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Photoinduced ionic conductivity in poly(ethylene glycol) containing malachite green leuco hydroxide

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SUMMARY

Photoinduced ionic conductivity in poly(ethylene glycol)400 (PEG400)/malachite green leuco hydroxide (MGLOH) was analyzed with photochemical reaction of MGLOH in its matrix. The resonance structure in photogenerated cation lay in the favor of 4,4'-(dimethylamino) triphenylmethylcation (MG^+) under UV irradiation. The change in the ionic conductivity was discussed with that in glass transition temperature (Tg) of the matrix on UV irradiation.

Introduction

Solid polymer electrolytes have much attention because of possible application to some new electrochemical microdevices(1,2). Addition of photofunction in their applications, such as control of the ionic conductivity by photoirradiation, will make a solid polymer electrolyte more attractive materials. In order to control the ionic conductivity by photoirradiation, either the number of conductive carrier ions or the mobility of ions should be controlled because the ionic conductivity is proportional to the product of the number of carrier ions and the mobility of ions. We have already reported the unique solid polymer electrolyte with photochemical controllable conductivity, whose mechanism is based on the control of segmental motion by the photodimerization of anthryl groups covalently bound to polymer matrix(3). That solid polymer electrolyte is classified as the system in which the mobility of ions is controlled, because the mobility of ions is deeply affected by the segmental motion in the polymer matrix(4). The present paper is concerned with the fundamental research for new system, in which the number of conductive carrier ions is controlled by means of photoionization of MGLOH. MGLOH is well known as photochromic material which dissociates into MG^+ and hydroxy anion by UV irradiation(5). If photogenerated ions act as conductive carrier in the matrix, resulting matrix is expected as a new type of photofunctional solid polymer electrolytes. The change in ionic conductivity by UV irradiation was discussed with the photoionization process of MGLOH. The change of resonance structure in MG^+ was also studied at the standpoint of interaction of this cation and PEG.

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Experimental

PEG400 (Kanto Chemical Co., Inc.) was dried in vacuo at 100°C for 24 h. MGLOH (Aldrich Chemical Company, Inc.) was recrystallized twice with diethyl ether/n-hexane, and was obtained as white crystal. The solutions were irradiated with 500 W Xe lamp through the U330 filter (HOYA Color Filter Glass, transparent ranging 240-410 nm) at constant intensity. During the irradiation, the temperature was controlled at 30°C with thermostat under a nitrogen atmosphere. UV-Vis absorption spectra of the sample solutions were obtained with double beam spectrophotometer (Shimazu UV-2200). Tg was determined by DSC (Mac Science DSC-3100) method. A scanning rate was 20°Cmin^{-1} over the temperature range from -120 to 100°C. The ionic conductivity of the solutions was measured with conductivity meter (Horiba DS-14) at 25°C.

Results and discussion

Photochemical reaction of MGLOH was investigated in PEG400 solution as the model matrix for solid polymer electrolyte. Fig. 1 shows the change in absorbance of MGLOH characteristic bands with the irradiation time. At the initial stage, the absorbances at 311 and 632 nm corresponding to MG^+ increased and that at 266 nm corresponding to MGLOH decreased gradually by UV irradiation. These results suggest that ionic dissociation of MGLOH proceeds in PEG400 solution. However at about 1 h after irradiation, the absorbance at 632 nm gradually decreased via maximum point. For this change in spectrum corresponding to MG^+, we note that there is a resonance structure in MG^+ as described in scheme 1. In order to obtain some information on this resonance structure, photochemical ionic dissociation of triphenylmethyl alcohol [$(C_6H_5)_3COH$] (TPMOH) was analyzed in PEG400. TPMOH is also well known to dissociate into triphenylmethylcation and hydroxy anion by UV irradiation. TPMOH however have no dimethylamino group as auxochrome, and resulting photogenerated cation do not show resonance in its structure as seen in MG^+. The increase of absorbance only at 310 nm was observed when the photodissociation of TPMOH was carried out in PEG400 by UV irradiation. These results indicate that resonance structure in MG^+ lies in the favor of triphenylmethylcation (Scheme 1-a). It is well known that alkali metal cation is coordinated by PEG similarly to crown ether, because PEG has electron-donating ether oxygen in their unit structure. When the spectra of PEG containing $LiClO_4$ was analyzed as a function of $LiClO_4$ concentration, the absorbance at 280 nm was found to decrease with increasing $LiClO_4$ concentration as shown in Fig. 2. This was probably attributed to the interaction between PEG and dissociated ions, because such a spectral change was not observed when non-ionic substance was dissolved into PEG400. When the spectra of PEG400 containing MGLOH was analyzed after irradiation, the same spectral change was revealed to be observed as shown in Fig. 3. Namely, the absorbance at 286 nm gradually decreased by UV irradiation. This indicates that photogenerated ions interact with PEG400. Actually, the Tg of PEG400 containing 10 wt% MGLOH

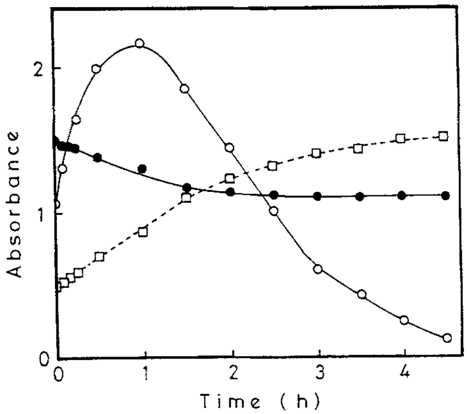
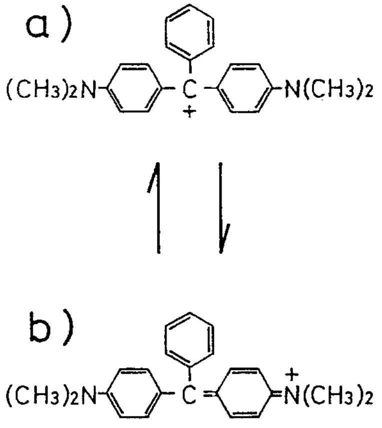


Fig. 1 Time dependence of absorbance for MGLOH in PEG400 under UV irradiation. [MGLOH]=0.1mM.
●, 266nm; □, 311nm; ○, 632nm.



Scheme 1

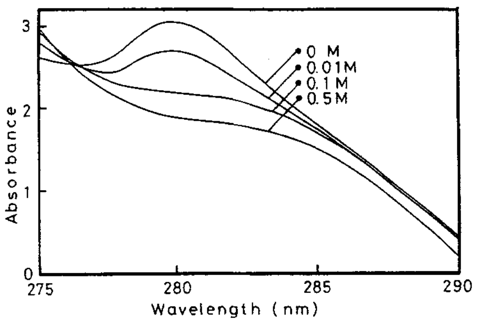


Fig. 2 Variation of absorption spectra for PEG400 solution of $LiClO_4$.

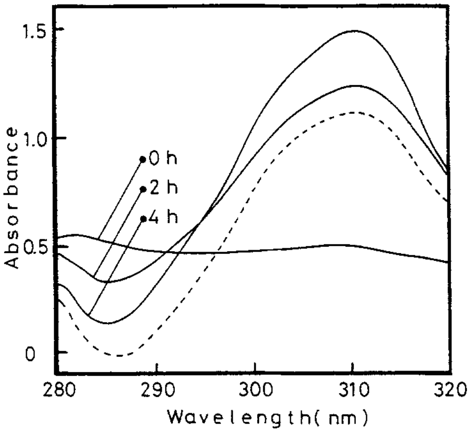


Fig. 3 Absorption spectra for MGLOH in PEG400 under UV irradiation. Broken line, dark 12 h after irradiation for 4 h. [MGLOH]=0.1mM

increased from -72.1°C to -70.8°C under UV irradiation after 10 h (Table 1). This result supports that photogenerated ions interact with PEG as a solvent. On the other hand, the photoionized MG^+ and hydroxy anion are well known to show backward reaction into MGLOH under dark. In this system, the absorbance at 311 nm corresponding to MG^+ gradually decreased under dark, but that at 286 nm corresponding to interaction did not return. This was attributed to the strong coordination of ionic species by PEG (6).

Table 1 Glass transition temperature for MGLOH in PEG400 under UV irradiation.

Irradiation Time(h)	Tg(°C) [a)]
0	-72.1
10	-70.8

a) Determined by DSC method; [MGLOH]=10 wt%.

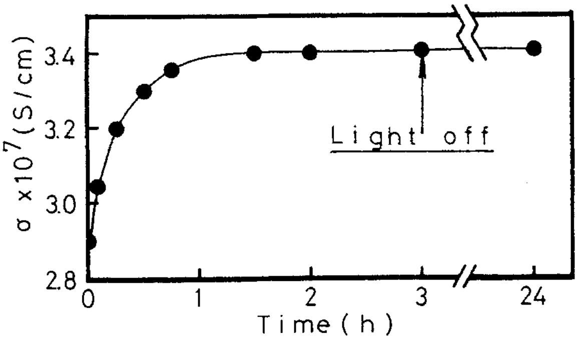


Fig. 4 Time dependence of ionic conductivity for MGLOH in PEG400 under UV irradiation at 25°C. [MGLOH]=10mM

Time dependence of ionic conductivity was measured for PEG400 containing MGLOH under UV irradiation (Fig. 4). The ionic conductivity increased by UV irradiation. However, increased ionic conductivity did not go back in the absence of irradiation. This suggests that photogenerated ions act as conductive carrier, but backward reaction in the absence of irradiation does not proceed because of the stabilization of ionic species by PEG400 matrix. This was also supported by the increase of Tg for the matrix after irradiation. The technique using this photoinduced ionic conductivity will be also effective to analyze the ionic dissociation and conductive properties in solid polymer electrolyte. Further investigation is now in progress, and will be reported in the near future.

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