

Relations between the Molecular Aggregation State and Ionic Conductivity in Photopolymerized Crosslinking Polymers with Oligo(oxyethylene) Chains

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ABSTRACT: A mixture of a vinyl monomer and a crosslinking agent was photopolymerized to form a crosslinked polymer film. Methacrylate with pendant oligo(oxyethylene) chain and poly(ethylene glycol) dimethacrylate were used as the vinyl monomer and crosslinking agent, respectively. The ionic conductivity of the film increased with an increasing concentration of LiClO₄ and then decreased. The size of the quasicrystalline aggregation phase composed of pendant and crosslinking chains in the film decreased with an increasing concentration of LiClO₄. The amorphous pendant and crosslinking oxyethylene chains gave rise to increased segmental motion and conductivity. The dissolution was depressed for a decrease in the ionic

conductivity at a high LiClO₄ concentration at which the interactions among ions became stronger and the crystal phase of LiClO₄ was formed. The amount of the dissolution of the aggregation phase increased with an increasing crosslinking agent concentration. The quasicrystalline aggregation phase became larger with an increasing length of the pendant chains, and an increase in the size of the aggregation phase resulted in a decrease in the ionic conductivity. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1272–1277, 2002

Key words: photopolymerization; conducting polymers; crosslinking; glass transition; structure-property relations

INTRODUCTION

It is well known that segmental motion in amorphous regions mainly contributes to ionic conductivity. Dissociated ions contained in solid polymer electrolytes and a high degree of segmental motion bring about high ionic conductivity. Solid polymer electrolytes may be used as ionic conductors in solid cells in which it is necessary to lower the interface resistance between an electrode and the electrolyte. If a polyaniline electrode is used as an anode, the interface resistance between the electrode and the solid polymer electrolyte can be lowered by plasma grafting of the electrolyte, which is directly formed on the electrode.^{1,2}

Polymers composed of oxyethylene chains become ionically conductive when LiClO₄ and LiCF₃SO₃ are dissolved in the polymer matrix.³ Oxyethylene chains in polymers tend to aggregate with one another to form a crystalline phase.⁴ The formation of the crystalline phase depresses ion mobility and results in the lowering of ionic conductivity. The formation of crosslinking chains between polymer chains is effective for depressing fluidization, which originates from ionic compounds. Comblike polymers with oligo(oxyethylene) side chains have been investigated as solid polymer electrolytes.^{5–9}

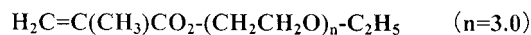
In this work, mixtures of a vinyl monomer and a crosslinking agent were photopolymerized to prepare crosslinked polymer films. Methacrylate with pendant oligo(oxyethylene) chain was used as the vinyl monomer, and poly(ethylene glycol) dimethacrylate (PEGDMA) was used as the crosslinking agent. The relationships between the state of aggregation and ionic conductivity were investigated for photopolymerized films containing LiClO₄.

EXPERIMENTAL

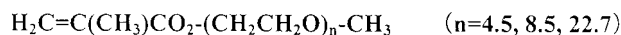
Preparation of the crosslinked polymer films containing LiClO₄

Figure 1 shows the chemical structures of the monomers and crosslinking agent used in this work. Poly(ethylene glycol) ethyl ether methacrylate (PEGEEMA) and poly(ethylene glycol) methyl ether methacrylate (PEGMEMA) were used as the monomers, and PEGDMA was used as the crosslinking agent. The average number of repeat units of the oxyethylene chain of PEGEEMA was 3.0; those of PEGMEMA were 4.5, 8.5, and 22.7; and

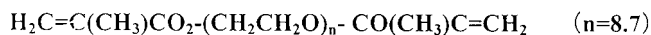
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PEGEEMA



PEGMEMA



PEGDMA

Figure 1 Chemical structures of PEGEEMA, PEGMEMA, and PEGDMA.

that of PEGDMA was 8.7. After a mixture of the monomer and crosslinking agent was poured into a frame of silicon rubber that adhered closely to a stainless steel plate, it was irradiated with a 100-W mercury lamp for 3 h, and then an acetonitrile solution of 0.4M LiClO₄ was poured on the mixture. The mixture was polymerized in the dark at 293 K for 48 h to form a crosslinked polymer film and then was dried in vacuo at 293 K for 48 h.

Measurements of the dynamic viscoelastic and thermal properties and X-ray analysis of the molecular aggregation state

The temperature dependence of the dynamic viscoelastic properties in the crosslinked polymer film was measured at frequencies of 3.5–110 Hz at a heating rate of 1 K/min with a Rheovibron DDV-III-EP dynamic viscoelastometer (Orientec Co., Ltd., Tokyo, Japan). The glass-transition behavior of the films was measured at a heating rate of 5 K/min at a nitrogen-flow rate of 2 mL/min with a DSC200 differential scanning calorimeter (Seiko Denshikogyo Co., Ltd., Chiba, Japan). The weight of the sample was 5 mg.

X-ray diffraction intensity curves were measured with a Rigaku Rint 1200 X-ray diffractometer (Rigaku Denki Co., Ltd., Tokyo, Japan). After the instrumental broadening was corrected with a quartz standard, the half-value width of the diffraction peak was evaluated so that the size of the quasicrystalline aggregation phase of oligo(oxyethylene) chains could be estimated.

Evaluation of the ionic conductivity

Complex impedances of the films, for which two stainless steel plates were used as electrodes, were measured at 293 K in a frequency range of 1 mHz to 100 kHz with a Hioki LCR Hi Tester 3522 (Hioki Denki Co., Ltd., Nagano, Japan). The bulk resistance of the films was evaluated from an impedance plot. The ionic conductivity (σ) was calculated as follows:

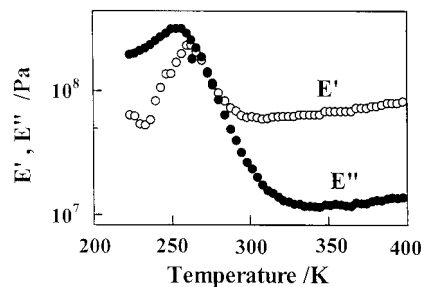


Figure 2 Temperature dependence of E' and E'' in a PEGDMA/PEGEEMA (10/90) film containing no LiClO₄.

$$\sigma = d/R_b A$$

where R_b is the bulk resistance of the film, d is the thickness of the film, and A is the area of the film. The temperature dependence of the ionic conductivity was measured with a cryostat.

RESULTS AND DISCUSSION

Analysis of the dynamic viscoelastic properties

Figure 2 shows the temperature dependence of the storage modulus (E') and loss modulus (E'') in the film formed by the photopolymerization of a PEGDMA/PEGEEMA mixture in which the molar fraction of PEGDMA was 10 mol %. This film is called the PEGDMA/PEGEEMA (10/90) film. No ionic compound was contained in the film. After E' largely decreased above 270 K, it increased slightly above 310 K. E' increased with the temperature increasing below 270 K because the aggregation phase of the oligo(oxyethylene) chains that formed in nonequilibrium via quenching for the measurement was rearranged to a stable state during the measurement. Figure 3 shows an Arrhenius plot displaying the relationship between the frequency and the reciprocal of the peak temperature at the E'' peak that appeared around 260 K. The Arrhenius plot gives a straight line, and the activation energy determined from the slope was 239 kJ mol⁻¹. It

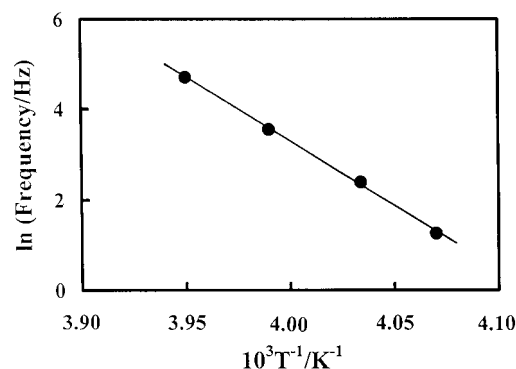


Figure 3 Arrhenius plot of the E'' peak around 250 K in a PEGDMA/PEGEEMA (10/90) film containing no LiClO₄.

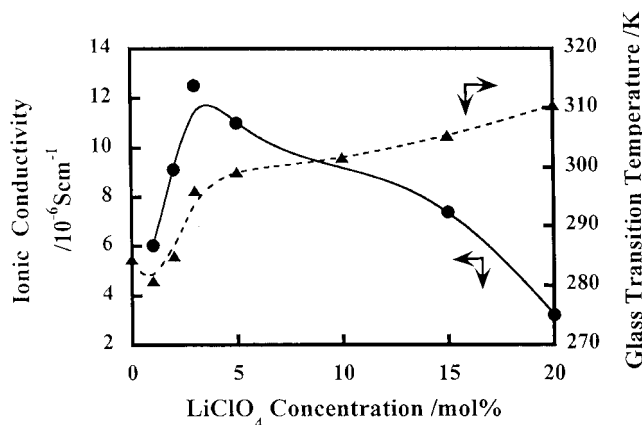


Figure 4 LiClO_4 concentration dependence of the ionic conductivity and glass-transition temperature in a PEGDMA/PEGEEMA (1/99) film.

can, therefore, be presumed from the value of the activation energy that the E'' peak around 260 K was associated with the segmental motion of the side and crosslinking chains composed of oligo(oxyethylene). The glass-transition temperature of the side and crosslinking chains, which was evaluated with differential scanning calorimetry (DSC), was 288 K and was higher than the temperature of the E'' peak. This result means that the glass-transition temperature depended on the heating rate in the measurement.

Effects of the LiClO_4 concentration on the ionic conductivity and thermal properties

Figures 4 and 5 show the LiClO_4 concentration dependence of the ionic conductivity and glass-transition temperature in the films formed by the photopolymerization of the PEGDMA/PEGEEMA (1/99) and PEGDMA/PEGEEMA (10/90) mixtures, respectively. The molar fractions of PEGDMA in the PEGDMA/PEGEEMA (1/99) and PEGDMA/PEGEEMA (10/90)

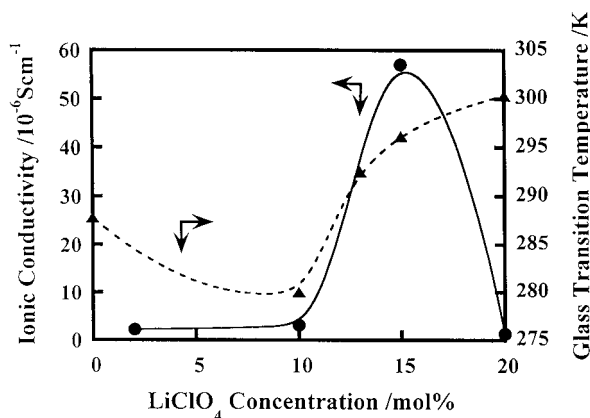


Figure 5 LiClO_4 concentration dependence of the ionic conductivity and glass-transition temperature in a PEGDMA/PEGEEMA (10/90) film.

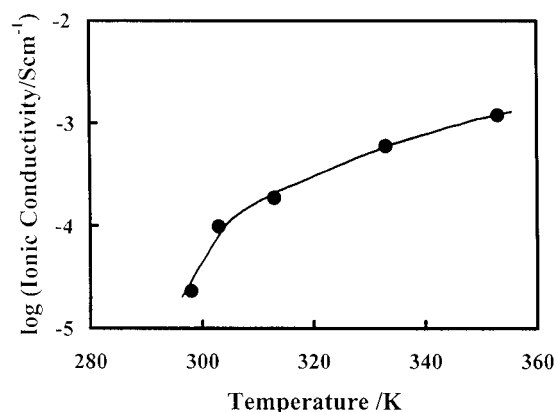


Figure 6 Temperature dependence of the ionic conductivity in a PEGDMA/PEGEEMA (10/90) film containing 15 mol % LiClO_4 .

mixtures were 1 and 10 mol %, respectively. The film formed from the PEGDMA/PEGEEMA (1/99) mixture is called the PEGDMA/PEGEEMA (1/99) film. The glass-transition temperatures were measured with DSC. The segmental motion of the side and crosslinking chains took place at the glass-transition temperature, as shown in Figure 3. The ionic conductivity of the films increased with increasing LiClO_4 concentration and then decreased. However, the glass-transition temperature decreased with increasing LiClO_4 concentration and then increased. An increase in the ionic conductivity originated from increases in both the concentration and mobility of carriers formed by the dissociation of LiClO_4 . The mobility of the carriers increased with the segmental motion of the side and crosslinking chains. However, a decrease in the ionic conductivity originated from a decrease in the mobility of the carriers, which interacted more strongly with one another to form ionic aggregates. The LiClO_4 concentration at the maximum ionic conductivity was higher than that at the minimum glass-transition temperature. Therefore, it was confirmed that the ionic conductivity depended on both the mobility and concentration of carriers. The LiClO_4 concentration at the maximum ionic conductivity in the PEGDMA/PEGEEMA (10/90) film was higher than that in the PEGDMA/PEGEEMA (1/99) film. This observation showed that the concentration of the mobile carriers increased with an increasing fraction of PEGDMA.

Figure 6 shows the temperature dependence of the ionic conductivity in the PEGDMA/PEGEEMA (10/90) film. The concentration of LiClO_4 in the film was 15 mol %. The ionic conductivity increased with increasing temperature, and the magnitude of the increase was larger below about 300 K because the segmental motion of the side and crosslinking chains initiated around the glass-transition temperature of 296 K and became more frequent above the glass-transition temperature.

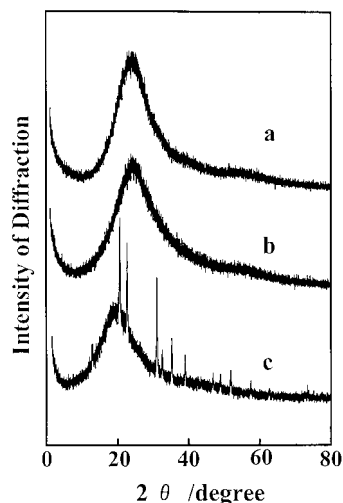


Figure 7 X-ray diffraction curves in PEGDMA/PEGEEMA (10/90) films containing (a) 0, (b) 10, and (c) 40 mol % LiClO_4 .

Effect of the LiClO_4 concentration on the molecular aggregation state

Figure 7 shows X-ray diffraction curves in PEGDMA/PEGEEMA (10/90) films in which the concentration of LiClO_4 was 0–40 mol %. The peak became broad by containing LiClO_4 . The crystalline phase of LiClO_4 was distinctly formed above the LiClO_4 concentration of 40 mol %. The films contained an amorphous phase and a quasicrystalline aggregation phase of oligo(oxyethylene) chains. The broad peak was composed of the diffraction peaks, which originated from the amorphous phase and the quasicrystalline aggregation phase of oligo(oxyethylene) chains, according to the distance between oligo(oxyethylene) chains. Because the peak intensity of the aggregation phase was much stronger than that of the amorphous phase, the half-value width of the peak was mainly affected by the aggregation state of oligo(oxyethylene) chains. Figure 8 shows the half-value width as a function of the

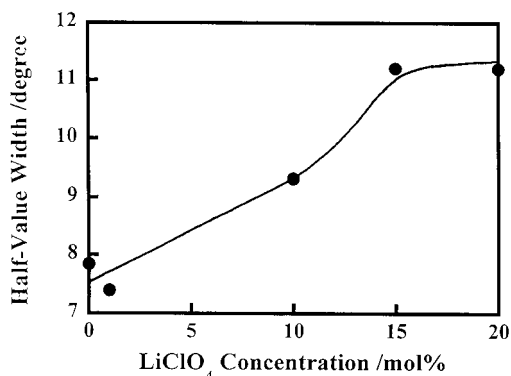


Figure 8 Half-value width of the X-ray diffraction peak as a function of the LiClO_4 concentration in a PEGDMA/PEGEEMA (10/90) film.

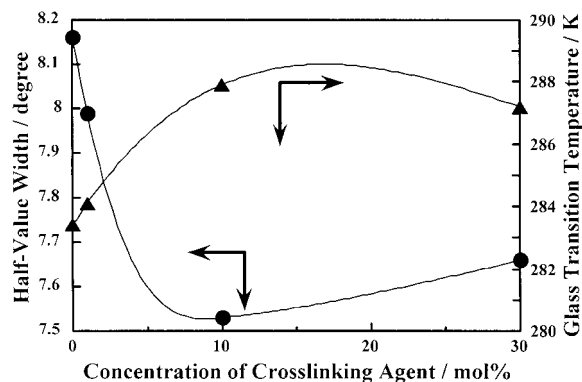


Figure 9 Half-value width of the X-ray diffraction peak and glass-transition temperature as a function of the crosslinking agent concentration in a PEGDMA/PEGEEMA film containing no LiClO_4 .

LiClO_4 concentration in the PEGDMA/PEGEEMA (10/90) film. The half-value width increased with increasing LiClO_4 concentration and then became almost constant. This fact shows that the aggregation phase was dissolved by the presence of LiClO_4 and was changed into the amorphous phase. The LiClO_4 concentration above which the half-value width became almost constant was 15 mol % and agreed with that of the maximum ionic conductivity, as shown in Figure 5. Above 15 mol %, an increase in LiClO_4 no longer resulted in dissolution of the aggregation phase; therefore, the dissociation of LiClO_4 no longer took place because the dissociation of LiClO_4 increased with the dissolution of the aggregation phase. Such a depressed dissociation of LiClO_4 was supported in the range of high LiClO_4 concentrations by the appearance of diffraction peaks that originated from the crystalline phase of LiClO_4 , as shown in Figure 7.

Effect of the crosslinking agent on the ionic conductivity and molecular aggregation state

Figure 9 shows the half-value width evaluated from the X-ray diffraction curve and glass-transition temperature as a function of the crosslinking agent concentration in the films formed by the photopolymerization of a PEGDMA/PEGEEMA mixture. The LiClO_4 concentration was 0 mol % in the films. The half-value width largely decreased with an increasing concentration of the crosslinking agent and then changed a little above 10 mol %, whereas the glass-transition temperature increased with an increasing concentration of the crosslinking agent and then changed a little above 10 mol %. It may be concluded from Figure 9 that the quasicrystalline aggregation phase of oligo(oxyethylene) in the side and crosslinking chains formed and its size increased with an increasing concentration of the crosslinking agent. How-

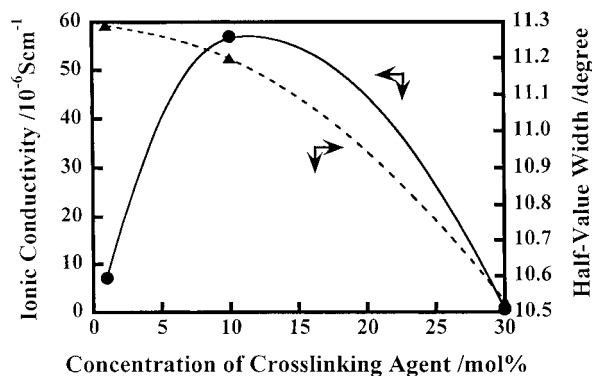


Figure 10 Ionic conductivity and half-value width of the X-ray diffraction peak as a function of the crosslinking agent concentration in a PEGDMA/PEGEEMA film containing 15 mol % LiClO_4 .

ever, an increase in the aggregation phase was depressed above 10 mol % by an increase in the fraction of crosslinking chains, by which the aggregation of the side chains was disturbed.

Figure 10 shows the ionic conductivity and half-value width as a function of the concentration of the crosslinking agent in the films formed by the photopolymerization of a PEGDMA/PEGEEMA mixture. The LiClO_4 concentration was 15 mol % in the films. The film containing no crosslinking agent was fluidized by the presence of 15 mol % LiClO_4 . Below the crosslinking agent concentration of 10 mol %, the ionic conductivity increased with an increasing concentration of the crosslinking agent, despite a small decrease in the half-value width. An increase in the ionic conductivity originated from an increase in LiClO_4 dissociated by the dissolution of the aggregation phase. The half-value width largely decreased above the crosslinking agent concentration of 10 mol %. This result shows that dissociation of the aggregation phase was depressed by an increase in the crosslinking chains above the crosslinking agent concentration of 10 mol %; therefore, the ionic conductivity decreased. Such a depression of the dissolution originated from an increase in the cohesive force of oligo(oxyethylene) in the quasicrystalline aggregation phase composed of the side and crosslinking chains because the average chain length of the crosslinking chains was longer than that of the side chains.

Effect of the length of the side chains on the ionic conductivity and molecular aggregation state

Figure 11 shows the ionic conductivity and half-value width as a function of the average number of repeat units in the side chain in the films formed by the photopolymerization of PEGDMA/PEGMEMA mixtures in which the molar fraction of PEGDMA was 10

mol %. The film is called the PEGDMA/PEGMEMA (10/90) film. The LiClO_4 concentration was 15 mol % in the films. The ionic conductivity and half-value width decreased with an increasing average number of repeat units. Because the size of the aggregation phase became larger in longer side chains, the fraction of the amorphous region decreased with an increasing length of the side chains. It became apparent in the film with the longest side chains that the crystalline aggregation phase of oligo(oxyethylene) chains was distinctly formed because an endothermic peak appeared around 311 K in the DSC curve. It was obtained from the heat of fusion in poly(oxyethylene) that the crystallinity of the film was 35%. Therefore, the mobility of the carriers was depressed by the formation of the crystalline aggregation phase, and the ionic conductivity decreased.

The glass-transition temperature of the PEGDMA/PEGMEMA (10/90) film in which the average number of repeat units of oxyethylene in PEGMEMA was 4.5 was lower than that of the PEGDMA/PEGEEMA (10/90) film. The glass-transition temperature was affected by the species of the alkyl group, which was the end group of the side chains. Therefore, the mobility of the carriers was larger in the PEGDMA/PEGMEMA (10/90) film at the measurement temperature of the ionic conductivity than that of the PEGDMA/PEGEEMA (10/90) film. Because of the higher mobility of the carriers, the ionic conductivity of the PEGDMA/PEGMEMA (10/90) film was higher at 15 mol % LiClO_4 than that of the PEGDMA/PEGEEMA (10/90) film, as shown in Figures 5 and 11.

CONCLUSIONS

Materials composed of side and crosslinking oxyethylene chains should be mostly amorphous and have a low glass-transition temperature for high ionic conductivity to be obtained. The size of the quasicrystal-

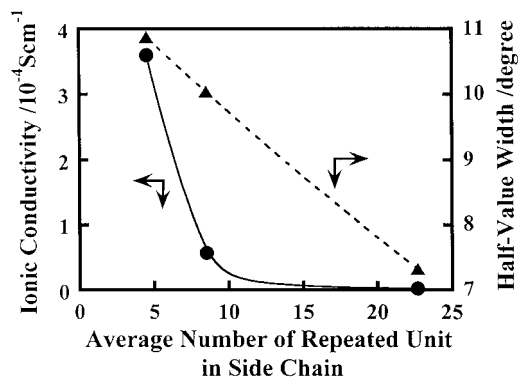


Figure 11 Ionic conductivity and half-value width of the X-ray diffraction peak as a function of the average number of repeat units in the pendant chain in a PEGDMA/PEGMEMA (10/90) film containing 15 mol % LiClO_4 .

line aggregation phase of the side and crosslinking chains decreased with increasing LiClO_4 concentration. Such a partial dissolution of the aggregation phase brought about both the formation of the carriers and the activation of segmental motion of the side and crosslinking chains, and the ionic conductivity increased with increasing concentration. The dissolution of the aggregation phase was depressed in the range of high LiClO_4 concentrations, at which the interactions among the carriers became stronger, and the ionic conductivity decreased with increasing concentration. The introduction of a crosslinking agent with oligo(oxyethylene) chains brought about an increase in the size of the quasicrystalline aggregation phase composed of oligo(oxyethylene) chains. Below the crosslinking agent concentration of 10 mol %, the amount of dissolution increased with an increasing concentration of the crosslinking agent in the presence of LiClO_4 to bring about an increase in the ionic conductivity. In the polymer with longer side chains, the aggregation phase became crystalline, the size of the

phase increased, and the ionic conductivity decreased, depressing the mobility of the carriers.

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