

## UNIQUE BEHAVIORS OF POLYMERS HAVING METALLOPORPHYRIN AS THEIR SIDE CHAINS

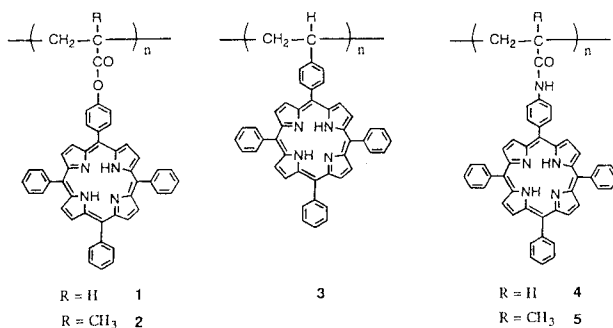
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**Abstract:** Several kinds of polymers having tetraphenylporphyrin (TPP) or some metallotetraphenylporphyrin (AgTPP, CuTPP, VOTPP or ZnTPP) moieties as their side chains have been prepared by the radical polymerization of the corresponding vinyl monomers. Visible spectra of these polymers show the clear hypochromism in the Soret bands of the tetraphenylporphyrin moieties as compared with those of the corresponding monomers. Polymer effects were clearly observed in the magnetic behaviors and the oxygen adsorption of paramagnetic metalloporphyrin moieties. In addition, polymer effects on photophysical and photochemical behaviors of ZnTPP were found in the amphiphilic polymers covalently tethered with small amounts of ZnTPP and hydrophobic substituents above a critical content, which form hydrophobic domains due to aggregation of the hydrophobic groups in aqueous solution.

## INTRODUCTION

Although polymer formation from vinyl monomers containing porphyrin moieties as their side chains have been prepared as a smaller amount of composition in their copolymers with other vinyl monomers [Refs. 1-3], no high molecular weight homopolymer has been reported to be produced in the polymerization of vinyl monomers containing porphyrin moieties in their side chains [Ref. 4]. This was considered to be due to the steric effect of the porphyrin moieties in ionic or radical polymerizations. We have succeeded in the preparation of high molecular weight polymers of acrylate, methacrylate, acrylamide, methacrylamide and vinyl monomer containing porphyrin moieties in the side chains by radical polymerizations of 5-(4-acryloxyphenyl)-10,15,20-triphenylporphine (AOTPP) (1) and 5-(4-methacryloxyphenyl)-10,15,20-triphenylporphine (MOTPP) (2), 5-(4-vinylphenyl)-10,15,20-triphenylporphine (VTPP) (3) [Refs. 4-6], 5-(4-acrylamidophenyl)-10,15,20-triphenylporphine (AATPP) (4) and 5-(4-methacrylamidophenyl)-10,15,20-triphenylporphine (MATPP) (5) [Refs. 4-7]. 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. Accordingly, we considered that



polymers having paramagnetic species in their side chains might be new magnetic materials, because an ordering of the spins of paramagnetic species through an exchange interaction of unpaired electrons seemed to be possible in the polymers.

Secondly, unique polymer effect on the oxygen adsorption in polymers having silver-tetrakis(4-phenylphenyl)porphyrin (AgTPP) moieties in their side chains is shown [Ref. 8]. In the course of ESR study on the polymer effect on the magnetic behavior, we came across the fact that the intensities of the ESR spectra decrease with lowering the temperature. Since such a change in intensity is not observed in the ESR measurement of the corresponding monomers, polymer chain is considered to play an important role in the oxygen adsorption.

Thirdly, we paid attention to photoactive function of polymers containing metalloporphyrin. Amphiphilic polyelectrolytes which load hydrophobic substituents above a critical content form hydrophobic domains due to aggregation of the hydrophobic groups in aqueous solution [Refs. 9,10]. In the amphiphilic polymers covalently tethered with small amounts of zinc(II)-tetrakis(4-phenylphenyl)porphyrin (ZnTPP), recently, we found that photochemical and photophysical behaviors of ZnTPP moieties were remarkably different in aqueous solution from those of ZnTPP moieties in homogeneous system [Refs. 11-13].

In this paper, I will present polymer effects on functionality of porphyrin moiety, which have been found in my laboratory.

## RESULTS AND DISCUSSION

### Hypochromism

UV-visible spectra of AATPP and polyAATPP are shown in Figure 1 [Ref. 10]. Both compounds have the Soret band at 411 nm and Q-bands in the region from 500 to 700 nm, as shown in the spectra of metalloporphyrins. The wavelength of the Soret band of polyAOTPP is similar to that of TPP. However, the molecular extinction coefficient of the former is smaller than that of TPP, which can be ascribable to the hypochromism due to the electronic

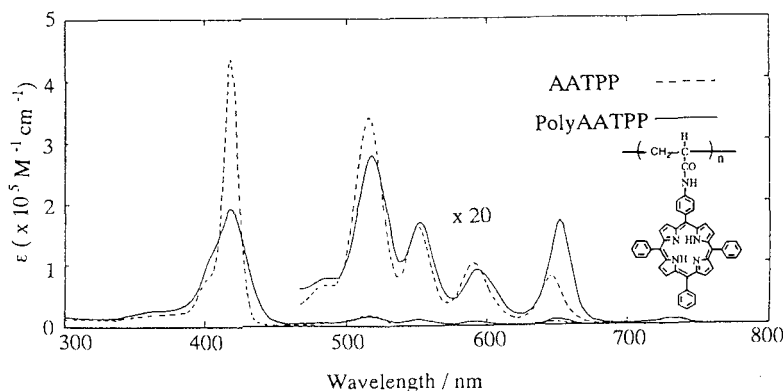


Figure 1. UV-Visible spectra of AATPP and PolyAATPP.

interaction of TPP moieties bonded to the polymer. Since the spectrum of the polymer does not change with the dilution of the concentration, the interaction is ascribable to the interaction of the TPP moieties of a polymer chain. Accordingly, if polymers, which have paramagnetic metalloporphyrin (M-TPP)] as their side chain, can be prepared, magnetic interaction might appear between paramagnetic metalloporphyrin bonded to a polymer chain.

### Magnetic Properties

We prepared the polymers having tetraphenylporphyrin (TPP) moieties, which had paramagnetic metal ions (Cu(II), Ag(II), VO(II), and Co(II)) into TPP moieties of polymers 1-5 and investigated their magnetic properties by ESR and magnetic susceptibility measurements ( $\chi_M$ ) [Refs. 4-6, 10, 11].

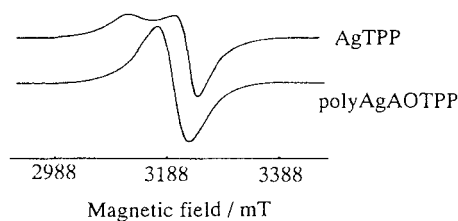


Figure 2. ESR spectra of AgTPP and polyAgAOTPP powders at room temperature.

ESR spectra of the polymer with Ag(II) and the corresponding monomer are shown as an example in Figure 2. The ESR spectrum due to AgTPP moieties is a symmetrical single line in the polymer, while that of the corresponding monomer is composed of anisotropic line shape. This finding shows that the exchange interaction between Ag(II) ions is easier in the polymer than in the corresponding monomer. Similar polymer effect was observed in the polymer with other paramagnetic metal ions such as Cu(II), VO(II), and Co(II).

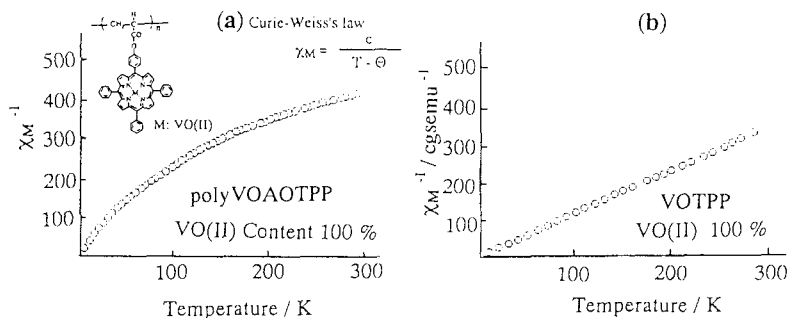


Figure 3. Temperature dependence of magnetic susceptibility of polyVOAOTPP (a), VOTPP (b).

The measurements of temperature dependence of the magnetic susceptibility of these polymers were performed. As an example, result of polyVOAOTPP is shown in Figure 2 along with that of VOTPP [Ref. 11], indicating that paramagnetic species bound to polymer chain interact antiferro-magnetically, and that the interaction is much larger than that of the corresponding monomer units [Refs. 4-6]. Similar polymer effects on magnetic interaction were observed in the measurements of the magnetic susceptibility of polymer with other paramagnetic metal ions. Although polymer effect was clearly observed in the magnetic

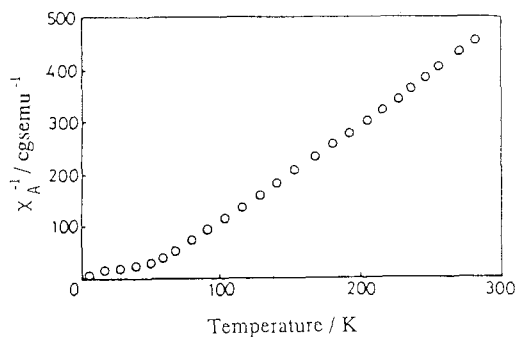


Figure 4. Temperature dependence of magnetic susceptibility of poly(CuAOTPP-co-VOAOTPP).

behavior, magnetic interaction observed was always antiferromagnetic. In order to get ferromagnetically interacting polymer, we attempted to expand this study to polymers containing different paramagnetic ions. Copolymers containing both CuATPP and VOTPP in their side chains were prepared by the radical copolymerization of CuAOTPP and VOAOTPP, whose metal ions have  $d^9$  and  $d^1$ , respectively [Ref. 9]. The temperature dependence of the magnetic susceptibility follows the Curie Weiss law with  $\theta=50$  K (Figure 4), indicating the existence of the ferromagnetic interaction between CuATPP and VOTPP moieties. Since magnetic behaviors of PolyCuAOTPP and polyVOAOTPP are respectively antiferromagnetic, the ferromagnetic behavior of the copolymer is probably ascribable to the ferromagnetic interaction of Cu(II) and VO(II).

Organic ferromagnetic polymers seem to be possible in the future, although there are a lot of problems to be solved for appearance of magnetic materials.

### Oxygen Adsorption

The temperature dependence of ESR signal was measured on the powder samples of the monomer and polymers containing the porphyrin moieties under various atmospheres. Figure 5 shows the results for polyAgAATPP and AgAATPP under air. The spectral shapes were

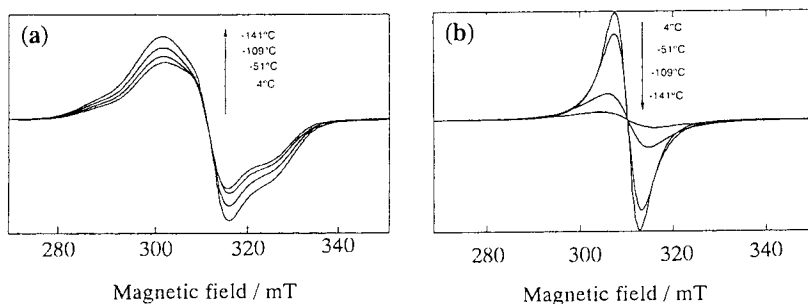


Figure 5. ESR spectra of AgAATPP and PolyAgAATPP.

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 [Ref. 12]. Figure 5(a) and 5(b) show the plots of the relative intensity of the ESR signal against temperature for AgAATPP and polyAgAATPP, respectively. In the case of the monomer, the signal intensity increased with a decrease in temperature under all conditions studied. In the case of the polymer, the signal intensity increased with a decrease in temperature under vacuum, while it decreased under air and under an oxygen atmosphere. The intensity started to decrease at a

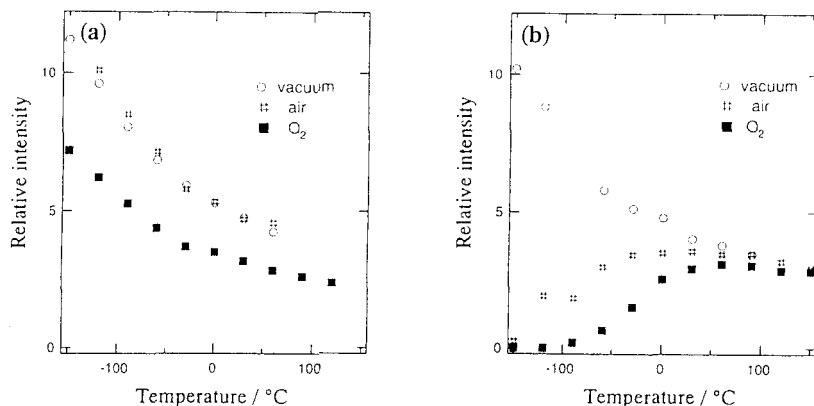


Figure 6. Temperature dependence of signal intensity  
(a) AgTTP, (b) polyAgAATPP.

higher temperature under an oxygen atmosphere than under air. Based on these facts, we suspected that the AgTTP moieties in the polymer interacted with dioxygen molecules at low temperature to form an ESR inactive species. When temperature was raised again, the signal intensity became larger, indicating that the behavior was reversible. Spectra of polyAgAOTPP under vacuum and in the presence of air are shown in Figure 6(b), respectively. Signal intensities increased with lowering the temperature under high vacuum, while the intensity decreased with lowering the temperature in the presence of air. Since the signal intensity of AgTTP increased in all cases with lowering the temperature, as shown in Figure 6(a), the decrease in the signal intensity in the presence of air and dioxygen is an unusual behavior [Ref. 12].

In order to get further information on the appearance of ESR inactive species due to the interaction between dioxygen molecules and AgTTP, 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 IR spectroscopy, new peak appeared at 728 cm<sup>-1</sup> in the presence of oxygen when the sample was cooled by liquid nitrogen, while the peak was not observed under an N<sub>2</sub> atmosphere even in the same temperature (Figure 7). When the same measurements were performed under 1 atm of <sup>18</sup>O<sub>2</sub>, the peak shifted to lower wave number (isotope effect). Accordingly, the peak at 728 cm<sup>-1</sup> is assignable to O<sub>2</sub> adduct of AgTTP moieties. In Raman spectroscopy, new peak appeared at 545 cm<sup>-1</sup> in the measurement under an O<sub>2</sub> atmosphere at -180 °C, while no peak was observed in an N<sub>2</sub> atmosphere even below -180 °C. Therefore, the peak is assigned to the adduct of O<sub>2</sub> and AgTTP moieties. This is polymer effect on O<sub>2</sub>-adsorption [Ref. 12].

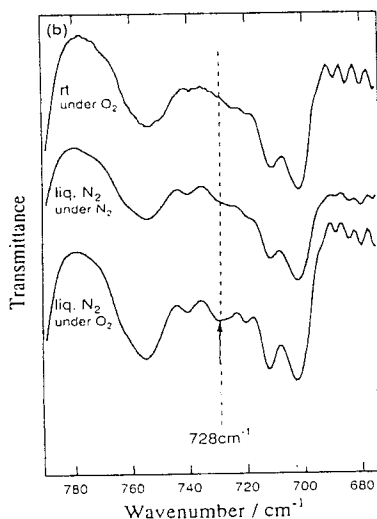
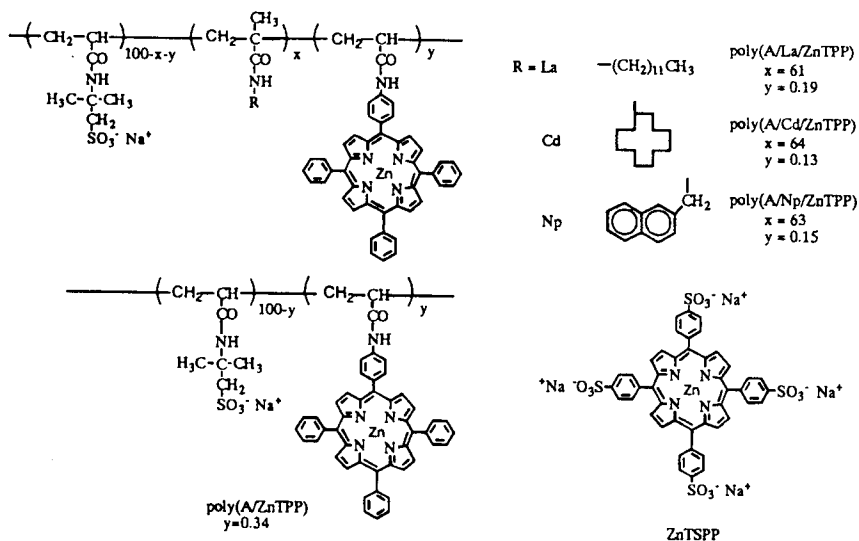


Figure 7. IR spectra of polyAgAATPP under various conditions.

### Photophysical and Photochemical Behavior

Amphiphilic polyelectrolytes with a small amount of ZnTPP moieties, as shown in the following scheme [Refs. 7, 13, 14], were prepared by terpolymerizations of sodium 2-



Scheme 1

acrylamide-2-hydrophobic groups [R: lauryl (La), cyclododecyl (Cd), and 2-naphthylmethyl (Np)], and small amounts of [5-(4-acrylamidephenyl)-10,15,20-tetraphenyl porphinato-

zinc(II)] (ZnAATPP) by their radical terpolymerizations [Refs. 7, 13-16]. Photophysical behavior of amphiphilic polyelectrolytes containing ZnTPP in aqueous solution was studied by absorption, fluorescence, phosphorescence, and transient spectroscopy. For comparison, polyelectrolytes with small amounts of ZnTPP were prepared by radical copolymerizations of AMPS with small amounts of ZnAATPP, and its photophysical behavior was investigated. Absorption spectra of terpolymer and copolymer containing a few amounts of ZnTPP moieties are shown in Figure 8. The absorption maximum of the Soret band shifted longer wavelength than that in DMSO (425 nm) which completely dissolves amphiphilic polyelectrolyte, while those of the copolymer and ZnTSPP were shorter than that in DMSO,

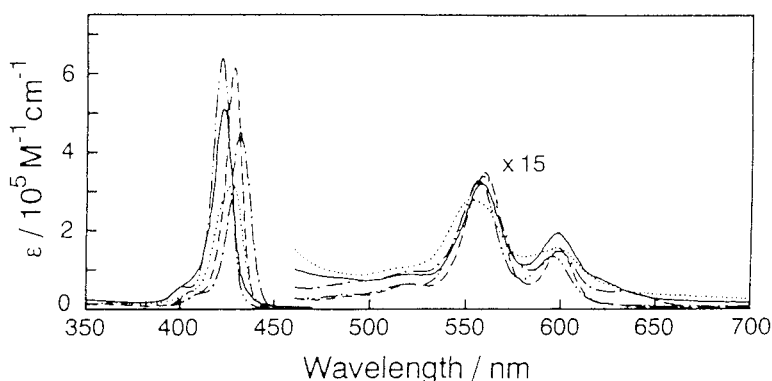


Figure 8. Absorption spectra of the terpolymers and the reference copolymer in aqueous solution: — — —, poly(A/La/ZnTPP); - - - -, poly(A/Cd/ZnTPP); — · — ·, poly(A/Np/ZnTPP); —, poly(A/ZnTPP); · · · ·, ZnTSPP.

indicating that the environments of ZnTPP moieties are more hydrophobic in the terpolymer than those of the reference copolymer. Since quantum yield of phosphorescence from excited state of ZnTPP has been reported to be 0.9 [Ref. 17], we measured the transient spectra of the terpolymer and copolymer and lifetime of the triplet of ZnTPP moieties by laser photolysis. Results are shown in Table 1 [Ref. 7]. Although the lifetime of the triplet of ZnTPP moieties was almost the same in DMSO, it was much longer in the amphiphilic terpolymer in aqueous solution than that in homogeneous system.

Phosphorescence and thermally activated delayed fluorescence of the ZnTPP moieties were first observed in aqueous solution at room temperature (Figure 9). Since the hydrophobic domain is formed in aqueous solution of amphiphilic polyelectrolyte as shown in Figure 8, these unusual phenomena are reasonably ascribable to the compartmentalization of ZnTPP moieties by hydrophobic domains whose size and properties have been estimated by dynamic light scattering and spin-probe methods [Ref. 14].



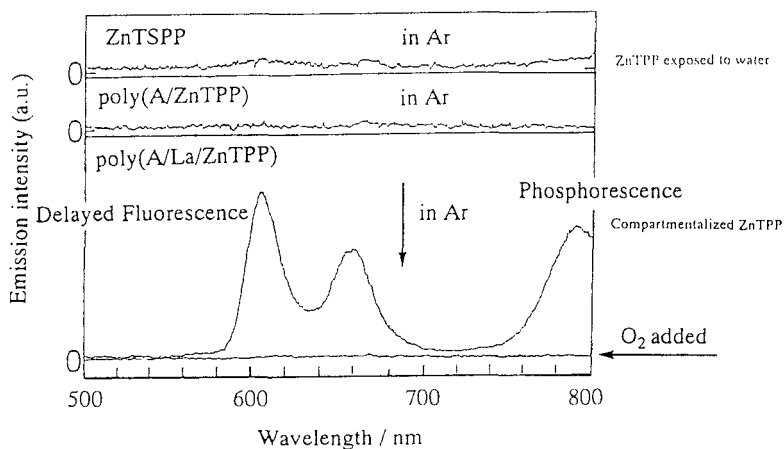


Figure 9. Delayed emission spectra in aqueous solution at 25 °C (delay time: 5 ms).

Table Initial absorbances ( $Abs_0$ ) and lifetimes of triplet excited state ( $\tau_t$ ) for ZnTSPP and the co- and terpolymers

sample code	DMF solution		aqueous solution	
	$Abs_0$	$\tau_t$ / ms	$Abs_0$	$\tau_t$ / ms
poly(A/ZnTPP)	0.38 <sup>a</sup>	3.0 <sup>a</sup>	0.26	3.0
poly(A/La/ZnTPP)	0.42	3.7	0.45	12
poly(A/Cd/ZnTPP)	0.42	4.3	0.25	20
poly(A/Np/ZnTPP)	0.41	3.8	0.33	19
ZnTSPP			0.53	3.5

<sup>a</sup> Solvent: DMF/water = 9/1 (V/V).

The effect of the compartmentalization on photochemical behavior was investigated by photoinduced electron transfer reaction of excited ZnTPP to electron acceptors such as methylviologen and phenylmethylphenacyl-sulfonium *p*-toluenesulfonate (PMPS). Although no transient absorption due to  $MV^{+\bullet}$  was observed in the copolymer, its clear transient spectra (Figure 10) and ESR spectra (Figure 11) due to  $ZnTPP^{+\bullet}$  were observed in the terpolymers, indicating that the lifetime of  $ZnTPP^{+\bullet}$  is longer in terpolymer.

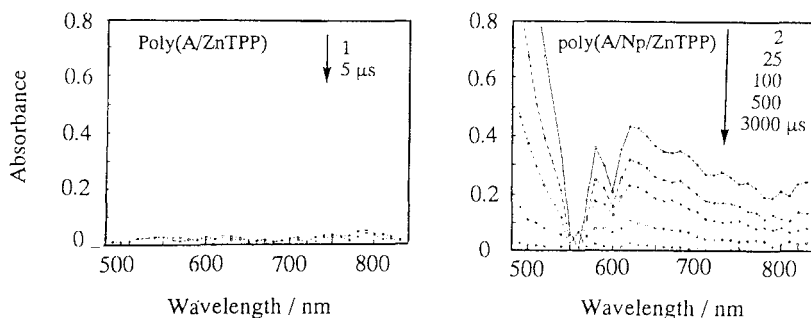


Figure 10. Time-resolved transient absorption spectra in the presence of  $MV^{2+}$  in aqueous solution:  $[ZnTPP] = 100 \mu M$ ;  $[MV^{2+}] = 5 \text{ mM}$ .

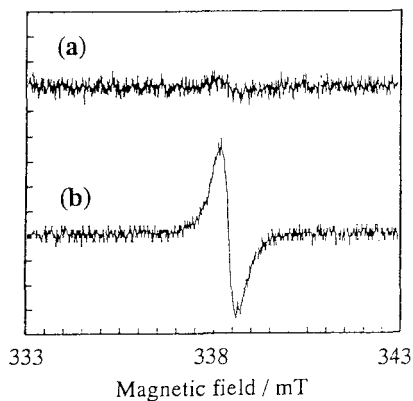


Figure 11. ESR spectra of  $TPPZn^{\bullet+}$   
(a) poly(A/TPPZn), (b) poly(A/Np/TPPZn).

The fact that accumulation of photoproducts,  $ZnTPP^{\bullet+}$  and  $MV^{\bullet+}$ , were found in the microsecond time region in the terpolymers is due to the retardation of the reversible electron transfer system which takes place in diffusion-controlled rate in homogeneous system. When phenylmethylphenacyl-sulfonium *p*-toluenesulfonate (PMPS) was used as irreversible electron acceptor [Ref. 14], the  $ZnTPP^{\bullet+}$  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  $ZnTPP^{\bullet+}$  moieties and other compounds by the compartmentalization.

## ACKNOWLEDGMENT

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