

Polymer Gel Electrolytes Prepared from P(EG-co-PG) and Their Nanocomposites Using Organically Modified Montmorillonite

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ABSTRACT: Polymer gel electrolytes were prepared by thermal crosslinking reaction of a series of acrylic end-capped poly(ethylene glycol) and poly(propylene glycol) [P(EG-co-PG)] having various geometries and molecular weights. Acrylic end-capped prepolymers were prepared by the esterification of low molecular weight (M_n : 1900–5000) P(EG-co-PG) with acrylic acid. The linear increase in the ionic conductivity of polymer gel electrolyte films was observed with increasing temperature. The increase in the conductivity was also monitored by increasing the molecu-

lar weight of precursor polymer. Nanocomposite electrolytes were prepared by the addition of 5 wt % of organically modified layered silicate (montmorillonite) into the gel polymer electrolytes. The enhancement of the ionic conductivity as well as mechanical properties was observed in the nanocomposite systems. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 894–899, 2004

Key words: polymer gel electrolyte; poly(EG-co-PG); nanocomposite

INTRODUCTION

Many types of ionically conducting polymers, generally classified as polymer electrolytes, have been developed and characterized in recent years.^{1–3} Special interest today is focused on the polymer systems having high ionic conductivity as well as desirable mechanical stability at ambient temperature. They are applied for separators in high-power, versatile, rechargeable lithium batteries.^{4–6} Polyether-based solid electrolytes are one of the most intensively studied ionic conductors.⁷ A target ionic conductivity of $\sim 10^{-3}$ S/cm at ambient temperatures is required in the area of rechargeable batteries. In general, the increase in the ionic conductivity is observed with an increase in the molecular mobility of lithium salts. To enhance the ionic conductivity, the crystallinity of the polymer matrix should be lowered by adding proper solvents or plasticizers for facile movement of ions. However, the incorporation of liquid plasticizers results in worsening of mechanical properties and increased reactivity toward the metal electrode. Therefore, the key issue to develop polymer electrolyte systems is having high ion conductivity, desirable

mechanical properties, as well as proper electrochemical stability.

For this purpose, the gel-type polymer electrolyte has been introduced as a possible candidate to fulfill the optimum properties. The gel-type electrolytes are obtained by the immobilization of liquid solutions of lithium salts in polymer matrices. Because the liquid electrolyte molecules can solvate lithium ions, coordinating polymers such as poly(ethylene oxide) (PEO) may be replaced by mechanically tough polymers such as polyvinylidene fluoride (PDVF), polyacrylonitrile, and poly(methyl methacrylate). A small amount of solvent can be incorporated into the gel polymers, which successfully reduces the glass transition temperature of the polymer and hence increases the ionic mobility at a given temperature. However, gel electrolyte systems also suffer the disadvantages of worsening the mechanical properties, releasing the volatiles, and increasing the reactivity toward the metal electrode. To compensate the disadvantage of the above-mentioned gel electrolyte systems, chemically crosslinked permanent networks systems were introduced by Kono et al.^{8–12} The chemically crosslinked permanent network provides the systems with enhanced mechanical properties as well as better capability of storing liquid electrolytes.

It has been known that the formation of composite polymeric electrolytes by adding inorganic fillers to polymer electrolyte systems as a third component is one of the most effective ways of preparing highly conductive polyether solid electrolytes while retaining

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good mechanical properties over a wide temperature range.^{13–18} The improvement of ionic conductivity observed in some polyether composite systems has been assigned to the decrease of polymer crystallinity by the addition of the fillers.^{19–21} The other aspect affecting conductivity is known as a doping effect of inorganic filler.^{22,23}

In these regards, we tried to prepare the new type of polymer electrolyte systems equipped with high ionic conductivity as well as good mechanical properties by employing the concept of combining the systems of chemically stable gel and inorganic/polymer nanocomposite. We studied the polymer gel systems based on polyether having acrylate end groups and their nanocomposites by using organically modified Montmorillonite (MMT). The polyether copolymers are composed of poly(ethylene glycol) and poly(propylene glycol) [P(EG-co-PG)]; their molecular weights are relatively low (M_n : 1900, 2500, 2800, 3500, 5000). The P(EG-co-PG) copolymer systems were chosen to prevent the crystalline domain formation. The terminal acrylate group was introduced by esterification reaction of hydroxy end group of copolymer with acrylic acid. The terminal acrylate functionality could provide the copolymer system with chemical crosslinking sites to form a gel polymer. This type of gel polymer could provide the system with suitable mechanical properties. The acrylate end-capped copolymers were mixed with Li salt solutions and an organically modified layered silicate, MMT nanoclay. The prepolymer mixture is finally heated to induce thermal crosslinking reaction to form polymer gel electrolyte nanocomposite films.

In this article, the synthetic methods and the physical properties of polyether-based polymer gel electrolytes and their MMT nanocomposites were described.

EXPERIMENTAL

Materials

The polyether copolymers having molecular weights of 1900, 2500, 2800, 3500, and 5000 were obtained from Aldrich. Acrylic acid (Junsei), LiCF_3SO_3 (Aldrich), propylene carbonate (PC, Aldrich), and ethylene carbonate (EC, Aldrich) were used without further purification. A peroxide initiator [percadox-16, bis(4-*t*-butylcyclohexyl) peroxydicarbonate] was kindly provided by Akzo nobel. Ethoxylated oligomer (SR903S), ethoxylated trimethylpropane triacrylate ester, was supplied by Sartomer. Organically modified MMT was purchased from Southern Clay (Texas). Methyl, bis-2-hydroxyethyl tallow ammonium ion (95 mequiv of MT2EtOH/100 g of MMT: 30BTM) was chosen in this study as an organic modifier, where tallow is predominantly octadecyl chains with small amounts of lower homologues ($\sim 65\%$ of C_{18} , $\sim 30\%$ of C_{16} , and

$\sim 5\%$ of C_{14}). The anion used for MT2EtOH is Cl^- . The typical plate size of the modified clay particles is $\sim 2\text{--}16\ \mu\text{m}$.

Preparation of gel polymer electrolyte film

Acrylate end-capped polyether was synthesized by the esterification of hydroxy-terminated P(EG-co-PG) with acrylic acid.¹⁰ In the preparation of liquid electrolyte, LiCF_3SO_3 was dissolved in the mixture of PC and EC (4 : 1 by volume) to yield 1M solution. Acrylate end-capped prepolymer was added in the electrolyte solution (weight ratio 1 : 3) and 1 wt % of the peroxide initiator was added to the solution. In the case of nanocomposite preparation, 5 wt % of MMT nanoclay was added to the prepolymer solution. This solution was mixed homogeneously and cast onto a glass plate. Gelation of prepolymer occurred in a convection oven at 80°C. The thickness of resulting film was $\sim 200\ \mu\text{m}$.

DSC measurement

DSC data were obtained between -80 and 100°C by using Seiko Exstar 6000 (DSC 6100) scanning calorimeter equipped with a liquid nitrogen autocooling accessory. A sample was cooled to -80°C , held at that temperature for 5 min, heated to 100°C , held for 5 min, and cooled, and the cycle was then repeated. All heating and cooling rates were $10^\circ\text{C}\ \text{min}^{-1}$.

Stress-strain test

Stress-strain test was performed by using Toyoseiki Stograph VI-C. Maximum load was 50 kgf and strain rate was 20 mm/min. The sample dimension was 1 cm \times 4 cm \times $\sim 500\ \mu\text{m}$.

X-ray diffraction measurement

The molecular structure of the polymer gel electrolyte composites was examined by wide-angle X-ray diffraction (Rigaku Rotaflex D/MAX System, Rigaku, Japan). The $\text{CuK}\alpha$ radiation ($\lambda = 0.154\ \text{nm}$) and curved graphite crystal monochromator were used in the measurement. The applied voltage and current of the X-ray tubes was 30 kV/100 mA, respectively. The 2θ was scanned between 2° and 30° at $3^\circ/\text{min}$.

Ionic conductivity measurement

An interfacial resistance between gel electrolyte and a stainless steel electrode was measured by complex impedance method by using computer-controlled impedance analyzer (Solatron 1255B, Multi Stat, USA) for SUS/gel electrolyte/SUS cell (surface area: $1.767\ \text{cm}^2$). The cell housing was equipped with heating

TABLE I
Compositions of Acrylate End-Capped P(EG-co-PG)

Polymer	M_n	Structure	EG (wt %)	Type
P2800D ^a	2800	Linear	10	Block
P1900D ^a	1900	Linear	50	Block
P3500T ^b	3500	Three-arm	50	Block
P5000T ^b	5000	Three-arm	70	Block
P2500D ^c	2500	Linear	75	Random
SR9035 ^d	935	Three-arm	100	Homo

^a P(EG-*b*-PG-*b*-EG).

^b P(EG-*b*-PG).

^c P(EG-*ran*-PG).

^d Sartomer reagent: ethoxylated trimethylpropane triacrylate esters $\text{CH}_3\text{CH}_2-\text{C}[\text{CH}_2-(\text{CH}_2\text{CH}_2\text{O})_5-\text{OCOCH}=\text{CH}_2]_3$.

wire to controlled temperature. During the ionic conductivity measurement, frequency was swept from 0.1 Hz to 1 MHz, under AC 0.1 mA with 10 MV. The data were obtained in the 298–353 K range.

RESULTS AND DISCUSSION

Preparation of gel polymer electrolyte film

The acrylic acid group was successfully reacted with the low molecular weight hydroxy-terminated P(EG-co-PG) in the presence of a catalytic amount of *p*-toluenesulfonic acid as described in the literature.¹⁰ The excess amount (~50% molar excess) of acrylic acid was used to give nearly 90% conversion. Aromatic solvents such as benzene and toluene were used for reaction medium to offer a condition for azeotropic removal of water. The formation of a terminal double bond was confirmed by FTIR spectroscopy by observ-

ing vibrational motion of vinyl groups assigned at 1637, 1618, and 1407 cm^{-1} . The product was also confirmed by 500 MHz ¹H-NMR in which several peaks were observed at the following chemical shifts: [δ : 1.12 (3H, CH₃), 1.23 (1H, CH), 3.58 (2H, CH₂), 5.82 (1H, —CH=CH₂—), 6.13 (1H, —CH=CH₂—), 6.41 (1H, —CH=CH₂)].

The acrylic end-capped prepolymers were mixed with LiCF₃SO₃/EC/PC salt solutions and peroxide initiator and the solution was successively heated to form polymer gel electrolyte films. FTIR spectroscopy revealed that the acrylic end groups totally converted to network structure. The structure, composition, and the molecular weight of a series of gel films used in this experiment are described in Table I.

The morphology of the resulting films was examined by using differential scanning calorimetry (DSC) technique monitoring the presence of crystalline residues. A typical thermograms of hydroxy-terminated P(EG-co-PG) and its gel electrolyte are shown in Figure 1. The DSC study reveals that the gel electrolyte films do not show any melting transition, which means that any crystalline regions do not exist in the gel electrolyte films. This might be due to the low molecular weight of copolymer structure as well as the system having a large amount of electrolyte solution.

It has been known that the ionic conductivity of polymer electrolyte is governed by various factors, such as the content of lithium salt, the presence of plasticizer, the molecular weight of host polymer, etc.¹ In this study, the ionic conductivity was measured as a function of molecular weight between crosslinks of the gel electrolyte film. Two different geometries of P(EG-co-PG) were investigated having a linear shape

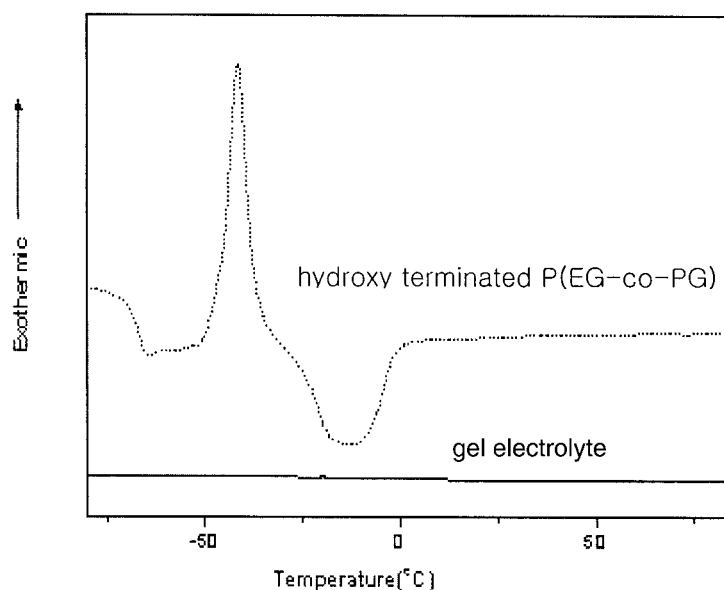


Figure 1 Typical DSC thermograms of hydroxy-terminated P(EG-co-PG) (---) and polymer gel electrolyte film P3500T (—).

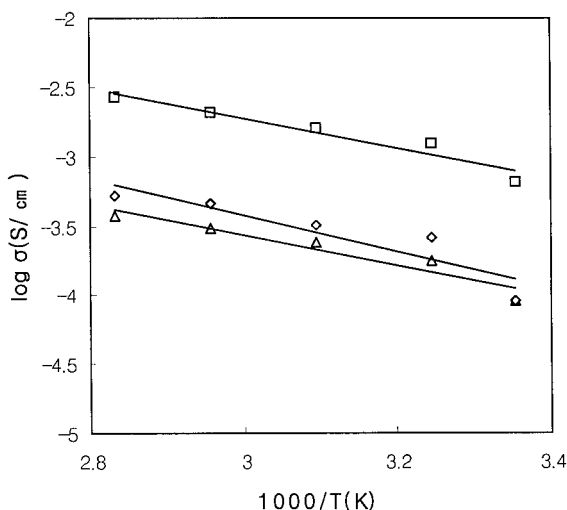


Figure 2 Arrhenius plots of ionic conductivity of gel electrolyte prepared from linear-type prepolymer [P2800D (\square ; $E_a = 20.42$ kJ/mol), P2500D (\diamond ; $E_a = 25.06$ kJ/mol), P1900D (\triangle ; $E_a = 21.03$ kJ/mol)].

and a star shape with tree arms. All the gel electrolyte films contain 75 wt % of 1M LiCF_3SO_3 liquid electrolyte solution in EC/PC mixed medium. The ionic conductivity was measured by using AC impedance analyzer. Figures 2 and 3 show the ionic conductivity of gel electrolyte film prepared from linear and three-arm star-shaped prepolymers. The ionic conductivity is plotted as a function of reciprocal temperature to present the Arrhenius behavior. As shown in the figures, the conductivity increases with the increase in temperature and the activation energy ranges between 10 and 25 kJ/mol depending on the structures. There is no slope change related to PEO crystallization or

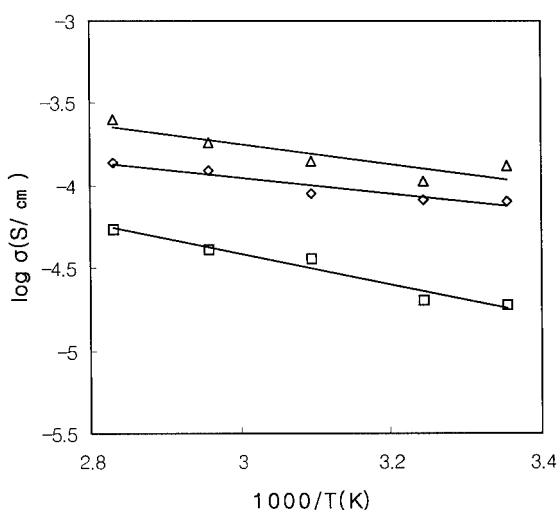


Figure 3 Arrhenius plots of ionic conductivity of gel electrolyte prepared from three-arm star-type prepolymer [SR9035 (\square ; $E_a = 17.74$ kJ/mol), P3500T (\diamond ; $E_a = 9.27$ kJ/mol), P5000T (\triangle ; $E_a = 11.74$ kJ/mol)].

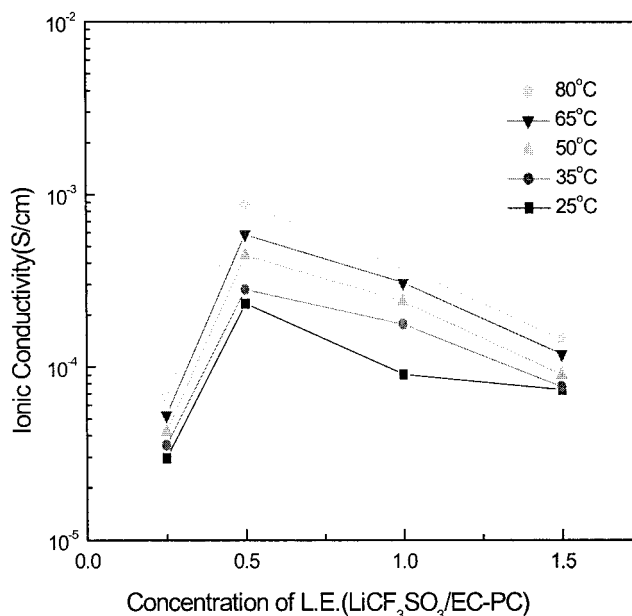


Figure 4 Ionic conductivity of gel electrolytes depending on liquid electrolyte contents at various temperatures. (\diamond : 80°C; ∇ : 65°C; \triangle : 50°C; \circ : 35°C; \square : 25°C).

fusion, which is a result coherent with the absence of crystallinity of the materials.⁸ It is also observed that the ionic conductivity increases with increasing molecular weight of precursor polymers. In the crosslinked systems, it is generally accepted that the decrease in molecular weight between crosslinks results in more restricted movement of polymer chain.¹⁸ Therefore, enhanced molecular mobility might be offered in the gel system prepared from higher molecular weight prepolymers, which consequently results in higher ionic conductivity. It can also be seen that the copolymer composition and the structure do not seem to give significant influences on the overall ion mobility.

To obtain high ionic conductivity, it is necessary to increase the number of carrier ions. Gel electrolytes having different salt concentrations were prepared to examine the effect of the salt content on ion conductivity. Figure 4 shows the ionic conductivity depending on the liquid electrolyte concentration. The ionic conductivity increases with the salt concentration; however, it subsequently decreases at higher concentration regions of $>0.5M$. The decrease in ionic conductivity may be attributed to the formation of ion complexes at high salt concentrations as described in the literature.²⁴ These complexes diffuse more slowly than dissociated ions in gel electrolytes.

Nanocomposites of polymer gel electrolyte/clay

It has been known that one of the most promising ways to improve the morphological and electrochem-

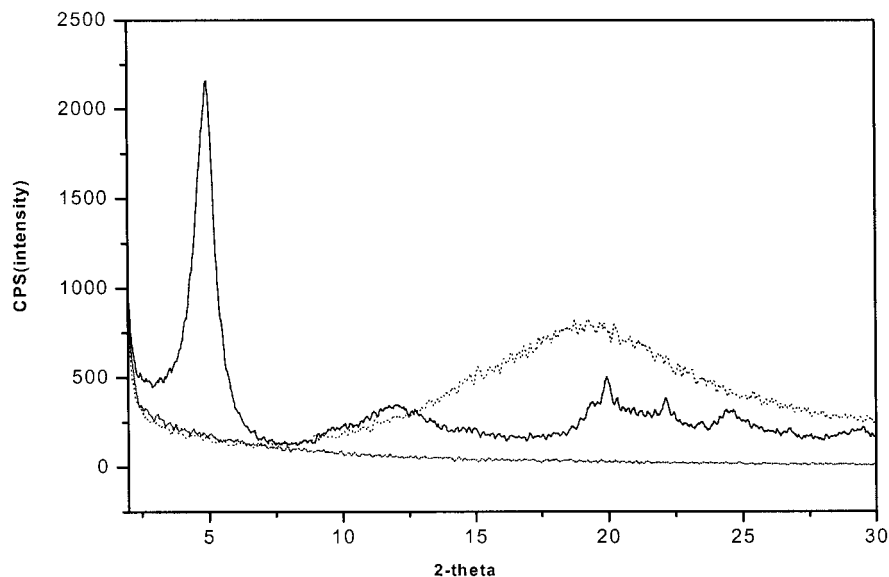


Figure 5 XRD spectra of nanoclay (—), gel electrolyte prepared from P1900D (···), and nanocomposite (- - -).

ical properties of polymer electrolytes is by the addition of ceramic fillers.^{13–18} In our experiment, a layered silicate, MMT [$M_xAl_{4-x}Mg_xSi_8O_{20}(OH)$], is used, which belongs to a family of phyllosilicates (2 : 1) composed of two tetrahedral silica thin layers with a central octahedral sheet of magnesia. Isomorphic substitution within the layers creates intrinsic surface negative charges primarily because of the alkali cation(s) residing in the interlayer. Therefore, the forces that hold the stacks together are ionic in nature and are relatively weak. It can be clearly seen that “intercalation of molecules between the layers” is favorable. To achieve high rendering of various ions, organoclaying processes are typically favored, benefiting from low surface tension. The nanocomposite formation of PEO by using various nanoclays has been reported in several articles.^{25,26} The authors claimed that PEO successfully intercalated into the clay structures, which resulted in an increase in interlayer distance at higher loading of PEO. Furthermore, a decrease in crystallinity of PEO has been observed in the intercalated structure, which resulted in enhanced ionic conductivity.

X-ray diffraction technique was used in our experiments to identify the structure of nanocomposites by using Bragg’s relationship. Figure 5 compares the representative wide-angle X-ray diffraction (WAXD) patterns for nanoclay, polymer gel electrolyte, and their nanocomposite samples. It can be seen that interlayer spacing (d_{001}) of MMT nanoclay is 1.78 nm and there is no indication of basal spacing in the polymer gel electrolyte and composite films. This identifies the finding that the polymer gel electrolyte film does not have any crystallinity, which has been confirmed by DSC measurement. It has been mentioned that polymer gel electrolyte films prepared from low molecular weight

prepolymer and a large amount of salt solution are totally amorphous in nature. In addition, the characteristic peak representing d -spacing of MMT clay disappears in the nanocomposite film. The absence of the gallery height at 1.78 nm in nanocomposites indicates that the regular spacing in nanocomposite is collapsed or the MMT layers are homogeneously dispersed. Consequently, it may be reasonable to mention that the nanoclays are exfoliated in the polymer matrix. This might be due to the strong interaction between the ammonium functional group (methyl, bis-2-hydroxyethyl, quaternary ammonium) in the clay surface and P(EG-co-PG) copolymer gel molecules.

It is thought that the use of clay to obtain nanocomposites with controlled ionic conductivity values is a fascinating method, because it could directly affect the mobility of the cations while avoiding the mobility of the anions (charged silicate layers). Figure 6 shows the Arrhenius plots of ion conductivity of several representative examples of novel nanocomposite polymer gel electrolyte systems compared with the MMT-free polymer gel electrolyte. The ionic conductivity of nanocomposite is nearly five times higher than that of MMT-free one. In the case of the lowest molecular weight sample (SR9035, M_n : 935), the addition of nanoclay enhances the ionic conductivity by nearly 20 times higher than the MMT-free system. Also, it should be mentioned that there is no transition point of conductivity in the Arrhenius plot, which means that there is no transition point between the crystalline and amorphous states as demonstrated in the previous DSC experiments.

It has been known that the increase in ionic conductivity of PEO-based nanocomposites is mainly due to the reduced crystallinity of intercalated PEO compos-

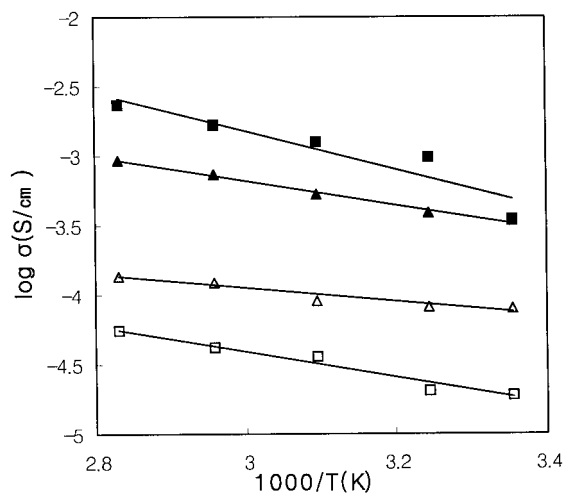


Figure 6 Arrhenius plots of ionic conductivity of gel electrolyte nanocomposites [SR 9035 (\square); $E_a = 26.53$ kJ/mol), SR9035 + 30B (\blacksquare); $E_a = 16.49$ kJ/mol), P3500T (\triangle); $E_a = 9.27$ kJ/mol), P3500T + 30B (\blacktriangle); $E_a = 17.74$ kJ/mol)].

ite structures.²⁷ However, the polymer gel electrolyte samples used in this experiment are totally amorphous, and thus, the reduction of crystallinity might not be the main reason for the increase in conductivity. One of the propositions used to explain the enhancement of the conductivity might be related to the formation of a space region which can modify the conductivity by creating a new kinetic pathway to the conduction.^{27–30} There might exist a special interaction, a so-called Lewis acid–base interaction, between the surface of nanoparticles and the polymer chains. This allows Li^+ ions to move more freely on the surface of the nanoparticles or through a polymer phase at the interface, which results in enhanced ionic conductivity.

As shown in Table II, it should be mentioned that the mechanical properties, such as tensile strength and modulus, of the nanocomposite films is increased because of the reinforcing effects of nanoparticles having enormous surface interactions with host polymers.^{31–33} The incorporation of nanoparticle into the gel resulted in the increase in the tensile strength by $\sim 60\%$ as well as modulus by $\sim 150\%$.

TABLE II
Tensile Strengths and Moduli of Gel Polymers and Nanocomposites

	P1900D	P1900D/clay	SR9035	SR9035/clay
Tensile strength (MPa)	0.35	0.58	0.84	1.33
Modulus (MPa)	0.04	0.15	0.44	1.69

Overall, the incorporation of nanosized platelets in P(EG-co-PG) gels increase the conductivity as well as mechanical properties, which could expand the applicability of PEO-based polymer gel electrolytes.

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