

MOLECULAR DESIGN OF FUNCTIONAL POLYMERS BASED ON UNIQUE PROPERTIES OF POLYMER CHAINS

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Abstract The inclusion complex formation of α -CD, β -CD, and γ -CD with various water-soluble polymers has been investigated, and the relationship between the chain cross-sectional areas of the polymers and the diameters of the cavities of cyclodextrins (molecular recognition) was found. Polyrotaxanes and tubular polymers were prepared on the basis of molecular recognition. Several kinds of polymers having tetraphenylporphyrin (TPP) and paramagnetic metallotetraphenylporphyrin (AgTPP, CuTPP, VOTPP or ZnTPP) have been prepared by radical polymerization of the corresponding monomers. Visible spectra of these polymers show hypochromism in the Soret bands of TPP moieties as compared with those of monomers. Polymer effects were observed in the magnetic behavior and oxygen adsorption of paramagnetic metallotetraphenylporphyrin moieties. Moreover, polymer effects on photophysical and photochemical behavior were found in the amphiphilic polymers covalently tethered with small amounts of zinc(II)-tetraphenylporphyrin (ZnTPP).

Keywords Molecular recognition, Tubular polymer, Photofunction, Magnetic function, Oxygen adsorption

Polymer synthesis has developed remarkably along with the progress of petroleum chemistry, and the large number of polymer molecules plays an important role in human life as a class of materials, because polymers can be endowed with special functions ascribable to the physical and chemical properties of functional groups bonded to a polymer chain^[1, 2]. When special behavior of the polymer chain is added to the physical and chemical properties of the functional groups, new functions, which cannot be observed in the functional group itself, appear in the polymer. Unique behaviors of enzymes are examples of the polymer chain effect^[3]. Accordingly, a variety of papers have reported on the preparation of functional polymers to realize various kinds of function^[4]. Furthermore, in biological systems, unique properties may appear owing to molecular recognition and/or self-organization of polymer chains, suggesting further developments in polymer science. In my laboratory, my coworkers and I have performed research on three fields i.e., basic research on radical polymerization using ESR spectroscopy, new polymer synthesis, and the study of polymer chain effect on functions. In this review, I will mention a unique molecular recognition of polymer chains and the preparation of some new types of polymers on the basis of the recognition, and unique behaviors caused by the self-organization or aggregation of side groups of a polymer chain.

TUBULAR POLYMER SYNTHESIS ON THE BASIS OF MOLECULAR RECOGNITION

Molecular Recognition^[4, 5]

Numerous papers have been published on the inclusion complexes of cyclodextrins with low molecular mass organic compounds^[6, 7]. However, to our knowledge, there has been no report on the formation of complexes of cyclodextrins with polymers^[8]. We have undertaken research on the inclusion complexes of cyclodextrins with polymeric compounds since 1988.

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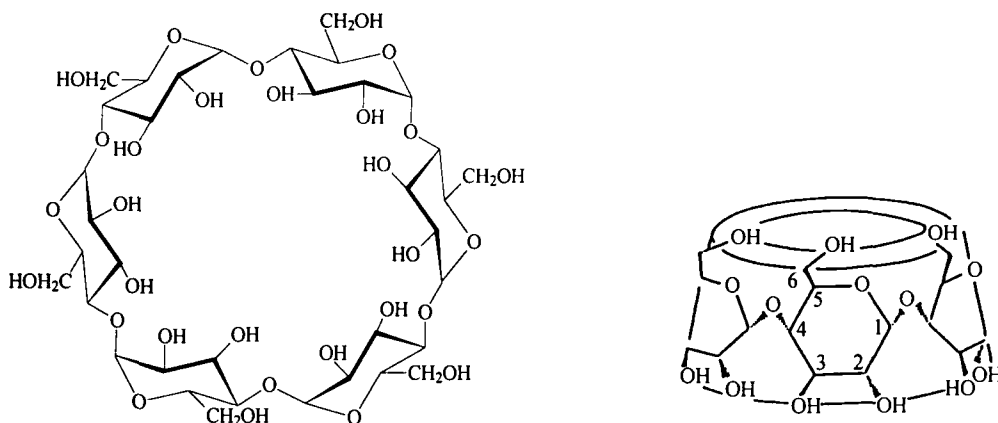


Fig. 1 Structure of α -cyclodextrin

We have observed (Fig. 1) that polyethylene glycol (PEG) selectively forms a complex with α -CD (diameter of cavity: 0.45 nm) in high yield; while polypropylene glycol (PPG), which has a larger cross-sectional area than PEG, selectively forms complexes with β -CD and γ -CD (diameter of cavity: 0.70 and 0.85 nm, respectively) in high yields; and polymethylvinyl ether (PMVE), which has the largest cross-sectional area, selectively forms a complex only with γ -CD in high yield. Table 1 shows the complex formation of three hydrophilic polymers with cyclodextrins^[9]. The results indicate that the relationship between the chain cross-sectional area of the polymers and the diameter of the cavities of cyclodextrins is very important in the complex formation of polymers with cyclodextrins. Studies on molecular models also show that a PEG chain can penetrate the α -CD cavity and has a good fit with this cavity. Although a PEG chain can penetrate the β -CD cavity it is too thin to fit in the cavity. While a PPG chain can penetrate both the β -CD and γ -CD cavities and fit in the cavities, this is not the case for α -CD. A PMVE chain can only penetrate the γ -CD cavity and fit in the cavity^[10]. These facts derived from the model are in accordance with our results shown in Table 1.

Table 1. Comparison of hydrophilic polymers with various chain cross-sectional areas in formation of crystalline complexes with cyclodextrins

Polymer	Structure	Yield (%)		
		α -CD ^a	β -CD ^b	γ -CD ^c
PEG ($M_w = 1000$)	$-(\text{CH}_2\text{CH}_2\text{O})_n-$	92	0	trace
PPG ($M_w = 1000$)	$-(\text{CH}_2\text{CHO})_n-$	0	96	80
	$\begin{array}{c} \text{CH}_3 \\ \\ -(\text{CH}_2\text{CHO})_n- \end{array}$			
PMVE ($M_w = 2 \times 10^4$)	$\begin{array}{c} \text{O} \\ \\ \text{CH}_3 \end{array}$	0	0	67

a) α -CD saturated aqueous solution, 1.5 mL; polymers, 15 mg; b) β -CD saturated aqueous solution, 7 mL; polymers, 15 mg; c) γ -CD saturated aqueous solution, 2 mL; polymers, 15 mg

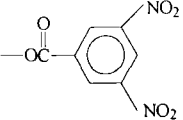
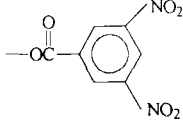
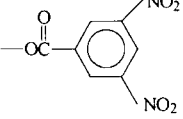
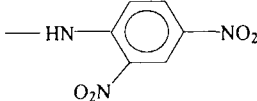
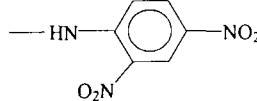
These findings suggest that a polymer chain can penetrate the cavities of cyclodextrins.

In order to confirm this suggestion, the complex formation between α -CD and PEG with various end groups was investigated. Results are shown in Table 2.

PEGs with small end groups, such as hydroxyl, methyl and amino groups can form complexes with α -CD in high yield, while PEG having a 3,5-dinitrobenzoyl group or a 2,4-dinitrophenyl group, which cannot go through the α -CD cavity at both ends, does not form any complexes with α -CD. On the other hand, polypropylene glycol does not form a complex except when the polymer has a bulky group at one end and a methoxy group at the other end. In order to get more quantitative information on the complex formation, we drew the continuous variation

plot between α -CD and PEG. Results are shown in Fig. 2. The plot shows a maximum at the molar ratio of 0.33 (α -CD), suggesting that the ratio of ethylene glycol units to CD is 2.

Table 2. Complex formation between CD and PEG with various end groups

R-(CH ₂ CH ₂ O) _n -CH ₂ CH ₂ R'			Yield (%)	
R	R'	M _w	α -CD	β -CD
-OH	-OH	1000	90	0
-NH ₂	-NH ₂	1450	90	0
-OCH ₃	-OCH ₃	1000	93	0
		900	0	0
	-OCH ₃	900	77	10
		3700	0	0

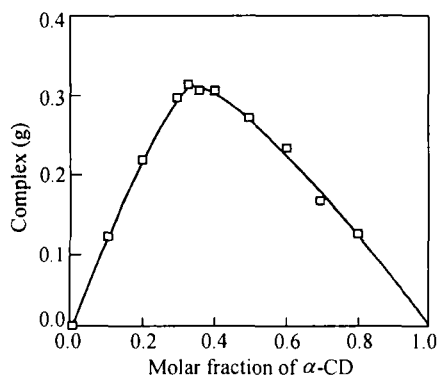


Fig. 2 Continuous variation plot for the complex formation between α -CD and PEG ($M_w = 1000$). The total amount of α -CD and ethylene glycol unit of PEG was fixed at 1.13×10^{-3} mol/L.

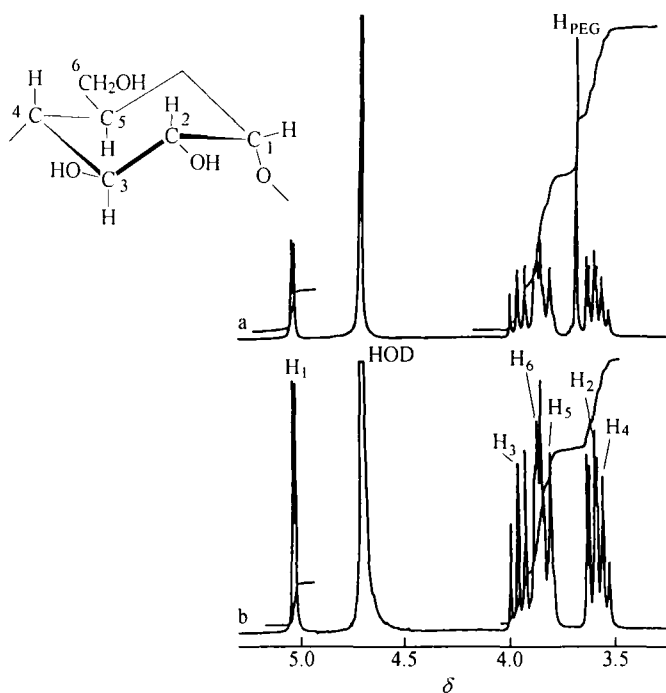
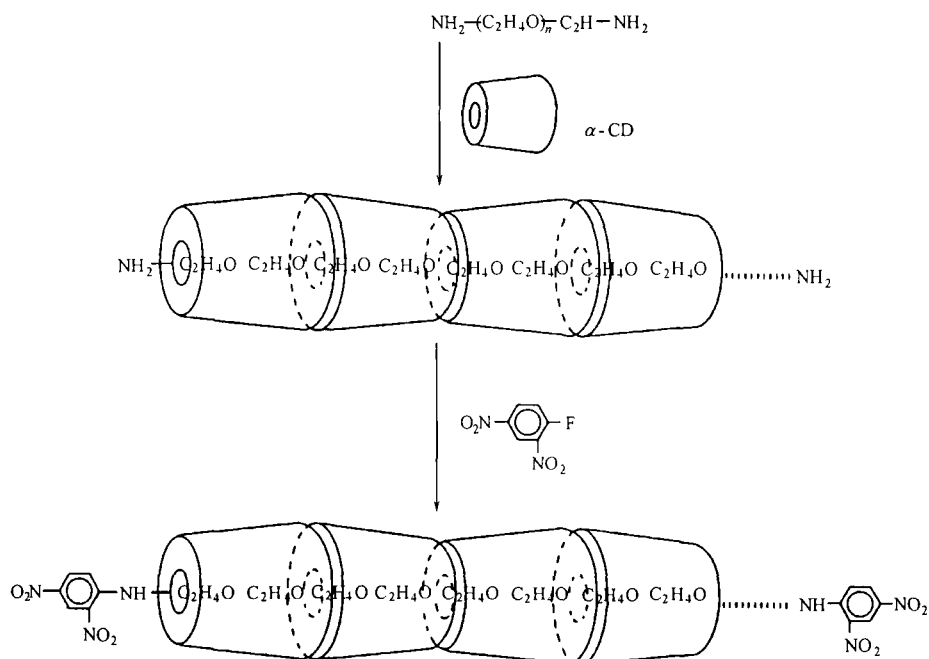


Fig. 3 270 MHz ¹H-NMR spectra of α -CD-PEG-600 complex a) and α -CD b) in D₂O at 30°C

¹H-NMR spectra of α -CD and its complex with PEG are shown in Fig. 3. In the spectrum of the complex (Fig. 3a), an extra signal due to methylene protons of the ethylene glycol unit was clearly observed. Since the peak due to proton bonded with C1 carbon was clearly observed in this spectrum, we could estimate the ratio of the ethylene glycol unit to CD by using this extra signal. The ratio is 8 to 6, which means that CD cavity has two

Polyrotaxane^[12a, b]

We prepared polyrotaxanes by the method shown in Scheme 1. PEG with amino groups was used as starting material. The inclusion complex obtained from α -CD and the PEG were allowed to react with 2,4-dinitro-1-fluorobenzene in DMF to form polyrotaxane which has amino groups at both ends. The reaction was followed by column chromatography on Sephadex G-50 with DMSO as the solvent. Absorption at 360 nm due to dinitrophenyl group and optical rotation due to CD were used for detection and the elution curve obtained is shown in Fig. 7. F1 was detectable by both detectors. F2 was detected by absorption, while F3 was detected by optical rotation. NMR spectra of each fraction in DMSO- d_6 at room temperature are shown in Fig. 8. F2 is assigned to PEG with dinitrophenyl substituents at both ends, F3 is cyclodextrin itself, and F1 belongs to polyrotaxane.



Scheme 1

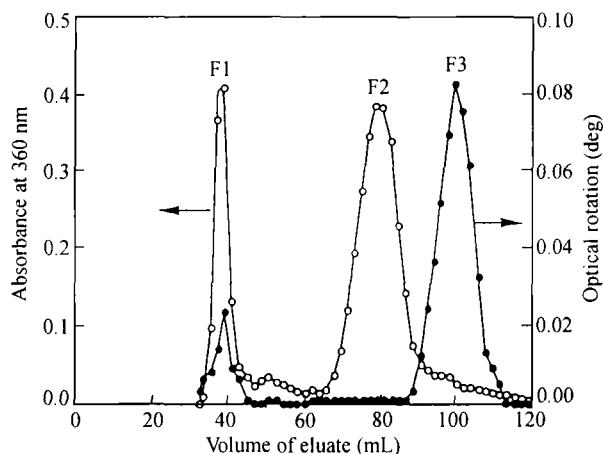


Fig. 7 Elution diagram of the reaction mixture of the α -CD-PEGBA-1450 complex with 2,4-dinitro-1-fluorobenzene
 A Sephadex G-50 column (1.7 $\times$ 70 cm) with DMSO solvent was used.

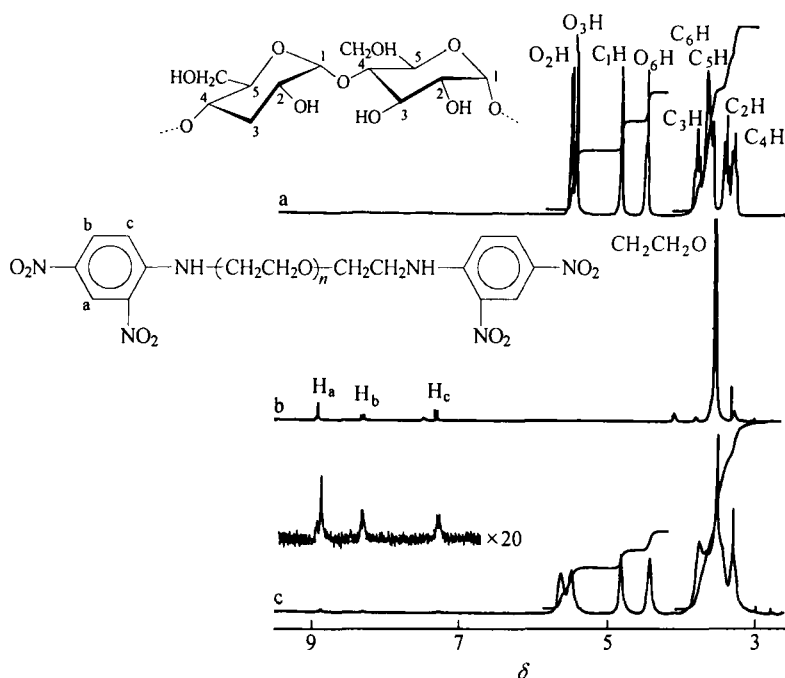


Fig. 8 270 MHz ^1H -NMR spectra of α -CD a), PEG-DNP₂ b) and MN-3350 c) in $\text{DMSO-}d_6$ at 30°C

It is observable that the ^1H -NMR spectrum of α -CD in $\text{DMSO-}d_6$ at room temperature shows sharp peaks, because α -CD can move freely in the solution. But for polyrotaxane, the situation is quite different as we can see in Fig. 8, which shows broadened peaks of α -CD.

The 2D NOESY NMR spectrum of rotaxane MN-3350 is shown in Fig. 9. The spectrum shows that the signals of H-3 and H-5 protons of α -CD, which are directed toward the inside of the cavity of α -CD, correlate with the resonance of the CH_2 of PEG, and the H-1, H-2 and H-4 protons, which are located outside the cavity, do not correlate with PEG. These results indicate that a PEG chain is included in the cavities of α -CD.

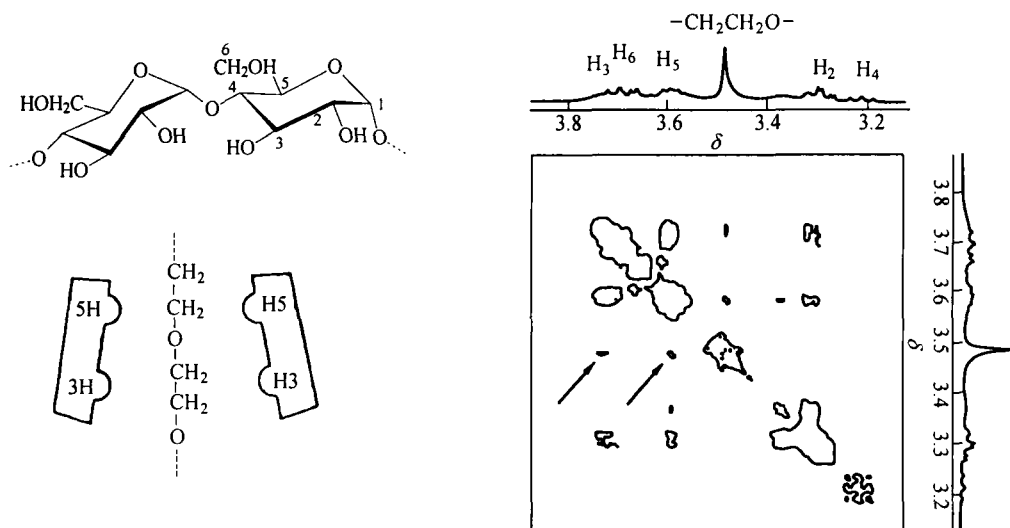


Fig. 9 2D NOESY NMR spectrum of MN-3350 in $\text{D}_2\text{O-NaOD}$ at 30°C . Arrows show the correlation peaks.

Rotaxanes of different molecular weight were prepared by a similar method. The molar ratio of ethylene glycol units to α -CD in polyrotaxanes prepared from α -CD-PEGBA gels is higher than 2:1 and increases with the increase in molecular weight of PEGBA used (Table 3). This is consistent with the fact that both included parts and non-included parts of PEG exist in the α -CD-PEG gel, and that the ratio of non-included parts of PEG to included parts increases with the increase in the molecular weight of PEG.

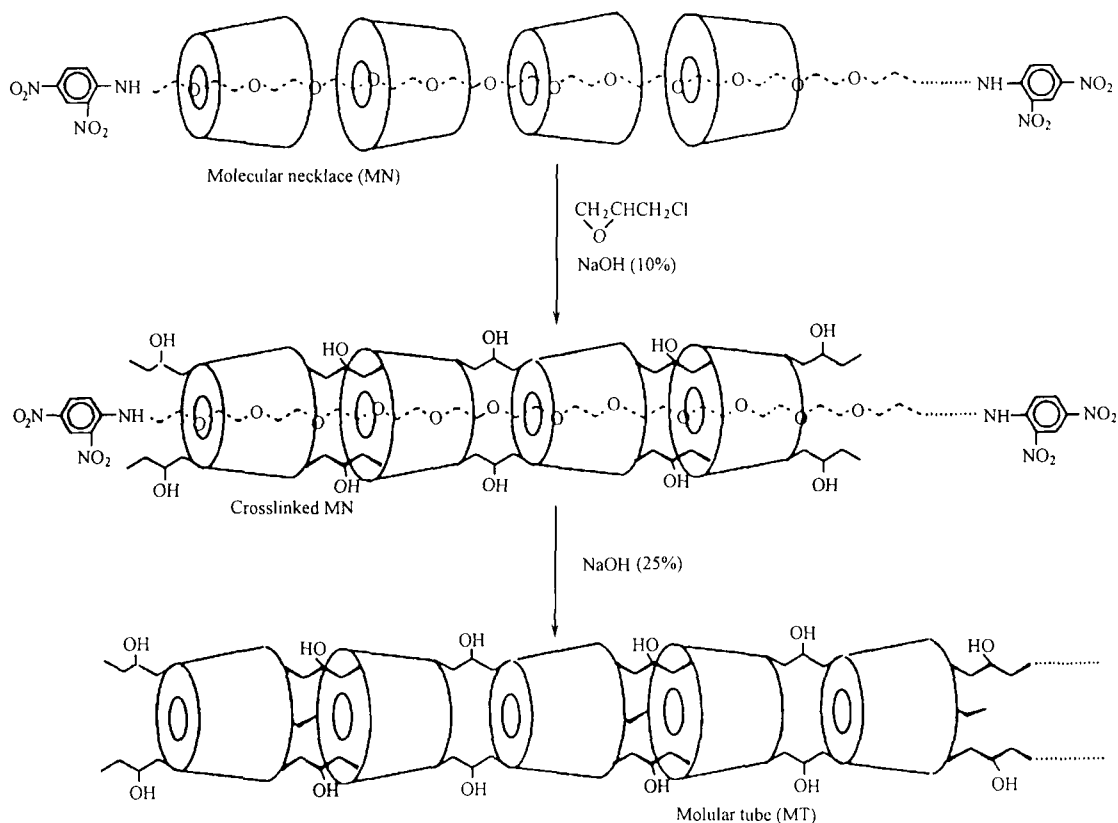
Table 3. Polyrotaxanes prepared from PEGBA with various molecular weight

Polyrotaxane	Molecular weight ^b	Number of ethylene glycol units (included+ non-included)	Number of threaded α -CD ^b	Molar ratio of ethylene glycol units to α -CD
MN-1450	16500	33 (33 + 0)	15	2.2
MN-2000	20000	45 (36 + 9)	18	2.5
MN*-2001 ^a	19000	45 (34 + 11)	17	2.6
MN-3350	23500	77 (40 + 37)	20	3.9
MN-8500	44000	193 (72 + 121)	36	5.4
MN-20000	89000	454 (140 + 314)	70	6.5

a) prepared from Jeffamine ED-2001, b) calcd. from UV-vis spectra, optical rotation and ¹H-NMR spectra

Tubular Polymers^[13]

The preparation of molecular tubes (MT) is shown in Scheme 2. To crosslink the α -CDs, the polyrotaxane was dissolved in 10% NaOH solution, to which epichlorohydrin was then added. The solution was stirred at room temperature for 36 h. The reaction mixture was neutralized by the addition of HCl. The yellow solid was precipitated from ethanol. In order to remove the bulky stoppers at both ends, the cross-linked polyrotaxane was treated with concentrated strong base (25% NaOH) at 45°C for 24 h. The reaction mixture was cooled and then neutralized with HCl. The product was separated by gel filtration and precipitation from THF.



Scheme 2 The preparation of molecular tubes (MT)^[11]

The molecular tubes are soluble in water, DMF and DMSO, although polyrotaxanes are insoluble in water and DMF, and soluble in DMSO. The product was characterized by elemental analysis, GPC, IR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectroscopy.

Figure 10 shows the elution diagram of the reaction mixture of polyrotaxane (MN-1450) with 25% NaOH a), the cross-linked MN-1450 b), the reaction mixture of the cross-linked MN-1450 with 25% NaOH c) obtained from a Sephadex G-25 column. After MN-1450 was treated with 25% NaOH and the solution was neutralized before bridging, two peaks were observed in the low molecular weight range of the diagram (Fig. 10a): one could be detected only by UV-vis (360 nm), which is assigned to the removed stopper dinitrophenol (DNP), and the other, which could be detected only by optical rotation, is identified as the dethreaded α -CD. In this case, α -CD was recovered. On the other hand, the cross-linked MN-1450 was eluted at the void volume of the column and was detected by both UV-vis and optical rotation as shown in Fig. 10b), which indicates that the cross-linked MN-1450 has high molecular weight and contains both dinitrophenyl group and α -CD. After the cross-linked MN-1450 was treated with concentrated strong base, two peaks appeared (Fig. 10c): one at the void volume, which is detected only by optical rotation, is identified as the product, the molecular tube (MT-1450). The second peak, which was detected only by UV-vis (360 nm), is assigned to dinitrophenol (DNP).

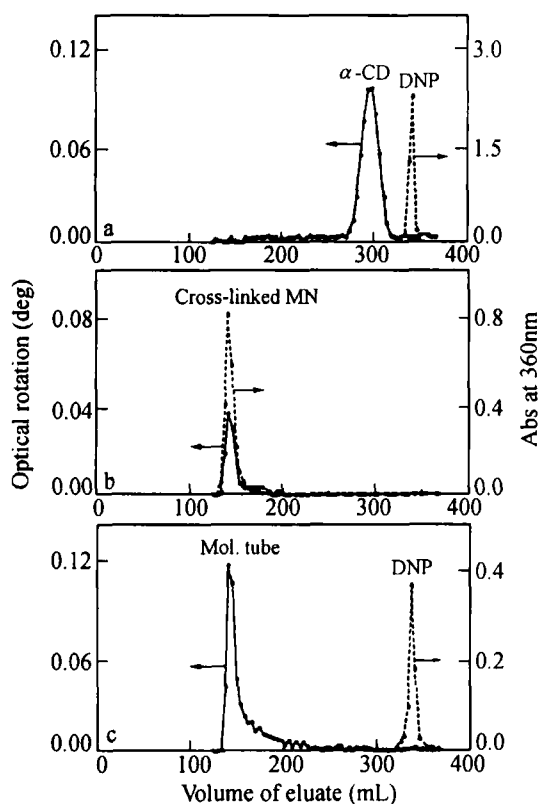


Fig. 10 Elution diagrams of the reaction mixture of polyrotaxane with 25% NaOH a), the cross-linked polyrotaxane (MN-1450) b), the reaction mixture of the cross-linked MN-1450 with 25% NaOH c) A Sephadex G-25 column (2.2×93 cm) with water eluate was used. Absorbance was measured at 360 nm with cell length 1 cm and optical rotation was measured at 589 nm with cell length 10 cm.

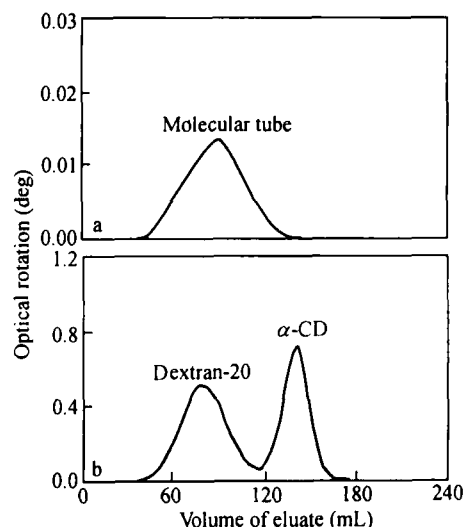


Fig. 11 Elution diagram of the molecular tube (MT-1450) a) and a mixture of dextran ($M_w = 2 \times 10^4$) and α -CD b) A Sephadex G-100 column (1.8×55 cm) with water eluate was used. Optical rotation was measured at 589 nm with cell length 10 cm.

Figure 11 shows the elution diagram of the molecular tube (MT-1450) obtained from a Sephadex G-100 column together with that of a mixture of dextran ($M_w = 2 \times 10^4$) and α -CD. The exclusion limit of a Sephadex

G-100 column is $4 \times 10^3 \sim 1 \times 10^5$. From a comparison between the two diagrams, it can be seen that the molecular tube was eluted just after dextran ($M_w = 2 \times 10^4$)^[13].

MAGNETIC PROPERTIES^[14]

Our attention was focussed on the functions of porphyrin and its derivatives which play an important role in photochemical systems and living systems^[15]. Polymers of vinyl monomers containing porphyrin moieties in their side chains have been prepared as a smaller amount of composition in their copolymers with other vinyl monomers^[16]. No high molecular weight homopolymer has been reported to be produced in the polymerization of vinyl monomers containing porphyrin moieties in their side chains. We succeeded in the preparation of high molecular weight polymers of acrylate and methacrylate containing porphyrin moieties in the side chains by radical polymerizations of 5-(4-acryloyloxyphenyl)-10,15,20-triphenylporphine (AOTPP) (1) and 5-(4-methacryloyloxyphenyl)-10,15,20-triphenylporphine (MOTPP) (2)^[17-19]. Hypochromism in the Soret band of porphyrin moieties of these polymers was clearly observed in the measurements of UV and visible spectra, indicating that there is an electronic interaction between porphyrin moieties in the polymers (Fig. 12). When paramagnetic metal ions were introduced into porphyrin moieties, an ordering of the spins through an exchange interaction of unpaired electrons was observed in the polymer. Furthermore, a unique polymer effect was apparent as oxygen adsorption in these polymers, which is not observed in the corresponding monomers. We prepared the polymers containing tetraphenylporphyrin (TPP) moieties, which had paramagnetic metal ions (Cu(II), Ag(II), VO(II), and Co(II)) in the TPP moieties of polymers 1 and 2, and investigated their magnetic properties by ESR and magnetic susceptibility measurements (χ_M)^[17].

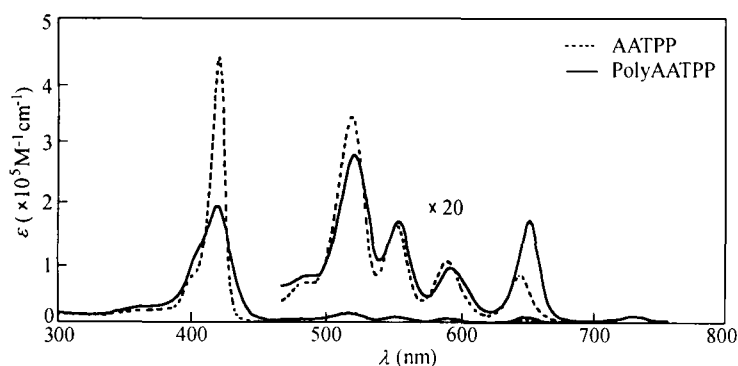
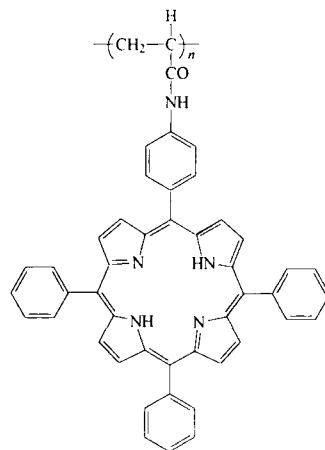


Fig. 12 UV-visible spectra of AATPP and polyAATPP



ESR spectra of the polymer with Ag(II) and the corresponding monomer are shown in Fig. 13. The ESR spectrum of the polymer is a symmetrical single line, while that of the corresponding monomer has anisotropic line shape. This finding shows that exchange interaction between Ag(II) ions is easier in the polymer than in the corresponding monomer. A similar polymer effect was observed in the polymer with other paramagnetic metal ions such as VO(II) and Cu(II).

The measurements of temperature dependence of the magnetic susceptibility of these polymers showed that paramagnetic species bound to polymer chains interact antiferromagnetically (Fig. 14), and that the interaction is much larger than that of the corresponding monomer units^[17-19]. Especially, a remarkable polymer effect on the magnetic behavior was clearly observed in the case of polyAOTPPAg(II), and the origin of the antiferromagnetic behavior in the polymer has been ascribed to the superexchange interaction through the C=O group between Ag(II) ions. We attempted to extend our study to polymers containing different paramagnetic ions. Copolymers containing both TPPCu(II) and TPPVO(II) in their side chains were prepared by the radical copolymerization of

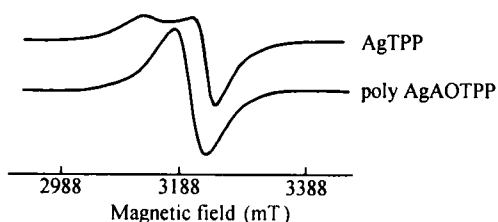


Fig. 13 ESR spectra of TPPAg (II) and polyAOTPP Ag (II) powders at room temperature

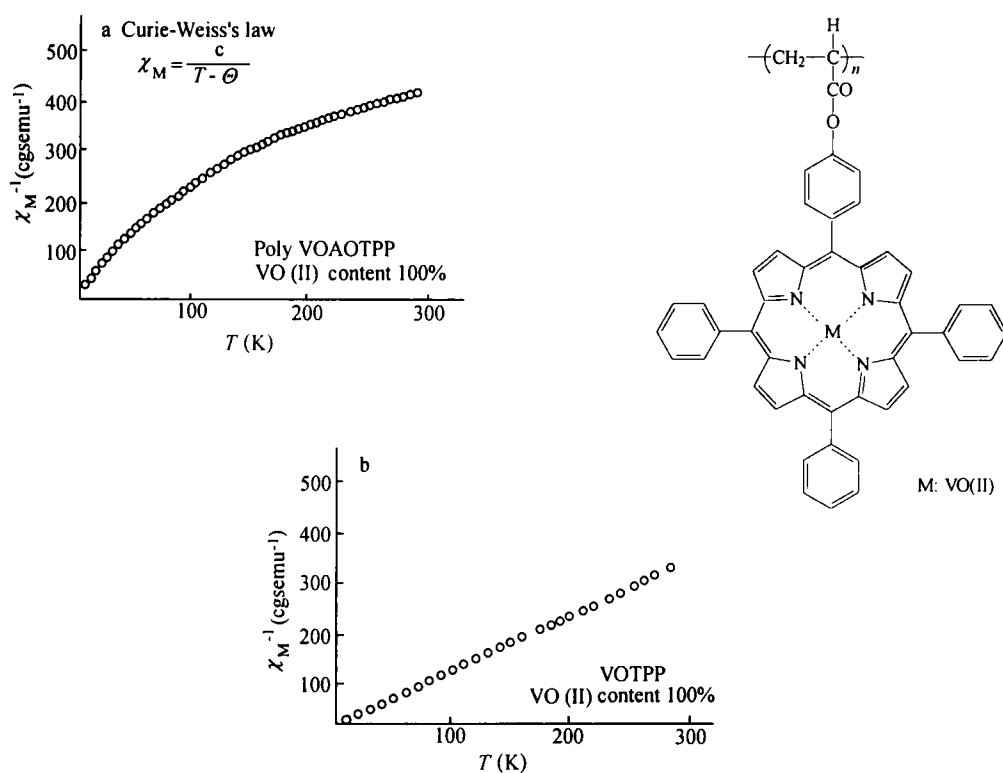


Fig. 14 Temperature dependence of magnetic susceptibility of polyVOAOTPP a), VOTPP b)

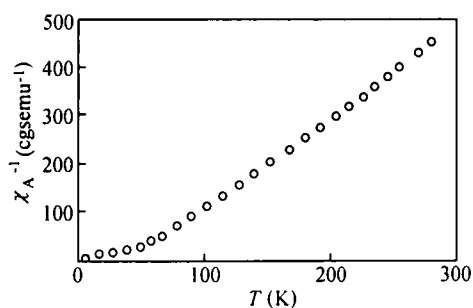


Fig. 15 Magnetic behavior of poly(AOTPPCu(II)-co-AOTPPVO(II))

AOTPPCu(II) and AOTPPVO(II), whose metal ions have d_9 and d_1 , respectively^[20]. The temperature dependence of the magnetic susceptibility follows the Curie Weiss law with $\theta = 50$ K (Fig. 15), indicating the existence of

ferromagnetic interaction between TPPCu(II) and TPPVO(II) moieties. Since the magnetic behaviors of both polyAOTPPCu(II) and polyAOTPPVO(II) are antiferromagnetic, the ferromagnetic behavior of the copolymer can be ascribable to the ferromagnetic interaction of Cu(II) and VO(II).

It appears that organic ferromagnetic polymers will be available in the future, although many problems will have to be solved in the production of magnetic materials.

OXYGEN ADSORPTION^[21]

The temperature dependence of ESR signals was measured on powder samples of the monomer and polymer containing the porphyrin moieties under various atmospheres. Figure 16 shows the results for polyAgAATPP and AgAATPP under air. The spectral shapes were different between the monomer and the polymer because of the spin exchange interaction in the polymer side chain, as reported previously for other Ag-porphyrin polymers. As a result, the anisotropy observed in AgAATPP disappeared in its polymer form^[21]. Figures 17a) and 17b) show the plots of the relative intensity of the ESR signal against temperature for AgAATPP and polyAgAATPP, respectively. In the case of the polymer, the signal intensity increased with a decrease in temperature under vacuum, but it decreased under air and under oxygen. The intensity started to decrease at higher temperature in an oxygen atmosphere than under air. Based on these facts, we suspected that AgTPP moieties in the polymer interacted with dioxygen molecules at low temperature to form an ESR inactive species. When the temperature was raised again, the signal became more intense, indicating that this behavior was reversible.

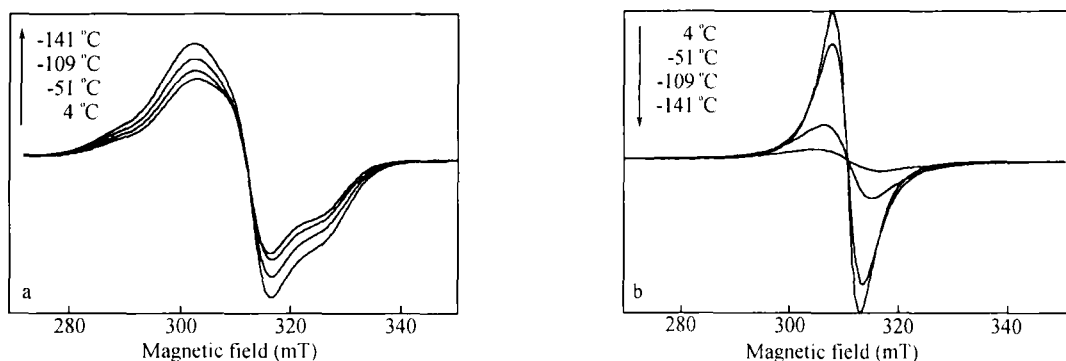


Fig. 16 Temperature dependencies of ESR spectra of AgAATPP a) and polyAgAATPP b) under air

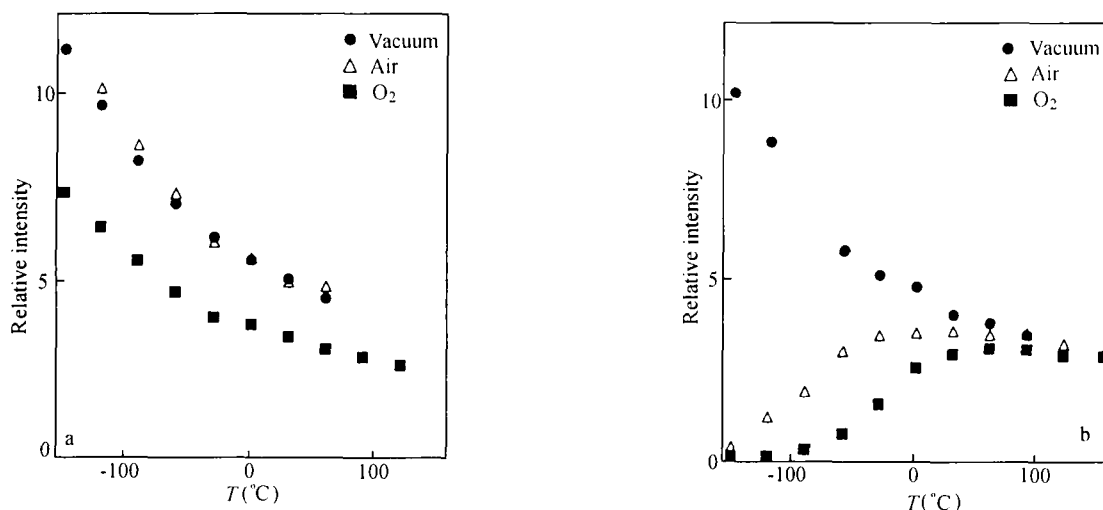


Fig. 17 Temperature dependencies of ESR spectra of AgAATPP a) and polyAgAATPP b)

In order to get further information on the appearance of ESR inactive species due to the interaction between

dioxygen molecules and AgTPP, IR and Raman spectra of the polymer were measured in the temperature region from 20°C to -180°C under oxygen and compared with those of the corresponding monomer. In the IR spectrum, a new peak appeared at 728 cm⁻¹ in the presence of oxygen when the sample was cooled by liquid nitrogen, and this peak was not observed in a nitrogen atmosphere even at low temperature. When the same measurements were performed under 1.01×10^5 Pa of ¹⁸O₂, the peak shifted to lower wave number (isotope effect). Accordingly, the peak at 728 cm⁻¹ is assignable to an oxygen adduct of AgTPP moieties^[21]. In the Raman spectrum, a new peak appeared at 545 cm⁻¹ in an oxygen atmosphere even below -180°C (Fig. 18). Therefore, this peak can be assigned to the adduct of O₂ and AgTPP moieties. This is a polymer effect on O₂ adsorption.

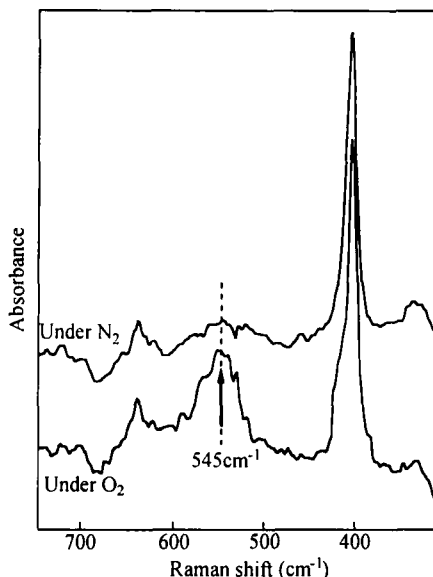


Fig. 18 Raman spectra of polyAgAATPP at 88 K, under N₂ (upper curve) and under O₂ (lower curve)

PHOTOCHEMICAL BEHAVIOR^[22~25]

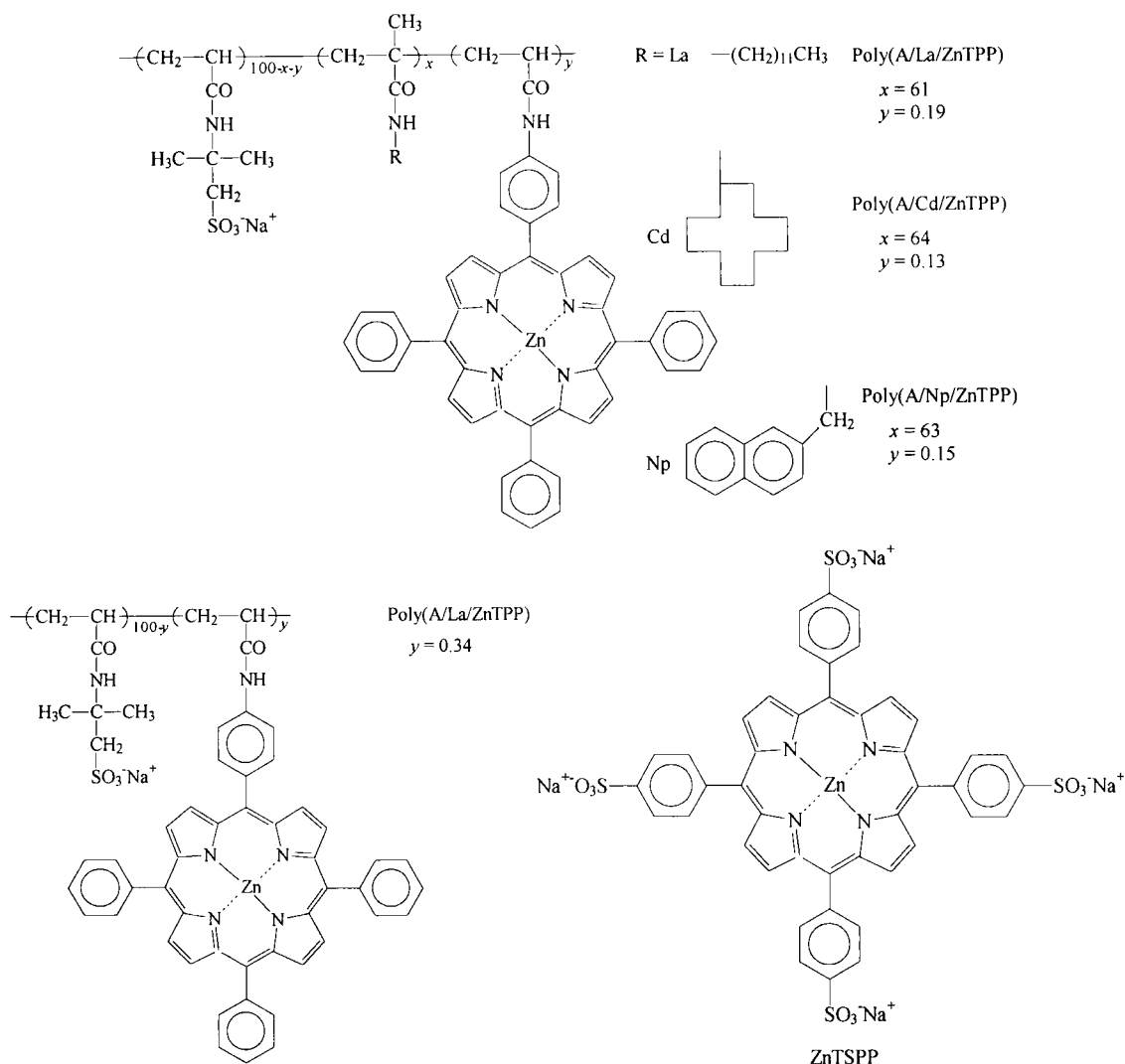
Thirdly, we paid attention to the photoactive function of polymers containing metalloporphyrin moieties for further investigation of polymer functionality. Amphiphilic polyelectrolytes which load hydrophobic substituents above a critical content form hydrophobic domains due to aggregation of the hydrophobic groups in aqueous solution^[22].

Amphiphilic Polyelectrolyte and Referenced Polyelectrolyte

Amphiphilic polyelectrolytes with a small amount of ZnTPP moieties, as shown in the Scheme 3, were prepared by terpolymerizations of sodium 2-acrylamido-2-methylpropane sulfonate (AMPS), *N*-substituted methacrylamide containing bulky hydrophobic groups [R: lauryl (La), cyclododecyl (Cd), and 2-naphthylmethyl (Np)], and small amounts of [5-(4-acrylamidophenyl)-10,15,20-tetraphenylporphinatozinc(II)] (ZnAATPP)^[23, 24]. For comparison, polyelectrolyte with small amounts of ZnTPP, which is used as a reference copolymer, was prepared by radical copolymerizations of AMPS with small amounts of ZnAATPP.

Photophysical Behavior

The photophysical behavior of the amphiphilic polyelectrolytes containing ZnTPP was studied by absorption, fluorescence, phosphorescence, and transient spectroscopy. For comparison, the photophysical behavior of a polyelectrolyte with a small amount of ZnTPP and tetrakis(4-sulfonatophenyl)porphinatozinc (ZnTSPP) was also investigated under the same condition. Absorption spectra of the amphiphilic polyelectrolytes, reference copolymer, and ZnTSPP are shown in Fig. 19.



Scheme 3 Structures of amphiphilic polysulfonates and reference polyelectrolyte with ZnTPP moieties, and their abbreviation

In aqueous solution, the absorption maxima for the Soret band of the amphiphilic polyelectrolytes were red-shifted by 5–9 nm as compared to those of the reference copolymer and ZnTSPP, whose ZnTPP moieties are exposed to water. In DMF, the Soret band of the amphiphilic polyelectrolytes is the same as those of the reference copolymer and ZnTSPP. These observations indicate that in aqueous solution the ZnTPP moieties in the amphiphilic polyelectrolytes and those in the reference copolymer and ZnTSPP exist in different environments. The results show that ZnTPP moieties in the amphiphilic polyelectrolytes are expected to exist in hydrophobic domains of the polymers in aqueous solution, while those in the reference copolymer and ZnTSPP are exposed to the aqueous solution. Fluorescence spectra of amphiphilic polyelectrolyte and reference copolymer in aqueous solution at 25°C are shown in Fig. 20. Fluorescence bands of amphiphilic polyelectrolyte shift to lower wave length about 10 nm lower than those of reference copolymer, which indicates that the ZnTPP moieties of the amphiphilic polyelectrolyte and those of the reference copolymer in aqueous solution exist in different environments. Typical examples of the time-resolved transient absorption spectra for the amphiphilic polyelectrolytes and the reference copolymer are shown in Fig. 21.

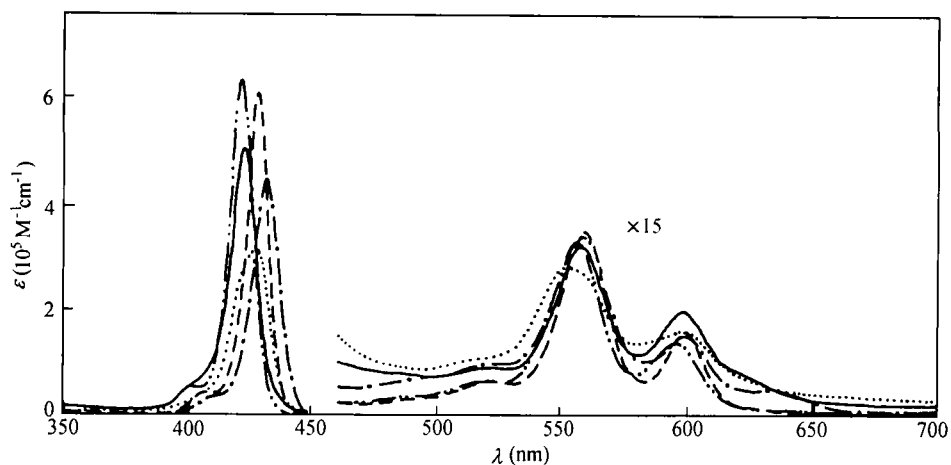


Fig. 19 Absorption spectra of the amphiphilic polyelectrolytes, reference copolymer, and ZnTSPP in water
 - - - poly(A/La/ZnTPP); - · - · - poly(A/Np/ZnTPP); ····· poly(A/Cd/ZnTPP);
 — poly(A/ZnTPP); - - - - - ZnTSPP

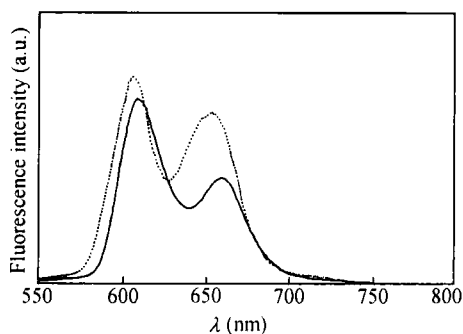


Fig. 20 Fluorescence spectra in aqueous solution by excitation at the maxima of the Soret band at room temperature
 — poly(A/Cd/ZnTPP); - - - poly(A/Cd)

The spectra were reasonably assigned to the T-T absorption band of the triplet state of ZnTPP moieties by comparing with the spectra of ZnTPP itself^[25-27]. Moreover, the triplet absorption bands of the amphiphilic polyelectrolytes persist for a longer time than those of the reference copolymer. Lifetimes of the T_1 state of the terpolymers and the reference copolymers were estimated from the decay profile of T_1 absorption at 480 nm. The estimated lifetimes for the amphiphilic polyelectrolytes and the reference copolymers in water and in DMF are shown in Table 4.

Lifetimes of the triplet states of the ZnTPP moieties in the amphiphilic polyelectrolytes at room temperature were much longer than that of the reference copolymer and those of small molecular weight ZnTPP moieties reported so far. Phosphorescence and thermally activated delayed fluorescence in the ZnTPP moieties in the amphiphilic polyelectrolytes were found, for the first time, in aqueous solution at room temperature. These unusual phenomena are reasonably ascribable to the compartmentalization of the ZnTPP moieties by the hydrophobic domains. Triplet lifetimes of ZnTPP itself have been reported to be 1.19 and 1.25 ms in ethanol and toluene solution at 300 K, respectively, while its phosphorescence lifetimes have been reported to be 25 and 26 ms in ethanol and toluene rigid glasses at 77 K, respectively. Unusually long lifetimes observed in the present study for the amphiphilic polyelectrolytes in aqueous solution at room temperature are due to a remarkable effect of the compartmentalization. The hydrophobic residues around the compartmentalized ZnTPP moieties serve not

only as protection groups for the chromophores but also as a rigid matrix for the chromophores similar to glasses at 77 K even though the amphiphilic polyelectrolytes are in fluid solution. The delayed emission spectrum for the amphiphilic polyelectrolytes in aqueous solution at 25°C is shown in Fig. 22. The emission bands were assigned to the fluorescence bands and phosphorescence bands. The reference copolymer and ZnTSPP did not showed such emission. Although ZnTPP has been reported to show both fluorescence and phosphorescence in rigid glasses at 77 K^[28–30], there is no paper which has reported both fluorescence and phosphorescence at room temperature in fluid solution. The delayed emission spectrum of the terpolymer was completely quenched under aerated condition as shown in Fig. 22, although fluorescence was far less sensitive to oxygen.

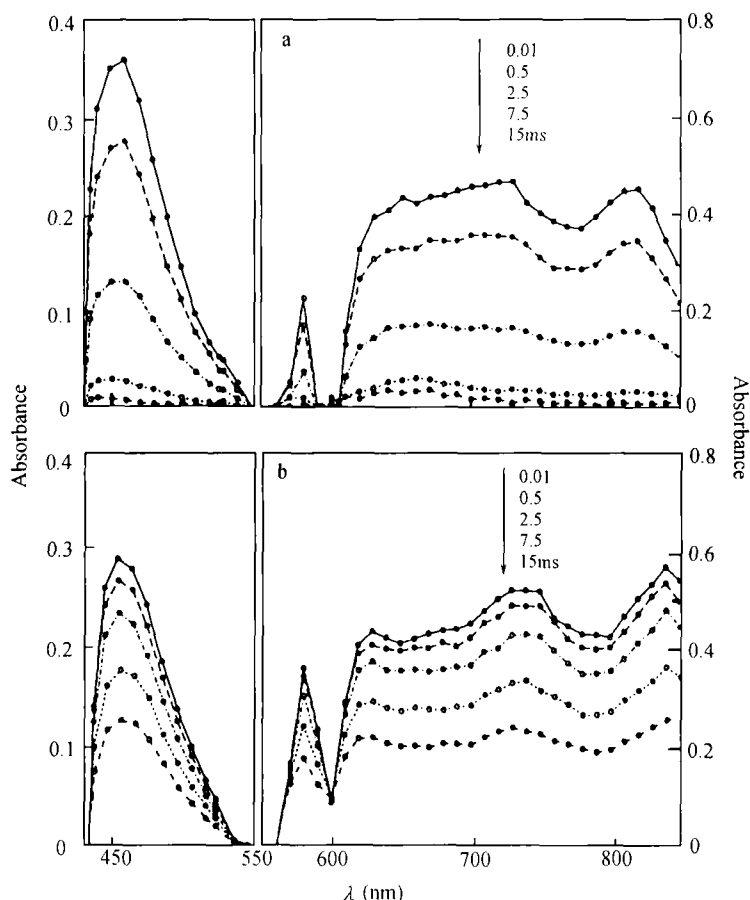


Fig. 21 Comparison of the time-resolved transient absorption spectra in aqueous solution at room temperature
a) poly(A/ZnTPP); b) poly(A/Cd/ZnTPP)

Table 4. Lifetimes of triplet excited states (τ_T) for the ZnTPP moieties in the terpolymers and reference copolymer at room temperature

Polymer	τ_T (ms)	
	In water	In DMF
Poly(A/La/ZnTPP)	12	3.7
Poly(A/Cd/ZnTPP)	20	4.3
Poly(A/Np/ZnTPP)	19	3.8
Poly(A/ZnTPP)	3.0	3.0*

* A mixture of DMF and water (9/1 volume ratio) was used for solubility reasons.

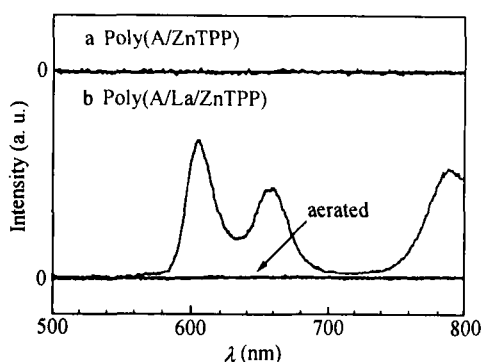


Fig. 22 Delayed emission spectra of poly(A/Cd/ZnTPP) and poly(A/ZnTPP) in aqueous solution at 25°C

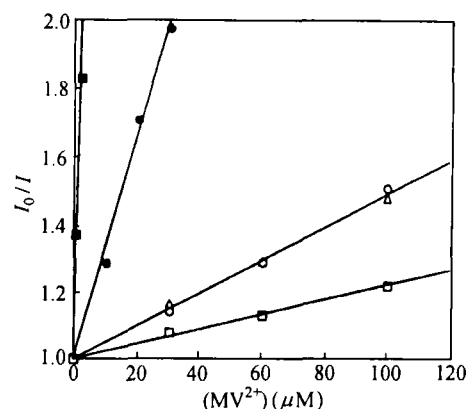


Fig. 23 Stern-Volmer plots for the ZnTPP fluorescence quenching by MV^{2+} in aqueous solution
 □ poly(A/Cd/ZnTPP), ○ poly(A/Na/ZnTPP),
 △ poly(A/La/ZnTPP), ■ poly(A/ZnTPP),
 ● ZnTSPP

Accordingly, it is concluded that the delayed fluorescence originates from the excited singlet state which was regenerated by the thermal activation of the triplet state. The observation of the phosphorescence and the delayed fluorescence at room temperature for the amphiphilic polyelectrolytes in aqueous solution is considered to arise from the unusually long lifetime of the ZnTPP moieties compartmentalized in the hydrophobic domain of the amphiphilic polymer.

Photochemical Behavior

The fluorescence spectra for ZnTSPP, poly(A/ZnTPP), and poly(A/CD/ZnTPP) in the absence and presence of MV^{2+} in aqueous solution were measured, and their Stern-Volmer plots are shown in Fig. 23. The Stern-Volmer constants obtained from the slope of the straight lines through the plots decrease in the following order: poly(A/ZnTPP) > ZnTSPP > poly(A/LA/ZnTPP) > poly(A/Nap/ZnTPP) > poly(A/CD/ZnTPP)^[25]. This order shows that ZnTPP moieties in the amphiphilic polyelectrolytes are compartmentalized by the hydrophobic domain.

Electron transfer quenching of the singlet excited state (S_1) of the ZnTPP moiety is known to occur in the presence of MV^{2+} ^[25, 27]. The effect of the compartmentalization on photochemical behavior was investigated in photoinduced electron transfer reaction of excited ZnTPP to methylviologen (MV^{2+}). We measured time resolved transient absorption spectra of the amphiphilic polyelectrolytes and poly(A/ZnTPP) reference copolymer in the presence of MV^{2+} . Typical examples are shown in Fig. 24. No transient absorption spectrum was observed for the reference copolymer, which is reasonably ascribable to electron back transfer reaction. In the amphiphilic polyelectrolyte accumulation of photoproducts, $ZnTPP^{+•}$ and $WV^{+•}$, was found on the microsecond time scale in spite of the reversible electron transfer system. When phenylmethylphenacylsulfonium *p*-toluenesulfonate (PMPS) was used as irreversible electron acceptor, the $ZnTPP^{+•}$ persisted over 20 min was detected by ESR spectroscopy, although no signal was observed in the homogeneous system.

These results are ascribable to the suppression of the reaction between the $ZnTPP^{+•}$ moieties and other compounds by the compartmentalization.

CONCLUSION

Inclusion complex formation of α -CD, β -CD, and γ -CD with various water-soluble polymers has been investigated, and the relationship between the chain cross-sectional areas of the polymers and the diameters of the cavities of cyclodextrins (molecular recognition) was established. Polyrotaxanes and tubular polymers were prepared on the basis of molecular recognition. Several kinds of polymers having tetraphenylporphyrin (TPP)

and paramagnetic metallotetraphenylporphyrin (AgTPP, CuTPP, VOTPP or ZnTPP) have been prepared by radical polymerization of the corresponding monomers. Visible spectra of these polymers show hypochromism in the Soret bands of TPP moieties as compared with those of monomers. Polymer effects were observed in magnetic behavior and oxygen adsorption of paramagnetic metallotetraphenylporphyrin moieties. Absorption and emission spectra of ZnTPP moieties covalently linked to an amphiphilic polyelectrolyte in aqueous solution show that the ZnTPP moieties are compartmentalized in hydrophobic microdomains, which were constructed by the aggregation of hydrophobic substituents. The triplet excited lifetime of the compartmentalized ZnTPP moieties at room temperature was found to be much longer, and phosphorescence and delayed fluorescence were observed even at room temperature.

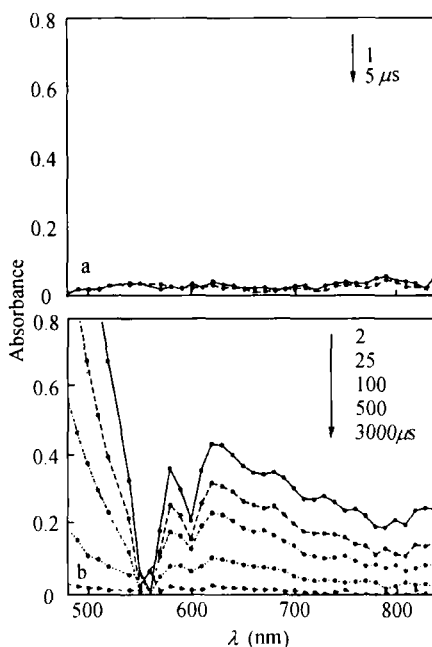


Fig. 24 Time resolved transient absorption spectra of poly(A/ZnTPP) a) and poly(A/CD/ZnTPP) b) in the presence of MV^{2+} [$ZnTPP$ moiety] = 100 μ mol/L; [MV^{2+}] = 5 mmol/L

The electron transfer reaction from ZnTPP moieties to MV^{2+} was investigated by fluorescence spectroscopy and transient absorption spectroscopy. In the amphiphilic polyelectrolytes, $MV^{+•}$ was clearly observed in transient spectroscopy, indicating that electron back transfer reaction is retarded significantly owing to the compartmentalization of ZnTPP moieties.

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REFERENCES

- 1 Morawetz, H., "Macromolecules in Solution", 2nd Ed., (High Polymer Series XXI), Wiley, New York, 1974
- 2 Plate, N.A., Litmanovich, A.D. and Noah, O.N., "Molecular Reactions", John-Wiley, New York, 1995
- 3 Kyte, J., "Mechanism in Protein Chemistry", Garland, New York, 1995
- 4 Harada, A. and Kamachi, M., "Functional Monomer and Polymer". 2nd Ed., ed. by Takemoto, K., Ottenbrite, P.M. and

- Kamachi, M., Marcel Dekker, New York, 1997
- 5 Harada, A. and Kamachi, M., "New Macromolecular Architecture and Function", ed. by Kamachi, M. and Nakamura, A., Springer Verlag, Berlin, 1996
 - 6 Bender, M.L. and Komiyama, M., "Cyclodextrin Chemistry", Springer-Verlag, Berlin, 1978
 - 7 Szejtli, J., "Cyclodextrins and Their Inclusion Complexes", Akademia Kiado, Budapest, 1982
 - 8 Harada, A. and Kamachi, M., *Macromolecules*, 1990, 23: 2821
 - 9 Harada, A., Li, J. and Kamachi, M., *Macromolecules*, 1993, 26: 5698
 - 10 Harada, A., Li, J. and Kamachi, M., *Chem. Lett.*, 1993, 237
 - 11 Harada, A. and Kamachi, M., *Macromolecules*, 1994, 27: 4534
 - 12 a) Harada, A., Li, J. and Kamachi, M., *Nature*, 1992, 356: 325; b) Harada, A., Li, J. and Kamachi, M., *J. Org. Chem.*, 1993, 58: 7524
 - 13 Harada, A., Li, J. and Kamachi, M., *Nature*, 1993, 364: 516
 - 14 Kamachi, M., "Functional Monomer and Polymer", 2nd. Ed., ed. by Takemoto, K., Ottenbrite, P.M. and Kamachi, M., Marcel Dekker, New York, 1997, p.149
 - 15 Hawson, W.D. and Hager, L.P., in "The Porphyrins", Vol. 7, Part B, ed. by Dolphin, D., Academic Press, New York, 1979, p.295~332
 - 16 Tsuchida, E. and Nishide, H., *Top. Curr. Chem.*, 1986, 132: 63
 - 17 Kamachi, M., Akimoto, H., Mori, W. and Kishita, M., *Polym. J.*, 1984, 16: 23
 - 18 Nozakura, S. and Kamachi, M., *Makromol. Chem. Suppl.*, 1985, 12: 255
 - 19 Kamachi, M., Cheng, X.S., Kida, T., Kajiwarra, A., Shibasaka, M. and Nagata, S., *Macromolecules*, 1987, 20: 2665
 - 20 Kamachi, M., Cheng, X.S., Aota, H., Mori, W. and Kishita, M., *Chem. Lett.*, 1987, 2331
 - 21 Aramata, K., Kajiwarra, A., Kamachi, M., Umehara, Y. and Yamagishi, A., *Macromolecules*, 1998, 31: 3397
 - 22 Morishima, Y., Seki, M., Nomura, S. and Kamachi, M., *Proc. Japan, Acad., Ser. B*, 1993, 69: 83
 - 23 Morishima, Y., Nomura, S., Ikeda, T., Seki, M. and Kamachi, M., *Macromolecules*, 1995, 28: 2874
 - 24 Aota, H., Morishima, Y. and Kamachi, M., *Photochem. Photobiol.*, 1993, 57: 989
 - 25 Aota, H., Araki, S., Morishima, Y. and Kamachi, M., *Macromolecules*, 1997, 30: 4090
 - 26 Harriman, A., *J. Chem. Soc., Faraday Trans. 2*, 1981, 77: 1281
 - 27 Harriman, A., Porter, G. and Searle, N., *J. Chem. Soc., Faraday Trans. 2*, 1981, 75: 1515
 - 28 Richoux, M.C. and Harriman, A., *J. Chem. Soc., Faraday Trans. 1*, 1981, 78: 1873
 - 29 Hopf, F.R. and Whitten, D.G., in "Porphyrins and Metalloporphyrins", ed. by Dolphin, D., Elsevier, Amsterdam, 1975, p.667
 - 30 Hopf, F.R. and Whitten, D.G., in "The Porphyrins", Vol. 2, Part B, ed. by Dolphin, D., Academic Press, New York, 1979, p.161