Polymerization and Copolymerization of Some Monomers as Adducts with β-Cyclodextrin

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ABSTRACT

The feasibility of chemical bond formation, especially in the chain-transfer reaction between polymer and β-cyclodextrin (β-CD) molecules in the products of the radiation polymerization of β-CD with vinylidene chloride (VDC) its adducts has been considered. The lack of these bonds in the polymerization products of similar β-CD adducts with methyl methacrylate (MM), styrene (St), a mixture of VDC and allyl chloride (AC) and a mixture of VDC and MM (10:90 molar ratio) has been established. On the basis of the results obtained the lack of chemical bonds in the polymerization product of β-CD·VDC adduct is suggested.

The feasibility of synthesis of polyrotaxanes (polymers of rotaxane topological structure, Fig. 1) with poly(vinylidene chloride) (PVDC) and β-cyclodextrin (β-CD) adduct (Fig. 2) as an intermediate product has been recently investigated [1]. Stable polymeric products (molecular weight about 20,000) have been obtained by radiation polymerization of crystalline monomeric adduct of vinylidene chloride
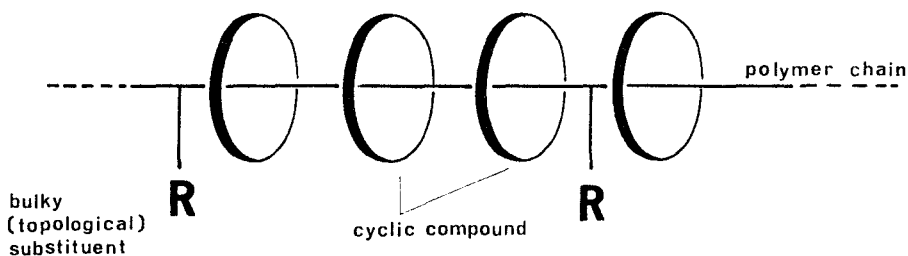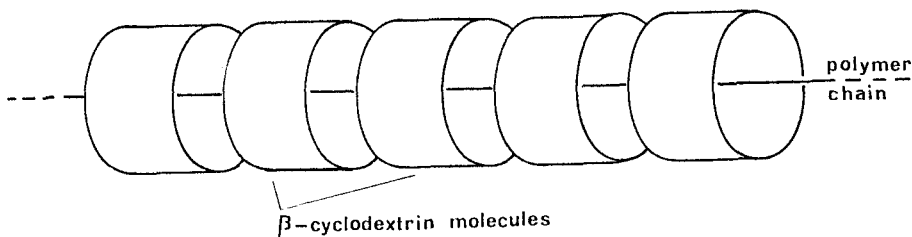
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FIG. 1. Scheme of polyrotaxane structure.

FIG. 2. Scheme of β-cyclodextrin-polymer adduct.

(VDC) and β-CD. The products contained molecules of β-CD (80 wt %) linked to the VDC polymer chain (20 wt %). Considering the high stability of the system, the authors suspected nonchemical linkage between the polymer and β-CD molecules, though they did not exclude the possibility of chemical bonds, which could form, e. g., in grafting or in chain transfer to the β-CD molecule.

The polymerization of adducts of β-CD with other monomers and monomer compositions that were tested threw some light on the problem of linkage between PVDC chain and β-CD molecules.

The crystalline adducts of β-CD with methyl methacrylate (MM), styrene (St) and the MM and St composition prepared according to Cramer [2] were polymerized by γ-irradiation (5 Mrad). It was found that the polymerization products, unlike those of the polymerization of β-CD·VDC products [1], were unstable and dissociated when purified with hot water. They behaved like low molecular compounds isolated in the same conditions from adducts with β-CD [3].

The results indicate the lack of the chain transfer on β-CD molecules in the polymerization of vinyl monomers included in an adduct. If it occurred in the case of β-CD·VDC polymerization, its

contribution to the polymerization of β-CD with other monomer adducts
would be also observed, because the chain-transfer reaction is fairly
common. Although the chain-transfer reaction constant in the VDC
polymerization is higher than in the case of MM or St because of the
higher reactivity of the growing PVDC macroradical [4, 5], it would
be less possible if the constant was zero in the case of MM and St.
Furthermore in the case of MM and VDC, the crystal structures are
identical (Table 1), so the conditions of the polymerization in the β-CD
crystalline lattice cells are approximately the same. It even seems
that the mobility of growing chain in the lattice is higher, e. g., in
the case of MM polymerization than that of VDC, and it would be more
likely to facilitate the chain transfer reaction. The evidence of
mobility of the forming channel MM-polymers in the β-CD crystal-
line lattice is the crystal structure of the polymerization product.
It is identical with that of monomeric adduct (Table 1), so there is
enough place for the reaction to proceed without destroying the crystal
structure. On the other hand, in the case of β-CD·VDC polymeriza-
tion [1], complete destruction of the crystal structure and formation
of an amorphous product are observed. Further evidence of the high
mobility of the reacting molecules in the β-CD·MM polymerization is
the feasibility of spontaneous polymerization without outside initiation.
This case is rather unusual, because polymerization of a monomer
in a crystalline phase requires generally strong initiation. The
spontaneous polymerization was also observed in the case of β-CD
adduct with a composition of MM and VDC with large excess of MM
(90:10 molar ratio). It appears that the conditions for polymerization
are more or less similar to those of the polymerization in a liquid
phase. A characteristic phenomenon accompanying the spontaneous
polymerization in the presence of water is the recrystallization of
the adduct: it changes from a powder form to single large crystals.

The possibility of chain transfer on β-CD molecules in VDC adduct
polymerization is contradicted by previous findings [1] on the
polymerization of an adduct of β-CD and a VDC-allyl chloride (AC)
composition. Stable systems of copolymer and β-CD molecules were
also obtained. The reactivity of a monomer like AC in the polymeri-
zation produces competition for the chain transfer on β-CD molecule
and on an allyl monomer.

Chain transfer on β-CD:

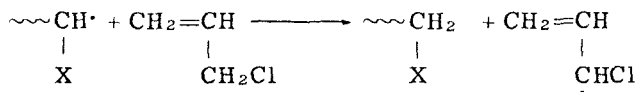$$\sim\!\sim\!CH^{\bullet} + \;-\overset{|}{\underset{|}{C}}- \;\longrightarrow\; \sim\!\sim\!CH_2 + \;-\overset{|}{\underset{\bullet}{C}}-$$
$$\quad\; \underset{X}{|} \qquad \underset{H}{|} \qquad\qquad\quad \underset{X}{|}$$

Chain transfer on AC:

TABLE 1. d Values Obtained from X-Ray Patterns of Adducts

			d value (Å)[a]		
β-CD·VDC (liquid)	β-CD·MM (liquid)	Polymer of β-CD·MM (liquid)	β-CD·VDC (vapor)	β-CD·MM (vapor)	Polymer of β-CD·(VDC + AC)
–	–	–	14.8 m	14.8 m	14.8 vw
–	–	–	13.55 s	13.2 w	–
14.2 vw	14.9 w	12.5 vw	12.85 s	12.7 w	12.99 vw
9.87 w	9.71 w	9.81 vw	–	9.75 vw	–
9.03 w	9.11 m	–	8.998 vw	8.96 vw	9.11 vw
8.32 s	8.35 s	8.32 s	7.93 m	–	–
7.43 s	7.59 vs	7.54 m	7.56 vs	7.56 vs	7.62 s
7.11 vs	7.12 vs	7.11 vs	7.11 w	7.07 vw	–
–	–	–	–	6.60 vs	–
6.14 s	6.12 s	6.06 w	6.21 w	6.19 w	6.07 w
–	5.91 w	–	–	5.81	–
5.72 w	5.70 s	5.74 m	5.73 w	–	5.64 w
5.53 m	5.54 w	5.49 w	5.44 w	–	–
5.21 m	5.21 m	5.18 s	5.20 s	5.22 m	–
5.11 m	5.12 s	–	–	–	–
–	–	–	5.04 vs	5.07 m	5.02 vs

4.96 s	4.99 s	–	–	–
4.86 m	4.84 s	–	4.90 s	–
4.73 s	4.72 vs	–	–	–
4.64 s	–	4.68 w	–	–
4.57 s	4.53 vs	4.51 m	–	–
–	–	–	4.44 w	4.43 w
4.24 vs	4.24 vs	4.20 m	4.25 w	4.30 w
4.19 s	4.15 m	–	–	–
–	4.03 vw	–	4.03 vw	–
3.88 m	3.80 s	–	–	–
3.77 w	–	3.79 w	3.76 vw	3.73 m

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

$$\sim\sim\text{CH}\cdot + \text{CH}_2\text{=CH} \longrightarrow \sim\sim\text{CH}_2 + \text{CH}_2\text{=CH}$$

$$\quad\quad | \quad\quad\quad\quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad | \quad\quad\quad\quad\quad\quad\quad |$$

$$\quad\quad\text{X} \quad\quad\quad\quad\text{CH}_2\text{Cl} \quad\quad\quad\quad\quad\quad\text{X} \quad\quad\quad\quad\quad\overset{\centerdot}{\text{CHCl}}$$

Consequently, the final product of the adduct copolymerization of β-CD, VDC, and AC should contain considerably less β-CD than that of VDC homopolymerization, if we assume binding of dextrin with the polymer chain to be an effect of the chain-transfer reaction. According to the literature data [1], the amount of β-CD bonded to AC and VDC copolymer is even higher (87 weight %) than in the case of VDC homopolymer (80 weight %).

It should be stressed that the β-CD content in the VDC and AC copolymerization product (87.55 weight %) corresponds to the value (86.4 weight %) calculated on the basis of the specific rotation measurements [1] with the assumption that β-CD was chemically unchanged in the copolymerization product.

The chemical identify of β-CD in polymerization products of various adducts can be evidenced by x-ray patterns. Although the products crystallized in different degrees, the x-ray patterns demonstrate that β-CD is in a chemically unchanged form in the product of β-CD (VDC + AC) polymerization. One evidence for this is the similarity of the β-CD crystal lattice in the polymeric and monomeric adducts, e. g., β-CD·VDC (vapor) or β-CD·MM (vapor). The same d values in the x-ray patterns (Table 1) suggest the identical chemical compound, i. e., β-CD molecules in all cases. The same x-ray patterns in the case of direct polymerization product and product of heating (water extraction of unbonded β-CD and monomeric adducts at 70°C) were obtained (Table 1). Therefore, the water-insoluble product of β-CD·(VDC + AC) polymerization [1] is not a chemical compound but an adduct-structural combination. A similar structure should be suspected in the case of the β-CD·VDC polymerization product.

The lack of chemical bonds in the combination PVDC·β-CD is confirmed additionally by studies of stability of copolymerization product of the β-CD adduct with VDC and MM mixture. It was worthwhile knowing the nature of difference between a monomer forming a stable polymer system with β-CD and, on the other hand, a monomer forming an unstable one.

The x-ray patterns of β-CD adducts with VDC and with MM were identical so the adducts must have identical crystal structures (Table 1). This situation should be conducive to the simultaneous presence of both monomers' molecules in the empty spaces (channels) of the β-CD crystal lattice. In order to avoid an excess of free monomer, adducts were obtained not by treating the aqueous solution of β-CD with liquid organic phase as usual [2] but by treatment with monomers vapors at room temperature. The crystal structure of
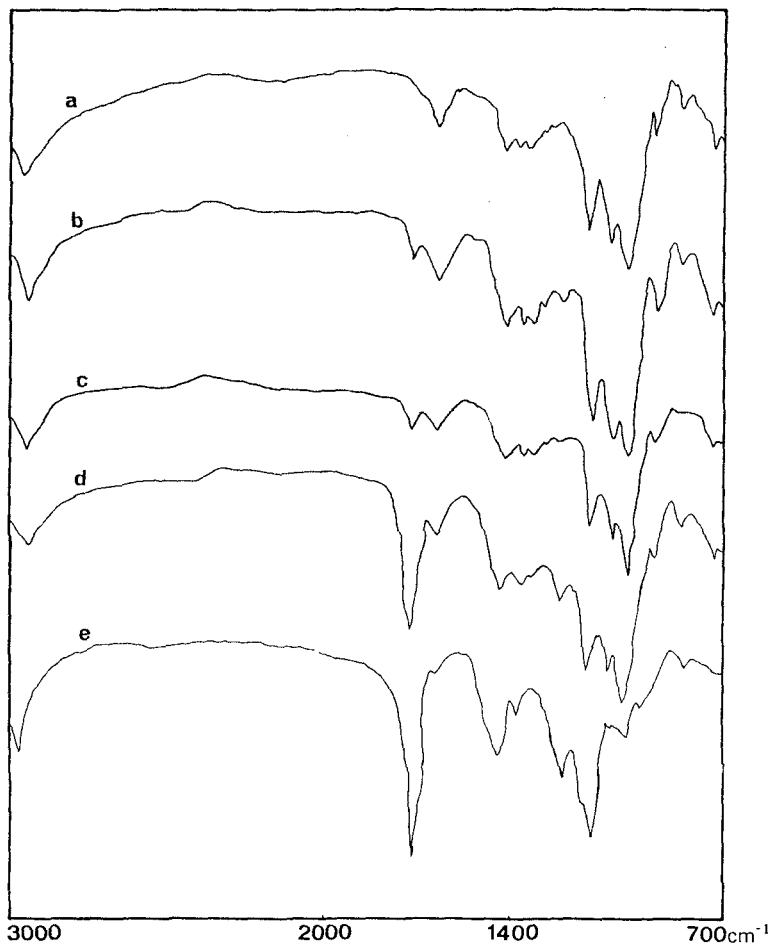
FIG. 3. IR spectra: (a) β-cyclodextrin (β-CD); (b) copolymer of β-CD·(VDC + MM) with VDC:MM mole ratio in the monomer mixture of 20:80; (c) copolymer of β-CD·(VDC + MM) with VDC:MM mole ratio in the monomer mixture of 35:65; (d) copolymer of β-CD·(VDC + MM) with VDC:MM mole ratio in the monomer mixture of 50:50; (e) copolymer of β-CD·(VDC + MM) with VDC:MM mole ratio in the monomer mixture of 10:90.

adducts obtained from monomers in gaseous phase differs from that
of adducts with liquid monomers, but it is also identical in the case of
both monomers (Table 1). The polymerization products were boiled
with water for 1 hr in order to remove monomeric adducts and free
β-CD molecules, then washed with acetone for 24 hr in order to remove
free poly(methyl methacrylate).

From initial mixtures of composition by weight of 80:20, 65:35, and
50:50 MM:VDC, polymerization products of approximately constant
chlorine content (13-15 weight %) were obtained. This amount did
not differ from chlorine content in the polymerization product of
β-CD·VDC (about 14 weight %) [1].

From the IR spectra it is evident that when reaction mixture was
enriched in MM, the content of MM mers in the product increases
(increase of the intensity of the absorption band at 1730 cm^{-1} in
patterns b - d, Fig. 3). With stable chlorine content, this means a
decrease in β-CD content in the polymerization product. This is
evidence that the "inclusion" forces decrease in the polymer -
β-CD molecules system on "dilution" of the PVDC chain with MM
mers and that the tendency for the system to dissociate increases
if the reaction product is an adduct. On the contrary, the "dilution"
of the PVDC chain by AC mers (1.2 mole of VDC and 0.66 mole of AC)
increased the content of carbohydrate in the adduct (87 weight % of
cyclodextrin [1]), probably on account of the high tendency of chlorine
derivatives to form adducts with cyclodextrins in general [2].

It should be stressed, however, that on further increasing MM mers
content in the copolymer with VDC, the latter, containing only 10
weight % of VDC mers loses practically all β-CD molecules when
treated with hot water. The polymerization products dissociate
nearly completely into free polymer (Fig. 3, compare the spectrum e
with a in the region 1000-1160 cm^{-1}) and ring molecules, though the
molecular weight of the polymer is very high (170,000 by membrane
osmometry). In the case of small content of VDC there are only
scattered VDC mers in the copolymer chain and that is probably the
reason for the lack of stability of the compound. It may be assumed
that the stability of such a system would be very low and similar
to that of monomer β-CD·VDC adduct. That means the absence of any
stronger binding than that of van der Waals character in this β-CD
copolymer compound. That also means that the absence of chemical
bonds in the β-CD·VDC polymerization product is feasible. Other-
wise, copolymer containing 10 weight % VDC mers should link about
30 weight % of β-CD, proportionally to β-CD content in β-CD·VDC
polymerization product [1]. The IR spectra give no evidence of it,
in any case (see spectra a and e, Fig. 3).

To recapitulate, it should be stated that of the two structure (chemi-
cal and inclusion) of the β-CD·VDC polymerization product the inclu-
sion structure is more probable. The nonchemical character of the

β-CD·(VDC + AC) polymerization product seems obvious, at least in the light of x-ray investigations.

ACKNOWLEDGMENTS

REFERENCES

[1] M. Maciejewski and G. Smets, paper presented at 2nd Conference on Modification of Vinyl Polymers, Wrocław, Poland, 1973; Sci. Papers Inst. Org. Technol. Plastics Wrocław Tech. Univ., 16, 57 (1975).
[2] F. Cramer and F. M. Henglein, Chem. Ber., 90, 2561 (1957).
[3] F. Cramer, Einschlussverbindungen, Springer-Verlag, Heidelberg, 1954.
[4] O. K. Nozaki, Discussions Faraday Soc., 2, 337 (1947).
[5] H. F. Mark, N. G. Gaylord, and N. Bikales, Eds., Encyclopedia of Polymer Science and Technology, Vol. 3, Interscience-Wiley, New York-London-Sydney, 1965 p. 596.