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Photoinduced ionic conductivity in poly[(ω-methoxy)oligo(oxyethylene)methacrylate] doped with triphenylmethane derivatives

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SUMMARY

The solid film of poly[(ω-methoxy)oligo(oxyethylene) methacrylate] [P(MEO)] doped with malachite green leuco hydroxide (MGLOH) or triphenylmethylalcohol (TPMOH) has been prepared as a new type of solid polymer electrolyte with controllable ionic conductivity upon photoirradiation. The ionic conductivity for P(MEO) film doped with 0.1mol% MGLOH or 0.05mol% TPMOH increased with UV irradiation. This suggests that the photogenerated ions act as conductive carrier in the matrix. In particular, for the TPMOH doped film, the effect of TPMOH content on the ionic conductivity change has been analyzed with the change of glass transition temperature (Tg) upon UV irradiation.

INTRODUCTION

Since the report on solid polymer electrolytes to be applicable to electrochemical devices, this field has stimulated considerable attentions. Actually, there have been many papers on solid state battery(1-3), electrochromic display(2, 4, 5) and so on. Further, some applications to microelectrochemical devices such as transistor(6) have been reported. Our interest is to prepare a new type of solid polymer electrolytes with photofunctions, for example, the solid polymer electrolyte with controllable ionic conductivity upon photoirradiation. The ionic conductivity (σ) can be expressed by the following equation,

$$\sigma = \Sigma q n \mu$$

where q, n, and μ are the charge of ions, the number of carrier ions, and the mobility of ions, respectively. If n or μ was controlled by photo-stimuli, solid polymer electrolytes with controllable ionic conductivity would be realized. We have already reported the photofunctional solid polymer electrolyte in which μ is controlled upon photoirradiation(7). Anthryl groups covalently bound to the polymer were used as the photofunctional group in the matrix. As anthryl group is well known to show dimerization behavior upon photoirradiation, the progress of photodimerization effects the decrease of segmental motion of the polymer matrix. μ was decreased upon photoirradiation because μ in solid polymer electrolytes was facilitated by segmental motion and, consequently, the conductivity decreased. We have also reported

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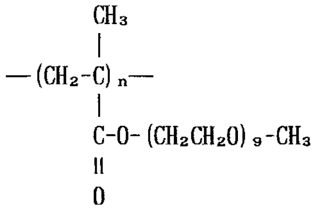
that n is controlled upon photoirradiation to PEG400 (Polyethylene glycol with molecular weight of 400)/MGLOH as the model matrix for solid polymer electrolyte(8). MGLOH and TPMOH are well known as a photochromic material which dissociates into MG cation or triphenylmethyl cation and hydroxy anion upon UV irradiation(9, 10). The conductivity actually increased upon photoirradiation.

The aim of the present work is to develop photoinduced ionic conduction behavior for MGLOH or TPMOH to solid matrix. This matrix will be effective to apply the photoinduced ionic conduction behavior to devices. The correlation of photochemical reaction of these dyes and the change in the ionic conductivity is discussed.

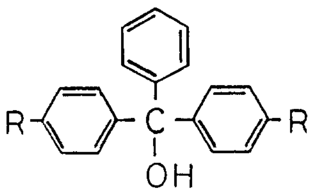
EXPERIMENT

MGLOH (Aldrich Chemical Co.) and TPMOH (Tokyo Kasei Co.) were crystallized twice with diethyl ether/n-hexane. Poly(ethylene glycol)400 (PEG400, Kanto Chemical Co.) was dried in vacuo at 100°C for 24 h. 2,2'-Azobisisobutylonitrile (AIBN, Kanto Chemical Co.) was crystallized with methyl alcohol. [(ω-Methoxy) oligo(oxyethylene) methacrylate] (MEO, Nippon Oil & Fats Co.) was polymerized with AIBN as the initiator under nitrogen at 50°C in distilled THF for 24 h. The polymer [P(MEO)] was precipitated twice from diethyl ether. P(MEO) and MGLOH or TPMOH were dissolved in distilled THF, and the resulting solution was cast onto ITO glass electrode. The film on the electrode was dried in vacuo at 40°C for 24 h, and was contacted with Au sputter-deposited on the quartz glass. Cell constitution was ITO/P(MEO) film doped with the dye/Au-quartz glass. The cell was completely sealed with resin to prevent the solid polymer electrolyte from the absorption of moisture. The cell was irradiated from Au-quartz electrode side with 500W Xe lamp through the U330 filter (HOYA Color Filter Glass, transparent ranging 240-410nm) at constant intensity. Ionic conductivity was calculated by the complex impedance method (Solartron 1260 Impedance Analyzer). Tg was determined by DSC method (Mac Science DSC 3100). Details of the preparation and measurements were reported earlier(8).



$$-\left(\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{C{-}O{-}(CH_2CH_2O)_9{-}CH_3}\\ \|\\ \mathrm{O}}}{\overset{\substack{\mathrm{CH_3}\\ |}}{\mathrm{C}}}\right)_n-$$

P (MEO)



R= $-N(CH_3)_2$, MGLOH
R= -H, TPMOH

RESULTS AND DISCUSSION

Fig. 1 shows the change in UV-Vis spectra for P(MEO) film doped with 0.1mol% MGLOH upon UV irradiation at 20°C. Upon UV irradiation, the absorption at 266 nm assignable to MGLOH decreased, and that at around 310 nm and 630 nm assignable to MG cation increased. These indicate that photodissociation of MGLOH is proceeded in solid film. However, the absorption at around 630 nm turned to decrease when this film was irradiated for more than 5 min. The similar manner was also observed in PEG400/MGLOH system(8). When the film was exposed to moisture after disappearance of the absorption at around 630 nm, This absorption was appeared again. This suggests that MG cation does not decompose in the matrix upon UV irradiation. This manner is probably related to the resonance structure of MG cation in the matrix as described in the previous paper concerning PEG400/MGLOH system(8). This was analyzed with photochemical reaction for TPMOH, which did not show resonance in its cation structure, in PEG400/TPMOH system. Namely, the resonance structure in MG cation also lies in favor of 4,4'-(dimethylamino) triphenylmethyl cation in P(MEO) matrix upon UV irradiation. Time dependence of ionic conductivity was measured for P(MEO) film doped with MGLOH upon UV irradiation (Fig. 2). The ionic conductivity for P(MEO) film doped with 0.1 mol% MGLOH (vs. ethylene oxide unit) increased upon UV irradiation. This suggests that the photogenerated ions act as conductive carrier in P(MEO) matrix irrespective of the resonance in its cation structure.

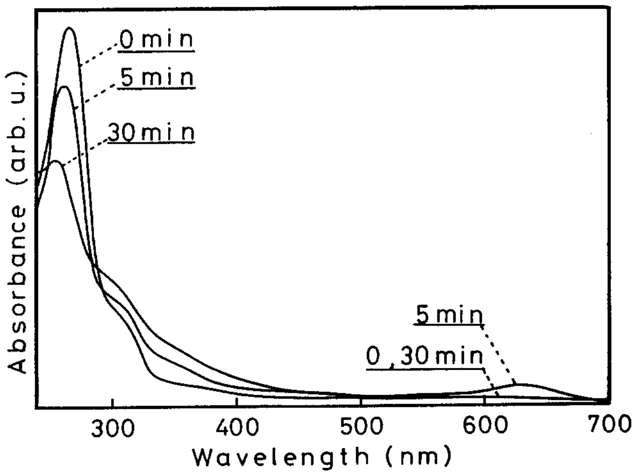


Fig. 1 Absorption spectra for P(MEO) film doped with 0.1 mol% MGLOH upon UV irradiation at 20°C

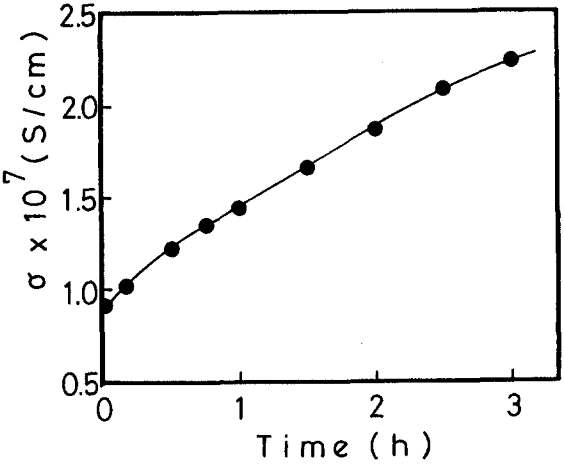


Fig. 2 Time dependence of ionic conductivity for P(MEO) film doped with 0.1 mol% MGLOH upon UV irradiation at 30 °C.

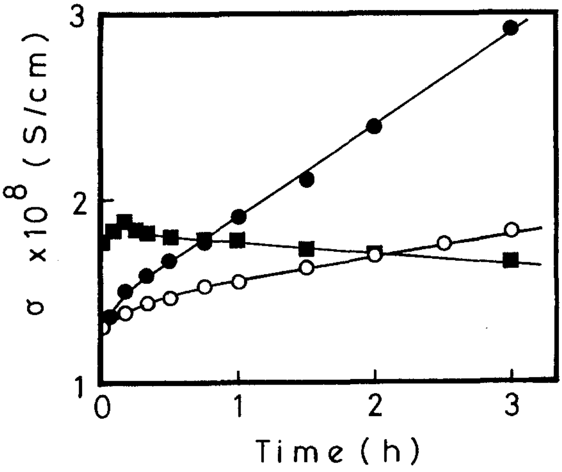


Fig. 3 Time dependence of ionic conductivity for P(MEO) film doped with TPMOH upon UV irradiation at 30 °C.
[TPMOH] : ●, 0.05 mol%; ○, 0.1 mol%; ■, 0.5 mol%.

Photoinduced ionic conductivity for P(MEO)/TPMOH film was also analyzed, because triphenylmethyl cation photogenerated from TPMOH showed no resonance in its structure. Fig. 3 shows the time dependence of ionic conductivity for P(MEO) film doped with TPMOH upon UV irradiation. P(MEO) film doped with 0.05 mol% TPMOH showed larger increase of ionic conductivity upon UV irradiation. Ions photogenerated from TPMOH also acted as conductive carrier. But the time dependence of ionic conductivity upon photoirradiation varied with the increase of TPMOH concentration. The increment of the ionic conductivity upon

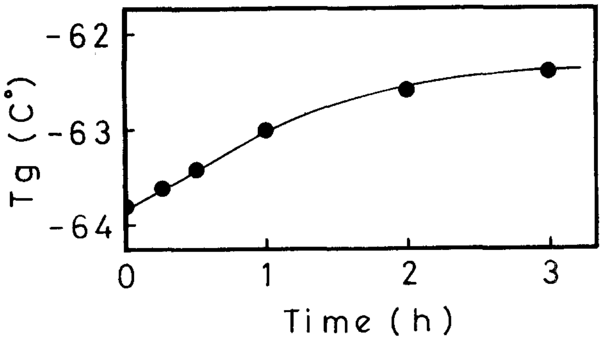


Fig. 4 Time dependence of Tg for P(MEO) film doped with 1.0 mol% TPMOH upon UV irradiation.

UV irradiation for P(MEO) film doped with 0.1 mol% TPMOH was smaller than that with 0.05 mol% TPMOH. Further, at the TPMOH concentration of 0.5 mol%, the ionic conductivity at first increased upon UV irradiation, but turned to decrease through a maximum after about 10 min. The change of n caused by the photoionization of TPMOH is assumed to effect this difference. Generally, the ionic conductivity for solid polymer electrolytes is strongly related to salt concentration(11,12). The increase of salt concentration leads to the increase of ionic conductivity for solid polymer electrolytes at a range of low salt concentration. The maximum was, however, found in the salt concentration dependence of the ionic conductivity. Namely, ionic conductivity at first increases, passes through a maximum, and then decreases as the salt concentration is increased. This decrease of ionic conductivity is attributed to the decrease of μ explained by the increase of Tg with increasing the salt concentration. The two opposing effects of salt concentration on n and μ lead to such a change of ionic conductivity upon salt concentration. Time dependence of Tg for P(MEO) film doped with 1 mol% TPMOH upon UV irradiation is shown in Fig 4. The Tg of this film increased upon UV irradiation. This suggests that photogenerated ions interact with polymers as generally observed in solid polymer electrolytes. The continuous UV irradiation facilitated the photodissociation of MGLOH, resulting further increase of the ionic concentration in the matrix. Therefore, the change of ionic conductivity as shown in Fig. 3 was probably influenced by the factor of μ as well as n. Namely, the increase of ionic conductivity in P(MEO) film doped with 0.05 and 0.1 mol% TPMOH was considerably due to the increase of n upon UV irradiation. On the other hand, for the film doped with 0.5 mol% TPMOH, the change in the ionic conductivity was due to the increase of n upon UV irradiation at first 10 min. The increase of n in the matrix caused the decrease of μ because of ion-polymer interaction and, consequently, the ionic conductivity decreased upon irradiation. The similar change in the ionic conductivity was also found for the film doped with 1 mol% MGLOH. The difference in the ionic conductivity change upon UV irradiation for the film doped with MGLOH and TPMOH at the same concentration may be attributed to the interaction of polymer and MG cation or triphenylmethyl cation. Consequently, the photoinduced ionic conductor has become feasible to dope the dye, which dissociates into the ions upon photoirradiation, into the matrix for solid polymer electrolytes.

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