the polymer by no chemical bonds. Though these results indicate the low stability of the linkage between some  $\beta$ -CD molecules and polymer, they imply that at least in the case of some  $\beta$ -CD molecules the lack of chemical bonds in  $\beta$ -CD·DH PVDC is obvious. Consequently, it can be stated that  $\beta$ -CD·DH PVDC has at least partially nonchemical character, and so the same is true of the character of the product of monomeric adduct direct polymerization ( $\beta$ -CD·PVDC). The action of fluorobenzene on  $\beta$ -CD·DH PVDC is rather clear, because of the tendency of  $\beta$ -CD to form an inclusion compound with it. Fluorobenzene precipitates  $\beta$ -CD quantitatively from aqueous solution [6]. In case of  $\beta$ -CD·DH PVDC, fluorobenzene probably causes dissociation of the adduct and forms transitionally its own adduct with  $\beta$ -CD taken from the polymeric one. It should be noticed also that simultaneously with the free  $\beta$ -CD formation there appears again lower fractions ( $K_{av} = 0.259$  and  $0.377$ ) which were absent in fraction A. They occur in products  $A_2$ ,  $A_3$  and  $A_3'$  obtained from A (Fig. 3, diagrams 4, 5 and 6). So as a result of the dissociation process, two new products appeared: free  $\beta$ -CD and fractions of  $K_{av} = 0.259$  and  $0.377$ , i. e., fractions of lower molecular weight than A ( $K_{av} = 0.0489$ ) from which they were created. All fractions obtained as a result of partition according to Scheme 2 are characterized by the content of  $\beta$ -CD (IR).

Relevant information concerning the retention of cyclic structure by carbohydrates in polymer could be obtained from studies of fraction  $A_3'$ . This fraction was formed as a result of precipitation with fluorobenzene, which is typical of cyclic dextrans only. The molecular weight of fraction  $A_3'$  is 1800, so one molecule contains one  $\beta$ -CD ring ( $M = 1135$ ).

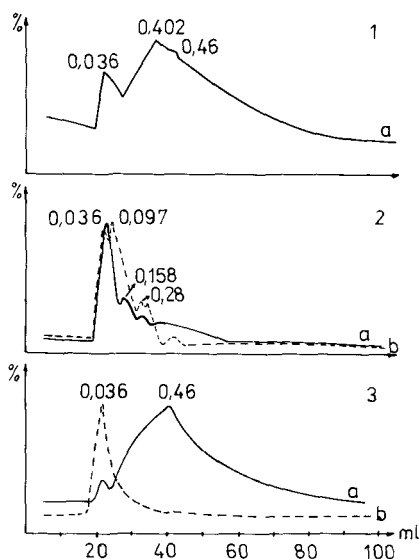


FIG. 4. Elution graphs (a determined according to RI, b according to UV) of fractions according to Scheme 2: (1) monocrystal fraction B; (2) fraction B<sub>2</sub>; (3) fraction B<sub>1</sub>. Numbers at tops of the bands are the values of  $K_{av}$ .

#### Monocrystal Fraction of $\beta$ -CD·DH PVDC

Small amounts of monocrystal fraction always form when the filtrate obtained from precipitation of product A (Scheme 2) is allowed to stand for some time (several weeks). Its IR spectrum in the "fingerprint" range corresponds precisely to that of  $\beta$ -CD. The fraction contains about 95% of  $\beta$ -CD according to  $[\alpha]$ . The x-ray investigations demonstrated that it was a homogeneous substance, and even its space group could be determined [9]. The crystalline structure of this fraction is different than that of pure  $\beta$ -CD and that of low molecular weight  $\beta$ -CD adducts (e. g. with styrene, methyl methacrylate, vinylidene chloride, toluene, and fluorobenzene). Chromatographically, however, the monocrystal fraction is not homogeneous. When introduced into water solution it demonstrates in elution (Fig. 4, diagram 1) the presence of some subfractions including free  $\beta$ -CD ( $K_{av} = 0.036, 0.402, \text{ and } 0.46$ ). The treatment



of the fraction with fluorobenzene results in separation of two parts:  $B_1$  and  $B_2$  (Scheme 2). Chromatography (Fig. 4, diagram 2) shows the lack of free  $\beta$ -CD in part  $B_2$ , which was not precipitated from aqueous solution by means of fluorobenzene. It absorbs UV in the range of the whole subfraction determined by RI. The substance, however, is not a pure polymer because of its high content of linked  $\beta$ -CD (IR). The second part of the monocrystal fraction precipitated with fluorobenzene ( $B_1$ ) (Fig. 4, diagram 3) is a mixture of two subfractions. The main one (95%) is free  $\beta$ -CD, as shown by the position of its area in the elution graph ( $K_{av} = 0.46$ ). The lack of UV absorption in the whole range demonstrates a lack of polymer in the subfraction. The amount of free  $\beta$ -CD separated in this stage of fractionation constitutes 83 weight % in relation to the whole monocrystal fraction. The second subfraction is a polymer (UV absorption) bonded with  $\beta$ -CD (able to be precipitated with fluorobenzene).

### $^{13}\text{C}$ -NMR Investigations of Reaction Products

It was established by means of fluorobenzene treatment that 28% of  $\beta$ -CD in the total product  $\beta$ -CD·DH PVDC was not chemically bonded to the polymer. Additional information concerning the problem of bonds in the products could be expected to be obtained from the comparison of  $^{13}\text{C}$ -NMR spectra of the reaction products with that of free  $\beta$ -CD. A very clear spectrum of free  $\beta$ -CD can be obtained (Fig. 5, spectra 1 and 3) and the intensity ratio of peaks coming from each glucopyranose ring carbon atoms easy can be calculated (Table 2). It was assumed that the intensity ratio of  $\beta$ -CD peaks should not differ from that of  $\beta$ -CD, PVDC and  $\beta$ -CD·DH PVDC, if  $\beta$ -CD exists in these compounds chemically unchanged. There are 6 carbon atoms groups in the  $\beta$ -CD molecule, each containing 7 equivalent carbon atoms. If any chemical reaction proceeds at any carbon, the intensity of the corresponding signal would decrease by a 1/7, that is to say by 15% in the relation to the analogous peak of free  $\beta$ -CD. This change of the spectrum can be observed in the case of  $^{13}\text{C}$ -NMR. However, in the case of polymers, the equivalency of  $\beta$ -CD carbon atoms in the respective groups seems not to be strictly maintained. Actually, there is double or triple splitting of some signals in the spectrum of  $\beta$ -CD·PVDC (DMF soluble part) and the spectrum is impossible to analyze. Better results were obtained for oligomeric products, e. g., the product of copolymerization of vinylidene chloride with allyl chloride in  $\beta$ -CD adducts [ $\beta$ -CD·P(VDC + AC)]. Spectra of good resolution were obtained (Fig. 5, spectrum 2), which allowed one to establish the conformity of the peaks' intensities

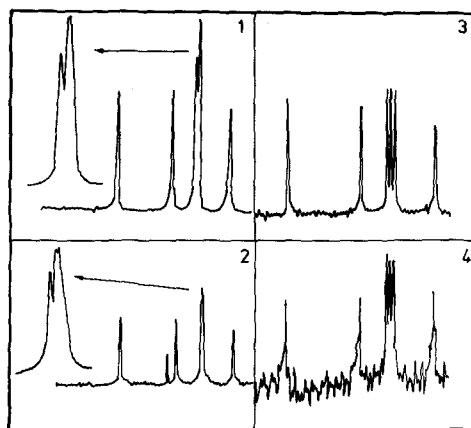


FIG. 5.  $^{13}\text{C}$ -NMR spectra: (1)  $\beta$ -CD in DMSO; (2)  $\beta$ -CD·P(VDC + AC); (3)  $\beta$ -CD in NaOD solution; (4) fraction  $A_3$  (Scheme 2) in NaOD solution.

related to that of standard  $\beta$ -CD. All the relative intensities of corresponding peaks in  $\beta$ -CD·P(VDC + AC) are practically identical except that of  $C_6$ , which is lower by 1/14 from the corresponding value for free  $\beta$ -CD (Table 2). This means that only every second  $\beta$ -CD molecule could react chemically, if not to consider other possibilities of  $C_6$  peak intensity decrease. It means also that at least half of  $\beta$ -CD molecules in  $\beta$ -CD·P(VDC + AC) are bonded to the polymer nonchemically. These investigations confirm the structure proposed previously [3] on the basis of x-ray diffraction studies in which nonchemical bonding between the VDC - AC copolymer chain and  $\beta$ -CD molecules exists.

It should be noted that chemical shifts of  $\beta$ -CD peaks are almost identical with that of  $\beta$ -CD·P(VDC + AC). The latter compound can be used, to some extent, as the model one for  $\beta$ -CD·PVDC and be another evidence of the nonchemical bonding in this system.

The  $^{13}\text{C}$ -NMR spectrum of the total produce  $\beta$ -CD·DH PVDC is less clear than that of  $\beta$ -CD·P(VDC + AC). There are some regions of continuous absorption instead of individual peaks, but for the low molecular weight fraction relatively well resolved spectra can be obtained.

The spectrum of fraction  $A_3'$  (according to Scheme 2) characterized by molecular weight 1800 was compared with that of  $\beta$ -CD

(Fig. 5, spectrum 4). The spectra appeared to be similar in respect of chemical shifts in corresponding region, though fraction  $A_3'$  contains no free  $\beta$ -CD. The  $A_3'$  spectrum, however, cannot be quantitatively interpreted because of the intensity of the peaks relative to background noise is too low, in spite of the length of sample exposure in the apparatus (NT 95,000). Nevertheless, the qualitative analysis is quite reliable. The  $A_3'$  spectrum in the range 400-1350 Hz (DMSO as standard) has the same character as that of  $\beta$ -CD. All the peaks of  $A_3'$  cyclodextrin parts were only slightly shifted down-fields (from 0.05 for  $C_3$  to 0.18 for  $C_6$ ) relative to the spectrum of free  $\beta$ -CD (Table 2). These shifts are lower than those observed by Uekama et al. [10] in the case of adducts of  $\beta$ -CD with sulfathiazole, also studied in NaOD solution (from 0.09 for  $C_3$  to 0.59 for  $C_4$  up-fields). Chemical shifts of carbons  $C_1$  and  $C_4$  show the cyclic structure of  $\beta$ -CD to be unchanged in  $A_3'$  and probably in the total product of dehydrochlorination. Colson et al. [11] observed a distinct difference in shifts for these carbon atoms between cyclic molecules ( $\alpha$ -CD,  $\beta$ -CD) and the linear ones (amylose, maltotriose). These differences in the case of amylose and  $\beta$ -CD in the alkaline medium equaled 1.1 ppm for  $C_1$  and 2.4 ppm for  $C_4$ . The slight differences in chemical shifts of corresponding carbons of  $A_3'$  (Table 2) indicate a cyclic structure of  $\beta$ -CD in this product. The same consideration is true of  $\beta$ -CD·P(VDC + AC).

### Structure of the Polymer Main Chain

The difference between the mass spectrum of the product of VDC and  $\beta$ -CD adduct polymerization and that of free PVDC was determined previously [4]. It seems that the reason for the difference is not the dissimilarity of the general structure of the polymer chains, but the polymer existing in  $\beta$ -CD channel which impedes formation of condensed rings derivatives (the lack of the tetrachloronaphthalene parent ion in mass-spectra) during pyrolysis. When extracted with a cyclohexanone-water mixture,  $\beta$ -CD·PVDC gives traces of free PVDC (IR spectrum, Fig. 6, spectrum a) not differing essentially in its structure from the polymer obtained without  $\beta$ -CD (Fig. 6, spectrum c). On treatment with dimethylformamide,  $\beta$ -CD·PVDC yielded in about 10% the substance of a lowered  $\beta$ -CD content (the content of  $\beta$ -CD decreased from 80 weight % for the starting product to 29 weight % for the extracted one) which gave in the IR spectrum bands at 1044,

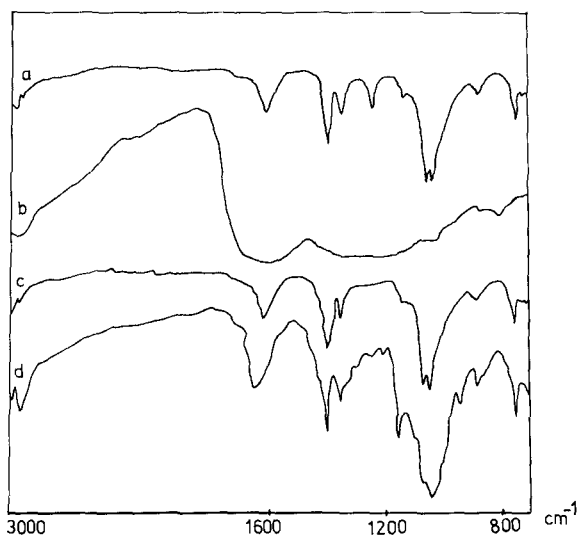
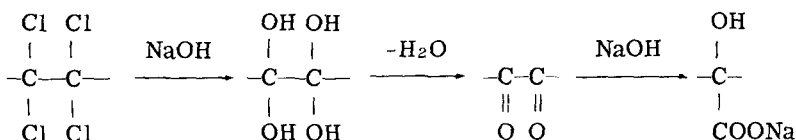


FIG. 6. IR spectra (KBr pellets): (a) PVDC extracted with cyclohexanone from  $\beta$ -CD·PVDC; (b) product of  $\beta$ -CD·DH PVDC hydrolysis; (c) PVDC obtained without  $\beta$ -CD; (d)  $\beta$ -CD·PVDC washed with DMF.

1071, 1360, and 1410  $\text{cm}^{-1}$  typical of PVDC absorption (Fig. 6, spectrum d). This shows that the rest of PVDC which was not washed off from  $\beta$ -CD·PVDC with cyclohexanone is also most probably a normal PVDC chain. The ordinary structure of the PVDC chain in  $\beta$ -CD·PVDC is evidenced to some extent by the IR spectrum (Fig. 6, spectrum b) of  $\beta$ -CD·DH PVDC acid hydrolysis which should cause complete removal of carbohydrates from the compound. The IR spectrum of the hydrolysis product corresponds to that of poly(vinylidene chloride) dehydrochlorinated to a weight loss of 60.5%, published by Dacey and Barradas [12].

The groups  $-\text{C}\equiv\text{C}-$  (2200-2030  $\text{cm}^{-1}$ ) and some quantities of  $>\text{C}=\text{O}$  (1720  $\text{cm}^{-1}$ ) characterize the majority of  $\beta$ -CD·CH PVDC fractions. However, surprising is the presence of acid groups in  $\beta$ -CD·DH PVDC which can acidify 1% water solution of product of pH = 2.4. Acid groups should not form as a product of dehydrochlorination of a normal PVDC chain. Though it is probable that some head-to-head structures occur in the  $\beta$ -CD·PVDC chain and as a result of dehydrochlorination the following reactions proceed [13]:



Considering the possibility of head-to-head structure in the polymers investigated, it is worthwhile noticing that polymerization of adducts of vinyl monomers with  $\beta$ -CD should lead at least partially to such a structure. The basis for this assumption are x-ray diffraction investigations [9]. According to the results obtained, the unit cell of the adduct crystal contains two  $\beta$ -CD molecules which are most probably placed symmetrically with respect to each other. This means that  $\beta$ -CD molecules in the crystalline lattice are probably turned from each other from one side with primary hydroxyl groups and with secondary ones from the other side (compare with Fig. 7). This would mean also that monomer molecules are placed in the crystalline lattice channels symmetrically, i. e., head to head, and this structure should be retained in the polymerization product, if the mobility of monomer molecules is limited. No polymers of head-to-head structure were obtained by polymerization of styrene, methyl methacrylate, methyl acrylate, nor methacrylonitrile [3, 4]. Most probably, in the case of vinylidene chloride polymerization at least part of the head-to-head structure was retained because of the limited mobility of the monomer which was confirmed by studying the molecular models [3].

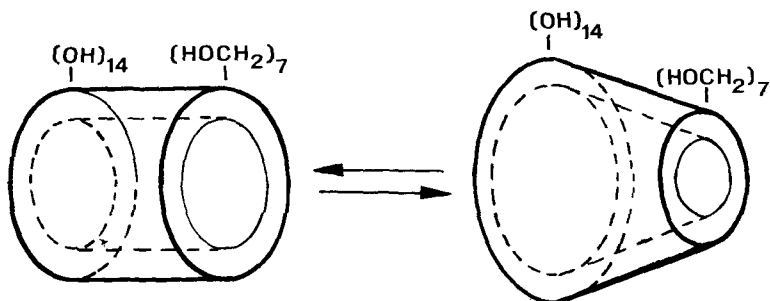


FIG. 7.

Further investigations of the problem with the use of other monomers are planned.

### Topological Bonding in the Polymeric Compounds of $\beta$ -CD

In all cases [1-4] of polymer syntheses in the presence of  $\beta$ -CD nonchemical reaction products occurred. In some conditions they could be also defined as topological type systems [2, 4]. This refers to adducts of  $\beta$ -CD with siloxane oligomers, poly(vinylidene chloride), and the copolymer of vinylidene chloride with allyl chloride. The nonchemical character of the latter was supported by the present paper. The occurrence of nonchemical bonding in the compound of  $\beta$ -CD with dehydrochlorinated poly(vinylidene chloride) ( $\beta$ -CD·DH PVDC) was also proved. Analogously to the compounds investigated previously,  $\beta$ -CD·DH PVDC seems to have topological character too. This assumption is confirmed to some extent by the results of gel chromatography. In this case, however, the cyclic molecules bonded weakly to the polymer, and the dissociation in the fractionation process (a part of  $\beta$ -CD molecules in total product and A) should be differentiated from the molecules linked to the polymer in more stable manner (e. g.,  $\beta$ -CD in fraction  $A_3$ ). Nothing can be said

about the latter type of bonding, but in the case of dissociating molecules the occurrence of unstable topological systems can be postulated. The behavior of  $\beta$ -CD·DH PVDC (especially A) in water solution leads to the assumption that it is not an inclusion compound. If it was an adduct, there should be in the solution large quantities of free  $\beta$ -CD staying in equilibrium with it, because, as completely soluble in water, it would be unstable. According to the published data [6], even by formation of insoluble (stable) adducts free  $\beta$ -CD dissolved in water stays in equilibrium with the precipitate (except of an adduct with fluorobenzene and chlorobenzene). The elution graphs of total  $\beta$ -CD·DH PVDC and A (Fig. 3, diagrams 1 and 2) show rather only traces of free  $\beta$ -CD in the solution. I conclude from this that topological bonds in  $\beta$ -CD·DH PVDC are likely.

As for the topological bonds, the possibility of existence of this sort of bonding was considered, as there were no large (topological) substituents which could bond the cyclic molecules to the polymer [1, 3]. So, the term "topological substituent" must be related not only to a bulky group like tert-butyl or triphenylmethyl, but also to a corresponding configuration of the polymer chain or a cyclic molecule linked with it.

Let me consider, therefore, what sort of topological bonds can occur in the products investigated. It seems obvious that the stability of the product of polymerization of vinylidene chloride in adduct

TABLE 3. Topological System-Forming Ability

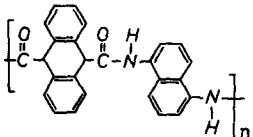
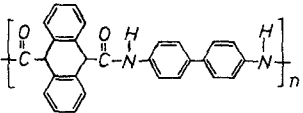
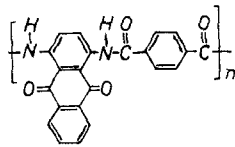
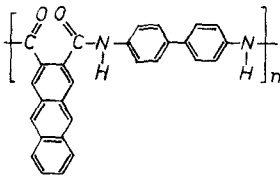
System	Ability of $\beta$ -CD molecules on the polymer chain to form a topological system <sup>a</sup>		
	With polymer	With copolymer containing single topological substituents	With copolymer containing at least two neighboring topological substituents
Polyethylene, single chain and double chain	-	-	-
Ethylene-acenaphthylene copolymer		-	+
Ethylene-vinylcarbazole copolymer		+	+
Polystyrene	-		
Poly(vinyl chloride)	-		
Vinyl chloride-styrene copolymer		-	-
Poly(vinylidene chloride)	-		
VDC-acenaphthylene copolymer		+	+
VDC-vinylcarbazole copolymer		+	+
VDC-vinyl naphtoate copolymer		+	+
VDC-vinyl benzoate copolymer		-	-
Poly(methyl methacrylate)	-		
Polyacrylonitrile	-		
Poly(vinyl acetate)	-		
Poly(vinyl bromide)	-		
	-		

TABLE 3. (cont.)

System	Ability of $\beta$ -CD molecules on the polymer chain to form a topological system <sup>a</sup>	
	With polymer	With copolymer containing at least two neighboring topological substituents
	-	
	+	
	+	

<sup>a</sup>Described as the ability (-) or inability (+) of ring molecules free mobility along the polymer chain.

( $\beta$ -CD·PVDC) depends on the presence of chlorine and it can only have an inclusion character [6]. The chlorine atoms are probably too small to form topological bonds here (Table 3). The topological bonds, however, may occur in acetylated  $\beta$ -CD·PVDC [1]. If one looks more closely at a model built according to Casu and Reggiani [14], it is easily noticed that the cyclodextrin molecules have a cylindrical shape, at the basis of which only primary OH groups are at one side and only secondary ones at another (Fig. 7). The glucose residues



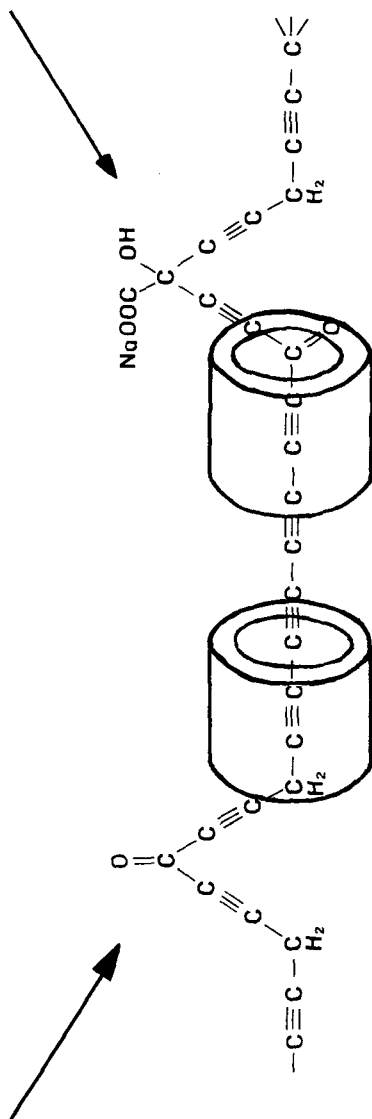


FIG. 8.

perform limited rotations around the 1,4- $\alpha$ -glycoside bonds placed along the circumference at the half the height of the cylinder. It causes an increase of the diameter of one base along with a decrease of another base diameter. Certainly, the decrease of either base diameter favors the formation of topological bonds between the cyclodextrin molecule and the polymer chain. A conversion from a cylindrical conformation to a conic one is especially favored in cyclodextrin acetate. In this case, the cyclodextrin molecule should take a conic shape in order to place all acetyl groups on the secondary OH side.

The possibility of  $\beta$ -CD and polymers producing a topological system with aid of different substituents, according to my observations on space filling molecular models, are shown in Table 3. The  $C_1$  conformation was assumed for the glucose residues [14].

It is rather difficult to answer the question, what would be the cause of formation of topological bonds in  $\beta$ -CD·DH PVDC, considering that at least several possibilities seem probable. In the first place, we should take the configuration of the main polymer chain under consideration. If we include the valence angles in the chain backbone which contains  $-C\equiv C-$  groups and some amounts of  $>C=O$  and  $HO-\overset{|}{C}-COONa$  ones, beside  $sp$  carbon atoms as well as the  $sp^2$  and  $sp^3$  ones, the scheme in Fig. 8 can be presented. The places in the chain marked with arrows can be considered as large substituents giving thus a base for topological bonds. This can occur also in  $\beta$ -CD·PVDC, as the polymer is already colored, and it probably contains a number of unsaturated bonds. These systems can reveal a topological character during treatment of  $\beta$ -CD·PVDC with hot water [4].

It seems also highly probable that, contrary to monomeric adducts, the polymeric ones may be stable even if they contain no bulky substituents in the chain. But then the polymer should contain some active groups which would either attract the cyclodextrin molecules (e. g., chlorine atoms in  $\beta$ -CD·PVDC) or repel them (e. g., acetylene groups in  $\beta$ -CD·DH PVDC) [1, 7]. In the first case the cyclic molecules would be "placed" on the active centers; in the second one they would oscillate between them. One would deal with typical adducts in systems with the attraction centers, while the repulsive centers would form compounds of a topological polyrotaxane type. Multiplicity of active centers occurring along the polymer chain would guarantee the stability of cyclodextrin-polymer systems.

## CONCLUSIONS

In the investigations the following has been established: (1) the presence of high molecular fraction (37,000) and the oligomeric ones

(2900) in  $\beta$ -CD·DH PVDC, (2) the nonchemical character of bonding between polymer (oligomer) chain and at least part of  $\beta$ -CD molecules in  $\beta$ -CD·DH PVDC,  $\beta$ -CD·PVDC and  $\beta$ -CD·P(VDC + AC), (3) the confirmation of essentially normal structure of PVDC in  $\beta$ -CD·PVDC, (4) the probability of occurrence of some quantity of head-to-head structures in the  $\beta$ -CD·PVDC polymer chain, (5) the retention of  $\beta$ -CD cyclic structure in the reaction products, (6) the probability of formation of topological bonding in the products investigated.

Some topology in compounds of  $\beta$ -CD with PVDC and their derivatives has been theoretically indicated. On the ground of model investigations, various polymers with large substituents and  $\beta$ -CD molecules have been found to be suitable for polyrotaxanes synthesis.

#### ACKNOWLEDGMENT

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#### REFERENCES

- [ 1 ] M. Maciejewski and G. Smets, paper presented at 2nd Conference on Modification of Vinyl Polymers, Wroclaw, Poland, 1973; Sci. Papers Inst. Org. Technol. Plastics Wroclaw Tech. Univ., 16, 57 (1975).
- [ 2 ] M. Maciejewski, M. Panasiewicz, and D. Jarmańska, J. Macromol. Sci.-Chem., in press.
- [ 3 ] M. Maciejewski, J. Macromol. Sci.-Chem., in press.
- [ 4 ] M. Maciejewski, A. Gwizdowski, P. Pęczak, and A. Pietrzak, J. Macromol. Sci.-Chem., in press.
- [ 5 ] F. Cramer and H. Hettler, Naturwiss., 54, 625 (1967).
- [ 6 ] F. Cramer and F. M. Henglein, Chem. Ber., 90, 2561 (1957).
- [ 7 ] F. Cramer, Einschlussverbindungen, Springer-Verlag, Heidelberg, 1954.
- [ 8 ] G. T. Cori, M. A. Swanson, and C. F. Cori, Fed. Proc., 4, 234 (1945).
- [ 9 ] Z. Durski, M. Maciejewski, et al., unpublished work.
- [ 10 ] K. Uekama, F. Hirayama, and H. Koinuma, Chem. Letters, 1977, 1393.
- [ 11 ] P. Colson, H. J. Jennings, and J. C. P. Smith, J. Am. Chem. Soc., 96, 8081 (1974).

- [ 12 ] J. R. Dacey and R. G. Barradas, Can. J. Chem., 41, 180 (1963).
- [ 13 ] B. H. Nicolet and A. E. Jurist, J. Am. Chem. Soc., 44, 1136 (1922).
- [ 14 ] B. Casu and M. Reggiani, Staerke, 18, 218 (1966).

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