Synthesis of Microphase-Separated Solvent-Free Solid Polymer Electrolyte Nanocomposite Films Using Amphiphilic Urethane Acrylate Precursors

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ABSTRACT: A new solvent-free solid polymer electrolyte (SPE) films could be fabricated through bulk copolymerization process of amphiphilic urethane acrylate nonionomer (UAN). Amphiphilic UAN chain having polypropylene oxide-based hydrophobic segment and polyethylene oxide-based hydrophilic segment can not only dissolve lithium salt by complex formation with lithium cations but also be copolymerized with various monomers to form microphase-separated polymeric matrix. Unlike conventional SPE systems showing higher conductivity with polar polymers and polar solvents, our SPE films prepared by copolymerization of UAN and hydrophobic monomers exhibited relatively higher conductivity. Dissolving lithium salts in UAN/hydrophobic monomer mixtures caused hydrophilic/hydrophobic microphase separation, which was more favorable for ionic conduction of lithium ions, result-ing in the higher ionic conductivity than the SPE films fabricated using UAN/hydrophobic monomer mixture. This microphase-separated structure of SPE films could be also confirmed by transmission electron microscope (TEM) images. Ionic conductivity of our SPE films could be also improved by dispersing clay minerals within SPE films. Three types of clay having different surface properties were used to fabricate clay/SPE nanocomposite films. Ionic conductivity of nanocomposite films depended on dispersiblity of clay nanoparticles with a SPE film, which was confirmed by measuring X-ray diffraction and TEM. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1359–1367, 2007

Key words: solvent-free solid polymer electrolytes; amphiphilic urethane acrylate; nanocomposite; microphase separation; clay nanoparticles

INTRODUCTION

It is widely recognized that solid polymer electrolytes (SPEs) can be potentially applied in many solid electrochemical devices such as high-energy density batteries, electro-chromic windows, and light emitting devices. Among SPEs, complexes of lithium salts in amorphous forms of poly(ethylene oxide) (PEO) have been largely used for fabrication of solvent-free SPEs.[1–4] However, low ambient conductivities in ambient temperature and poor mechanical property have prohibited their applications. To increase conductivity at ambient temperature of SPEs, gel-type polymer electrolytes containing low molecular weight solvents have been attempted; however, these systems could not avoid leakage of dissolved salts and decreased mechanical property of polymer matrix.[5–7]

There have been several approaches to solve low ambient conductivities of solvent-free SPEs in ambient temperature. SPE systems based on poly(vinyl alcohol)[8], polysiloxanes,[9] polyacrylonitrile (PAN)[10] have been fabricated for this purpose. Also, specially designed polymers, such as amphiphilic polytetrahydrofuran copolymers, poly(ethyleneoxide)-based borates, highly porous poly(vinylidene fluoride), and poly(ethylene oxide-co-ethylene carbonate) have been used for this purpose.[11–17] Recently, polyurethane-based or polyurethane acrylate-based polymers have also received attention as a possible candidate matrix of SPEs because of possibility of increased mechanical property of electrolyte films because of their microphase-separated structure.[18–22] Especially, polyurethane acrylates could be fabricated as polymer electrolyte films via UV-coating process without use of large amount of solvents.

In this study, we represent the synthesis of new SPE films using copolymers of amphiphilic urethane acrylate and several monomers having different polarity. In most cases, mechanical properties and ion conductivity of polyurethane-based polymer electrolytes films strongly depended on microphase separation between soft and hard segments at polymer matrix.[18–22] However, in our system, we suggest

here the possibility of improving ion conductivity of SPE films through controlling microphase separation between hydrophilic and hydrophobic segments within polymer matrix. Since urethane acrylate non-ionomer (UAN) chains used in this study have hydrophobic polypropylene oxide (PPO)-based urethane-linked backbone and hydrophilic polyethylene oxide (PEO) segment at the same backbone, UAN can form microphase-separated structure at various conditions via hydrophilic/hydrophobic microphase separation.[23–25] So, unlike conventional polyurethane-based SPE films, it could be expected that SPE films synthesized through copolymerization of UAN/various monomers would have very different microstructures with type of monomer used, which may strongly influence their ion conductivity.

Here, we first present fabrication of solvent-free SPE films via UV-initiated copolymerization process of UAN/monomer mixtures. And changes of conductivity with composition and type of the monomers used for fabrication of SPE films will be presented and discussed it in relation to the different microstructures anticipated for these SPE films. In addition, clay dispersed UAN/monomer solutions were also prepared to fabricate clay/SPE nanocomposite films. Recently, it has been reported that clay minerals dispersed at SPE films could improve ion conductivity by formation of complex with lithium ions.[26–28] So, solvent-free SPE films were also synthesized using clay/UAN/monomer solutions at various compositions to increase conductivity and mechanical property of the films. To investigate effect of nature of clay mineral, three types of clay minerals were used for the synthesis of SPE films.

EXPERIMENTAL

Materials

In the synthesis of amphiphilic urethane acrylate nonionomer (UAN) precursor chains, poly(propylene oxide triol) (PPO triol, $M_w = 1000$, Korea Polyol Ltd., Ulsan, Korea), 2,4-toluene diisocyanate (TDI, Junsei Chemical, Tokyo, Japan) 2-hydroxyethyl methacrylate (2-HEMA, Aldrich Chemicals, Milwaukae, WI), and poly(ethlylene glycol) (PEG, $M_w = 1500$, Aldrich Chemicals) were used. PPO triol and PEG were dried and degassed at 80°C and 3–5 mmHg for 2 days.

Butyl acrylate (BA), Acylonitrile (AN), Styrene and Methyl methacrylate (MMA) were purchased from Aldrich Chemical and used as monomers for mixing with UAN. Lithium perchlorate (LiClO$_4$, Aldrich Chemicals) and (1-hydroxycyclohexyl)-phenyl-methanone (Irgacure 184, Ciba Geigy Chemical) were used as lithium salts and a photoinitiator for UV curing, respectively.

Three types of clay (Cloisite® Na$^+$,15A, and 30B) were purchased from Southern Clay Products and used as received. Cloisite® Na$^+$ is a natural montmorillonite, Cloisite®15A is a natural montmorillonite modified with a quaternary ammonium salt, which is $(CH_3)_2N^+(HT)_2$ where HT is hydrogenated tallow ($\sim$ 65%C18; $\sim$ 30% C16; $\sim$ 5% C14), and Cloisite® 30B is a natural montmorillonite modified with a quaternary ammonium salt, which is $(C_2H_4OH)_2N^+(CH_3)T$ where T is tallow ($\sim$ 65%C18; $\sim$ 30% C16; $\sim$ 5% C14).

Synthesis of UAN

Amphiphilic UAN precursor chain was synthesized by using an established three-step process as described in previous publication.[23–25] Each reaction was performed in a 500 mL four-neck vessel equipped with stirrer, thermometer, and an inlet system for nitrogen gas. Synthesis procedure and molar ratio of UAN chain was described in detail in our previous reports.[23–25] The polystyrene equivalent molecular weight of synthesized UAN chains is a 6700 (g/mol) weight average molecular weight with a polydispersity of 1.93. Expected molecular structure of UAN chain was schematically illustrated in Figure 1.

Preparation of solvent-free SPE film based on UAN/monomers

To fabricate solvent-free SPE films, UAN precursor chain was first mixed with various monomers such as styrene, BA, MMA, and AN at various weight ratio at room temperature for 2 h, and then lithium salt, LiClO$_4$ (3 wt %), was added and mixed for 24 h to prepare reaction solutions. After complete dissolving
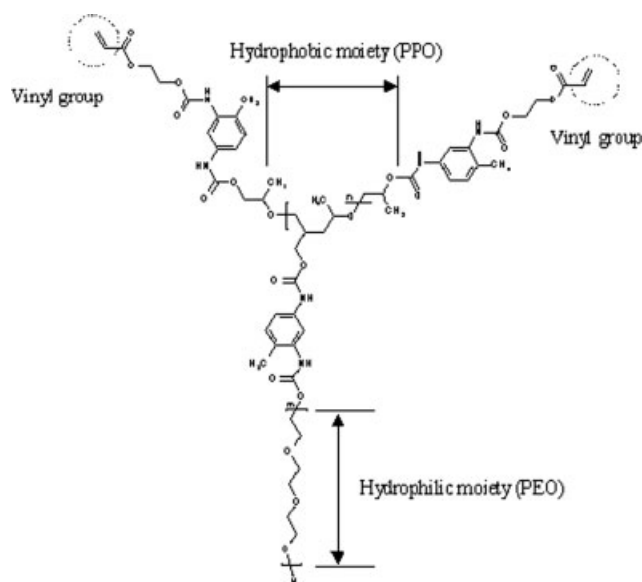
Figure 1 Schematic presentation of UAN chain.

TABLE I
Recipes for Fabrication of SPE Films

Sample	Ingredients (g)					
	UAN	Styrene	BA	MMA	AN	LiClO$_4$
UAS-1	4	1	–	–	–	0.15
UAS-2	4	2	–	–	–	0.18
UAS-3	4	3	–	–	–	0.21
UAS-4	4	4	–	–	–	0.24
UAB-1	4	–	1	–	–	0.15
UAB-2	4	–	2	–	–	0.18
UAB-3	4	–	3	–	–	0.21
UAB-4	4	–	4	–	–	0.24
UAM-1	4	–	–	1	–	0.15
UAM-2	4	–	–	2	–	0.18
UAM-3	4	–	–	3	–	0.21
UAM-4	4	–	–	4	–	0.24
UAA-1	4	–	–	–	1	0.15
UAA-2	4	–	–	–	2	0.18
UAA-3	4	–	–	–	3	0.21
UAA-4	4	–	–	–	4	0.24

lithium salts, Irgacure 184 (3 wt %), photoinitiator, was added and mixed at prepared solutions for UV-initiated crosslinking polymerization, and then the solutions were coated on the ITO glass frame and UV-initiated crosslinking polymerized for 5 min (UV-Lamp; 450W, Ace Glass) Prepared samples were contained under vacuum at 80°C for 48 h. Recipes for the synthesis of these solvent-free SPE films are illustrated in Table I.

Preparation of solvent-free SPE films containing clay nanoparticles

Three types of clay minerals having different hydrophobicity were first mixed with UAN at 40°C for 1 h, and then various monomers were added and mixed for another 1 h. After completion of mixing, lithium salt, LiClO$_4$ (3 wt %) was added at these UAN/monomer/clay mixtures and mixed for 24 h. Recipes for the synthesis of these solvent-free polymer electrolytes are illustrated in Table II. Irgacure 184 (3 wt %) photoinitiator was added and mixed at prepared mixtures for UV-initiated crosslinking polymerization, and then the solutions were coated on the ITO glass frame and UV-initiated crosslinking polymerized for 5 min (UV-Lamp; 450W, Ace Glass). Prepared samples were kept under vacuum at 80°C for 48 h.

Measurements

The ionic conductivity was measured by using a ZAHNER impedance analyzer in the frequency from 1 Hz to 1 MHz. Cells for measuring the ionic conductivity were prepared by sandwiching the polymer electrolyte between ITO glasses. The thickness of composite film was 100 μm. The impedance response was gauged in the air over the range from 30 to 80°C. Transmission electron microscope (TEM,

TABLE II
Recipes for Fabrication of Clay/SPE Nanocomposite Films

Sample	Ingredient (g)						
	UAN	Styrene	BA	LiClO$_4$	Cloisite® Na$^+$	Cloisite® 30B	Cloisite® 15A
Na-UAS-1	4	1		0.15	0.15	–	–
Na-UAS-1	4	2	–	0.18	0.18	–	–
30B-UAS-1	4	1	–	0.15	–	0.15	–
30B-UAS-2	4	2	–	0.18	–	0.18	–
15A-UAS-1	4	1	–	0.15	–	–	0.15
15A-UAS-2	4	2	–	0.18	–	–	0.18
Na-UAS-1	4	–	1	0.15	0.15	–	–
Na-UAS-1	4	–	2	0.18	0.18	–	–
30B-UAS-1	4	–	1	0.15	–	0.15	–
30B-UAS-1	4	–	2	0.18	–	0.18	–
15A-UAS-2	4	–	1	0.15	–	–	0.15
15A-UAS-2	4	–	2	0.18	–	–	0.18

|	UAN	MMA	AN	LiClO$_4$	Cloisite® Na$^+$	Cloisite® 30B	Cloisite® 15A
Na-UAM-1	4	1	–	0.15	0.15	–	–
Na-UAM-1	4	2	–	0.18	0.18	–	–
30B-UAM-1	4	1	–	0.15	–	0.15	–
30B-UAM-2	4	2	–	0.18	–	0.18	–
15A-UAM-1	4	1	–	0.15	–	–	0.15
15A-UAM-2	4	2	–	0.18	–	–	0.18
Na-UAA-1	4	–	1	0.15	0.15	–	–
Na-UAA-1	4	–	2	0.18	0.18	–	–
30B-UAA-1	4	–	1	0.15	–	0.15	–
30B-UAA-1	4	–	2	0.18	–	0.18	–
15A-UAA-2	4	–	1	0.15	–	–	0.15
15A-UAA-2	4	–	2	0.18	–	–	0.18

JEM 2020CX, JEOL), applying an acceleration voltage of 200 kV, was used to clarify the nanostructure of crosslinked polymer films. The films were embedded in an epoxy resin of Epon-812 supplied by SPI. Ultra-thin sections of the film with thickness of $\sim$ 70 nm were prepared at $-60°C$ by an ultramicrotome of Ultracut R made by Leica. Carbon was vacuum-evaporated on the thin sections to prevent accumulation of electrons during TEM observation. The films were immersed in OsO_4 (2 wt %) aqueous solution for 1 day and rinsed with water to stain the hydrophilic domains of the film. X-ray scattering experiments for the dried composite films were conducted with a Rigaku D/Max-2200 (Copper radiation, 40 kV, 100 mA, nickel filter).

RESULTS AND DISCUSSION

Effect of the type and the amount of the monomer

Four types of monomer having different polarities were used to investigate effect of monomer nature on ionic conductivity of the SPE films. Weight ratio of UAN and monomer is changed as 4 : 1, 4 : 2, 4 : 3, and 4 : 4. The standard recipe is illustrated in Table I. Ionic conductivity at various types and amount of monomer were measured and represented in Figure 2. As presented, the larger amount of monomer is added to UAN, the lower the ionic conductivity is. This indicates that UAN chains play more important role in ionic conduction of SPE films fabricated using UAN/monomer mixtures. In other words, polymerized UAN matrix have better performance for ion conduction compared to the polymeric matrix formed by polymerization of MMA, AN, BA, and styrene.

At the same weight ratio of UAN/monomer, SPE films fabricated using UAN/nonpolar monomers (styrene or BA) showed higher ionic conductivity than the films prepared using UAN/polar monomers (AN or MMA). This result is very opposite to that of conventional SPE films. In most cases, polar polymers or polar solvents, which can dissolve lithium salts, are generally used for fabrication of conventional SPE films to obtain acceptable high ionic conductivity.[5–10,29–31] Especially, for solvent-free SPE films, host polymers should be able to dissolve lithium salts. So, films fabricated using polar polymers such as PAN or poly(methyl methacrylate) exhibited relatively higher ionic conductivity.[8–10] For our system, styrene and BA used cannot dissolve lithium salts because of their nonpolarity, whereas AN and MMA can dissolve a lot of lithium without a solvent. So it could be expected based on conventional results that SPE films fabricated using UAN/AN and UAN/MMA would show higher ionic conductivity than the SPE films prepared using UAN/sty-
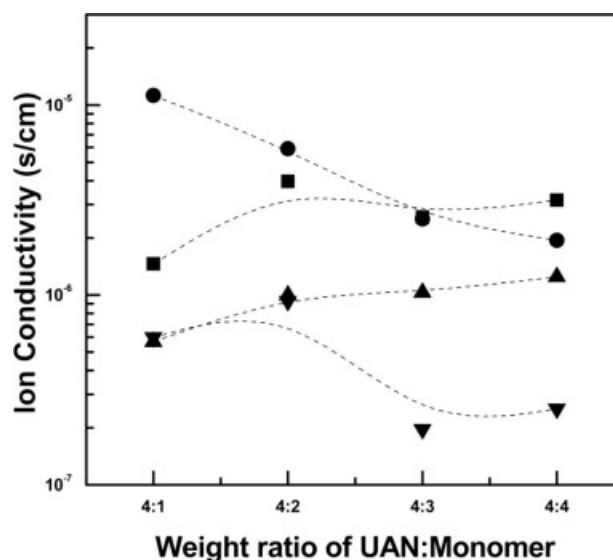

Figure 2 Ion conductivity of SPE films fabricated using UAN/monomer solutions at various weight ratio of UAN: monomer (-■- UAN/Styrene mixture, -●- UAN/BA mixture, -▲- UAN/MMA mixture, -▼- UAN/AN mixture).

rene and UAN/BA. However, our SPE films showed relatively higher ionic conductivity in UAN/styrene and UAN/BA mixtures. This very opposite tendency compared to ionic conductivity behaviors of conventional SPE films can be interpreted as due to microphase separated structure of our SPE films.

For SPE films fabricated using mixtures of UAN/polar monomers (MMA or AN), MMA and AN can not only dissolve whole UAN chains but also dissolve lithium salts, resulting in formation of homogeneous solutions. In addition, poly(MMA) and poly(AN) formed in the course of synthesis of SPE films may have better compatibility with polymerized UAN chains. So, it can be thought that SPE films fabricated using UAN/MMA or UAN/AN have relatively homogeneous microstructure and dissociated lithium salts may be homogeneously distributed whole polymer matrix.

For the films synthesized using UAN/hydrophobic monomers (styrene and BA), these monomers cannot dissolve lithium salts but dissolve whole UAN precursor chains. So, disappearance of added lithium salts by just mixing with UAN/styrene or UAN/BA mixtures can be interpreted as due to interaction between lithium salt and PEO segments of UAN chains. And added monomers in the mixtures just acted as viscosity thinner of UAN chains.
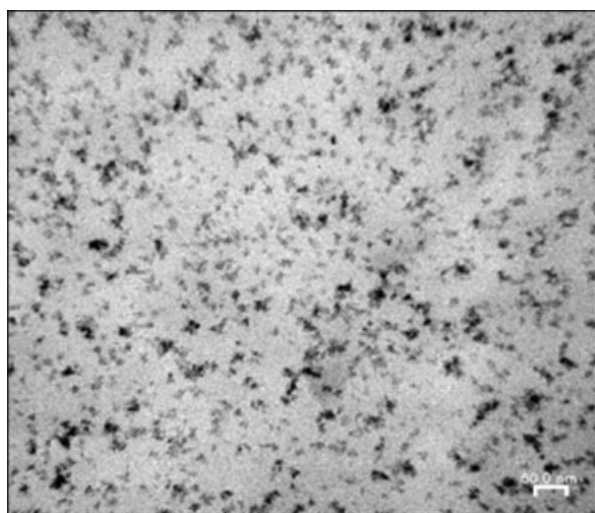
Figure 3 shows TEM image of the crosslinking polymerized UAN/styrene (4:2) films stained by OsO_4 aqueous solution. Since OsO_4 aqueous solution is absorbed only by hydrophilic PEO segments, it can be thought that the dark spots (about 10 nm) dispersed within a matrix represent the hydrophilic
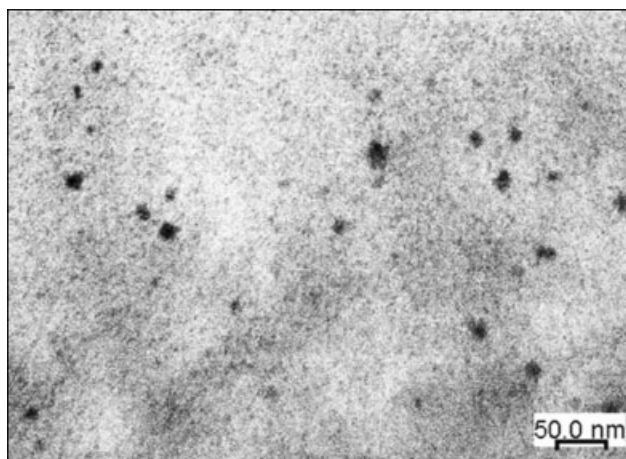
Figure 3 TEM image of microstructure of the film fabricated by crosslinking polymerization of UAN/styrene.

domains. It can be confirmed by this image that PEO segments of UAN are microphase-separated from PPO-based hydrophobic segment of UAN and styrene to form their hydrophilic domains through copolymerization of UAN and styrene. This microphase separated hydrophilic domains could be used as a nano-sized reactor for the synthesis of inorganic nanoparticles such as silver, iron oxide, and CdS.[18–20] Number of dark spots distributed at the matrix was smaller than expected. This result indicates that hydrophilic PEO segments of UAN chains are slightly microphase separated from hydrophobic PPO segments and styrene in the absence of lithium salts. This can be interpreted as due to the amphiphilic character of the ethylene oxide repeating units of PEO in UAN chains.[32,33]
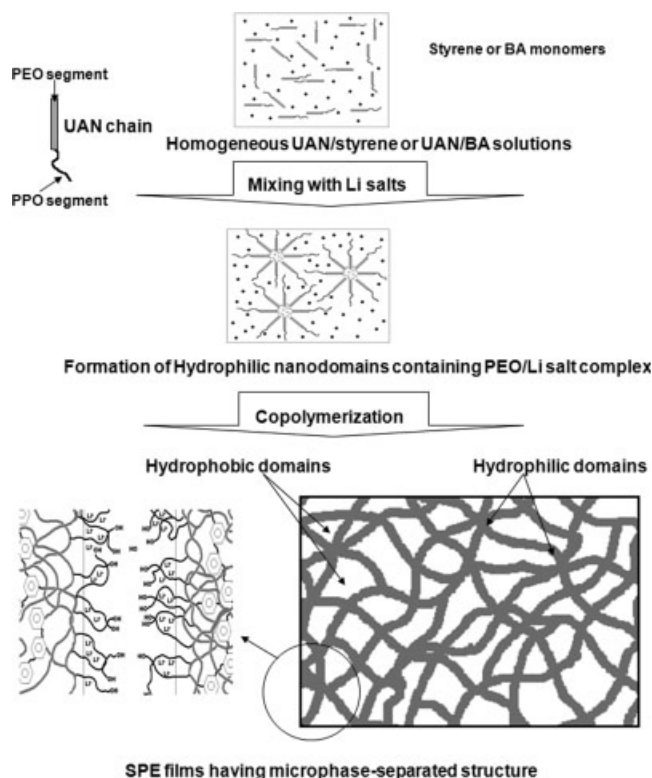
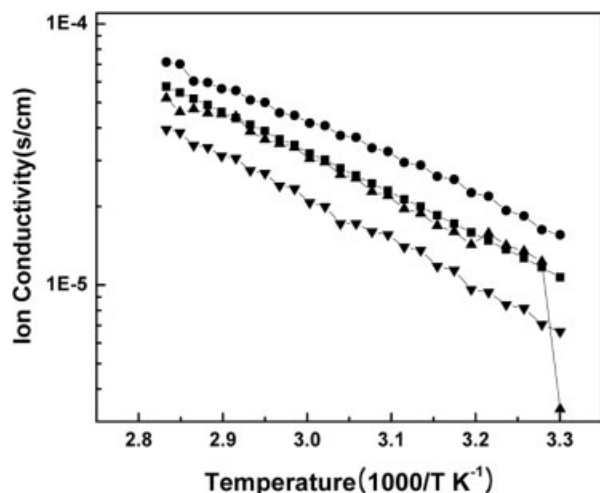Figure 4 shows TEM image of the films synthesized using UAN/styrene (4:2) solution containing

dissolved lithium salts (3 wt %). Since lithium salts can dissolve only at PEO segment of UAN chains, it can be expected that dissolved lithium salts should be located only at hydrophilic domains formed by association of PEO segments of UAN chain. As seen in TEM image of Figure 4, dark spots corresponding to hydrophilic domains containing dissolved lithium salts are distributed in whole matrix. This indicates that lithium salts are dissolved by PEO segment of UAN chains, resulting in formation of hydrophilic domains containing dissolved lithium salts, which are distributed within whole polymer matrix.

Therefore, it can be assumed by these results that on mixing lithium salt with UAN/styrene or UAN/BA mixtures, PEO chains in UAN are microphase-separated and form complex with lithium salts to dissolve it, whereas hydrophobic PPO-based segment in UAN and styrene monomers are homogeneously mixed with each other to form continuous hydrophobic domains. This microphase-separated structure is locked-in by radical copolymerization process. Consequently, dissociated lithium salts exist only in hydrophilic domains dispersed within crosslinked polymer matrix. So, it can be postulated that conduction of lithium cations take place exclusively through hydrophilic domains formed by hydrophilic/hydrophobic microphase separation, which is schematically illustrated in Figure 5.

Figure 5 Schematic presentation for formation of microphase separated SPE films.

Figure 4 TEM image of microstructure of the film fabricated by crosslinking polymerization of UAN/styrene containing dissolved lithium salts.

Figure 6 Arrehnius plot from 30 to 80 °C for SPE films fabricated using various UAN/monomer mixtures (-■- UAN/Styrene mixture, -●- UAN/BA mixture, -▲- UAN/MMA mixture, -▼- UAN/AN mixture).

By comparing TEM images of Figure 4 with that of Figure 3, it can be observed at Figure 4 that greater numbers of dark spots are distributed at whole matrix. So, it can be thought that degree of microphase separation of PEO segments from hydrophobic moieties is increased by dissociating lithium salts within UAN/styrene solution. In other words, since lithium salt can be dissociated only by PEO chains of UAN, the larger number of PEO chains are microphase separated to make complex with lithium ions by dissociating the salts, causing to increase the degree of hydrophilic/hydrophobic microphase separation. So, it can be thought by higher ion conductivity of SPE films fabricated using UAN/styrene or UAN/BA mixtures that microphase-separated structure formed in SPE films could enhance their ion conduction at the same weight % of lithium salts.

Figure 6 is the result of Arrehnius plot from 30 to 80°C for SPE films fabricated using various UAN/monomer solutions. Ionic conductivity of all SPE film increased with increase of temperature, which can be interpreted as increase of chain mobility of SPE films at elevated temperature. Like the result of Figure 2, SPE films fabricated using UAN/BA solutions also showed the highest conductivity among them. It is explained that BA is the lowest glass temperature among them.

Effect with the type of clay

It has been reported that clay minerals dispersed with SPE films can not only improve mechanical properties of SPE films but also increase their ionic conductivity by reducing crystallinity of host poly-

mers and dissolving lithium cations via formation of complex.[26–28] So, we first mixed three types of clay minerals with UAN/monomer solutions to disperse it at nano-scale. And then we added lithium salts at prepared solutions to fabricate clay/SPE composite films. The weight ratio of UAN to monomers is fixed as 4 : 1 and 4 : 2. Also, the amount of clay and Li salt is fixed as 3 wt %. Ionic conductivities of fabricated clay/SPE composite films were measured and presented in Figure 7. In comparison with neat SPE films, clay/SPE composite films exhibited very different degree of increase of ionic conductivity. For clay/SPE composite films fabricated using UAN/AN and UAN/MMA solutions, ionic conductivity of these composite films was a little higher than that of
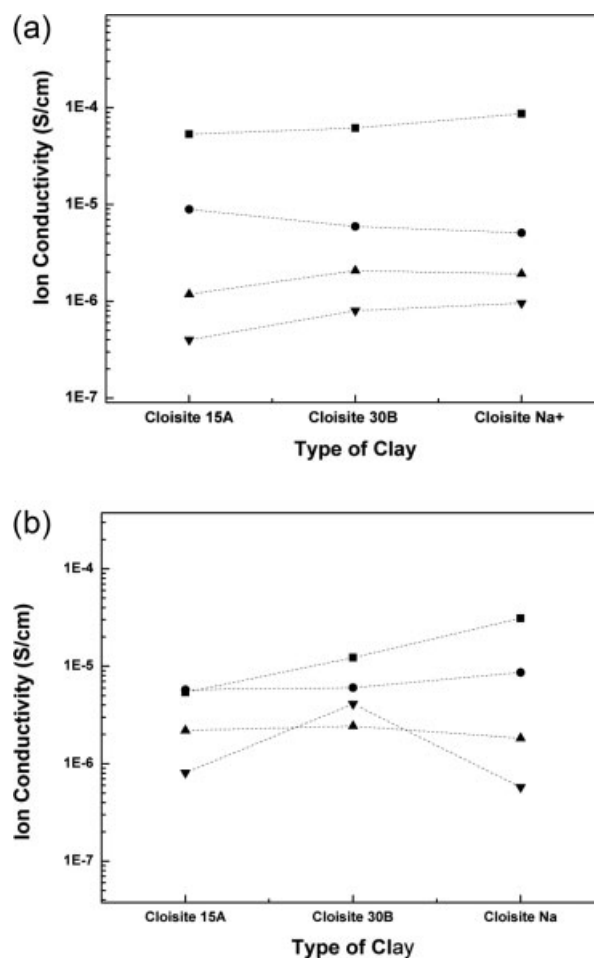
Figure 7 (a) Ion conductivity of clay/SPE nanocomposite films fabricated using clay/UAN/monomer solutions at 4:2 weight ratio of UAN: monomer (-■- clay/UAN/Styrene mixture, -●- clay/UAN/BA mixture, -▲- clay/UAN/MMA mixture, -▼- clay/UAN/AN mixture). (b) Ion conductivity of clay/SPE nanocomposite films fabricated using clay/UAN/monomer solutions at 4 : 1 weight ratio of UAN: monomer (-■- clay/UAN/Styrene mixture, -●- clay/UAN/BA mixture, -▲- clay/UAN/MMA mixture, -▼- clay/UAN/AN mixture).
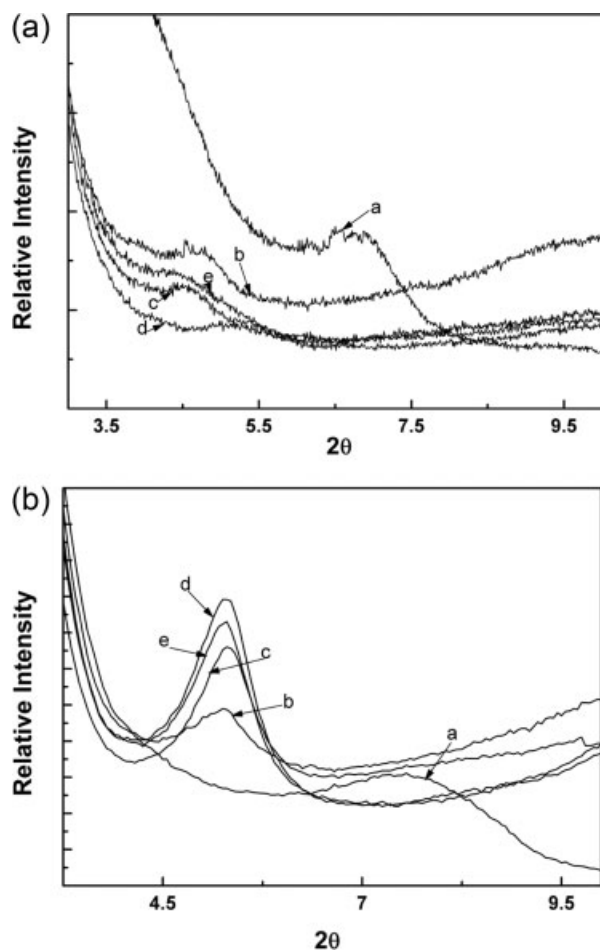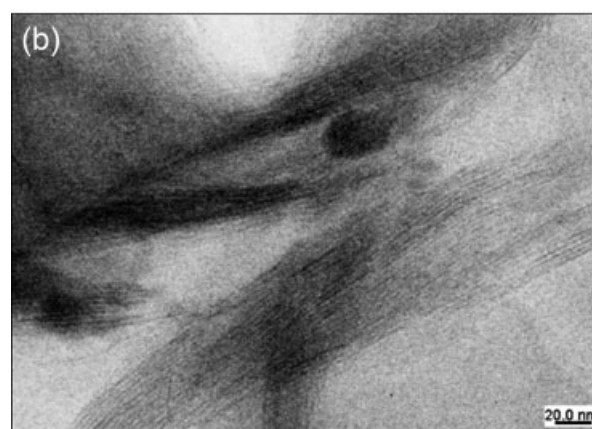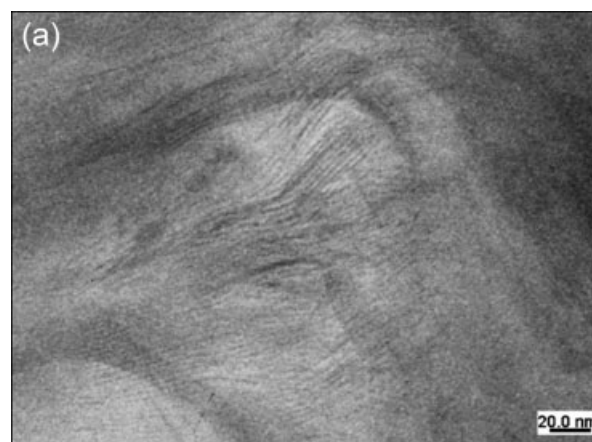
Figure 8 (a) XRD patterns of neat Cloisite® 15A and Cloisite® 15A/SPE nanocomposite films (-a- neat Cloisite® 15A, -b- Cloisite® 15A/UAN/Styrene mixture, -c- Cloisite® 15A/UAN/BA mixture, -d- Cloisite® 15A/UAN/MMA mixture, -e- Cloisite® 15A/UAN/AN mixture). (b) XRD patterns of neat clay Cloisite® Na^+ and Cloisite® Na^+/SPE nanocomposite films (-a- neat Cloisite® Na^+, -b- Cloisite® Na^+/UAN/Styrene mixture, -c- Cloisite® Na^+/UAN/BA mixture, -d- Cloisite® Na^+/UAN/MMA mixture, -e- Cloisite® Na^+/UAN/AN mixture).

rier, which is helpful for increasing ionic conductivity. At the same time, however, added clay also causes decrease of chain mobility of SPE because of increase of the viscosity of SPE, which is unfavorable for improving ionic conductivity. So, to obtain improved ionic conductivity of SPE films, clay minerals should be nano-dispersed within SPE system via exfoliation of their silicate layers. In other words, improved ionic conductivity of clay/SPE systems strongly depends on nano-dispersibliity of clay minerals within SPE matrix.

Therefore, the highest improved ionic conductivity of clay/SPE composite films fabricated using UAN/styrene solutions can be interpreted as due to the highest dispersibliity of clay minerals within UAN/styrene solutions. Decreased or a little increased ionic conductivity of clay/SPE composite films prepared using UAN/BA, UAN/AN, and UAN/MMA can be explained as poor dispersibliity of clay minerals at these SPE films. At same type of monomer and clay, the clay/SPE composite films showed the higher ionic conductivity at 4 : 1 weight ratio of UAN/monomer than 4 : 2 weight ratio of UAN/monomer. This result can also be interpreted as due

their pristine SPE films. The composite films prepared using clay-dispersed UAN/AN solutions showed decrease in ionic conductivity compared with that of their pristine SPE films. However, the composite films prepared using clay-dispersed UAN/styrene solutions showed the highest increase of ionic conductivity. These results can be interpreted as due to difference of dispersibility of clay within a given SPE films.

It has been reported that clay minerals can dissolve lithium salts by the formation of complex between lithium cations and silicate layers acting as Lewis base.[26–28] So, adding and dispersing clay minerals at SPE systems increase fraction of the free anions and make the recrystallization of dissolved lithium salts uneasily, resulting in higher charge car-

Figure 9 TEM images of microstructure of clay/SPE nanocomposite films fabricated using (a) Cloisite® 30B/UAN/styrene and (b) Cloisite® 15A/UAN/styrene.

to better dispersibliity of clay minerals at SPE films fabricated using 4 : 1 weight ratio of UAN/monomer.

X-ray diffraction (XRD) analysis is a powerful tool for examining dispersibliity of clay minerals at a given polymer matrix, because interlayer spacing of their silicate layers can be determined from the XRD peak using Bragg equation

$$\lambda = 2d \sin \theta$$

where d corresponds to the spacing between diffractional lattice planes, θ is the diffraction position, and λ is the wavelength of the X-ray. Figure 8 presents XRD patterns of various clay/SPE composite films. In Cloisite® 15A system, the basal interlayer spacing of monomers increased from 31.5 (neat Cloisite 15A) to 45.1, 44.2, 39.6, and 43.9 Å for UAN/styrene, UAN/BA, UAN/MMA, and UAN/AN, respectively. In Cloisite® Na$^+$ system, the basal interlayer spacing also increased from 11.7 (neat Cloisite Na$^+$) to 16.8, 16.6, 16.6, and 16.8 Å for UAN/styrene, UAN/BA, UAN/MMA, and UAN/AN, respectively. This indicates that silicate layers of clay minerals used are intercalated by insertion of polymer chains of our SPE system at some extent. The largest increase of basal interlayer spacing in UAN/styrene system also indicates that clay minerals have the higher dispersibliity at UAN/styrene mixture compared to the other UAN/monomer mixtures. Consequently, it can be confirmed by these XRD results that the highest ionic conductivity of clay/SPE composite films fabricated using UAN/styrene mixtures is due to the highest dispersibility of clay minerals at UAN/styrene system.

The intercalation of the silicate layers of clay was also examined by using TEM. Figure 9 shows TEM micrographs of clay/SPE composite film prepared using UAN/styrene/clay (3 wt % of Cloisite® 15A and Cloisite® 30B). The dark lines in the pictures correspond to the silicate layers of clay. Even though some silicate layer still maintain the ordered stacking morphology, some silicate layers are dispersed within crosslinking polymerized UAN-styrene matrix where the distance between the layers ranges from 3 to 5 nm. This indicates silicate layers are intercalated and dispersed at crosslinking polymerized UAN-styrene matrix.

CONCLUSIONS

We could fabricate solvent-free SPE films via bulk copolymerization of various monomers and amphiphilic UAN without use of a solvent and solvent evaporation process. Unlike conventional SPE systems showing higher conductivity with polar polymers and solvents, our SPE systems showed higher conductivity at the films prepared by copolymeriza-tion of UAN and nonpolar monomers, which was due to the formation of microphase-separated structures within SPE films via hydrophilic/hydrophobic microphase separation. That is, microphase-separated structure formed in SPE films enhanced ion conduction within SPE films. Ionic conductivity of our SPE films could be also improved by dispersing clay minerals within SPE films. Among clay/SPE composite films, the films fabricated using UAN/styrene/clay mixtures showed the highest conductivity and improvement of ionic conductivity, which was due to the best dispersibility of clay particles within these mixtures. So, it could be concluded that the highest conductivity could be obtained when clay nanoparticles were nano-dispersed within SPE matrix containing microphase-separated structure via hydrophilic/hydrophobic microphase separation.

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