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Polymer gel electrolytes prepared by thermal curing of poly(vinylidene fluoride)–hexafluoropropene/poly(ethylene glycol)/propylene carbonate/lithium perchlorate blends

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Abstract

In an effort to prepare a poly(vinylidene fluoride)–hexafluoropropene (PVdF–HFP) based polymer gel film electrolyte with higher mechanical strength and little volatility, a two component urethane system employing blocked multiisocyanate as a potential thermal crosslinking agent, and low molar mass poly(ethylene glycol) (PEG) as a hydroxy-functional coreactant was blended with the PVdF–HFP gel system, and the cure of the blends was examined as a function of temperature, molar mass of PEG, and PEG/blocked isocyanate ratio. The network forming reaction could not proceed below 100 °C, but it slowly took place above 120 °C by thermal deblocking of blocked multiisocyanate, followed by the reaction of regenerated free multiisocyanate with PEG in the absence and presence of PVdF–HFP, plasticizer (propylene carbonate, PC) and lithium perchlorate. The adduct of polymeric methylene diphenyl diisocyante (PMDI) with acetone oxime was used as a potential thermal crosslinking agent for this study. Network polymer gels having no PVdF–HFP were also prepared for comparison. The cured (PVdF–HFP/PEG/blocked PMDI/PC/$LiClO_4$) polymer gel networks were mechanically and dimensionally stable, and their thermal characteristics and electrochemical properties were investigated using FT-IR spectroscopy, differential scanning calorimetry, electrochemical impedance spectroscopy and linear sweep voltammetry.

Keywords: Thermal crosslinking; Blocked multiisocyanate; Polymer gel electrolyte

1. Introduction

Recently, there have been many efforts to develop thin film lithium batteries using polymer gel electrolytes [1–5]. Since light weight, small size and high efficiency of electrical machinery can be achieved, lithium polymer batteries are very promising systems in terms of energy density and power density [4,5]. Polymer gel electrolytes combine good mechanical properties with high ionic conductivity at room temperature. They consist of a relatively robust polymer matrix. A salt and a plasticizing liquid solvent in polymer gels are expected to increase the ionic conductivity of the system [6].

Polymer gel electrolytes are prepared by encapsulating organic electrolyte solutions into various matrix polymers such as PVdF [7], polyacrylonitrile (PAN) [8], poly(methyl methacrylate) (PMMA) [9], poly(vinyl chloride) (PVC) [10], poly(vinyl pyrrolidone) (PVP) [11] and poly(vinyl sulfone) (PVS) [12]. So far, PVdF (or its copolymer) has been the most extensively studied as a base polymer for the polymer gel electrolytes due to its high solvating power towards lithium salts. Nevertheless, PVdF/organic electrolyte system has low processibility at room temperature because of the thermoplastic nature of PVdF. The impregnation of a liquid electrolyte into PVdF results in softening of the polymer [3–5]. It has been also shown that PVdF/ethylene carbonate (or PC)/Li salt polymer gel electrolytes lose carbonate solvent by evaporation, when they are exposed to an open atmosphere [13]. This solvent loss causes variation of electrolyte composition as well as low ionic conductivity. Thus, a polymer gel electrolyte with high ionic conductivity and little or no volatility is desired. Several strategies have been exploited to overcome the problems, including the in situ film forming techniques [14,15] and membrane-supported polymer gel electrolyte approaches [16,17]. The use of oligomeric poly(ethylene glycol) dimethyl ethers as plasticizer was also reported to

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prepare polymer gel electrolytes with desirable thermal properties, especially their volatility [13,18,19]. Among them, crosslinking modification has proved to be one of the most important means towards improving the mechanical properties of the polymer gel electrolytes.

For crosslinking of poly(ethylene oxide)s (PEOs) (and/or PEGs), various methods can be introduced including chemical and radiation processes. PEOs were crosslinked by γ-irradiation [20,21] or by UV irradiation in the presence of benzophenone as a photoinitiator [22–24]. Chemical crosslinking of PEOs was also reported [25]. Several routes have been applied to obtain crosslinked PEO structures via urethane chemistry [26–28] and esterification chemistry [29]. Relatively fast crosslinking using isocyanates provides significant advantages for many applications over other methods. Although various isocyanates can efficiently crosslink PEOs (and PEGs), the crosslinking of PEGs with blocked isocyanates for polymer electrolyte applications has not yet been investigated.

The liquid-like nature of current PVdF-based gel systems is not desirable for many polymer electrolyte applications. In an effort to prepare a new class of PVdF-based polymer gel electrolyte with higher mechanical strength and little volatility consisting of chemically crosslinked network phase, we have attempted to synthesize an urethane network system based on blocked multiisocyanate and PEG, wherein lithium perchlorate salt, plasticizer and PVdF–HFP were incorporated. PEGs with hydroxyl groups can react with unblocked multiisocyanate to form crosslinked networks. The isocyanate group can be effectively 'blocked', however, by oximes [30]. The blocked multiisocyanate can consequently be introduced into a PVdF-gel system along with PEGs, later to be activated as a crosslinking agent. This allows for PVdF gel film formation to a preferred state prior to crosslinking. By then heating above the dissociation temperature (T_d) of the blocked multiisocyanate, the active isocyanate group is regenerated and crosslinking can occur. In other words, by the use of blocked multiisocyanate instead of unblocked multiisocyanate, crosslinking can be scheduled to follow film formation i.e. crosslinking takes place in the film state by partial incorporation of blocked multiisocyanate and PEG into PVdF–HFP gel electrolyte film (Scheme 1). This is because the isocyanate groups of multiisocyanate can be blocked in advance giving a stable derivative at ambient temperatures. On being mixed into the casting solution containing PVdF–HFP, PEG, PC and lithium salt, it will not react with the active hydrogen atoms of PEG. When the PVdF–HFP based film has been formed by solution casting technique, the crosslinking will not take place until the film is subjected to heat treatment.

In this paper, we report the effects of the amount of blocked isocyanate used in the blend mixture and the length of PEG segments on gel fraction yield and the thermal properties of the networks, as well as basic electrochemical properties.

2. Experimental

2.1. Materials

The seven kinds of PEGs used in this work were PEG200, PEG400, PEG600, PEG1000, PEG2000, PEG3400 and PEG4600 from Aldrich. PVdF–HFP copolymer (Kynar 2801) was from Elf Atochem. Toluene 2,4-diisocyanate from Aldrich and PMDI (MW ≈ 450, equivalent weight ≈ 225, functionality = 2.01–2.1) from Kumho-Mitsui Chemical Corp. were used as received. Acetone oxime from Aldrich was used as a blocking agent for isocyanates. Lithium perchlorate ($LiClO_4$, purity >99.99%) from Aldrich was used as a lithium salt. All other reagents were purchased from commercial sources (Aldrich or Fisher Scientific) and used without further purification unless otherwise noted. PEGs were dried under vacuum at room temperature for 48 h before use.

2.2. Sample characterization

A Varian Unity Inova spectrometer was used to obtain the ^{1}H NMR spectra of the blocked isocyanates. All data were for samples in $CDCl_3$. Tetramethylsilane (TMS) was used as an internal standard reference. The IR spectra of the samples were recorded on a Unicamx Mattson 500 FT-IR spectrometer using KBr plate technique.

The thermal characterization of the prepared polymer networks was carried out by Differential Scanning Calorimeter (DSC) with a heating and cooling rate of 10 °C/min on a DSC TA 2910 instrument. Samples of 5–9 mg were quenched from room temperature to −30 °C by liquid nitrogen and were run under a nitrogen atmosphere over a temperature range of 0–250 °C. Indium ($T_m = 156.6$ °C) was used for temperature calibration. Thermal stability of the sample was monitored by a TGA TA 2910 instrument.

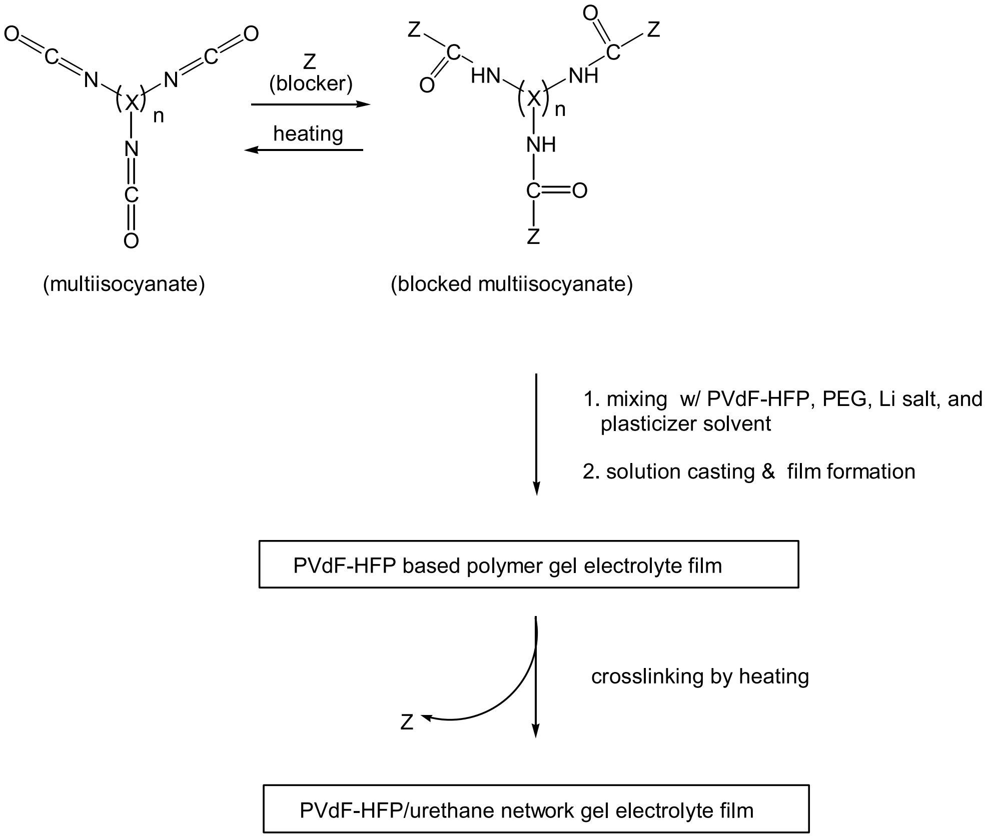
The mechanical strength of the polymer gel electrolyte films was determined from stress–strain measurements using an Instron Model 4204 universal testing instrument.

For the determination of gel fraction of network films, the cured PEG/blocked PMDI samples were weighed and then extracted with methanol for 24 h. After extraction, they were dried under vacuum and weighed. The gel fraction was simply calculated by ratio of initial weight of sample to weight of extracted sample:

$$\text{Gel Fraction (GF, \%)} = (W/W_0)100$$

where W_0 is the initial weight of sample and W is the weight of extracted sample.

Ionic conductivities of the prepared gel electrolytes were measured using frequency response analyzer (model 1025) from EG & G. Cells for measuring the ionic conductivity were prepared by sandwiching the sample (diameter 10 mm) between two stainless steel electrodes (diameter 20 mm). Ionic conductivity was measured in a dry chamber at room temperature. A potential difference of 5 mV was applied to



Scheme 1. Preparation of network polymer gel electrolyte film.

the sample for frequencies ranging from 10 mHz to 100 kHz. Bulk resistance was obtained from measured AC impedance (Nyquest plot). Ionic conductivity was calculated by the equation below:

$$\sigma(\text{Ionic Conductivity}) = t/(R_b A)$$

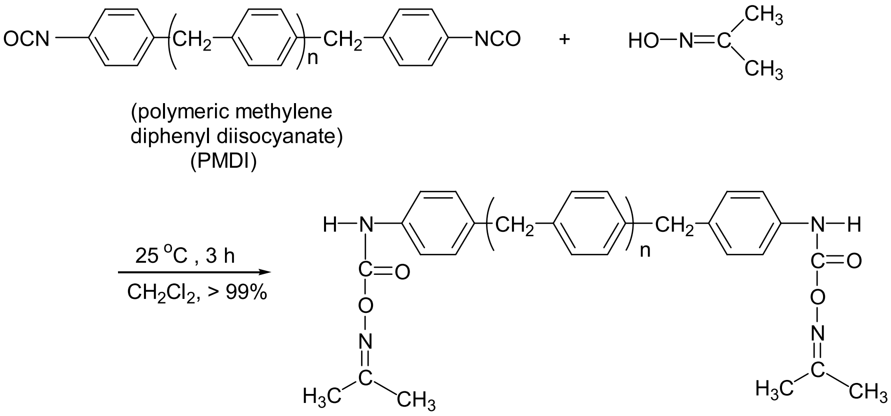
where t is the thickness of polymer network films, R_b, the bulk resistance of polymer network films, and A is the area of polymer network films. One of the important parameters for the characterization of any electrolyte is the extent of its electrochemical stability window. Electrochemical stability window of the prepared polymer gel samples was obtained by means of WBCS 3000 battery cycler from WonATech. It was evaluated with cells featuring a stainless steel working electrode, a lithium counter electrode and a reference electrode by linear sweep voltammetry at 25 °C. Voltage ranging was carried out from 0 to 5.0 V. Sweep rate was 1.0 mV/s.

2.3. Preparation of blocked isocyanates

Two blocked isocyanates used in this study (acetone oxime blocked toluene 2,4-diisocyanate and acetone oxime-blocked PMDI) have been synthesized and characterized according to the modified procedure of Ref. [30]. The synthetic route to acetone oxime-blocked polymeric MDI is shown in Scheme 2. In a 250 mL round-bottom flask were placed PMDI (5.00 g, 11 mmol), acetone oxime (1.75 g, 24 mmol), and methylene chloride (100 mL). The solution was stirred at 25 °C under N_2 for 3 h. The reaction mixture was then poured into water. The organic layer was separated and washed with aq HCl and water, respectively. The solvent was evaporated yielding a brownish oil: yield = 6.40 g (>99%).

2.4. Model reactions of acetone oxime-blocked toluene 2,4-diisocyanate with butanol in an electrolyte solution

Twenty milliliters of 1.0 M solution of $LiClO_4$ in PC was taken in a moisture-free three-necked flask, fitted with a condenser and a nitrogen gas inlet. The contents were heated to 30–50 °C with stirring. Catalysts such as triethyl amine or diazabicyclo-[2,2,2]octane(DABCO), 0.01–0.5% on the weight of blocked isocyanate, were added. Acetone oxime-blocked toluene 2,4-diisocyanate (1 g, 3.12 mmol) and butanol (0.51 g, 6.86 mmol) were added, and the reaction mixture was stirred at 120 °C under N_2 for 4 h. The reaction mixture was then poured into water. The organic layer was separated and washed with aq HCl and water, respectively. The solvent was evaporated yielding a brownish solid. The product so formed was washed with hexane, filtered and dried in a vacuum oven ((3-butoxycarbonylamino-4-methylphenyl)-carbamic acid butyl ester): yield = 1.00 g (3.102 mmol, 99.4%), mp 120 °C, ^1H NMR (500 MHz,



Scheme 2. Preparation of blocked PMDI by the use of acetone oxime.

$CDCl_3$), δ 0.95 (t, $J = 5.28$ Hz, 6H, $-CH_3$), δ 1.42 (m, 4H, $-CH_2CH_3$), δ 1.65 (m, 4H, $-OCH_2CH_2-$), δ 2.21 (s, 3H, $Ar-CH_3$) δ 4.15 (t, $J = 6.45$ Hz, 4H, $-OCH_2CH_2-$), δ 6.39 (s, 1H, *ortho* to –NH–), δ 6.58 (d, 1H, $J = 8.20$ Hz, *meta* to $-CH_3$), δ 7.07 (d, 1H, $J = 8.21$ Hz, *ortho* to $-CH_3$), δ 7.36 (s, 1H), δ 7.76 (s, 1H).

2.5. Preparation of acetone oxime-blocked PMDI/PEG network films

The blocked PMDI/PEG network films were prepared by a solvent-casting method. The reaction conditions for the thermal curing of various molecular weight PEGs are shown in Table 1. In a typical procedure, a mixture containing appropriate amounts of blocked PMDI (0.5 g), DABCO (5 mol% based on blocked PMDI) and PEG200 (0.5 g) was dissolved in tetrahydrofuran (THF, 8 ml). The resulting solution was poured into a glass dish, and the solvent was allowed to evaporate in air prior to thermal curing. The curing was carried out at 120 °C for ~10 h yielding a free-standing film.

2.6. Preparation of PVdF–HFP/PEG200/blocked PMDI/PC/LiClO₄ polymer electrolyte films

PVdF–HFP, PEG200, blocked PMDI and $LiClO_4$ were dried under vacuum before use. PEG 200 (1 g) was added under stirring into a 1.0 M solution of $LiClO_4$ in PC (10 g) containing blocked PMDI (3 g) and PVdF–HFP (4 g). The mixture was poured onto a glass plate or a 25 × 25 mm rectangular aluminum foil, and a free-standing film was formed when the excess amount of PC (~2 g) was evaporated at 60 °C. The casted gel film (sandwiched between two glass plates) was then transferred into a desiccator which, according to the cure schedule, was heated in an oven at temperature ranging from 100 to 120 °C for different times until the blocked isocyanate functionality was not detected by thin layer chromatography (TLC). The duration of chemical reaction was ~11 h. The thickness of

Table 1
Composition and measured gel fraction of the PEG/acetone oxime-blocked PMDI network films

Entry	Sample composition[a] (molar ratio)	Curing time (h)	Film forming property	Gel fraction (%)
1	PEG200/BPMDI = 1/1	3	Poor	10
2	PEG200/BPMDI = 1/1	6	Poor	21
3	PEG200/BPMDI = 1/1	10	Poor	35
4	PEG200/BPMDI/DABCO = 1/1/0.05	4	Poor	52
5	PEG200/BPMDI = 1/1.5	10	Poor	41
6	PEG200/BPMDI/DABCO = 1/1.5/0.075	4	Poor	55
7	PEG200/BPMDI = 1/2	10	Good	44
8	PEG200/BPMDI/DABCO = 1/2/0.15	4	Good	67
9	PEG200/BPMDI = 1/3	10	Good	80
10	PEG200/BPMDI/DABCO = 1/3/0.05	4	Good	93
11	PEG400/BPMDI/DABCO = 1/3/0.15	4	Poor	45
12	PEG600/BPMDI/DABCO = 1/3/0.15	4	Poor	32
13	PEG1000/BPMDI/DABCO = 1/3/0.15	4	Poor	14
14	PEG2000/BPMDI/DABCO = 1/3/0.15	4	Poor	13
15	PEG3400/BPMDI/DABCO = 1/3/0.15	4	Poor	12
16	PEG4600/BPMDI/DABCO = 1/3/0.15	4	Poor	9

Curing temperature: 120 °C.

[a] The code BPMDI represents blocked PMDI, and the PEGs are coded by molecular weights.

the network gel film obtained was measured with a micrometer and varied between 100 and 120 μm. The prepared polymer network films were stored in a desiccator.

3. Results and discussion

External stimulation such as heating and photo-irradiation induced crosslinking is of special interest in control of crosslink density of polymer gel electrolyte systems [5]. Especially, development of efficient thermal-latent crosslinkers is desirable for enhancement of both storage stability and handling of gel-forming resins. Potential candidates for this type of thermal-latent crosslinker should be inert under normal conditions (e.g. ambient temperature and solution), but show activity upon heating. For this purpose, the adduct of PMDI with acetone oxime was used as a novel potential thermal crosslinker for the present work. We also have designed some network polymer gel electrolyte systems that can be directly prepared by thermal crosslinking reactions of PVdF–HFP based gel electrolyte films containing acetone oxime-blocked PMDI as a crosslinker and PEG as a hydroxy-functional coreactant. This design allows the procedure of blending the blocked PMDI/PEG containing electrolyte solution with PVdF–HFP matrix in advance, followed by the crosslinking reaction upon heating, which would find many advantages for the application of this type of polymer gel electrolytes to lithium polymer batteries. Here, we report that crosslinking can be scheduled to follow free-standing gel electrolyte film formation i.e. crosslinking takes place in the film state by partial incorporation of a two component urethane system (blocked PMDI and PEG) into a PVdF–HFP based gel electrolyte film (Scheme 1).

3.1. Synthesis of blocked multiisocyanates

The highly reactive isocyanate group can be converted to a blocked isocyanate by reacting it with a suitable blocking agent. These adducts are relatively inert at room temperature, but they generate free isocyanates at a deblocking temperature, which then react with the available nucleophile (e.g. hydroxy-functional compounds) to form stable urethane [31]. The isocyanate can be blocked through one of the several methods [32]. In this study, isocyanate functionality of multiisocyanates such as PMDI and toluene 2,4-diisocyanate was blocked to make a thermal crosslinking reaction possible upon heating over 100 °C, but not higher than the boiling point of plasticizer liquid. Acetone oxime was the blocking agent of choice because of its high evaporation property (deblocking temperature: ca. 120 °C) Thus, blocked PMDI and toluene 2,4-diisocyanate were prepared in >99% yield by reacting isocyanates with acetone oxime (Schemes 2 and 3).

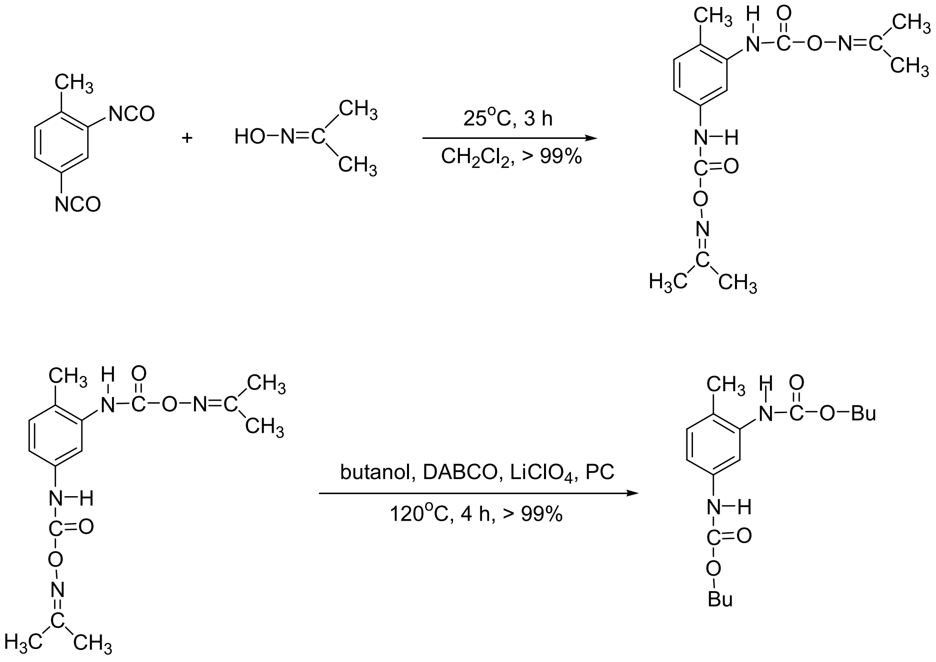
IR spectra of all blocked isocyanate adducts were recorded using a FT-IR unit in KBr pellets, and all adducts showed no NCO absorption band at ~2270 cm^{-1} (Fig. 1), and this indicated the complete blocking of isocyanate groups with acetone oxime. A stretching vibration band at 1210–1220 cm^{-1} showed the presence of C=O combined with N–H in all spectra. The formation of PMDI from the acetone oxime-blocked PMDI is observed in the FT-IR spectrum of heated blocked PMDI (Fig. 2). In the spectrum of acetone oxime-blocked PMDI the isocyanate stretching mode frequency, the 2270 cm^{-1} band, is absent, whereas in the heat-treated sample, the regeneration of the isocyanate group is clearly observed. The increase of the intensities of the isocyanate group with an increase in temperature is seen in Fig. 2. The FT-IR studies clearly demonstrate the formation of PMDI from the acetone oxime-blocked PMDI after heating at a temperature of ~110 °C for 5 min in the neat state.

3.2. Evaluation of the blocked isocyanate reactivity in the model reaction

In a preliminary set of experiments the reactivity of the blocked isocyanate was tested by model reactions of acetone oxime-blocked toluene 2,4-diisocyanate with butanol, a hydroxy-functional model compound, in the presence of a plasticizer and a lithium salt (Scheme 3). The reaction of acetone oxime-blocked toluene 2,4-diisocyanate and butanol with a feed molar ratio of 1:2.2 was carried out in 1.0 M solution of LiClO_4 in PC containing trace amounts of DABCO as catalyst. After the mixture was allowed to react at 120 °C for 4 h, the product was isolated in 99.4% yield. The 500 MHz ^{1}H NMR spectrum of the product is shown in Fig. 3. It should be noted that no signals due to acetone oxime (=C–CH_3) appeared at ~2.50 ppm of the product spectrum, and the ratio of peaks from the aromatic moiety to those from the butanol segment was in good agreement with a 1:2 adduct structure. The deblocking of the acetone oxime-blocked toluene 2,4-diisocyanate in the reaction mixture occurred at a lower temperature than the boiling point of PC (bp 240 °C), and the presence of PC and LiClO_4 did not suppress the urethane forming reaction. The present transformation is simple and highly selectively, and no side reaction products were detected. Having established the feasibility of the thermal curing reaction using blocked isocyanate and hydroxy-functional coreactant, we proceeded to study the constructions of different reaction schemes based on model reactions.

3.3. Thermal curing of PEGs with acetone oxime-blocked PMDI

The next step consisted in preparing networks using PEGs and acetone oxime-blocked PMDI (Table 1). The various studies were the [NCO]/[OH] ratio and the molecular weight of PEGs in order to vary the crosslink density and the dimensional stability of the network films. Appropriate quantities of the starting materials were mixed



Scheme 3. Model reaction of acetone oxime-blocked toluene 2,4-diisocyanate with butanol in an electrolyte solution.

at room temperature in THF with (or without) DABCO as catalyst. The reaction mixture was poured onto a glass plate in order to obtain a film ~100 μm thick, and THF was removed by heating at 60 °C. Then, the network was formed by heating the precursor film at 120 °C for 4–10 h. It was found that in the absence of catalyst PEG200 undergoes a crosslinking process with blocked PMDI when heated for relatively long periods of time (~10 h) at 120 °C to form a network film (Table 1, entries 1–3). In this case, the gel fraction of the PEG200/blocked PMDI network film as a function of curing time was measured to explore the thermal-crosslinking rate. The gel fractions were gravimetrically determined after extracting the thermally crosslinked network film by methanol. Even though the amount of blocked PMDI used guaranteed a stoichiometric ratio among the OH groups of PEG and blocked isocyanate

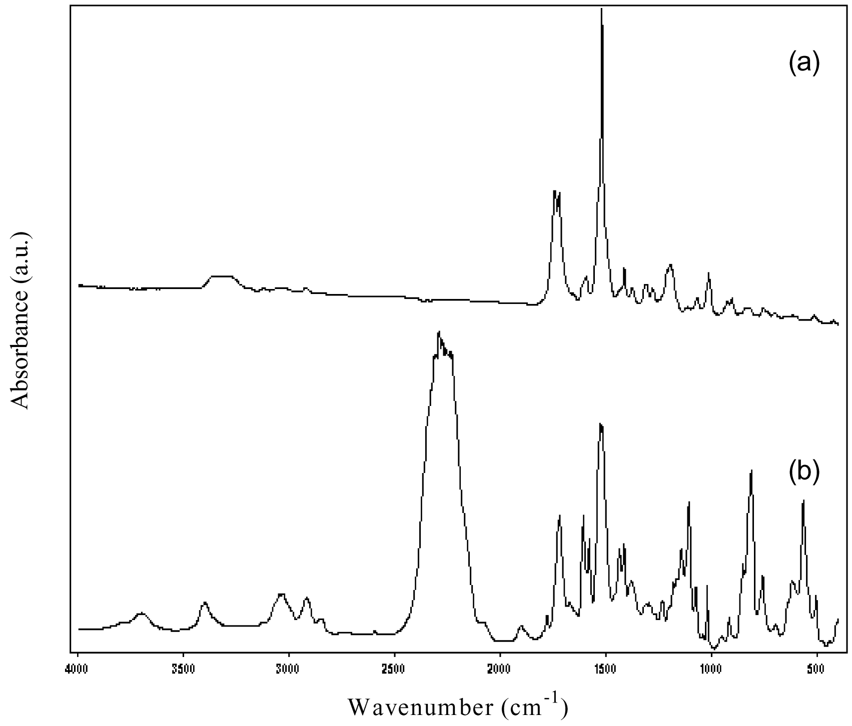


Fig. 1. FT-IR spectra of (a) acetone oxime-blocked PMDI and (b) PMDI.

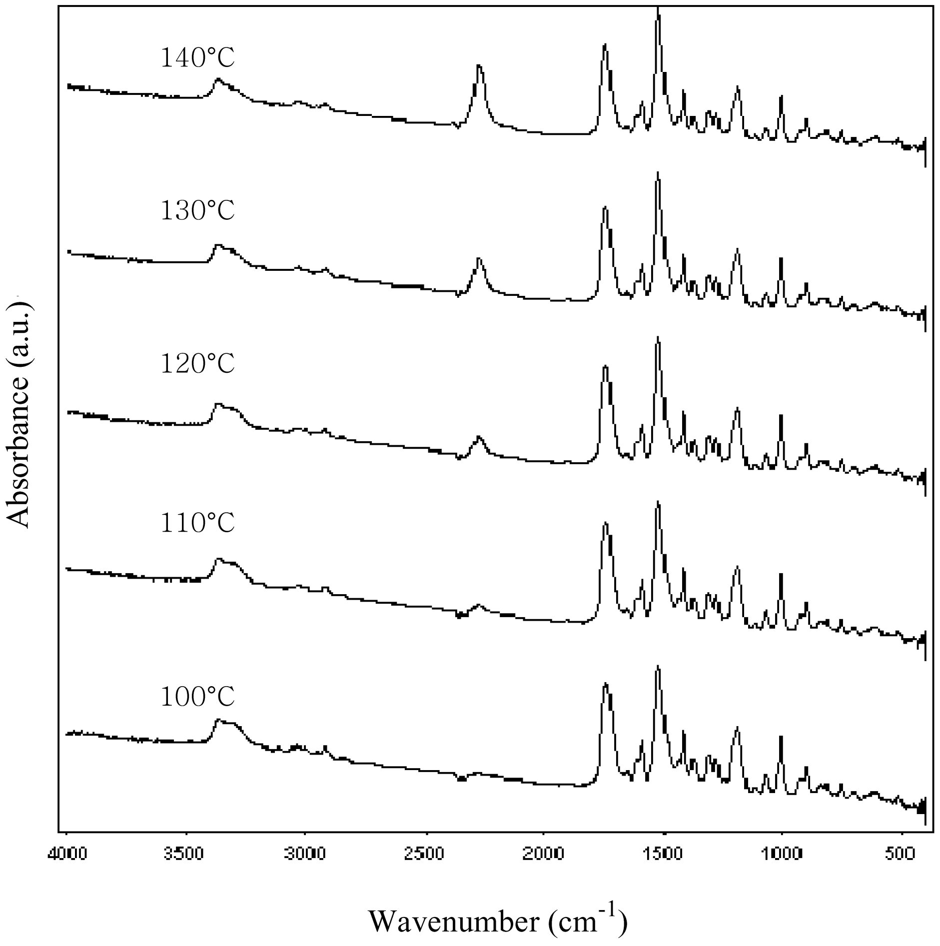


Fig. 2. FT-IR spectra of blocked PMDI at varying temperatures.

groups, the gel fraction did not reach close to 0.5 within the heating at 120 °C for 10 h. However, the degree of crosslinking could be controlled by tuning the heating time. In the presence of catalyst (5 mol% based on blocked PMDI) the crosslinking reaction was completed within 4 h (gel fraction = 52%, entry 4). Extending the heating time over 4 h did not provide greater amounts of gel fraction.

In order to investigate whether the crosslink density depends on the amount of blocked PMDI used, several samples of different composition were crosslinked under

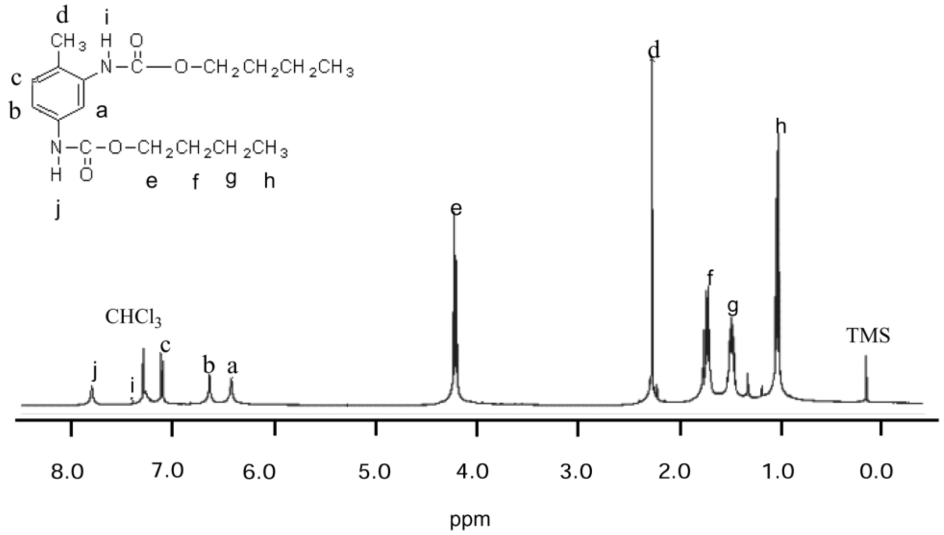


Fig. 3. A ^{1}H NMR spectrum of the reaction product from acetone oxime-blocked toluene 2,4-diisocyanate and butanol.

identical curing conditions. The ratio between PEG and blocked polymeric MDI was varied in the range of 1:1 to 1:3 mol of blocked isocyanate per mol of PEG. The data shown in Table 1 indicate that increasing the amount of blocked PMDI in the reaction mixture gives a higher value for gel fraction. PEG200/blocked PMDI (= 1/3) system in the presence of catalyst gave the free-standing network film with the highest gel fraction yield of 93% (entry 10). This is probably due to the increased amount of regenerated isocyanate groups formed with increasing blocked PMDI content.

For PEG200/blocked PMDI (= 1/3) systems, the catalyst has also demonstrated a great effect on the crosslinking between blocked isocyanate and hydroxyl groups. In general, the lower concentration of the catalyst was, the much slower the crosslinking proceeded. For instance, for the reaction between PEG and blocked PMDI without catalyst, it took more than 10 h for blocked isocyanate–urethane conversion to reach 90% (the conversion was estimated by the model reaction of unblocked PMDI with PEG without catalyst through the isocyanate titration method specified in ASTM D2572-91 before and after the curing).

The molar mass dependence of the efficiency of chemical crosslinking of PEG with blocked PMDI is also shown in Table 1. It was found that with regard to PEG network percent of gel formed decreases with larger molar mass of PEG. The amount of the insoluble PEG/blocked polymeric MDI (= 1/3) mixture upon curing decreases going from 93% for PEG of 200 Da to 9% for PEG of 4600 Da (Table 1, entries 10 and 16). It is likely that the proximity of hydroxy groups between PEG components in the sample is a very important factor for crosslinking reactions upon heating. Lower molar mass PEG favored better crosslinking, since the greater mobility of the polymer segments provides a increased number of contacts with regenerated free isocyanates. On the other hand, higher molar mass PEG chains are entangled to render the reaction of hydroxyl groups with regenerated free isocyanates difficult. From the various curing results, most of the compositions prepared proved unsuccessful in giving dimensionally stable network film except the samples containing the PEG200.

3.4. Thermal characterization

Uncrosslinked specimens of PEG/blocked PMDI (3 equiv.) were characterized by DSC measurement and the corresponding thermograms of the film are presented in Fig. 4. T_g and T_m were not observed in any curve in a temperature range from 50 to 250 °C. The urethane precursors (a mixture of PEG and blocked PMDI) are thermally stable compounds at ambient temperature because no exothermic event was discernible in the DSC heating trace even if they were scanned to as high as 120 °C. However, upon heating over 120 °C, a prominent exotherm manifested itself in the thermogram, indicating the occurrence of network forming process. This could be evidenced by the fact: the sample after being heated over 120 °C became hardened. Fig. 4 also shows that except for plain blocked PMDI/PEG system, all the catalyst containing systems exhibit exotherms in the thermograms with different peak temperatures (T_p). Clearly, lower molecular weight PEG specimens give lower T_p as they contain more reactive hydroxy groups per unit weight. For specimens containing no catalyst, the cure seems to proceed with difficulty and is incomplete even though the highest temperature of the specified temperature range is reached (Fig. 4(b)). It was found that a catalyst content greater than ca. 5 mol% based on blocked PMDI is necessary to ensure the completion of curing.

3.5. Thermal curing of PVdF–HFP/PEG/blocked PMDI/LiClO$_4$/PC blends

In further studies, various molecular weight PEGs and blocked PMDI were mixed with a liquid electrolyte (1.0 M solution of LiClO$_4$ in PC) (Table 2). The gel-forming reaction was initiated by solvent-casting techniques followed by heat treatment, which resulted in the formation of gel films consisting of a three dimensional PEG network containing the liquid electrolyte. All the PEG/blocked PMDI networks were completely transparent (not phase separated), irrespectively of the presence and absence of the electrolyte. However, these heat-cured polymer gel films were not dimensionally stable and difficult to handle even though the films could encapsulate up to 178 wt% liquid electrolyte based on the amount of solid components (Table 2, entry 2).

The polycondensation reactions employing the use of low molar mass PEGs and blocked PMDI in the absence and presence of a liquid electrolyte readily gave urethane networks. However, to improve the film-forming property of the urethane networks, PVdF–HFP was incorporated into the network system to give thin films with good mechanical properties. We also attempted to incorporate a lithium salt and a plasticizing liquid solvent into the network to increase the ionic conductivity of the system. In this experiment, before thermal crosslinking modification, PVdF–HFP based gel electrolyte films containing the urethane precursors (PEG/blocked PMDI/DABCO) plasticized with a solution of LiClO$_4$ in PC were prepared in advance by solvent-casting techniques (Scheme 1). When the film had been formed, the blocked isocyanate remained intact in the film, and crosslinking did not take place until the film was subjected to heat treatment. Then, crosslinking was scheduled to follow this film formation i.e. crosslinking took place in the PVdF–HFP gel electrolyte film state by heating the film. Since the isocyanate group of PMDI was blocked, a controlled crosslinking could take place in the gel film state by tuning the curing time and temperature. However, the addition of PVdF–HFP reduced the crosslinking reaction rate (curing time: ca. 7 h), but did not result

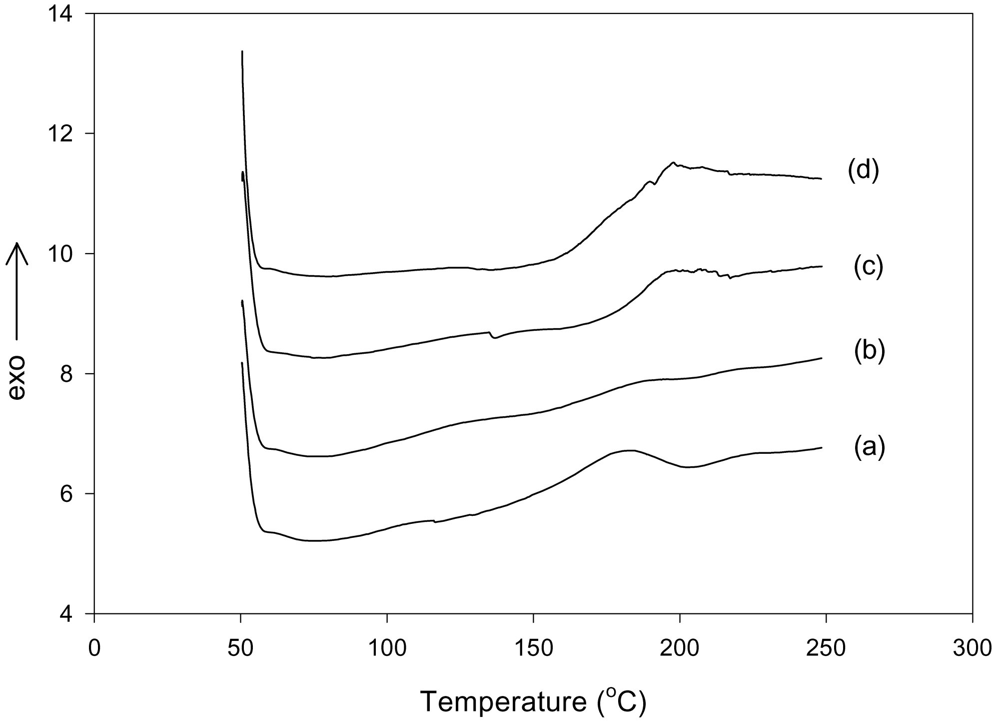


Fig. 4. DSC heating curves for PEG and blocked PMDI (3 equiv.) specimens containing DABCO (5 mol% based on blocked PMDI) and the corresponding plain sample (with no catalyst). Heating rate 10 °C/min: (a) PEG200, (b) PEG200 (with no catalyst), (c) PEG400, (d) PEG600.

in a remarkable decrease in the amount of liquid electrolyte encapsulated by a polymer host (Table 3). It was found that the capacity to retain the electrolyte solution in the network film is slightly dependent on the composition of the blend. The increasing incorporation of PEG200/blocked PMDI into the network results in higher tendency of the polymer network for phase separation (PEG-based urethane system is not dispersed in PVdF–HFP matrix at a molecular level). Also the capacity to encapsulate the electrolyte in the film decreases. However, gels with ≥ 50 wt% PVdF–HFP based on the total amount of solid components have been isolated as dimensionally stable free-standing films which are transparent and homogeneous (Table 3, entries 2–7). The films are able to embed high liquid electrolyte contents up to 156 wt% PC based on the amount of solid components (entry 3). From DSC experiments, the transition of the polymer in the gel electrolytes was not detected. Therefore, these gel electrolytes can be regarded as single-phase system. On the contrary, the DSC experiments of gel electrolytes on the basis of ≤ 25 wt% PVdF–HFP showed the signal which can be related to the melting of PVdF–HFP. Consequently, these gel electrolytes are heterogeneous materials. The gel electrolytes on the basis of (PEG200/blocked PMDI/PVdF–HFP = 1/3/4, weight ratio) system (Table 3, entries 2 and 3) are able to embed up to ~150 wt% PC, preserving high dimensional stability. In further discussions, the composition of the film will thus be restricted to PEG200/blocked PMDI/PVdF–HFP = 1/3/4.

3.6. Ambient-temperature storage stability of (PVdF–HFP/PEG200/blocked PMDI/LiClO$_4$/PC) gel films

A major drawback of PVdF-based gel systems is their poor processibility at ambient temperature [3–5]. They lose significant amounts of organic solvent by evaporation when they are exposed to an open atmosphere. In our study, the

Table 2
Thermal curing of (PEG/blocked PMDI/LiClO$_4$/PC) blends

Entry	Sample composition[a] (wt ratio)	Wt% of electrolyte[b] (after curing)
1	(PEG200/BPMDI/DABCO)[c]:electrolyte = 1:1	44
2	(PEG200/BPMDI/DABCO)[c]:electrolyte = 1:2	64
3	(PEG400/BPMDI/DABCO)[c]:electrolyte = 1:2	41
4	(PEG600/BPMDI/DABCO)[c]:electrolyte = 1:2	31

Curing temperature: 120 °C, curing time: 4 h.

[a] The code BPMDI represents blocked PMDI, and the PEGs are coded by molecular weights.

[b] Electrolyte: 1.0 M solution of LiClO$_4$ in PC.

[c] PEG/BPMDI/DABCO = 1/3/0.15 (molar ratio).

Table 3
Thermal curing of (PVdF–HFP/PEG/blocked PMDI/$LiClO_4$/PC) blends

Entry	Sample composition[a] (PVdF–HFP/PEG/BPMDI/electrolyte) (wt ratio)	Wt% of electrolyte[b] (after curing)	Appearance	Ionic conductivity (S/cm)[c]
1	20/7.5/22.5/50	38	Phase separated	–
2	25/6.0/19.0/50	46	Transparent	4.43×10^{-3}
3	15/3.6/11.4/70	61	Transparent	7.17×10^{-3}
4	30/5.0/15.0/50	45	Transparent	3.50×10^{-3}
5	35/3.5/11.5/50	44	Transparent	2.56×10^{-3}
6	40/2.5/7.50/50	39	Transparent	7.01×10^{-4}
7	50/0/0/50	32	Transparent	3.20×10^{-4}

Curing temperature: 120 °C, curing time: 7 h.

[a] The code BPMDI represents blocked PMDI, and the PEGs used are PEG200. 5 mol% DABCO based on blocked BPMDI was added.

[b] Electrolyte: 1.0 M solution of $LiClO_4$ in PC.

[c] All conductivities were measured by the complex impedance technique.

storage stability of PVdF-based gels can be improved by partial incorporation of PEG/blocked isocyanate network-forming system into the PVdF-based gel system, since such a network is chemically crosslinked and, therefore, shows an improved dimensional stability and maintains its mechanical integrity even at elevated temperatures.

In order to investigate solvent exudation upon storage at elevated temperature in (PVdF–HFP/PEG200/blocked PMDI/$LiClO_4$/PC) gel electrolyte, the weight percent of liquid electrolyte based on the total weight of the gel electrolyte film was measured as a function of storage time. Fig. 5 shows the time dependence of the weight percent of liquid electrolyte for PVdF–HFP/PEG200/blocked PMDI (= 4/1/3) gel film at 40 °C. Polymer gels having PVdF–HFP alone were also tested for comparison. A gel electrolyte containing 50 wt% (PVdF–HFP/PEG/blocked PMDI) and 50 wt% 1.0 M solution of $LiClO_4$ in PC lost 13, 26 and 40% of its mass after being stored at 40 °C for 0.8, 1.8 and 4 h, respectively, (Fig. 5(a)). It can clearly be seen that since the capacity of electrolyte impregnation for PVdF–HFP/PEG200/blocked PMDI system is relatively high compared to PVdF–HFP alone system, a much less loss of liquid electrolyte encapsulated in the polymer gel network film was observed (Fig. 5 (a) and (b)). The time evolution of the weight percent of liquid electrolyte curves obtained at 80 °C showed similar trends (Fig. 6). From these results, the capacity to retain the electrolyte solution in the PVdF–HFP based polymer gel film is found to be highly enhanced by the partial introduction of PEG/blocked PMDI network system.

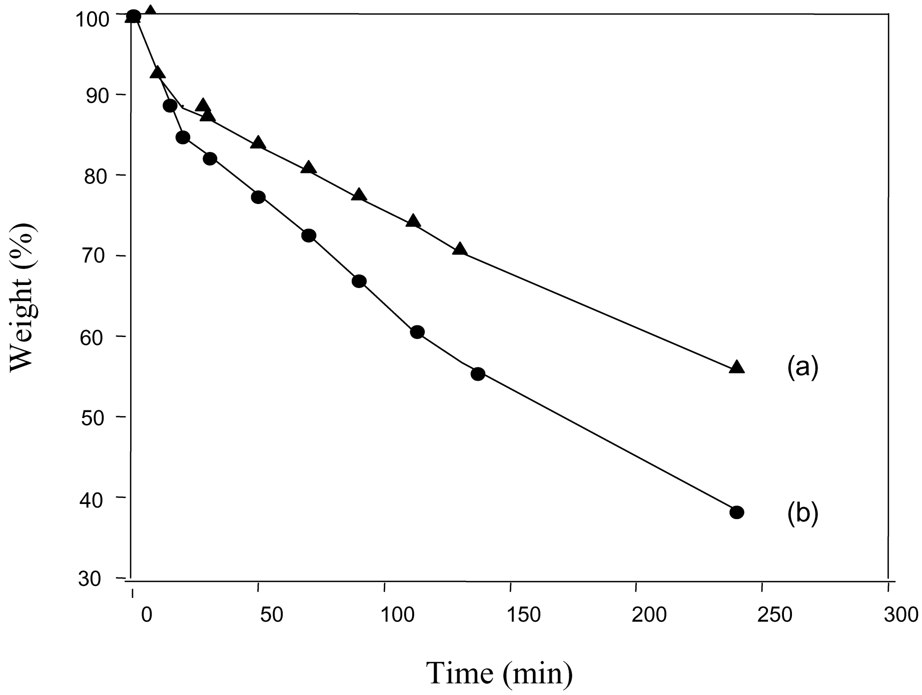


Fig. 5. Time evolution of the weight percent of liquid electrolyte for (a) PVdF–HFP/PEG200/blocked PMDI/electrolyte (= 0.50/0.125/0.370/1.00) and (b) PVdF–HFP/electrolyte (= 1/1) at 40 °C. Electrolyte: 1.0 M solution of $LiClO_4$ in PC.

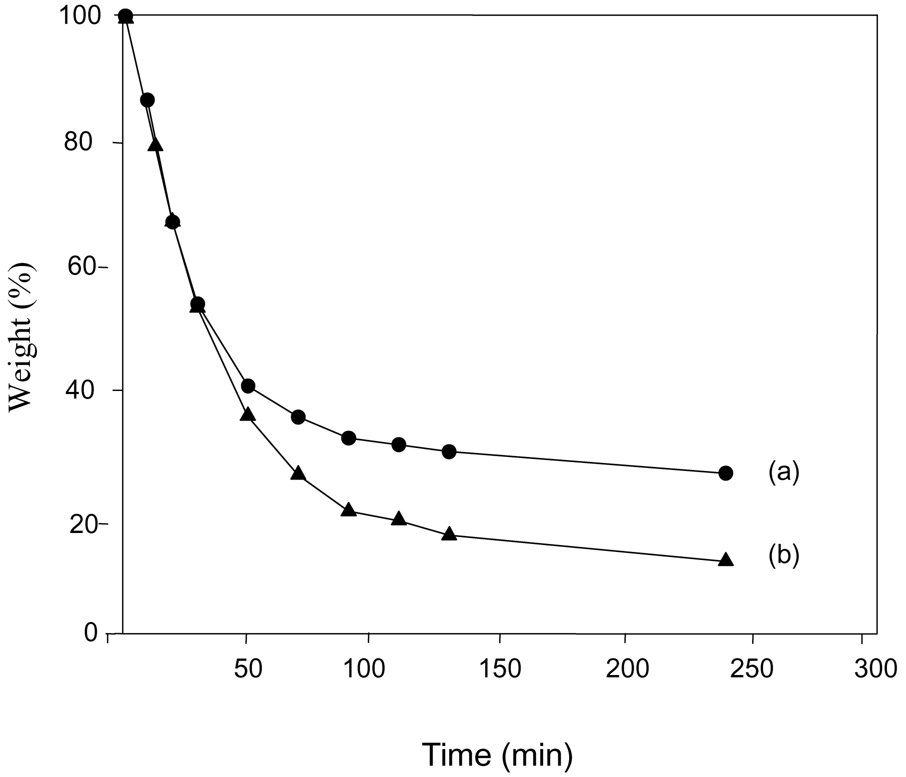


Fig. 6. Time evolution of the weight percent of liquid electrolyte for (a) PVdF–HFP/PEG200/blocked PMDI/electrolyte (= 0.50/0.125/0.370/1.00) and (b) PVdF–HFP/electrolyte (= 1/1) at 80 °C. Electrolyte: 1.0 M solution of $LiClO_4$ in PC.

3.7. Ionic conductivity of (PVdF–HFP/PEG/blocked PMDI/electrolyte) polymer gel films

Table 3 lists the ionic conductivity obtained from AC impedance spectra for the (PVdF–HFP/PEG200/blocked PMDI)-based gels prepared with 1.0 M solution of $LiClO_4$ in PC having different compositions. Electrolyte No. 7 was prepared by dissolving PVdF–HFP in an appropriate amount of PC–$LiClO_4$ solution and evaporating off the excess solvents until a film was formed. Alternatively, electrolytes No. 1–6 based on PVdF–HFP and (PEG200/blocked PMDI) were prepared by adding PVdF–HFP, PEG200 and blocked PMDI in the appropriate proportion to a PC–$LiClO_4$ solution and heating the preformed gel film at 120 °C to allow crosslinking of PEG with blocked PMDI. It was found that the ionic conductivity is slightly dependent on the composition of PVdF–HFP (or PEG200/blocked PMDI unit), which may be due to the ability of PEG200/blocked PMDI unit to impregnate electrolyte. The PEG portion is able to trap a relatively large amount of liquid electrolyte due to the good compatibility between the $-CH_2CH_2O-$ unit and PC. On the other hand, the PVdF–HFP portion in (PVdF–HFP/PEG200/blocked PMDI) has poor compatibility with PC from visual observation. The highest conductivity (7.17×10^{-3} S/cm at 25 °C) is thus found for PEG200/blocked PMDI/PVdF–HFP (= 1/3/4) with 61 wt% electrolyte impregnated (entry 3). For the PVdF–HFP polymer gel electrolyte without the PEG/blocked PMDI system, the amount of liquid electrolyte encapsulated in the polymer gel is low compared with PVdF–HFP/PEG200/blocked polymeric MDI system (entry 7). Most of the electrolytes prepared showed room temperature conductivities of greater than 10^{-4} S/cm.

3.8. Electrochemical stability window of (PVdF–HFP/PEG/blocked PMDI/$LiClO_4$/PC) polymer gel film

The electrochemical stability of (PVdF–HFP/PEG200/blocked PMDI (= 4/1/3))-based polymer gel film was evaluated by linear sweep voltametric measurements using a potentiostat. Experiments were carried out by applying an anodic voltage to a cell composed of the polymer gel film sandwiched between a lithium electrode and an inert stainless steel electrode. The decomposition voltage was considered as the potential at increase as the potential was swept. Fig. 7 shows the electrochemical stability window of (PVdF–HFP/PEG200/blocked PMDI)-based polymer gel electrolyte containing 61 wt% 1.0 M solution of $LiClO_4$ in PC. In the course of the scan, change of current was not nearly noticed in the range of 0 to 4.0 V, which implies that the (PVdF–HFP/PEG/blocked PMDI)-based polymer gel electrolytes are electrochemically stable in the given voltage range. However, the decomposition voltage is relatively low for high voltage cathode materials such as $LiCoO_2$. This may be associated with the decomposition of impurities present in the electrolyte. It was found that gel

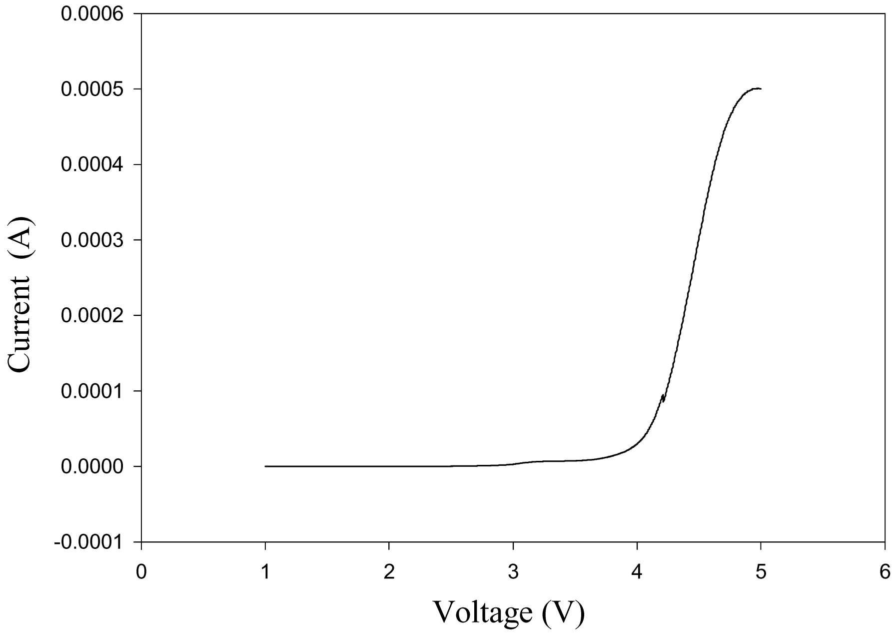


Fig. 7. Current–voltage curve of a Li/(PVdF–HFP/PEG200/blocked PMDI/$LiClO_4$/PC)/SS cell at 25 °C (sweep rate: 1.0 mV/s, SS: stainless steel).

electrolyte films contain trace amount of residual acetone oxime by-product, even though the precursor (acetone oxime-blocked PMDI)-containing blend mixture decomposed when heated to 120 °C for relatively long period of time.

3.9. Mechanical strength of (PVdF–HFP/PEG200/blocked PMDI/electrolyte) polymer gel film

The stress–strain data, plotted in Fig. 8 provide information on the mechanical property of the (PVdF–HFP/PEG200/blocked PMDI)-based polymer gel electrolytes. The strain of the electrolyte films varied markedly depending on the PVdF–HFP content. Tensile strength (stress) as high as 19 kg/cm^2 at an elongation-at-break value (strain) of 28% was observed (Fig. 8(a)). The much less elastic property of (PVdF–HFP/PEG/blocked PMDI)-based polymer electrolytes compared to PVdF–HFP based electrolytes is attributed to the chemically crosslinked network structure of the electrolyte.

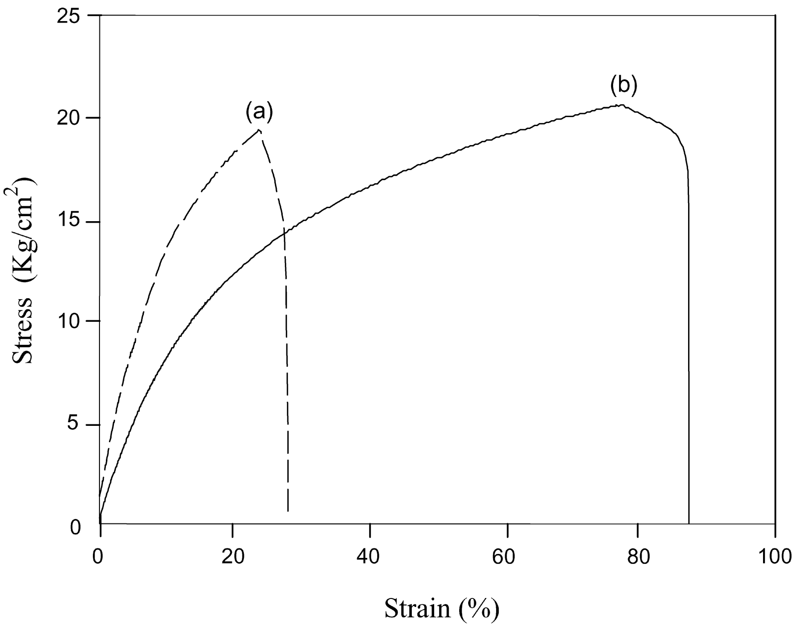


Fig. 8. Stress–strain plots for (a) (PVdF–HFP/PEG200/blocked PMDI)/electrolyte (61/39) and (b) PVdF–HFP/electrolyte (68/32). PVdF–HFP/PEG200/blocked PMDI = 4/1/3 (weight ratio). Electrolyte: 1.0 M solution of $LiClO_4$ in PC.

4. Conclusions

Here, we report that relatively robust PVdF–HFP/PEG/blocked multiisocyanate network films containing plasticizer and lithium salt can be obtained by the use of thermal crosslinking reaction of low molar mass, liquid PEGs with blocked isocyanates. A PMDI–acetone oxime addition compound has been used as a novel crosslinker to achieve good mechanical strength and improve the thermal properties of elastomeric gel films, especially their volatility. The relative molar composition of PVdF–HFP/PEG/blocked PMDI in the polymer gel films proved to play a critical role in determining the crosslink density and the capacity to retain electrolyte solution within the network film. The ionic conductivity and electrochemical stability window of the optimized polymer gel electrolyte were found to be 7.17×10^{-3} S/cm and 4.0 vs. Li/Li$^+$, respectively. From these results, it is expected that the (PVdF–HFP/PEG/blocked PMDI)-based gel film is a promising material as a polymer electrolyte for a lithium polymer battery. More detailed studies on the battery performance of lithium polymer cells employing (PVdF–HFP/PEG/blocked PMDI/electrolyte) systems are in progress.

Acknowledgements

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