Table 1. The initial quantum yield (Q_i) of the obtained polymer by the irradiation ($\lambda=300$ nm) of air-free acrylic acid derivates in methanol containing 5×10^{-3} M photoinitiator[a]

Monomer ($X_{monomer}$)	Photoinitiator (5×10^{-3} M)		
	BEE	BIE	BP
AA (0.08)	8.34	6.18	4.67
MA (0.08)	2.21	1.83	1.45
MMA (0.08)	1.37	1.13	0.93
AA (0.04)+MA (0.04)	1.34	1.05	0.88
AA (0.04)+MMA (0.04)	0.43	0.35	0.24
MA (0.04)+MMA (0.04)	0.31	0.26	0.15

[a]The initial quantum yield of the copolymers was calculated on the assumption that copolymerizations were carried out by the 1 : 1 combination of monomers.

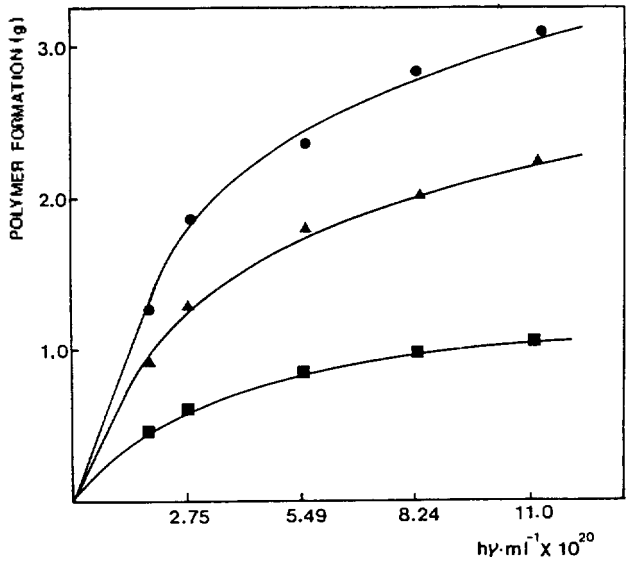
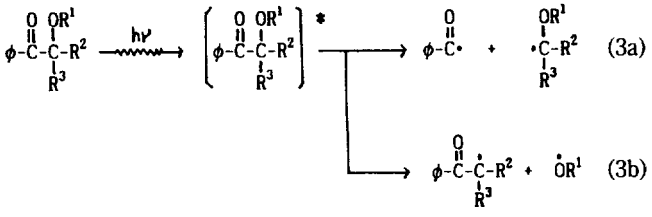


Figure 2. Polymer formation of acrylic acid in methanol with 5×10^{-3} M benzophenone as a function of the number of quanta. Mole fractions of acrylic acid are 0.129 (●), 0.084 (▲), and 0.041 (■).



This primary reaction of excited aromatic carbonyl compound could explain the relatively low polymer yield in the case of benzophenone. Since the size of ketyl radical in equation (1) is larger than the radicals of BE and BIE produced according to equation (3), it seems that it is more difficult for the ketyl radical to attack C_1 position (the first carbon atom) in monomer ($CH_2=CR\text{-}COOR'$, R and R'=H or CH_3) than the other radicals. Besides, the high polymer yield in the case of AA compared with MA and MMA under the same conditions might support the influence of steric hindrance.

The polymer yield as a function of number of quanta is shown in Figure 2. The polymer yield decreased with the number of quanta. One should note that a back reaction occured in the system; the obtained polymer was decomposed by the direct photolysis of polymer or by an attack of the radicals which were formed during the photochemical reaction.

In conclusion, polymer yields were found to be dependent on the bulk of the primary radicals which were produced by the electronically exited photoinitiators, and the ability of photopolymerization was affected by the molecular structure of monomers.

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Cleavage of *m*-Nitrophenyl Acetate in Ethylenediaminated and Diethylenetriaminated β-Cyclodextrin Media

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Cyclodextrins are cyclic oligosaccharides which possess a hydrophobic cavity. They have attracted great attention as enzyme mimics because of their ability to form inclusion complexes with a variety of substrates and large kinetic ef-

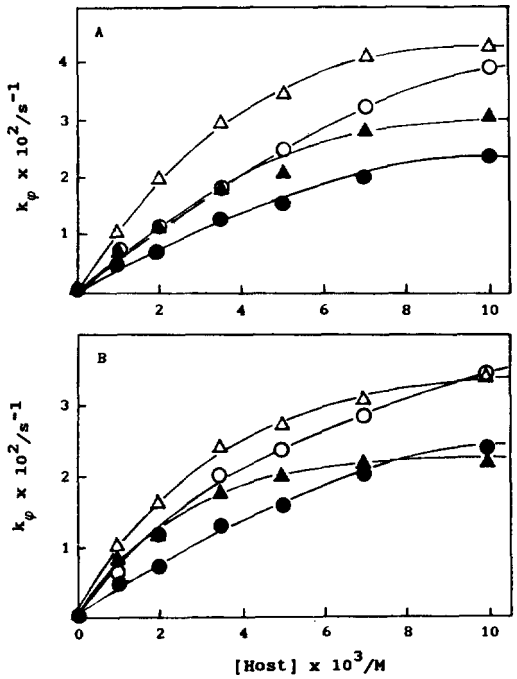
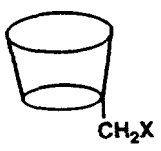


Figure 1. Effects of the concentration of the host for the cleavage of *m*-nitrophenyl acetate in the absence and in the presence of the metal ions: (A) ●, β-CD; ○, CDen; ▲, CDen-Zn^{2+} (1 : 0.25); △, CDen-Cu^{2+} (1 : 0.5); (B) ●, β-CD, ○, CDdien; ▲, CDdien-Zn^{2+} (1 : 0.75); △, CDdien-Cu^{2+} (1 : 0.75).

fects on the reactions of the inclusates.[1] Recently, efforts have been made into modifying cyclodextrins to enhance their kinetic effects.

We have been interested in functionalized β-cyclodextrins (β-CDs), and have shown that there are differences in reactivity and enantioselectivity among functionalized β-CDs.[2,3] Polyamine-functionalized β-CDs have metal-binding sites, and exhibit large metal ion effects on the binding affinity[4] and reactivity[5] of guest molecules. In this report, we present kinetics of the deacylation of *m*-nitrophenyl acetate in mono-6-deoxy-6[*N*-(2-aminoethyl)]amino-β-CD (CDen) and mono-6-deoxy-6-[*N*-(2-aminoethyl)-2-aminoethyl]amino-β-CD (CDdien) media in the presence and in the absence of divalent metal ions.

CDen (**2**) and CDdien (**3**) were prepared by a modification of the reported procedures.[4,5] Primary tosylate (3.00 g) of β-CD[6] was reacted with ethylenediamine (15 m*l*) at 90℃ for 1 h or diethylenetriamine (27 m*l*) at 50℃ for 5 h under N_2 atmosphere. After cooling the reaction mixture the product was precipitated by the addition of acetone. The product was dissolved in water and reprecipitated by the addition of acetone, and purified by ion-exchange chromatography on Sephadex CM-25 resin (eluent: 0.5 M NH_4HCO_3) and then Sephadex G-15 gel-filtration.



1: β-CD, X=OH

2: CDen, X=$NHCH_2CH_2NH_2$

3: CDdien, X=$NHCH_2CH_2NHCH_2CH_2NH_2$

Deacylation reactions of *m*-nitrophenyl acetate were initiated by adding 20 μ*l* of 0.02 M solution of the substrate in acetonitrile to 2.00 m*l* of the host (β-CD, CDen, or CDdien) solutions (0-10 mM) in 0.05 M pH 9.60 borate buffer (I=0.2 M) containing desired amount of a metal ion in a cuvette at 25℃. Reactions were followed by monitoring the formation of *m*-nitrophenol at 390 nm. The reactions obeyed pseudo-first-order kinetics with respect to the ester, regardless of the presence of the hosts and metal ions, and the first-order rate constants (k_φ) were determined both in the absence ($k_\varphi°$) and in the presence of various concentrations of β-CDs.

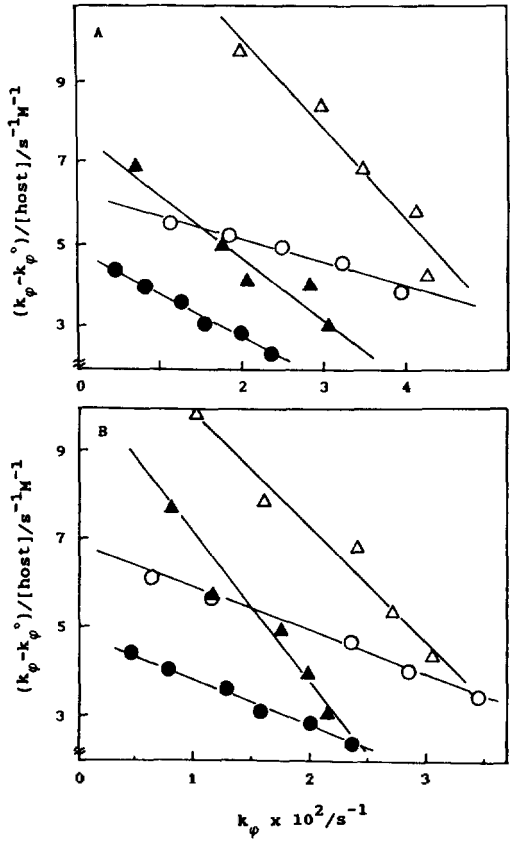


Figure 2. Plot of data of Figure 1 according to Eqn. (1). See Figure 1 for legends.

Figure 1 shows variation of k_φ for the cleavage of *m*-nitrophenyl acetate depending on the concentration of the host both in the absence and in the presence of the metal ions. The effects of the hosts on k_φ indicate different reaction rates for free and host-complexed substrates. Assuming 1 : 1 complexation between the substrate and host, k_φ and $k_\varphi°$ values are related with the rate constant k_φ^{CD} for the fully complexed substrate, and the binding constant K of the substrate to the host by Eqn. (1).[2,3,7]

$$(k_\varphi-k_\varphi°)/[\text{host}]=-Kk_\varphi+Kk_\varphi^{CD} \quad (1)$$

Data in Figure 1 were analyzed according to Eqn. (1) and the results are presented in Figure 2. K and k_φ^{CD} values were calculated from the slopes and intercepts of the lines in Figure 2, and are summarized in Table 1.

The K and $k_\varphi^{CD}/k_\varphi°$ values for β-CD agree well with the literature value:[7] k_φ^{CD} obtained in this work (pH 9.6) is about one-tenth of the reported value (pH 10.6), presumably due to the difference in pH of the reaction media. The dec-

Table 1. Constants for the Cleavage of *m*-Nitrophenyl Acetate in the Presence of Cyclodextrins and Metal Ions[a]

Host	M^{2+} ([host] : [M^{2+}])	K/M^{-1}	$k_\psi^{CD}\times10^2/s^{-1}$	$(k_\psi^{CD}/k_\psi^{\circ})^b$
β-CD	none	100	4.7	86
	none	125[c]	44.4[c]	96[c]
CDen	none	55	11	210
	Zn^{2+} (1 : 0.25)	150	5.1	94
	Cu^{2+} (1 : 0.50)	230	6.5	120
CDdien	none	95	7.1	130
	Zn^{2+} (1 : 0.75)	310	3.2	59
	Cu^{2+} (1 : 0.75)	260	4.8	89

[a] At 25℃, in 0.05 M pH 9.60 borate buffer (I=0.2 M). [b] k_ψ° is $5.4\times10^{-4}\,s^{-1}$; [c] Lit. values obtained in pH 10.60 carbonate buffer (ref. 9).

reasing order of the binding constant between host and the ester is β-CD≅CDdien>CDen, while that of k_ψ^{CD} is CDen >CDdien>β-CD. Addition of Zn^{2+} or Cu^{2+} to the media containing CDen or CDdien have a contrasting effect on the binding constant and k_ψ^{CD}: the binding constant increases, whereas k_ψ^{CD} decreases on the addition of the metal ions.

One possible explanation for the order of the binding constant is that the diethylenetriamine group is sufficiently hydrophilic to stay outside of the cyclodextrin cavity, and the environment and the depth of the cavity are not much different with those of β-CD itself, leading the binding constant of CDdien being essentially same with that of unmodified β-CD. On the other hand, the ethylenediamine group is expected to be included into the cavity, at least in part, causing the shallowness of the cavity and decreased binding of the substrate. This result is in line with our earlier report[2] of weaker binding of 1-benzyl-1,4-dihydronicotinamide, BNAH, with mono(6-O-tosyl)-β-CD, 6-Ts-CD, compared to that with β-CD itself. The fact that the rate constant k_ψ^{CD} for the fully complexed substrate is greatest in case of CDen implies that the substrate complexed with CDen is in better position for the nucleophilic interaction between the C-2 oxido group of the CD and the carbonyl carbon atom of the substrate.[8].

The effects of the divalent metal ions on the binding constants and k_ψ^{CD} for CDen and CDdien can be attributed to the interaction between the metal ion and the amino group.[4,5,9] The interaction of cyclodextrins functionalized with polyamines with Cu^{2+} or Zn^{2+} results in cyclodextrins flexibly capped by metal ions, which causes increased binding of the substrate.[4] The difference in the effects of Cu^{2+} and Zn^{2+} seems to arise from different coordination geometry and/or coordination number between Cu^{2+} and Zn^{2+}.[9,10] Contrast to the enhancement of the binding affinity of the substrate with CDen or CDdien by the addition of the metal ions, the k_ψ^{CD} value gets smaller and becomes not much different with that of β-CD itself. This suggests that the enhanced binding by the flexible capping does not give the proper geometry for the nucleophilic interaction between the C-2 oxido group of the CD and the carbonyl carbon atom of the substrate.

In conclusion, this work demonstrates that functionalization of β-CD with polyamines increases the reactivity of *m*-nitrophenyl acetate complexed with the host molecules. Addition of divalent metal ions enhances binding affinity of the ester, but decreases the reactivity of the complexed substrate.

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Nitrosation Products of *N*-Acyl-N'-Substituted Phenylhydrazines

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A large number of cytostatic 2-chloroethyl-nitrosoureas[1-12] have been synthesized and evaluated for antitumor activity against murine leukemia L1210 implanted either intraperitoneally or intracerebrally. The nitrosoureas decompose to yield an isocyanate and a variety of other reactive species.[13] The interaction of one or more of these reactive moieties with biologically active macromolecules is thought to be responsible for the anticancer activity and the cytotoxicity of