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Polymer Inclusion Compounds by Polymerization of Monomers in β-Cyclodextrin Matrix in DMF Solution

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ABSTRACT

The investigations of the synthesis of polyrotaxanes by the radical polymerization of monomers (vinylidene chloride, methyl acrylate, styrene, and methacrylonitrile) in DMF in the presence of β-cyclodextrin have been carried out. The possibility of formation β-cyclodextrin inclusion compounds with some vinyl monomers or some other organic substances in DMF solution has been established. We assume that the inclusion in presence of the solvent is related to the unusual phenomenon of β-cyclodextrin crystallization in hot DMF solutions. The polymerization of vinyl monomers in DMF solution at increased temperatures in the presence of β-cyclodextrin leads to compounds containing a great amount of cyclic compounds (up to 80%). Similar results have been obtained for monomers introduced as previously prepared adducts with β-cyclodextrin. Stable compounds of polymer and β-cyclodextrin have been obtained in the case of vinylidene chloride. The lack of carbohydrate moieties in the product obtained by polymerization of vinylidene chloride in the presence of linear dextrin suggest the inclusion character of the linkage between polymer and β-cyclodextrin molecules. The structure of a topological compound of polyrotaxane type is most feasible after dehydrochlorination.

INTRODUCTION

The formation of polyrotaxanes has been assumed as a result of directed synthesis [1] carried out by the solid-phase polymerization or copolymerization of β-cyclodextrin (β-CD) and monomer inclusion compounds.

In the case of vinylidene chloride (VDC) polymerization, the polymer created (50 weight % yield) retained a large quantity of cyclodextrin molecules in a stable manner. The weight of linked cyclodextrin constituted 400% that of included polymer chain.

Although a possibility of a prepolyrotaxane structure of this product was considered on account of its character (polymer chain included in a channel) and though it was used as an intermediate in the synthesis of polyrotaxanes, it could be considered also as a real polyrotaxane, at least when the boiling water acts on it. Under such conditions the product of included VDC polymerization behaves quite differently than typical cyclodextrin adducts, i. e., it does not dissociate into its components. This means that, even after inclusion forces are taken off by the action of boiling water [2], the compound is still stable. If there are no chemical bonds between polymer chain and β-CD molecules a topological linkage must be taken into consideration. Then polyrotaxane structure would be possible.

Before a rotaxane structure can be concluded to exist, the possibility of the existence of chemical bonds must be eliminated.

DISCUSSION

According to the authors [1] the polymerization of inclusion compounds was feasible only by means of initiation by radiation. In the radiation polymerization there is, however, a possibility of various side reactions leading to the grafting of the cyclodextrin molecules onto the polymer chain, which makes the unequivocal structure determination of the final products very difficult.

Although some recent investigations [3] suggest no chemical binding between β-CD molecules and the polymer chain in the radiation polymerization product, it is relevant to determine the conditions in which the polymerization of monomeric inclusion compounds would occur without radiation initiation. In fact, it has been found that monomeric inclusion compounds with β-CD can polymerize in the absence of ionizing radiation by radical initiation. In this case, the basic side reactions which could lead to chemical binding of cyclodextrin with the polymer chain are the chain-transfer reaction and reactions of the already formed polymer with cyclodextrin molecules.

Although preliminary experiments of the polyrotaxanes synthesis through radical (both bulk and solvent) polymerizations have failed [1], we considered it desirable to carry out some new attempts of polymerization of vinyl monomers in the presence of cyclodextrin dissolved in dimethylformamide (DMF).

Maciejewski [4] has observed an unusual crystallization of β-CD when dissolved in DMF on increasing temperature to about 100°C. On cooling of the solution, the crystals redissolve. The same effect was noticed earlier by Wolff and Rist in case of some polysaccharide carbanilates dissolved in organic solvents [5]. It should be added that the x-ray patterns obtained in our study of β-CD, both crystallized from DMF solution when heated and in cold state of evaporation of the solvent, demonstrate the identity of both crystal structures. These x-ray patterns also do not differ from those of β-CD crystals obtained from aqueous solution (Table 1, patterns 1, 2 and 3).

To complete the previous investigations [4] we have carried out experiments with some organic compounds added to DMF solutions of β-CD. We have found that in these cases, the crystals formed in the hot state appeared to be inclusion compounds of β-CD and introduced substances. The molar composition of these inclusion compounds is shown in Table 2. Conditions in DMF solution are especially favorable for polymerization of monomers included in the β-CD rings, which not only do not dissociate at increased temperatures (conditions of polymerization) but continue to form. Table 2 does not contain the data concerned with β-CD·VDC inclusion compound, though it is the main object of our studies. Because of the high volatility of VDC, the feasibility of formation of the β-CD·VDC adduct and its stability were analyzed according to DTA curves of suitable solutions investigated in sealed ampoules.) It was observed that when the solution of cyclodextrin in DMF contains VDC, crystallization is improved and "hot crystals" form already at 50°C. This is evidence for the cooperation of the monomer with cyclodextrin molecules in the crystal phase formation.

The DMF solutions tested were: an anhydrous β-CD solution; a solution of β-CD containing water of crystallization; a solution of previously prepared β-CD·VDC inclusion compound; solutions of the anhydrous β-CD and VDC added separately.

It must be emphasized that the thermal effects of crystallization processes investigated were probably not great, and we could not get well defined DTA curves; even then, some observations were possible.

TABLE 1. Interplanar Spaces d (Å)

d Spacings of β-cyclodextrin (Å)			d Spacings of Crystalline β-cyclodextrin adducts with different monomers (Å)			
Hot-crystallized from DMF	Cold-crystallized from DMF	Crystallized from water	Methacrylonitrile	Styrene	Methyl acrylate	Vinylidene chloride
		15.2 vw	15.54 w			
13.32 w	14.6 w	13.8 vw	14.81 m	14.86 m	13.90 vw	14.20 vw
9.91 w	9.85 w	9.15 m	13.32 s	13.36 s	9.81 w	9.87 w
8.22 m	8.35 M	8.19 m	12.65 s	12.71 s	9.11 w	9.03 w
7.62 s	7.79 m			9.20 vw	8.32 s	8.32 s
		7.72 m				
	7.54 s		8.03 m	7.93 m		7.43 s
7.02 s	7.06 s	6.94 vs	7.59 vvs	7.53 vvs	7.06 vvs	7.11 vvs
6.11 w	5.80 w	5.82 s	6.58 vw	6.58 vw	6.03 m	6.14 m
5.02 s	5.08 vs	5.49 m	6.11 w	6.09 w	5.74 s	5.72 m
4.77 vs	4.79 vs	4.85 vvs	5.79 w	5.74 w	5.51 w	5.53 m
	4.50 vs	4.65 s	5.20 s	5.22 s	5.18 s	5.21 m
4.27 s	4.29 vw	4.17 vw	5.02 vs	5.02 vs	4.97 s	4.96 s
3.82 w	3.85 m	3.88 m	4.89 vvs	4.89 vvs	4.70 s	4.86 m
3.78 w	3.75 w	3.72 w	4.77 s	4.77 s		4.64 w
3.57 m	3.61 m	3.63 w	4.62 m	4.60 m	4.53 vs	4.57 s

3.40 m	3.37 m	3.56 w	4.41 w	4.41 w	4.24 vs	4.24 vs
3.31 w	3.27 m	3.27 w	4.23 s	4.22 s	4.14 s	4.19 s
		3.11 vw	4.04 w	4.03 w	3.90 s	3.88 m
2.980 w		2.91 vw	3.77 m	3.77 m	3.78 w	3.77 w
2.800 w		2.79 vw	3.67 m	3.65 m	3.66 m	3.68 m
2.655 w			3.36 vw		3.54 m	3.55 m
2.515w			3.31 vw		3.47 m	3.46 w
			3.22 vw		3.28 s	3.29 s
			3.12 vs		3.11 w	3.11 w
			3.05 vw	3.03 vw	2.953 vw	2.955 vw
			2.898 vvw		2.869 w	2.859 w
			2.682 vvw		2.795 w	2.807 w
			2.612 vw	2.624 vw		2.653 vw
			2.538 w	2.546 w		2.608 w
			2.483 vw		2.570 m	2.563 w
			2.429 vw		2.508 w	2.518 w
			2.394 vw		2.447 w	2.437 w
			2.333 vw			2.357 w
			2.269 vw		2.302	2.295 vw
					2.261 w	2.256 w

(continued)

TABLE 1 (continued)

d Spacings of β-cyclodextrin (Å)			d Spacings of Crystalline β-cyclodextrin adducts with different monomers (Å)			
Hot-crystallized from DMF	Cold-crystallized from DMF	Crystallized from water	Methacrylonitrile	Styrene	Methyl acrylate	Vinylidene chloride
					2.216 w	2.231 w
					2.184 vw	2.183 vw
					2.117 vw	2.108 vw
						2.068 vw
					2.050 vw	2.037 vw
					2.013 vw	

[a] Intensity: vs = very strong; s = strong; m = medium; w = weak; vw = very weak.

TABLE 2. Composition of Inclusion Compounds

Organic compound	X (weight %)	Organic compound (weight %)	Mole ratio organic compound β-CD
1,1,2,2-Tetrachloroethane	10.48	12.45	1
1,2-Dibromoethane	4.71	5.53	0.35
o-Dibromobenzene	3.18	4.69	0.23
m-Dichlorobenzene	5.92	12.34	1.04
Bromobenzene	7.31	14.34	1.08
o-Chlorophenol	3.33	12.17	1.23

A relatively well defined endothermic effect beginning at 115°C, with a minimum on the curve at 133°C (Fig. 1) was observed. The same effect beginning at 150°C was observed in solution 2 (Fig. 1). In both cases the crystallization occurred above 100°C, i. e., in the region approximately covering the endothermic effects. It was impossible to obtain a clear curve than that in Fig. 1-4 for solution 4. However, the endothermic effect with an extreme at about 50°C, i. e., at the temperature when the solution 4 really crystallizes can be noticed. No endotherm and no crystallization have been observed in the case of solution 3, which contains β-CD·VDC as an inclusion compound.

These observations make clear that VDC affects the "hot" crystallization of the β-CD-DMF solution and, the β-CD·VDC inclusion compound remains stable in DMF solution and does not dissociate into VDC and β-CD. Otherwise, the DTA curve of solution 3 should be the same as that of solution 4.

The complexity of the DTA curve of solution 4 can be explained by the presence both free β-CD molecules and those linked with the monomer, probably in inclusion compound. This would be in agreement with a more complex mixture of polymerization products i. e., free poly(vinylidene chloride) (PVDC) in addition to PVDC-cyclodextrin adduct in such a system in comparison with the polymerization product obtained in solution 3 when no free PVDC was observed. It is not yet clear why the crystallization occurs when free components are added but does not when preprepared β-CD·VDC inclusion compound was dissolved. Perhaps some water molecules included in the adduct formed from aqueous solution play an essential role.

On the basis of the above observations the polymerization of

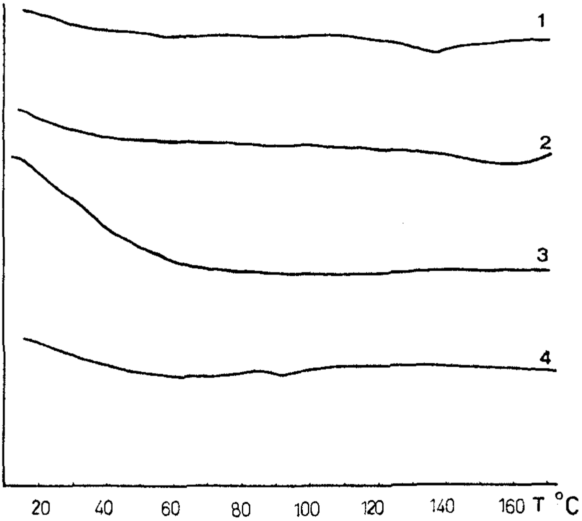

FIG. 1. DTA curves: (1) 20% solution of anhydrous β-cyclodextrin in DMF; (2) 20% DMF solution of β-cyclodextrin containing water of crystallization; (3) 20% DMF solution of β-cyclodextrin and vinylidene chloride inclusion compound; (4) 20% DMF solution of β-cyclodextrin with vinylidene chloride dissolve separately (weight ratio of vinylidene chloride/β-cyclodextrin is 1.2:1.0). All samples were investigated in sealed ampoules.

monomers in DMF solution in the presence of cyclodextrin was expected to proceed differently than in other typical solvent systems.

It is rather sure that the polymerization of VDC in an inclusion compound with β-CD would not occur in crystals isolated from DMF solution. This reaction could not be carried out conventionally in the solid phase [1]. (In the solution of a previously prepared adduct, crystallization does not generally occur.) It is suspected, however, the reaction occurs in associates of structure more labile than that of crystals. They probably form from single β-CD molecules containing VDC molecules in their free spaces. If the crystallization occurs, these associates probably remain in the phase equilibrium with crystals. It was found that, in fact, as the reaction developed, the crystal phase dissolves completely. The polymerization process is represented schematically in Fig. 2.

The formation of associates preceding the polymerization process was shown by investigations of the effect of the presence of β-CD

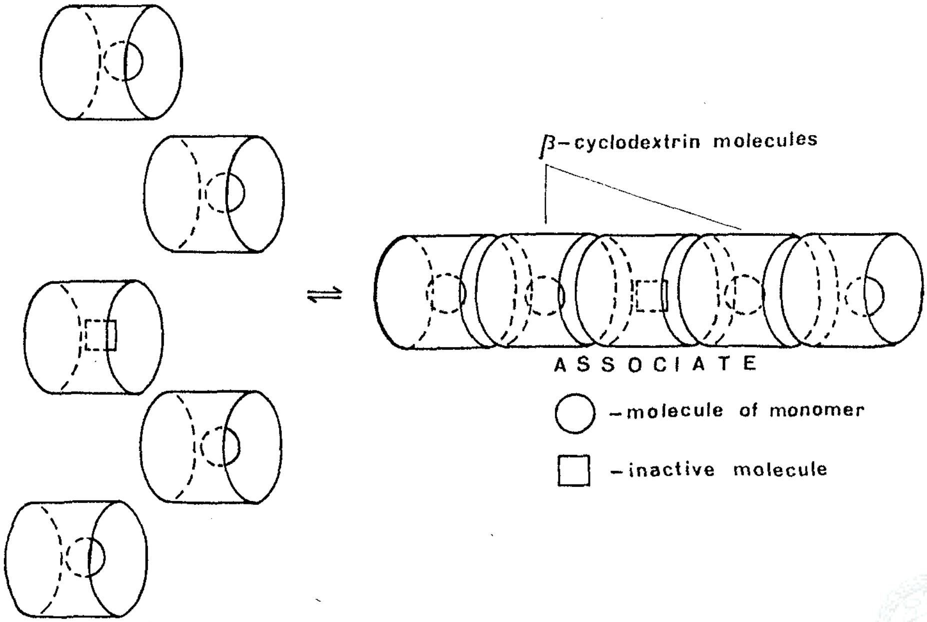

FIG. 2. Schematic diagram of the polymerization process.

inclusion compound containing inactive material in the solution on the molecular weight of the polymer. We used an adduct of β-CD with benzene as the inactive compound because of its inactivity also in the chain-transfer reaction. If the polymerization proceeded in the associates, they should also contain inactive adducts which would separate some of the monomer molecules and this would effectively decrease the polymer molecular weight.

The polymerization of the adduct of β-CD with styrene (St) in the presence of an inactive adduct was carried out. Polystyrene (PSt) formed in the reaction separated readily from the polymeric adduct and could be investigated in the isolated form. We observed a distinct decrease of the PSt molecular weight (viscosity) when the content of inactive adduct in the reaction mixture increased (Table 3). A similar effect of inactive molecules on the degree of polymerization was observed by Brown and White in the polymerization of monomers in adducts with thiourea [6].

We have carried out the polymerization of monomers in two different ways: (1) the free monomer was added to the DMF solution of β-CD; (2) the monomer was added to DMF as an inclusion compound

TABLE 3. Viscosity as a Function of Inactive Adduct

No.	Weight ratio β-CD·styrene/β-CD·benzene in initial mixture	Polystyrene relative viscosity η_{rel}
1	β-CD·styrene alone	1.1221
2	20:1	1.0488
3	15:1	1.0359
4	10:1	1.0174
5	5:1	1.0045

with β-CD. By polymerization of methyl acrylate (MA), methacrylonitrile (MAN) or styrene (St) by method 1, pure polymers free of carbohydrate were obtained (IR spectra, elemental analysis). Method 2 leads to a pure polymer in the case of MAN, unlike MA and St, which gave polymers containing considerable amounts of cyclodextrin (Fig. 3, IR spectra 1 and 2). These adducts dissociated into pure polymers and free cyclodextrin when heated with water. The IR spectra demonstrate an atactic microstructure [7] of all free polymers formed both during the polymerization itself and by dissociation of the polymeric adducts.

No relation between stability of products and crystal structure of the monomer-β-CD adducts has been found. The crystal structures have been analyzed comparatively by means of x-ray powder patterns of the monomeric inclusion compounds (Table 1). It has been established that the adducts of β-CD with MAN and St had the same crystal structure. Another similarity of crystal structures can be found in inclusion compounds of cyclodextrin with MA and VDC.

As in the radiation polymerization [1], of the monomers studied, VDC alone forms a product linked with the β-CD molecules in a stable manner. For VDC introduced as free monomer, the polymerization has been carried out in the temperature range between 50 and 140°C. In each polymerization a final product containing considerable amounts of linked cyclodextrin (from 35 to 72 weight %) was obtained. The detailed results are presented in Table 4. This shows the efficiency of the reaction, i. e., the ratio a of PVDC containing cyclic parts to homo-PVDC (the by-product of the reaction) and the content of cyclodextrin in the products obtained. With increasing temperature, the ratio of PVDC containing cyclic material to homopolymer increases while the content of cyclodextrin shows a maximum in the range 90-100°C. The products containing the cyclodextrin molecules dissolve in DMF, in contrast to the PVDC homopolymer. The

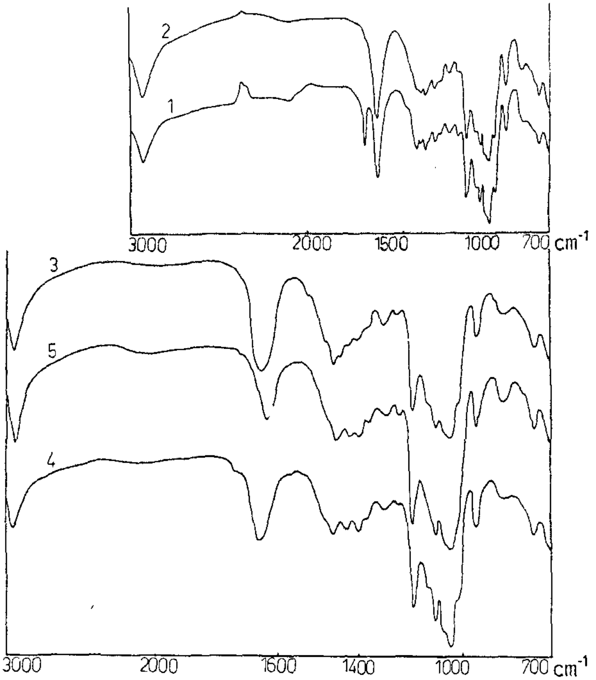

FIG. 3. IR spectra (KBr pellets): (1) product of the methyl acrylate/β-cyclodextrin adduct polymerization in DMF; (2) product of the styrene/β-cyclodextrin adduct polymerization in DMF; (3) free vinylidene chloride polymerization product in DMF in the presence of β-cyclodextrin; (4) product of the vinylidene chloride/β-cyclodextrin adduct polymerization in DMF; (5) β-cyclodextrin.

solubility of these products in dimethyl sulfoxide (DMSO) is low and often only partial. They are completely insoluble in other organic solvents like acetone, alcohols, diethyl ether, and dioxane. Because of the considerable content of cyclic dextrin, the IR spectra of these products coincide with the spectrum of pure β-CD (Fig. 3) in the range 4000-600 cm^{-1}. The structure of the basic polymer in the inclusion compound was determined by the mass spectrometry method used by Zeman [5]. The samples were introduced directly into the source of the mass spectrometer and heated to 350°C at 10^{-5} Torr, and the spectra of the degradation products were recorded. The analysis of the thermal treatment products carried out on PVDC by Zeman shows

TABLE 4. β-Cyclodextrin in Polymerization Products

Temperature of polymerization (°C)	Weight ratio of PVDC bonded with β-cyclodextrin to pure PVDC	Degree of vinylidene chloride conversion	β-cyclodextrin in polymerization product (%)
50	0.0048	0.575	37
80	0.0183	0.670	35
90	0.0420	0.564	72
100	0.0648	0.315	70
110	0.1480	0.316	69
120	0.2190	0.298	61
130	0.2220	0.411	41
140	0.8850	0.255	50

that the polymer loses molecules of hydrogen chloride in a two-step reaction, as is known. In the first step a polymer with the structure $-(CH=CCl)_n$ is formed, then as a result of Diels-Alder reaction, products with cycloalkene structure are obtained. These, in turn, liberate further molecules of hydrogen chloride, giving products with a condensed aromatic ring structure. This process finally leads to the carbonization of the polymer. The first step of the dehydrochlorination is characterized in the mass spectra by the presence of 1,3,5-trichlorobenzene (m/e = 180 and 182), and the second step by the presence of tetrachloronaphthalene (m/e = 264, 266, and 268). In the mass spectra of our products some peaks typical of pure β-CD have been observed (m/e = 57, 60, 73, 85, 98, 126) as well as peaks, according to Zeman, coming from homopolymer PVDC (1,3,5-trichlorobenzene molecular ion at m/e = 180 and 182). However, the molecular ion peak of tetrachloronaphthalene (m/e = 264, 266, and 268) has not been observed in the spectra. It should be stressed that mass spectra of products obtained by the radiation polymerization [1] also show no molecular ion peak of tetrachloronaphthalene. Therefore, it can be assumed that the products of the VDC polymerization carried out in the inclusion compounds both in the solid phase and in DMF solution have a similar structure. The mass spectrum of homo-PVDC formed as a by-product contains both usual peaks of trichlorobenzene and tetrachloronaphthalene.

It is worthy of notice that the polymerization of the β-CD·VDC adduct (method 2) contrary to the polymerization of free monomer, eliminates

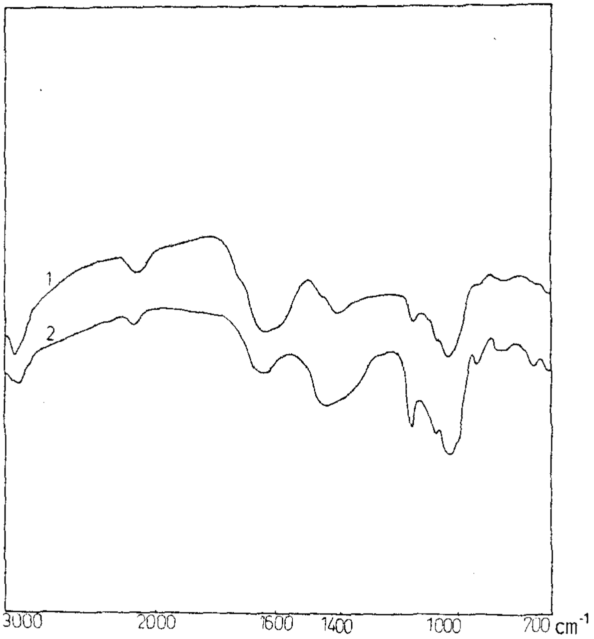

FIG. 4. IR spectra (KBr pellets): (1) insoluble fraction obtained as a result of the dehydrochlorination of the vinylidene chloride in DMF in the presence of β-cyclodextrin polymerization product; (2) soluble fraction obtained as above.

the simultaneous formation of homo-PVDC and leads to high β-CD content in the polymerization product (85 weight %). This result confirms the high stability of the β-CD·VDC inclusion compound dissolved in DMF. Besides other properties the substances are similar to the products obtained by radiation [1] with respect to chemical constitution and solubility properties. The transition from the polymerization products to the dehydrochlorination products is particularly typical. Easily water-soluble substances were obtained in our case, though no additional hydrophilic groups were formed as the result of the reaction. Dehydrochlorination leads mainly to unsaturated groups. There is a broadened absorption band at 1650-1550 cm^{-1} in the IR spectra (Fig. 4) related to the C=C bond and a band at 2200-2100 cm^{-1} typical of acetylene groups. The band at 1650-1550 cm^{-1} has been observed also by Burnett and Haldon [9] in the case of dehydrochlorination products of homo-PVDC. In

TABLE 5. Dependence of Solubility on Degree of Dehydrochlorination and Cyclodextrin Content

Adduct of poly(vinylidene chloride) with β-cyclodextrin		Dehydrochlorination products				
Temperature of polymerization (°C)	β-Cyclodextrin (%)	Water-soluble fraction		Water-insoluble fraction		Weight ratio of soluble fraction to insoluble fraction
		Chlorine (%)	β-Cyclodextrin (%)	Chlorine (%)	β-cyclodextrin (%)	
90	72	9	77	31	45	10.0
110	69	2	89	23	63	3.22
130	35	5	83	28	30	0.0073
140	50	4	83	30	31	0.785

addition to the water-soluble product some quantity of insoluble fraction was obtained in each case. There is a considerable dependence of the solubility upon the degree of dehydrochlorination and the cyclodextrin content (Table 5). The amount of soluble fraction decreases together with the content of cyclodextrin in the polymerization product. There is a small content of chlorine (less than 10%) and a large amount of β-CD (about 80%) in the soluble fraction, while the content of chlorine in the insoluble fraction increases to 30% and that of cyclodextrin is smaller than 40-60%. It seems probable that the solubility of the dehydrochlorination products is related to the transition from the inclusion structure of the polymerization products to the topological structure as a result of the considerable loss of chlorine atoms by the polymer chain when dehydrochlorinated [1]. The composition of the water-soluble and insoluble fractions corresponds to this statement. It is worthy of note that homo-PVDC, unlike our product described above, loses its solubility when dehydrochlorinated. In some cases it is completely insoluble after elimination of 1% chlorine [9]. If the structure of the compound studied was purely chemical, the dehydrochlorination reaction would decrease the solubility of the product.

As already stated, the solvent polymerization of VDC in the presence of cyclodextrin may produce chemical bonds between polymer and macrocycles, mainly by chain-transfer reaction. The possibility of the reaction of β-CD molecules with the already formed PVDC chain should also be taken into account. Both of these alternatives have been checked up in the following reactions: (1) the reaction of VDC with linear dextrin under the conditions of polymerization and (2) the reaction of PVDC with β-CD. In both cases the final products turned out to be polymers containing practically no carbohydrate (IR spectra, Fig. 5). This means that, as in radiation polymerization [1], the cyclic structure of β-CD is essential to link PVDC with the carbohydrate in the solvent polymerization product of the β-CD·VDC adduct and a rotaxane structure or at least an inclusion character for these products cannot be excluded.

RESULTS

Polymers containing considerable amounts of cyclic structures have been obtained by means of free-radical polymerization of vinyl monomers in the presence of β-cyclodextrin in dimethylformamide solution. Polymers containing β-cyclodextrin molecules were formed by polymerization in associates composed of β-cyclodextrin/monomer adducts.

An absence of chemical bonds between the poly(vinylidene chloride) chain and the β-cyclodextrin molecules seems probable.

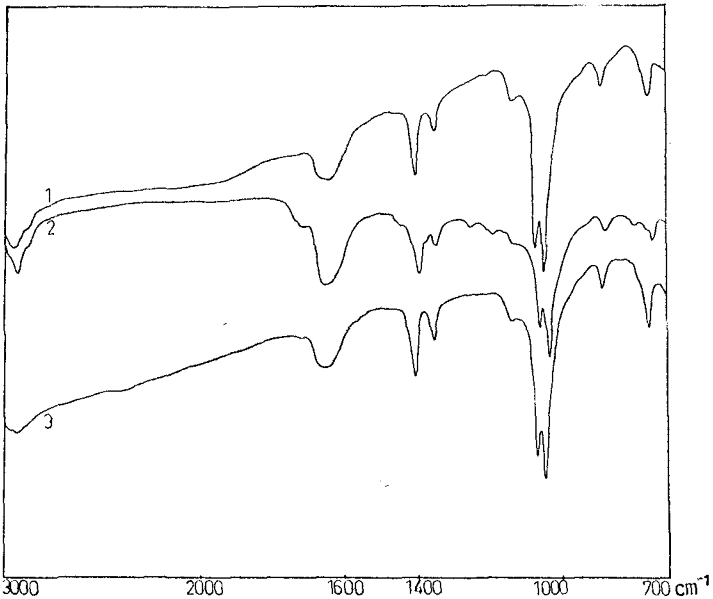

FIG. 5. IR spectra (KBr pellets): (1) pure poly(vinylidene chloride); (2) poly(vinylidene chloride) obtained in the presence of linear dextrin; (3) poly(vinylidene chloride) heated with β-cyclodextrin in DMF solution (conditions of polymerization).

Systems of stable combination of the β-cyclodextrin molecules with the polymerization product of vinylidene chloride have been obtained.

The polymerization of a previously prepared adduct of β-cyclodextrin and vinylidene chloride in dimethylformamide solution leads entirely to the polymer containing cyclic parts, whereas introduction of these ingredients to the solvent separately leads also to the poly(vinylidene chloride) as a by-product.

No fundamental differences in chemical and physicochemical properties have been found for polymer adducts obtained traditionally by radical polymerization and those obtained with radiation [1].

EXPERIMENTAL

Materials

β-Cyclodextrin (Corn Products Company) was recrystallized once, $[\alpha]_D^{25} = +162°$ (1, H_2O).

The identity of β-CD was proved by NMR and x-ray determinations. Linear dextrin (Merck) was identified by IR [10].

Vinylidene chloride (Koch-Light), methyl acrylate (Fluka), styrene (Koch-Light) and methacrylonitrile (Koch-Light) were freshly distilled before use.

Solvents and nonsolvents of analytical grade were freshly distilled before use.

Equipment

IR spectra were obtained with a Specord 71 IR spectrophotometer. The x-rays were measured with a 50 JM diffractometer (USSR). Mass spectra were obtained with a Varian MAT 111 instrument. A MOM Budapest OD 102 Derivatograph was used for DTA.

Preparation of Adducts of β-CD with Organic Compounds in DMF Solution

The organic compounds (halides) were added to 20% solution of β-CD in DMF in 1:1 weight ratio to β-CD. The solutions were heated to 100°C as immediate precipitation of crystalline material was observed. The precipitates were filtered off in the hot state and washed with boiling DMF, then with water. The IR spectra of the products correspond to that of pure β-CD in the range of 4000-600 cm^{-1}. The quantitative composition of the adducts obtained was determined from the halogen content (Table 2).

Polymerization of Free Vinyl Monomers in DMF Soltuion of β-CD

A mixture of 20 g of 20% DMF solution of β-CD, 4.8 g vinyl monomer, and 0.020 g AIBN as radical polymerization initiator was prepared in a glass ampoule. Ampoules were sealed under nitrogen atmosphere and heated in a thermostat.

Polymerization of Methacrylonitrile. The ampoule was heated at 110°C for 6 hr. A white polymer was precipitated on

TABLE 6. Polymerization of Vinylidene Chloride

Temperature of polymerization (°C)	Time of polymerization (hr)	Weight of product containing β-cyclodextrin (g)	Weight of pure poly(vinylidene chloride) (g)
50	72.0	0.022	2.738
80	15.5	0.090	3.155
90	10.0	0.395	2.634
100	6.5	0.307	1.420
110	3.0	0.677	1.306
120	2.0	0.616	1.095
130	0.75	0.540	1.612
140	0.50	1.153	0.650

adding 100 ml of water; it was further heated for 1/2 hr with an excess of water in order to purify it from free β-CD. The IR spectrum corresponded exactly to that of pure polymethacrylonitrile [7]. The elemental analysis showed: N, 20.65%; C, 68.66%; H, 7.75%.

Polymerization of Methyl Acrylate. The ampoule was heated at 110°C for 6 hr. The reaction product was divided into two phases which were separated and purified as described above. The IR spectra (KBr pellets) of both products were similar and correspond to that of pure poly(methyl acrylate) [7].

Polymerization of Vinylidene Chloride. The polymerization reactions were carried out in the range of temperatures 50-140°C. In every case a beige product precipitated on addition of 100 ml water. The precipitate was purified from free β-CD by boiling with water for 1/2 hr. The relation between conditions of the reaction and the yield is shown in Table 6. The IR spectra (KBr pellets) of all products were practically the same as that of pure β-CD (Fig. 3) in the range of 4000-600 cm^{-1}. The elemental composition is shown in Table 7.

Preparation of Vinyl Monomers Adducts with β-Cyclodextrin

The β-CD adducts with vinyl monomers were prepared by Cramer's procedure for adducts of organic compounds [11]. A 4 g portion of

TABLE 7. Elemental Composition of Poly(vinylidene Chloride) Adducts

Temperature of polymerization (°C)	N (%)	C (%)	H (%)	Cl (%)
50	0.78	32.16	3.78	44.01
80	0.77	32.58	3.77	44.41
90	0.23	37.51	5.51	18.98
100	0.34	37.19	5.32	20.74
110	0.17	36.53	4.96	22.62
120	0.34	36.91	4.83	26.23
130	0.46	33.80	4.36	39.39
140	-	32.91	3.90	37.23

β-CD was dissolved by heating in 100 g water. After cooling to the room temperature the solution was mixed vigorously with 2 g monomer for about 15 min and left to set for 12 hr. The precipitate was filtered off, carefully washed with water and dried over anhydrous Na_2SO_4 in an atmosphere of monomer vapors.

Polymerization of Monomers as Adducts with β-CD in DMF Solution

Every adduct of vinyl monomer and β-CD prepared as described above was dissolved in 16 g DMF; 0.020 g AIBN was added to each solution. The mixtures were placed in glass ampoules sealed under nitrogen and heated in thermostat at 110°C for 8 hr. The products of polymerization were precipitated on addition of 100 ml water. The products containing cyclodextrin were boiled with a new portion of water in order to dissociate into polymer and cyclodextrin if they were simple inclusion compounds [2]. Polymerization of methacrylonitrile resulted after precipitation in pure polymethacrylonitrile (IR [7]), elemental composition: C, 69.30%; H, 7.70%; N, 19.60%). Polystyrene and poly(methyl acrylate) free of β-CD (IR [7]) were obtained only after boiling with water. IR spectra of products of precipitation included all absorption bands typical of β-CD (1160, 1080, 1030, 950, and 700 cm^{-1}) in the cases both styrene and methyl acrylate. The styrene-β-CD adducts were polymerized also in the presence of benzene-β-CD adducts in various proportions. The isolated polymers were reprecipitated from 1% benzene solution on addition of an excess of methanol in order to purify. The results are shown in Table 3.

Polymerization of Vinylidene Chloride-β-CD Adduct in DMF Solution

The adduct was prepared and polymerized in the way described above. A part of the precipitated polymerization product was dissolved in DMF and reprecipitated with 10 times its volume of water. The elemental composition of the reprecipitate was: C, 39.10%; H, 5.55%; Cl, 13.70%. Another part of the polymerization product was boiled with water for 1/2 hr. The elemental composition of the product obtained was: C, 37.5%; H, 5.97%; Cl, 11.80%. The IR spectra of both products were identical and similar to that of pure β-CD in the range of 4000-600 cm^{-1} (Fig. 3).

Dehydrochlorination of the Poly(vinylidene Chloride)-β-CD Adduct

The PVDC·β-CD adducts obtained at different temperatures were dehydrochlorinated according to the following procedure.

A mixture of 1 g adduct, 1 g NaOH, and 50 ml ethyl alcohol was boiled for 1 hr. After cooling, a black precipitate was filtered off and washed with ethyl alcohol to neutrality. It was dried at 80°C for 1/2 hr then boiled with 50 ml water and centrifuged. In every case a deep dark solution and an insoluble sediment were obtained. The solution was treated with 250 ml of ethyl alcohol which caused the precipitation of a black product (A). This product was dried at 80°C for 1/2 hr. The insoluble sediment (B) was boiled again in water for several minutes and filtered off.

The relation between the conditions of polymerization and the yield of dehydrochlorination products A and B is described in Table 8.

In the IR spectra (KBr pellets) of the precipitates A and B (Fig. 4) some absorption bands typical of β-CD (1160, 1080, 1030, 970, and 700 cm^{-1}) and of dehydrochlorinated PVDC (1650-1550 and 2200-2100 cm^{-1}) appeared.

The elemental compositions of the dehydrochlorinated polymers are shown in Tables 9 and 10.

Control Reactions

Reaction of Vinylidene Chloride with Linear Dextrin in Conditions of Polymerization.

A 13.5% DMF solution (saturated at room temperature) of linear dextrin was prepared

TABLE 8. Yield of Dehydrochlorination Products

	Poly(vinylidene chloride) with β-cyclodextrin adduct		Dehydrochlorination products	
Dehydrochlorination reaction	Temperature of polymerization (°C)	Weighed portion for reaction (g)	A (g)	B (g)
1	90	0.452	0.151	0.015
2	110	0.677	0.280	0.078
3	130	0.460	0.009	0.124
4	140	1.000	0.200	0.255

TABLE 9. Dehydrochlorination Products

Dehydrochlorination reaction	Precipitate A			
	N (%)	C (%)	H (%)	Cl (%)
1	0.23	43.56	5.92	8.98
2	-	39.84	5.87	1.75
3	0.49	45.74	5.48	5.17
4	-	41.59	5.86	3.95

TABLE 10. Dehydrochlorination Products

Dehydrochlorination reaction	Precipitate B			
	N (%)	C (%)	H (%)	Cl (%)
1	0.86	40.25	4.18	30.98
2	0.98	48.87	3.73	22.10
3	1.11	51.63	3.40	28.28
4	0.57	49.80	3.16	30.25

and was heated in a glass ampoule at 110°C for 1/2 hr. No crystallization on heating was observed. After cooling, 0.013 g AIBN and 2.6 g vinylidene chloride were added. Then the ampoule was sealed under nitrogen and heated at 110°C for 3 hr. After reaction a two-phase system was obtained. The sediment (1.2 g) was filtered off and boiled in water for 1/2 hr in order to eliminate dextrins. The filtrate was treated with 100 ml water, after which some beige precipitate (0.008 g) was obtained. It was purified by boiling with water for 1/2 hr. The IR spectrum (KBr pellets) of both products were identical and comparable with that of pure poly(vinylidene chloride) (Fig. 5).

Reaction of Poly(vinylidene Chloride) with β-CD. A mixture of 1.42 g poly(vinylidene chloride) obtained by radical polymerization of vinylidene chloride in DMF at 110°C, 20 g of DMF solution of β-CD, and 0.020 g AIBN was heated in a sealed ampoule under nitrogen atmosphere in a thermostat at 110°C for 3 hr. The precipitate obtained was filtered off and purified from β-CD by boiling with water for 1/2 hr. Its weight was 1.045 g. A trace amount of the product was obtained from the filtrate by precipitation on addition of 100 ml water. It was purified in the way described above. The IR spectra (KBr pellets) of both products were identical in the range of 4000-600 cm^{-1} (Fig. 5) and similar to that of pure poly(vinylidene chloride).

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