Spectroscopic and electrochemical studies of PMMA-based gel polymer electrolytes modified with interpenetrating networks

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Abstract

This work reports the mechanical strength and ionic conductivity of poly(methyl methacrylate) (PMMA)-based polymer gel electrolytes that are modified with interpenetrating networks. A series of poly(ethylene glycol dimethacrylate) (PEGDMA) polymers with different numbers of repeating ethylene oxide units is utilized as the network former. The mechanical strength of the electrolytes is estimated from their stress–strain curves. To assess ionic distribution in the gel electrolytes, an analysis is made of the infrared absorption bands of the symmetric stretching modes of SO_3 in triflate anions that are incorporated as the lithium salt. The local viscosity around charge-carrying ions is estimated by means of the fluorescence depolarization method. Introduction of a PEGDMA network, in particular by modifying with lower molecular weight PEGDMA, is effective for increasing the mechanical strength of PMMA-based gel electrolytes. This feature can be explained by a cross-linking effect provided by the network former. In addition, the PEGDMA modification leads to an increase in ionic conductivity due to enhancement in both the free-ion fraction and the ionic mobility. This favorable feature probably results from the introduction of the ethylene oxide unit (as PEGDMA) which has a high donor number for Li^+ ions and high chain flexibility. Consequently, the use of higher molecular weight PEGDMA is advantageous for conductivity enhancement. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Gel polymer electrolytes; Interpenetrating networks; Ionic conductivity; Mechanical strength; Local viscosity

1. Introduction

At present, various gel-type polymer electrolytes that are made by immobilizing lithium salts and plasticizing organic solvents in polymer matrices are proposed in the literature for possible application as battery electrolytes [1–3]. In such gel-type polymer electrolytes, enhanced ionic conductivity through the addition of plasticizing organic solvents is a favorable characteristic. Nonetheless, many gel electrolyte systems which contain large amounts of organic solvents are not mechanically strong for practical applications, e.g. for large-scale coating processes. The addition of an extra amount of polymeric component may prove to be a simple way to increase the mechanical strength, but this is largely offset by the lower ionic conductivity that results from a higher local viscosity in polymer-rich gel electrolytes. Therefore, a better approach may be the addition or formation of mechanically stronger species in gel electrolytes, while minimizing the polymeric ingredient. Accordingly, in practical lithium-polymer cells, inorganic fillers (such as fumed silica, zeolite, Al_2O_3, γ-$LiAlO_2$ or glass fiber) are frequently added to improve the mechanical strength of electrolyte films [4–6]. Even if it is less efficient, deliberate control of the polymer–solvent affinity is an alternative approach to improve the mechanical strength of gel electrolytes [7,8]. When the polymer–solvent affinity is controlled to a low level by proper selection of polymer and liquid components, a microscopic phase separation between the polymer- and solvent-rich phases is commonly encountered, under which conditions the polymer gels possess a reasonable mechanical strength.

In this work, a further method for increasing the mechanical strength of gel electrolytes is investigated. This involves the incorporation of an interpenetrating polymer network into the given electrolyte. The underlying principle is to enhance the mechanical strength by providing chemical cross-linking while maintaining the polymer content at a low level [9]. In practice, a series of poly(ethylene glycol dimethacrylate) (PEGDMA) polymers with different amounts of ethylene oxide units is added, as a network former, into the poly(methyl methacrylate) (PMMA)-based gel electrolytes. In the resulting PEGDMA-modified PMMA-based gel electrolytes, as the cross-linking density is inversely proportional to the molecular weight of PEGDMA, the mechanically strongest gel film is likely

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made from the PEGDMA with the smallest molecular weight. It is also noted that PEGDMA carries an ethylene oxide unit that has a high donor number for Li^+ ions and high chain flexibility [10,11]. In our previous study [11], it was clearly demonstrated that the ion solvating ability of solvents or polymers is not correlated with their dielectric constants but is strongly dependent on the donor numbers. The free-ion fraction was found to be higher when polymers of a higher donor number were used as the gel-forming matrix. It is thus expected that the addition of PEGDMA may increase the ionic conductivity of PMMA-based gel electrolytes as the ethylene oxide unit with a high donor number may enrich the free-ion fraction while the high chain flexibility may allow a high ionic mobility.

In this work, to ascertain the above premises, the following studies have been performed. First, the mechanical strength and ionic conductivity of pristine PMMA-based gel electrolytes is examined as a function of PMMA content. Here, the ionic distribution and local viscosity changes are examined as a function of PMMA content by means of infrared and fluorescence spectroscopy. This allows the factor which controls the conductivity to be identified. Second, the effect of PEGDMA addition and its molecular weight on both mechanical strength and ionic conductivity of PEGDMA-modified PMMA-based gel electrolytes is investigated by means of electrochemical and spectroscopic techniques.

2. Experimental

2.1. Materials

PMMA (Aldrich, molecular weight ~120,000) was vacuum-dried at 60 °C for several days before use. Propylene carbonate (PC), ethylene carbonate (EC), tetrahydrofuran (THF), and lithium perchlorate ($LiClO_4$) were purchased from Tomiyama Co. as battery grade materials and were used without further purification. Lithium trifluoromethanesulfonate ($LiCF_3SO_3$, denoted hereafter as LiTf; >96%, Aldrich) was vacuum-dried at 120 °C for several days before use. Varieties of poly(ethylene glycol dimethacrylate) (M_n about 330, 536, and 875) (Aldrich) were purified by passage through an inhibitor removal column (Aldrich) and then stored with molecular sieve (4A). Benzoin ethyl ether (99%, Aldrich) was used as received.

For the preparation of PMMA-based gel electrolytes, PMMA was first dissolved in THF. After a homogeneous solution was obtained, an appropriate amount of liquid electrolytes was added to the polymer solution. The homogeneous solutions were casted on a piece of glass or Teflon sheet and stored at room temperature until the volatile THF was completely evaporated. The PEGDMA-modified gel electrolytes were prepared by first dissolving PMMA, PEGDMA and lithium salt in EC–PC mixed solvent and casting on a piece of glass sheet. For the curing of

PEGDMA, UV light (Osram, ULTRA-VITALUX, 300 W) was irradiated on the cast film for 5 min. Benzoin ethyl ether (0.1 wt.%) was used as the polymerization initiator. The cast film was covered with a quartz plate during irradiation with UV light to minimize solvent evaporation.

2.2. Instrumentation

The conductivity of the electrolytes was measured in a blocking-type cell which was fabricated by sandwiching the electrolyte film between two stainless steel (SUS 316) electrodes. Impedance data were obtained with a Zahner IM6e impedance analyzer in the frequency range 100 mHz–1 MHz at 30 °C. IR spectra were collected by means of a BOMEM MB 100 series FT-IR system with a resolution of $2 cm^{-1}$. The polymeric and liquid electrolyte samples were sealed with thin polyethylene films in an argon filled glovebox to avoid moisture interference. Individual absorption peaks in IR spectra were fitted with a trial function which consisted of a base line and a Lorenztian function. A nonlinear least squares method was used to fit the experimental data.

Fluorescence depolarization measurements were made with a luminescence spectrometer (AMINCO Bowman Series 2) equipped with a film polarizer. In order to avoid undesirable intermolecular energy transfer or spectral distortion due to self absorption, the concentration of the probe was maintained at a sufficiently low level (2 μM). The solid sample holder was placed at 60° against the excitation light in order to minimize reflectance. The emission intensity at 432 nm was measured in both the parallel and the perpendicular directions to the polarized excitation with the excitation wavelength fixed at 376 nm, from which the polarization ratio was calculated.

Tensile properties of polymer gel films were measured according to the ASTM 882 procedure with a universal tensile meter (UTM, Lloyd, LR 10K). The tensile rate was controlled at $1 cm min^{-1}$.

3. Results and discussion

3.1. Factors affecting ionic conductivity of pristine PMMA-based gel electrolytes

PMMA has a polar functional group so as to exhibit a high affinity for both lithium ions and plasticizing organic solvents. This feature allows the PMMA-based gel electrolytes to have a high ionic conductivity, even at sub-ambient temperature, and good solvent retention ability [11–15]. Despite this, the PMMA-based gel electrolytes exhibit such poor mechanical strength that a relatively large amount of PMMA is needed to make a dimensionally stable film. The ionic conductivity of the PMMA-based gel electrolytes containing $LiClO_4(1)EC(8.0)PC(3.5)$ by molar ratio is shown in Fig. 1 as a function of PMMA content. Even if
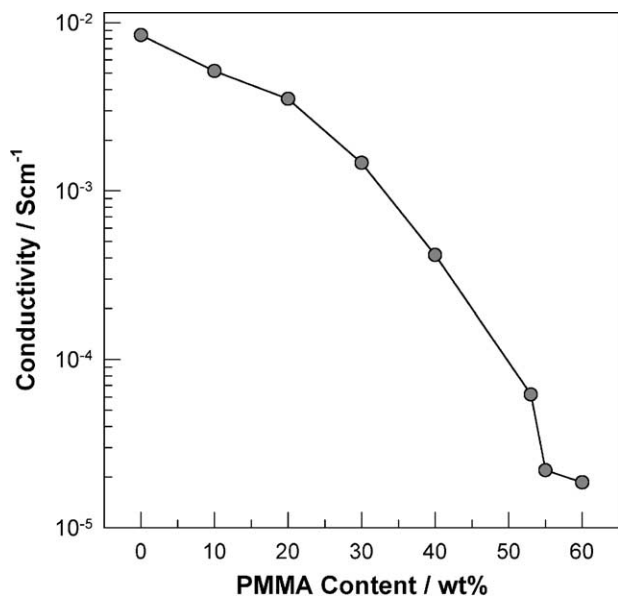
Fig. 1. Ionic conductivity of pristine PMMA-based gel electrolytes. The liquid component composed of LiClO$_4$(1)EC(8.0)PC(3.5) by molar ratio. Free-standing film obtained only after 50 wt.% of PMMA is added.

the conductivity is >10^{-3} S cm^{-1} when the PMMA loading is low (<30 wt.%), the polymer gels are still viscous liquids. The polymer gels become dimensionally stable only when the PMMA content is >50 wt.%, under which circumstances the ionic conductivity falls to 10^{-4} S cm^{-1}.

The decline in conductivity with increase in PMMA loading may arise from a decrease in either the charge carrier concentration or the ionic mobility. In order to examine the first possibility, the charge carrier concentration was estimated by means of IR spectroscopy. The IR spectra obtained from PMMA-based gel electrolytes containing LiTf(1)EC(7.7)PC(3.3) are shown in Fig. 2a; the PMMA loading is indicated. The background arising from the polymer absorption is subtracted for clarity. In order to analyze the ionic distribution in the polymer gels, the symmetric stretching modes of SO$_3$ in trifluoromethanesulfonate anions (CF$_3$SO$_3^-$, "triflate") are utilized as the probe because their absorption intensity is high and the degree of overlap with the polymer absorption is negligible. It is known that the non-degenerate vibrational mode of v_s(SO$_3$) appearing at 1030–1034 cm^{-1} comes from the free triflate anions, the 1040–1045 cm^{-1} absorption from the monodentate ion-paired triflates (LiX, LiX$_2^-$, LiX$_3^{2-}$), and the 1049–1053 cm^{-1} band from the more highly aggregated triflates such as Li$_2$X$^+$ and Li$_3$X^{2+}, respectively [16,17]. The relative intensity of three absorption bands that were obtained by fitting the spectra in Fig. 2a is shown in Fig. 2b. As seen, the PMMA loading leads to a slight increase in the ion-pair fraction at the expense of highly aggregated triflates, but the free-ion fraction remains largely the same within experimental error. Considering that the free ions are the major charge carriers in these polymer electrolytes, the rapid conductivity drop shown in Fig. 1 can not be explained
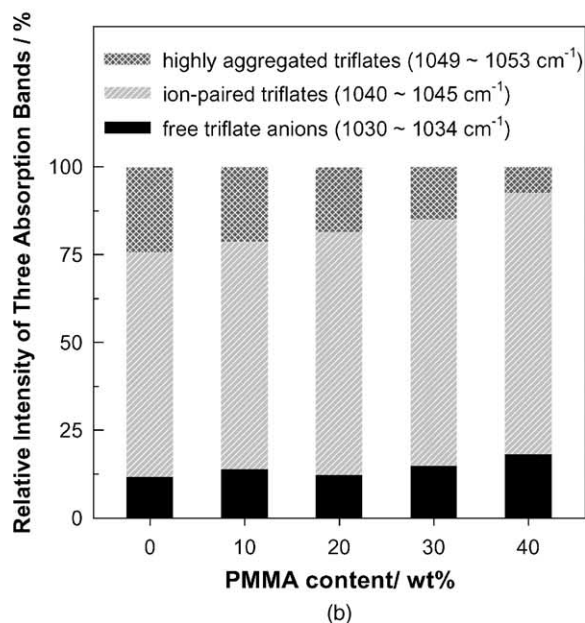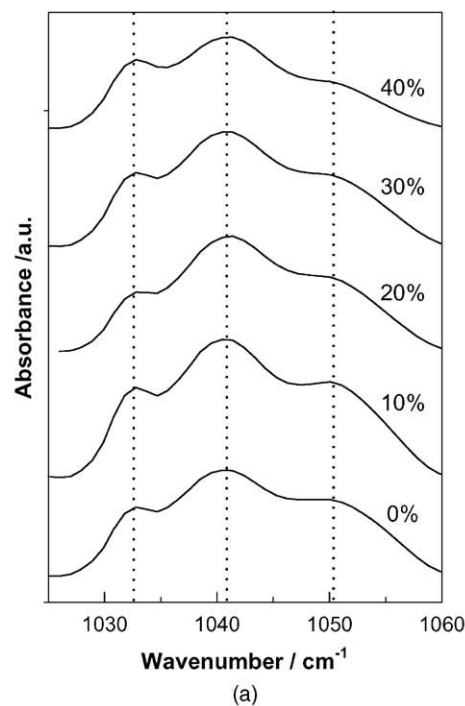

Fig. 2. (a) Infrared absorption spectra of pristine PMMA-based gel electrolytes containing LiTf(1)EC(7.7)PC(3.3) as liquid component. Only SO$_3$ symmetric stretching of triflate anion is provided. The wt.% of PMMA is indicated. (b) The relative intensity of three absorption bands.

by the decrease in charge carriers with PMMA addition, but by the decrease in ionic mobility as shown below.

Ionic mobility is not directly related to the macroscopic viscosity measured usually by rheometric methods [14,18]. Rather, the local viscosity surrounding charge carriers is the more important parameter affecting ionic mobility. In this work, the fluorescence depolarization method is used to probe the local viscosity of polymeric media. As the

fluorescence technique can sensibly detect structural alteration in the immediate local environment around probes, it has become a popular tool in polymer science to study structural, conformational and dynamic properties of polymer systems [19–22]. In the fluorescence depolarization experiment, the polarization ratio reflects directly the local viscosity of surrounding medium as the angular displacement of the fluorescent probe controls this parameter. The polarization ratio is expressed by the following equation.

$$P = \frac{I_\parallel - I_\perp}{I_\parallel + I_\perp} \tag{1}$$

Here, $I_\parallel$ and $I_\perp$ are the emission intensity parallel and perpendicular to the direction of polarized excitation, respectively. In this study, 9,10-diphenylanthracene is used as the probe since the anthracene group has an anisotropic planar structure and its molecular size is relatively small [21]. The typical fluorescence excitation and emission spectra of the probe, that was simply added to the PMMA-based gels, are shown in Fig. 3a. After the emission spectra parallel ($I_\parallel$) and perpendicular ($I_\perp$) to the direction of polarized excitation were obtained with variation in the PMMA content, the inverse of P was calculated. As shown in Fig. 3b, the $1/P$-values rapidly decrease with addition of PMMA. This indicates that the molecular motion in the polymer gel is significantly hindered as the polymer content increases. This leads to the conclusion that the decrease in mobility by the local viscosity enhancement in PMMA-rich gels is the major cause of the fall in conductivity shown in Fig. 1.

3.2. Mechanical strength and ionic conductivity of PEGDMA-modified PMMA-based gel electrolytes

The results presented so far suggest that the polymer content should be minimized to ensure a sufficiently high conductivity in PMMA-based gel polymer electrolytes. To minimize the polymer loading while maintaining a reasonable mechanical strength, an interpenetrating polymer network was introduced into the PMMA-based gel electrolytes via radiation polymerization of PEGDMA of different chain length. The molecular weight differs from about 330 to 536 and 875. The number of repeating ethylene oxide units (n) in the oligomers corresponds to 4.0, 8.7, and 16.4, respectively.
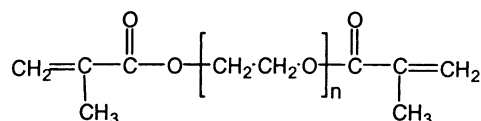
PEGDMA (n=4.0, 8.7, 16.4)

The visual appearance of gel electrolytes made with different compositions in PMMA, TEGDMA and LiClO$_4$(l)-EC(8.0)PC(3.5) is summarized in Fig. 4. In this particular experiment, tetraethylene glycol dimethacrylate (TEGDMA, $n = 4.0$) was used as the interpenetrating network former.
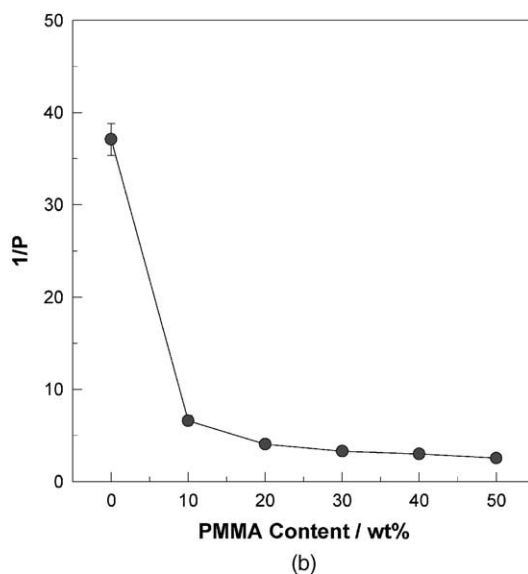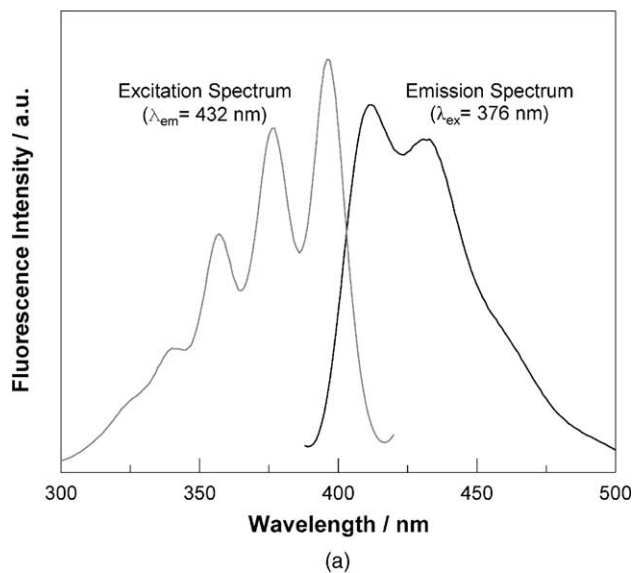
Fig. 3. (a) Fluorescence excitation and emission spectra of 9,10-diphenyl anthracene. (b) Inverse of polarization ratio ($1/P$) as function of PMMA content (wt.%) in polymer gels made with EC(8.0)PC(3.5) solution. A larger $1/P$-value corresponds to a lower local viscosity.

Without TFGDMA, at least 50 wt.% of PMMA is needed to obtain a free-standing film. The diagram indicates, however, that the total polymer content can be lowered down to 30 wt.% by incorporating the interpenetrating networks. For example, when 20 wt.% of TEGDMA is added, the PMMA content can be reduced to 10 wt.% to make a free-standing film. It is observed that this electrolyte film delivers an ionic conductivity of $>10^{-3}$ S cm^{-1}, which is one order of magnitude higher than that observed with a pristine PMMA (50 wt.%)-based gel electrolyte film. This observation clearly demonstrates that the mechanical strength of PMMA-based gel electrolytes can be enhanced by the introduction of PEGDMA networks while keeping the total polymer content low.
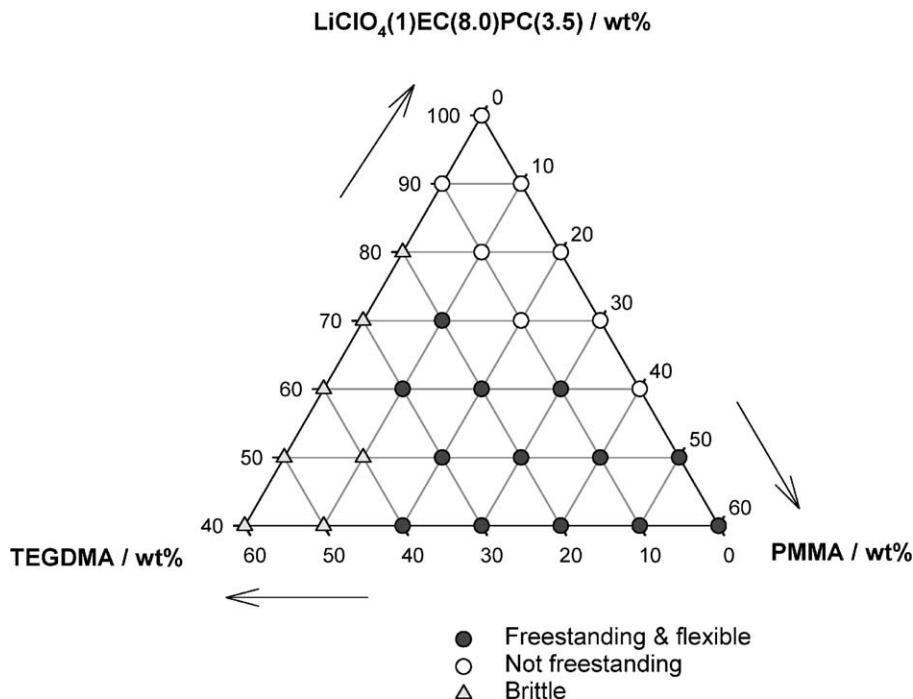
LiClO₄(1)EC(8.0)PC(3.5) / wt%

Fig. 4. Visual appearance of PMMA-based gel polymer electrolytes modified with TEGDMA ($n = 4.0$).

The stress–strain curves that reflect the mechanical strength of PMMA-based gel electrolyte films modified with PEGDMA of different molecular weight ($n = 4.0$, 8.7 and l6.4) are shown in Fig. 5. The elastic modulus (slope of stress–strain curve in the elastic region), ultimate tensile strength (stress at the break) and ultimate elongation (elongation at the break) are compared for the three polymer gel films. In general, the PEGDMA-modified polymer films exhibit a higher strength and lower extensibility than the pristine PMMA-based polymer film, even if the total polymer content is lower (i.e. 40 wt.% versus 55 wt.%). The higher elastic modulus and tensile strength, and lower elongation observed with the former films are the direct evidence of this feature. It is also noted that the film made with the PEGDMA of $n = 4.0$ has the highest mechanical strength and lowest extensibility, but the reverse features are shown by the film made with $n = 16.4$. This is the result of the difference in the cross-linking density provided by PEGDMA with different n-values. Clearly, the PEGDMA with $n = 4.0$ gives rise to the highest cross-linking density.

The free-ion fraction in PEGDMA-modified PMMA-based gel electrolytes is given in Fig. 6, which was obtained from the IR absorption spectra of the SO_3 symmetric stretching modes of triflate anions. The total amount of polymeric ingredient (PMMA + PEGDMA) was fixed at 40 wt.%. It is seen that the free-ion fraction grows with an increase in the ethylene oxide content in the polymeric media; that is, with an increase in both the PEGDMA loading content and the molecular weight (n-values) of the network formers. Considering that ionic distribution is

controlled either by the dielectric constant or by the donor number of the media, the strong correlation between the free-ion fraction and the ethylene oxide unit population in the gel electrolytes demonstrates the importance of donor number in affecting the ion-solvating ability of polymers. Note that the ether group in PEGDMA has a higher donor number but lower dielectric constant compared with the ester group in PMMA [23,24].
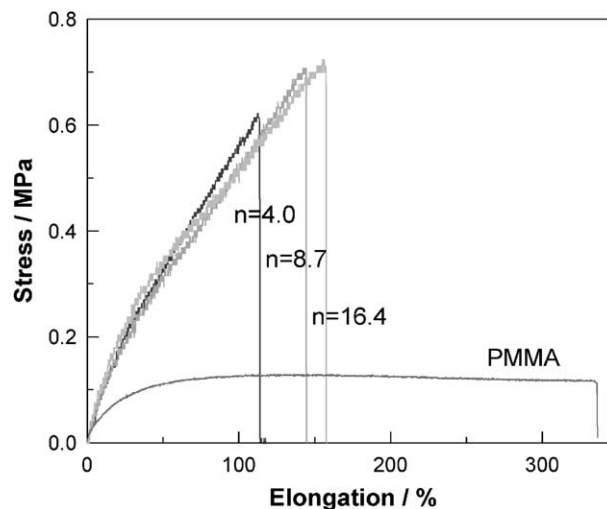

Fig. 5. Stress–strain curves of PMMA-based gel electrolytes modified with PEGDMA of different chain length. Each film consists of 20 wt.% of PMMA, 20 wt.% of PEGDMA and 60 wt.% of LiClO₄(1)EC(8.0)PC(3.5) solution. The pristine PMMA-based gel film, which contains 55 wt.% PMMA and 45 wt.% LiClO₄(1)EC(8.0)PC(3.5) solution is presented for comparison.
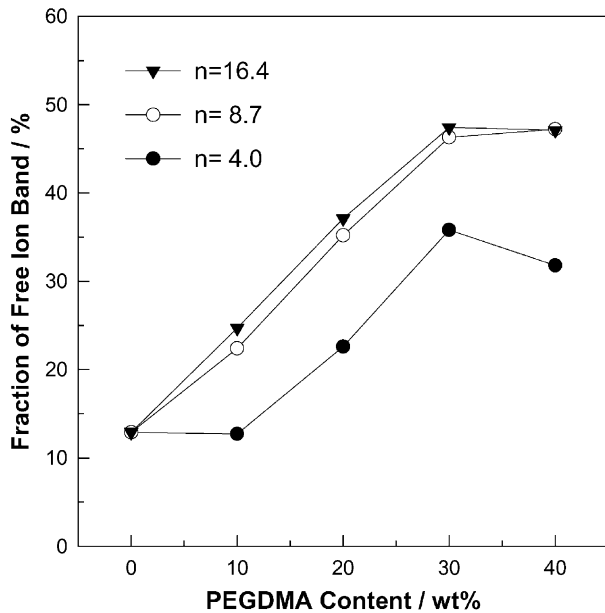
Fig. 6. Fraction of free-ion absorption band observed with PEGDMA-modified PMMA-based gel electrolytes. Experimental conditions as those for Fig. 2 except for PEGMDA modification. The total polymer content fixed at 40 wt.% in LiTf(1)EC(7.7)PC(3.3) solution. The *n*-values of PEGDMA are shown.

The variation of local viscosity in the PEGDMA-modified PMMA-based gel electrolytes as a function of both the loading content and *n*-values of PEGDMA is presented in Fig. 7. The results were obtained by means of the fluorescence depolarization method. It can be seen that the local viscosity of gel electrolytes, which is assessed from the 1/*P*-values, becomes smaller with increase in the ethylene oxide
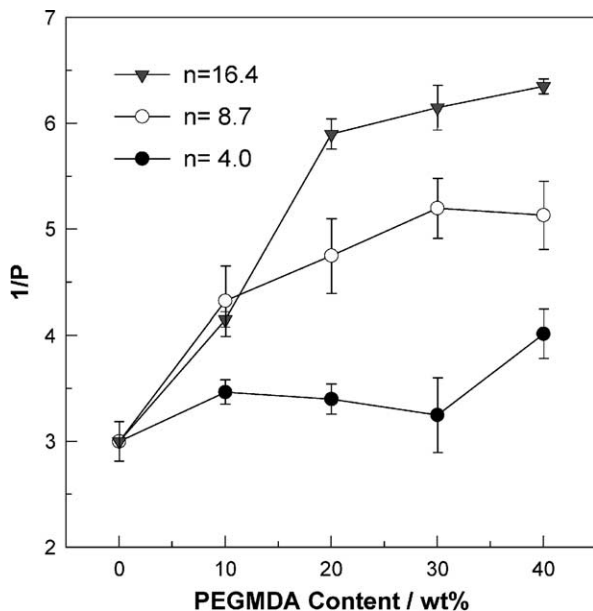

Fig. 7. Inverse of polarization ratio (1/*P*) observed for PEGDMA-modified PMMA-based gels. Experimental conditions same as those for Fig. 3 except for PEGMDA modification. The *n*-values of PEGDMA are indicated.

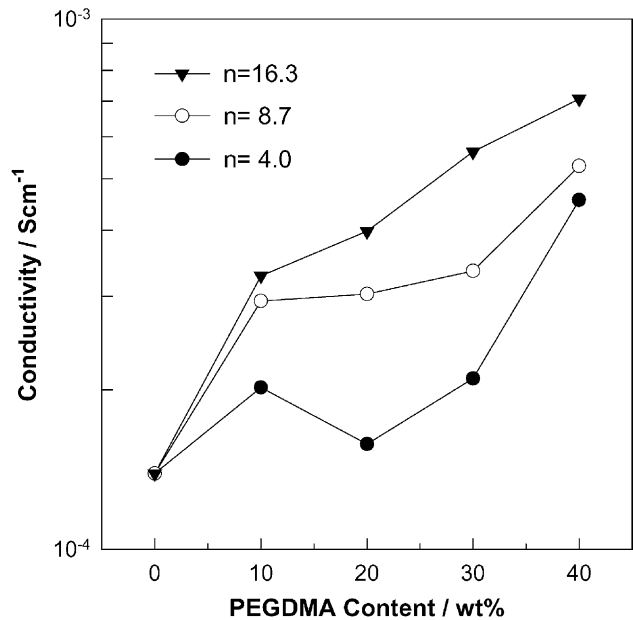Fig. 8. Ionic conductivity of PMMA-based gel electrolytes modified with PEGDMA of different chain length. Total polymer content fixed at 40 wt.% in LiClO$_4$(1)EC(8.0)PC(3.5) solution. The *n*-values of PEGDMA are indicated.

population in the polymeric media. This implies that the ethylene oxide chain is more flexible than PMMA. It is also apparent in Fig. 7 that the gel electrolytes made with PEGDMA of high molecular weight exhibit smaller local viscosity. This must result from the enhanced chain flexibility allowed by a larger gap between the cross-linking points in the PEGDMA with high *n*-values.

The results shown in Figs. 6 and 7 indicate that the incorporation of an interpenetrating network former provides favorable features in terms of both the free-ion fraction and the local viscosity of the polymer media. It is thus not difficult to expect a higher ionic conductivity in the polymer gel electrolytes made with higher PEGDMA loading, in particular, modified with PEGDMA with high *n*-values. Fig. 8 ascertains this feature.

4. Conclusions

(i) In pristine PMMA-based gel electrolytes, the ionic conductivity shows a steady decrease with an increase in PMMA content. A fluorescence study reveals that this is caused by a local viscosity increment with PMMA loading.

(ii) The addition of PEGDMA is effective in increasing the dimensional stability of PMMA-based gel electrolytes, which is due to a cross-linking effect exerted by the network former. In pristine PMMA-based gel electrolytes, at least 50 wt.% of PMMA is required to produce free-standing films. Due to the cross-linking effect, however, a free-standing film can be made even

if the total polymer content (PMMA + TEGDMA) is reduced to 30 wt.% in TEGDMA-modified gel electrolytes.

(iii) Ionic conductivity can also be enhanced with PEGDMA modification owing to the high donor number and high chain flexibility of the ethylene oxide units. As a consequence, the incorporation of higher molecular weight PEGDMA is more effective for conductivity enhancement.

Acknowledgements

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