

Synthesis of High Molecular Weight Polyoxyethylene with a Quaternary Catalyst and Study of Its Conductive Blends with Poly(2-vinyl pyridine)

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ABSTRACT: High molecular weight polyoxyethylene (PEO) was synthesized by using a quaternary catalyst composed of triisobutyl aluminum, phosphoric acid, water, and *N,N*-dimethylaniline (DMA). Optimum synthesis conditions and some properties of the product were studied. This catalyst showed high activity and the molecular weight of the polyoxyethylene obtained can approach one million. The activity of polymerization mainly depends upon the composition of catalyst. The optimum composition is as follows: $i\text{-Bu}_3\text{Al}:\text{H}_3\text{PO}_4:\text{H}_2\text{O}:\text{DMA} = 1 : 0.17 : 0.17 : 0.10\text{--}0.15$ (molar ratio). The active centers of the catalyst was thus proposed. The high molecular weight PEO synthesized by this catalyst was blended with poly(2-vinyl pyridine) (PVP) and then doped with LiClO_4 and TCNQ to obtain a conductive elastomeric material. Ionic, electronic, and mixed (ionic–elec-

tronic) conductivities of blends were investigated. At a Li/EO molar ratio of 0.1 and a TCNQ/VP molar ratio of 0.5, the mixed conductivity of the blend of PEO/PVP/ LiClO_4 /TCNQ is higher than the sum of ionic conductivity of PEO/PVP/ LiClO_4 and electronic conductivity of PEO/PVP/TCNQ, when the weight ratio of PEO to PVP is 6/4 or 5/5. It can reach 4×10^{-6} S/cm at room temperature. Differential scanning calorimetry, thermal gravimetric analysis, and the appearance of the blend showed that both TCNQ and LiClO_4 can complex with PEO and PVP, thus enhancing the compatibility between PEO and PVP. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 562–569, 2007

Key words: polyoxyethylene; catalyst for ring-opening polymerization; blend; conductivity; poly(2-vinyl pyridine)

INTRODUCTION

Polyoxyethylene (PEO) with high molecular weight is a water-soluble, thermoplastic, and crystalline polymer and has a lot of application, such as water soluble package material, coagulant, textile sizer, thickener, antistatic agent and agent for reducing water flow resistance etc. Hill et al.,¹ Miller and Price,² Vandenberg,³ Furukawa et al.,⁴ Osgan and Teysie,⁵ Hsieh,⁶ and Zhang and Shen⁷ used alkali-earth carbonate, aluminum isopropylate-zinc chloride, alkyl aluminum-water-acetylacetonate, diethyl zinc-aluminum oxide, bimetallic oxoalkoxide catalyst $[(\text{RO})_2\text{Al}-\text{O}-\text{Zn}-\text{Al}(\text{OR})_2]$, trialkyl aluminum-water-zinc acetylacetonate, and trialkyl aluminum-water-rare earth metal acetylacetonate as catalyst, respectively, to obtain high molecular weight polyoxyethylene. However, some of the catalysts were unstable,

some needed large amount, some showed low conversion or produced products whose molecular weights were not high. Xie⁸ found an active quaternary catalyst (trialkyl aluminum-phosphoric acid-water-tertiary amine) for polymerization of epichlorohydrin.

The area of electroactive polymers has become one of the most challenging and fruitful fields within the past two decades. Both electronic conductive polymers and ionic conductive polymer electrolytes have been prepared and studied. The mixed (ion–electron) conductive polymer displays better discharge characteristics as a polymer electrode in polymer electrolyte, because it can decrease contact resistance between the electrode and polymer electrolyte in a solid-state battery. Cui et al.⁹ reported the synthesis of poly(2-vinyl pyridine)-graft-poly(ethylene oxide) with well-defined structure and indicated that the graft copolymer, after doped with LiClO_4 and TCNQ, showed a mixed conductivity with a synergistic effect, which reached 4.4×10^{-5} S/cm at room temperature, but preparation of these polymers needs complicated synthesis and purification processes. Hence, it is of interest to develop an easier method for preparing mixed (ion–electron) conduc-

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tive polymers. Li and Khan^{10,11} examined PEO (MW 600,000)/poly(2-vinyl pyridine) (PVP) (MW 200,000) or poly(4-vinylpyridine) (MW 50,000) blend systems at weight ratio of 85/15 with LiClO₄, but only ionic conductivity was studied. Cui et al.¹² studied both the ionic and electronic conductive blends of PVP and PEG with molecular weight of 20,000, doped with LiClO₄ and TCNQ and obtained a mixed conductivity of 1.10×10^{-5} S/cm with a synergistic effect at room temperature. However, the blends were in the wax state.

This article deals with the optimum conditions for ring-opening polymerization of ethylene oxide by using the quaternary catalyst, both with respect to high conversion and high molecular weight. This article also concerns with the study of the ionic and electronic conductive blends of high molecular weight PEO synthesized by the quaternary catalyst with PVP and doped with LiClO₄ and TCNQ. This is because high molecular weight PEO will offer better mechanical strength to the blend. DSC and TGA of the PEO/PVP blend doped with LiClO₄ or TCNQ were also studied for understanding the compatibility of the components in the blend.

EXPERIMENTAL

Materials

Ethylene oxide was treated with potassium hydroxide, distilled, and stood over 4A molecular sieve. Toluene, benzene, and petroleum ether were chemically pure and used directly for polymerization after standing over 4A molecular sieve overnight. LiClO₄ was an analytical reagent and was dried at 160°C before use. Other reagents are all chemically pure. High molecular weight PEO was self-made using the quaternary catalyst and its molecular weight was determined by modified Bruss membrane osmometer to be about 1000,000. 7,7,8,8-Tetracyano-1,4-quinodimethane (TCNQ) was synthesized according to literature.¹³ Commercial 2-vinyl pyridine (VP) was purified by distillation under reduced nitrogen pressure over CaH₂ twice before use.

Polymerization of ethylene oxide using the quaternary catalyst

Quaternary catalyst was prepared under nitrogen atmosphere by adding ether solution of 85% phosphoric acid, in which the molar ratio of water to phosphoric acid is about 1 : 1, to a toluene solution of triisobutyl aluminum, followed by addition of *N,N*-dimethyl aniline (DMA). After addition of the catalyst to the toluene solution of ethylene oxide in a dried vessel under purified nitrogen atmosphere,

polymerization was carried out at 50°C for 20 h. Polymerization was stopped by adding toluene solution containing 0.5% antioxidant 264. After the solvent was evaporated, the product was dried in vacuum oven at 50°C to a constant weight. The rate of polymerization was determined by weighing the product after different times of polymerization carried out in different vessels under the same conditions.

Synthesis of poly(2-vinyl pyridine)

Poly(2-vinyl pyridine) was prepared by anionic polymerization of purified 2-vinyl pyridine in a mixture of benzene and tetrahydrofuran, using 1-methylnaphthalene lithium as initiator as follows. The initiator was synthesized by mixing 1-methylnaphthalene, lithium chips, and tetrahydrofuran with stirring under nitrogen atmosphere, and then kept in a refrigerator for 1 month. The concentration of the upper layer was determined by titration with 0.1M standard HCl solution, using methyl red as indicator. The initiator was added dropwise to the solution of VP in a mixture of benzene and tetrahydrofuran under nitrogen atmosphere until the light yellow color ceased to disappear, to scavenge impurities of the reaction system. The required amount of the initiator was then injected by means of a syringe, and the mixture appeared dark red immediately. Then the reaction was maintained at 25°C for 1 h, followed by termination with methanol. The product was precipitated and washed with petroleum ether (bp 60–90°C). The precipitate was dissolved in chloroform and filtered. The filtrate was precipitated again with petroleum ether. After drying under an IR lamp, the PVP was vacuum-dried at 80°C to constant weight. The number-average molecular weight of PVP used in blending with PEO was determined by Knauer VPO apparatus, using chloroform as solvent, to be 35,000.

Preparation of the blends

Blends of PEO, PVP, and LiClO₄ were prepared by dissolving PEO and PVP in dichloromethane, followed by addition of a methanolic or ethanolic solution of LiClO₄ with stirring for 3.5 h at room temperature. Blends of PEO, PVP, and TCNQ were obtained by dissolving PEO, PVP, and TCNQ in DMF during stirring for 5 h with slight heating. Blends of PEO, PVP, LiClO₄, and TCNQ were prepared by mixing PEO, PVP, and TCNQ in DMF, followed by addition of methanol solution of LiClO₄, during stirring for 5 h with slight heating. After evaporating the solvent, all the blends were dried in a vacuum oven at 60°C thoroughly for 24 h.

Measurement of conductivity

The blend sandwiched between two thin aluminum foils was hot-pressed in a die into a disc (about 2 mm thick and 14 mm diameter) at 110°C for the PEO/PVP/LiClO₄ blend and the PEO/PVP/LiClO₄/TCNQ blend, at 120–130°C for the PEO/PVP/TCNQ blend. Before measuring, all the discs were dried over fresh P₂O₅ thoroughly for at least 48 h.

The a.c. conductivities were measured at different temperatures with a DDS-11 conductometer using copper disc electrodes operated at a frequency of 1100–1200 Hz. The determination from 5 to 80°C was repeated once more. Usually, no further reduction in the conductivity at room temperature was observed.

Characterization

The inherent viscosity (η_i) of polyethylene oxide was determined in water solution of 0.1 g/dL concentration at 30°C. $[\eta]$ was calculated using the relation $[\eta] = \frac{\sqrt{2(\eta_{sp}-\ln \eta_r)}}{c}$. Molecular weight of polyethylene oxide was calculated from equation: $[\eta] = 1.25 \times 10^{-4} M_w^{0.78}$.¹⁴ Melt index (MI) was determined under 5 kg load at 180°C. Homopolymers of ethylene oxide was hot-pressed at 200°C, annealed at 140°C, and then quenched. Tensile strength and stress-strain curves were determined by a tensile tester.

DSC measurements were performed on a Perkin-Elmer DSC-2C Differential Scanning Calorimeter. The samples were first heated from room temperature to 200°C and maintained for 2 min, then the samples were quench-cooled quickly to -70°C before obtaining thermograms. The scanning rate was 10°C/min. The glass transition temperatures (T_g) were taken at the midpoints of the heat capacity changes, and the melting temperatures (T_m) were taken at the maxima of the enthalpy endothermic peaks. Thermal gravimetric analysis was performed on Perkin-Elmer TGS-2 apparatus with a heating rate of 20°C/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

Homopolymerization of ethylene oxide into high molecular weight product

Polymerization of ethylene oxide into high molecular weight polymer using the quaternary catalyst and study of its properties have not yet been reported. Our work shows that the quaternary catalyst can polymerize ethylene oxide into polymer with molecular weight of several hundred thousands to a million. The catalytic activity is high.

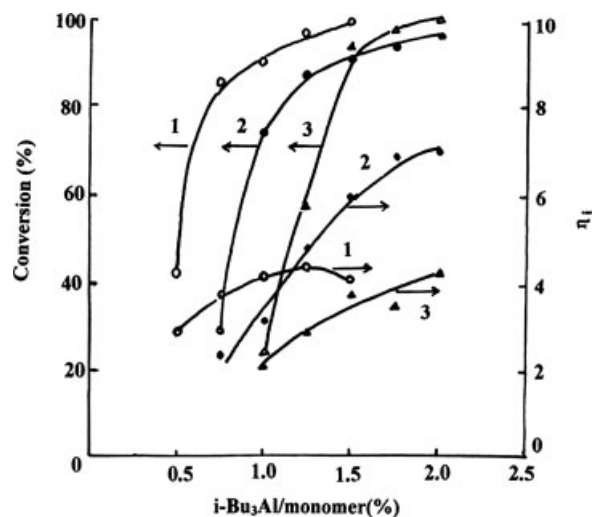


Figure 1 Effects of catalyst amount, monomer concentration, and molar ratios of PA/Al on monomer conversion and molecular weight of PEO [DMA/Al = 0.1, at 50°C for 20 h; (1) 15% M, PA/Al = 0.2; (2) 10% M, PA/Al = 0.17; (3) 10% M, PA/Al = 0.20].

The quaternary catalyst is composed of triisobutyl aluminum (Al), phosphoric acid (PA), water, and *N,N*-dimethylaniline (DMA). The activity of polymerization mainly depends upon the composition of catalyst. Without phosphoric acid, the activity of *i*-Bu₃Al-H₂O-DMA was quite low. There was no polymer yield when tributyl phosphate was used instead of phosphoric acid. Hence, the active hydrogen atoms in phosphoric acid are necessary for reaction with triisobutyl aluminum and then complexing with the electron donor to form the active sites. Since 85% phosphoric acid contain phosphoric acid and water in molar ratio of 1/1, change of 85% phosphoric acid amount can change the molar ratios of PA/Al and H₂O/Al. Water in the catalyst can enhance the molecular weight of the product. When PA/Al and H₂O/Al molar ratio are lower than 0.15 or higher than 0.25, both the conversion and molecular weight of the product are lower. In the range of PA/Al or water/Al molar ratio at 0.17–0.20 at a monomer concentration of 10 wt %, the conversion of ethylene oxide reaches over 90%, when the *i*-Bu₃Al/monomer weight ratio is over 1.5%, as shown in Figure 1. With increasing *i*-Bu₃Al/monomer weight ratio, the conversion increases rapidly at first and then gradually. The activity of the catalyst with PA/Al molar ratio at 0.17 seems higher than that of the catalyst with PA/Al molar ratio at 0.20. The η_i or molecular weight of PEO increases with the increase of *i*-Bu₃Al/monomer weight ratio. The molecular weight of PEO obtained at PA/Al molar ratio of 0.17 is also higher than that obtained at PA/Al molar ratio of 0.20. In the former case, when the amount of *i*-Bu₃Al/M increases to 1.75 wt %, the

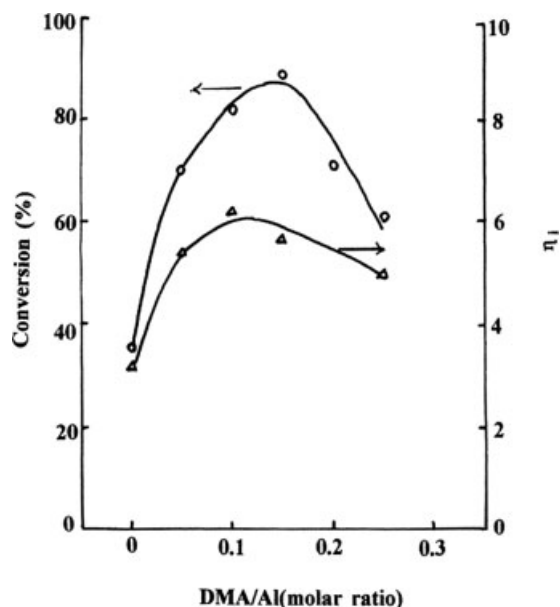


Figure 2 Effect of DMA/Al molar ratio on conversion and molecular weight of PEO ($i\text{-Bu}_3\text{Al}/\text{M} = 0.75\%$, $\text{PA}/\text{Al} = 0.17$, 20% M, 50°C).

molecular weight of PEO can reach over one million (η_i reaches 7). Figure 1 also shows that at PA/Al molar ratio of 0.2 and DMA/Al molar ratio of 0.1, when the monomer concentration increases from 10 to 15 wt %, the catalyst amount can be lowered to 1.0 wt % $i\text{-Bu}_3\text{Al}$, so as to reach the conversion of EO over 90% at 50 °C for 20 h. At the same catalyst amount, η_i of the product also increases with monomer concentration.

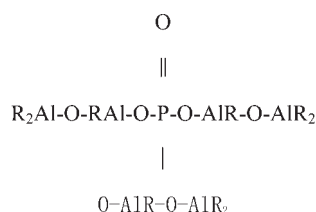
Figure 2 shows that in the absence of DMA both the conversion and molecular weight of PEO are lower. Both of them increase with increasing DMA/Al molar ratio. Hence, it is necessary to use tertiary amine as an electron donor in the catalyst. At 0.17 molar ratio of PA/Al, the optimum molar ratio of DMA/Al for the polymerization is in the range of 0.1–0.15. With decreasing PA/Al molar ratio, the optimum range of DMA/Al molar ratio becomes narrower and the molecular weight of the product becomes lower. With increasing PA/Al molar ratio, the optimum range of DMA/Al molar ratio becomes wider but the molecular weight of PEO decreases.

The catalyst is more effective when prepared in the right order, i.e., addition of ether solution of 85% phosphoric acid to a toluene of triisobutyl aluminum, followed by addition of DMA as electron donor, whereas it becomes less effective when prepared in other sequences. This is because the catalyst prepared in the former order is apparently homogeneous, whereas it appeared to be inhomogeneous when prepared in the other orders. The heterogeneous catalyst is less effective than the homogeneous catalyst.

Polymerization proceeds quickly at the beginning and then slows down, as shown in Figure 3. When the molar ratio of PA/Al is 0.17, the molecular weight of PEO increases abruptly at first and then decreases gradually, whereas when the molar ratio of PA/Al is 0.20, the molecular weight increases quickly at first and then keeps almost unchanged. This fact may be due to the occurrence of chain transfer in the later stage of polymerization, when more triisobutyl aluminum exists in the former case.

The optimum composition is as follows: $i\text{-Bu}_3\text{Al} : \text{H}_3\text{PO}_4 : \text{H}_2\text{O} : \text{DMA} = 1 : 0.17 : 0.17 : 0.10\text{--}0.15$ (molar ratio) or nearly 6 : 1 : 1 : 0.6–0.9.

According to the most favorable composition of the catalyst, the active site is presumed to be composed of:



which is complexed with the nitrogen-containing electron donor, DMA, to form active sites. Since nitrogen atom in DMA has lone pair electrons and acts as an electron donor, whereas Al atom in the reaction product of AlR_3 with water and phosphoric acid is electron acceptor, the complex formed can function as active center, somewhat similar to the Vandenberg catalyst composed of hydrolytic product of AlR_3 with acetylacetonate as electron donor.¹⁵

The polymerization is presumed to be of coordinated anionic type. The oxygen atoms of the EO molecules are first coordinated with the Al atoms

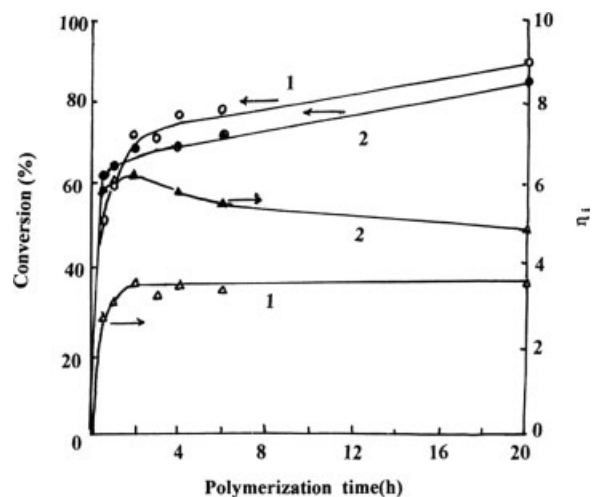


Figure 3 Effect of polymerization time on conversion and molecular weight of PEO [(1) PA/Al = 0.2, DMA/Al = 0.1, 15% M, $i\text{-Bu}_3\text{Al}/\text{M} = 1\%$, 50°C; (2) PA/Al = 0.17, DMA/Al = 0.1, 15% M, $i\text{-Bu}_3\text{Al}/\text{M} = 1\%$, 40°C].

TABLE I
Mechanical Properties of PEO Film Formed by Different Methods

η_i of PEO	Film formation method	Tensile strength (MPa)	Ultimate elongation (%)	Permanent set (%)
3.23	Solution cast	5.5	–	22
3.23	Cast and hot-pressed	7.7	60	32
5.60	Solution cast	7.1	560	470
6.30	Solution cast	8.4	648	492
6.30	Cast and hot-pressed	9.6	592	478

and then initiated by ring-opening reaction and propagate at the Al atoms complexed with the electron donors as the active sites. The presence of P–O–Al–O–Al bond in the active sites may enhance the propagation reaction and reduce the chain transfer or termination, thus increasing the molecular weight of the polymer.

Some properties of the high molecular weight polyoxyethylene

High molecular weight polyethylene oxide can dissolve in water, dichloromethane, dichloroethane, toluene, tetrahydrofuran, etc. Table I shows that the tensile strength of the film cast from dichloromethane solution reaches 5.0–8.5 MPa, which increases with the increase of molecular weight. The polyethylene oxide has a melting point of about 64°C and can be hot-pressed. After heated at 100°C for 15 min and cooled naturally, the film shows very large spherulites, which can be seen by eyes. Its tensile strength can be increased to about 10.0 MPa in this way, as shown in Table I.

The relationship between the melt index (MI, at 180°C and 5 kg load) and the inherent viscosity of PEO (η_i) in 30°C water is shown in Figure 4, or it may be represented by $\log MI = 2.01 - 0.554\eta_i$.

PEO/PVP/LiClO₄ blend system

Macrophase separation occurred in PEO(80)/PVP(20) blends, when no LiClO₄ was added to it. The blend with addition of LiClO₄ at a Li/EO molar ratio of 0.05 or EO/Li molar ratio of 20 shows apparently homogeneous but not transparent, indicating a microphase separation. As the concentration of LiClO₄ salt increases, the blend changes into a semi-transparent elastomer. When the Li/EO molar ratio reaches 0.1 or 0.2, this blend becomes a transparent elastomer. Lithium ions can interact with both the oxygen atoms of PEO and the nitrogen atoms of PVP due to the ion-dipole interactions. Because of the differences in the electronegativity between oxygen and nitrogen and in the steric hindrance of PEO and PVP, the complexing ability of PEO is superior to that of PVP. When the concentration of lithium salt is lower (Li/EO = 0.05, or EO/Li = 20), the lith-

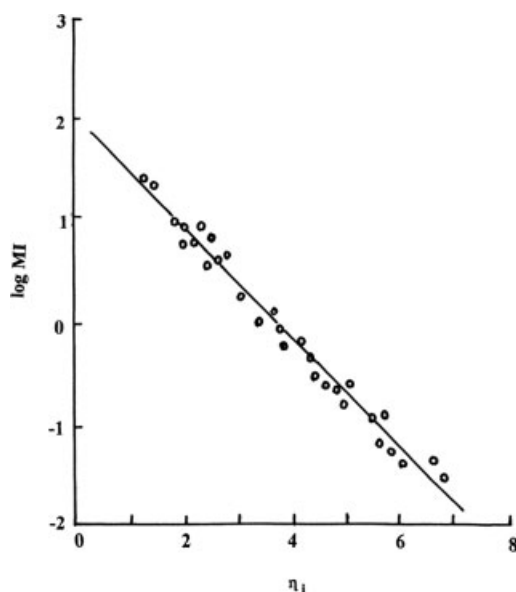


Figure 4 Relationship between melt index (180°C, 5 kg load) and inherent viscosity of PEO in water at 30°C.

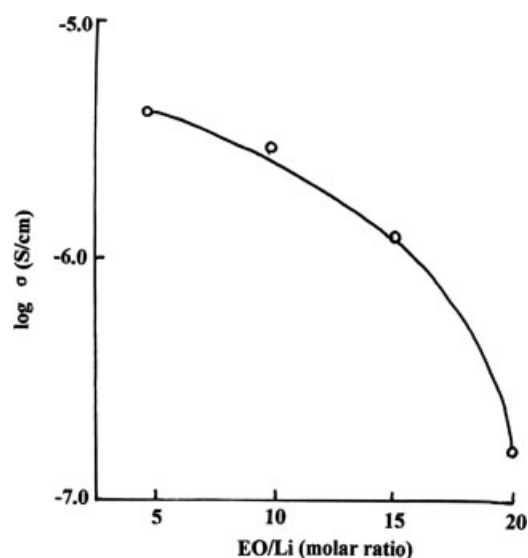


Figure 5 Effect of EO/Li molar ratio on conductivity of PEO(80)/PVP(20)/LiClO₄ blend at 25°C.

ium ion interacts with the oxygen of PEO, hence PEO and PVP exist as two microseparated phases. Through the increase in the amount of lithium salt, a part of the lithium salt can act as a compatibilizer between PEO and PVP, because lithium ion could interact with the oxygen of PEO and the nitrogen of PVP simultaneously. Optical transparency is one of the important criteria¹⁶ to illustrate the compatibility of two phases. Hence, the blend at a Li/EO molar ratio of 0.1 or 0.2 is a transparent elastomer. This indicates that PEO and PVP are compatible in the presence of a certain amount of lithium salt. This will be proved by DSC results discussed later.

When the content of PEO in the PEO/PVP blend decreases to 40 wt % or lower and the molar ratio of Li/EO is fixed at 0.10, this blend becomes phase-separated. The reason is that the phase separation is partially caused by deficiency in LiClO₄ salt. The PEO/PVP blend is elastomeric as the content of PEO is in the range of 50–80 wt %, while the PEO/PVP blend becomes nonelastomeric when the content of PEO is less than 50 wt %. After complexed with LiClO₄, crystalline phase of PEO changes into amorphous and PEO behaves as an elastomer. When the content of PEO is lower than that of PVP, the PEO/PVP blend behaves as a toughened plastic.

Figure 5 shows that the room temperature ionic conductivity (σ_T) decreases with decreasing LiClO₄ concentration, and the room temperature ionic conductivity of PEO(80)/PVP(20)/LiClO₄ blend at a EO/Li molar ratio of 5 or Li/EO molar ratio of 0.20 is 4.0×10^{-6} S/cm. We have found that this molar

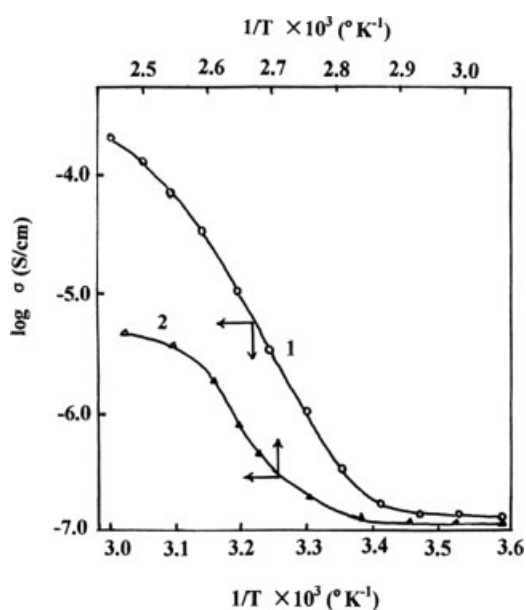


Figure 6 Arrhenius conductivity plots of PEO/TCNQ complex and PVP/LiClO₄ complexes (1, TCNQ/EO = 0.10; 2, Li/VP = 0.10).

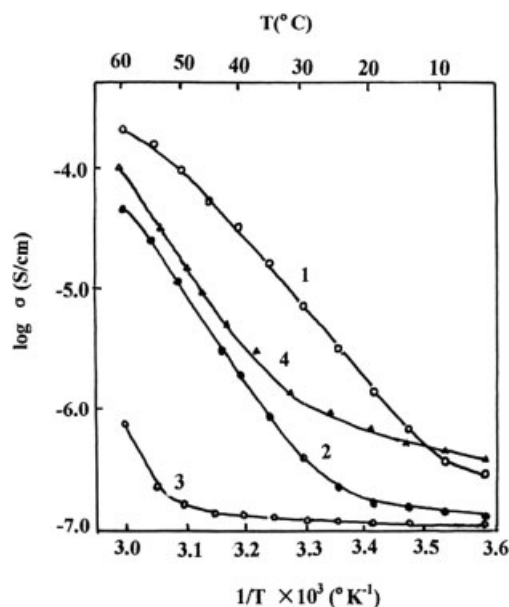


Figure 7 Arrhenius conductivity plots of PEO/PVP/LiClO₄ blends [(1) Li/EO = 0.10, PEO/PVP = 8/2; (2) Li/EO = 0.10, PEO/PVP = 5/5; (3) Li/EO = 0.10, PEO/PVP = 2/8] and of PEO/PVP/TCNQ blend [(4) TCNQ/VP = 1.0, PEO/PVP = 8/2].

ratio of Li/EO is higher than that in the general PEO/LiClO₄ system in which the optimum Li/EO is 0.05. This is because in the PEO/PVP/LiClO₄ blend, pyridyl groups of PVP could consume a part of LiClO₄ salt due to the ion-dipole interaction. Although PVP can also interact with lithium ion, its conductivity is low, as shown in Figure 6.

The ionic conductivity of PEO/PVP/LiClO₄ blend is mainly contributed by the PEO/LiClO₄ complex. Figure 7 shows that the conductivity of PEO/PVP/LiClO₄ at fixed molar ratio of Li/EO decreases with reducing PEO content. When the PEO content is lower, the conductivity increases slowly with temperature at lower temperature range. Since PEO becomes a dispersed phase in the PEO/P2VP blend with lower PEO content, the ionic conduction is difficult to take place.

TABLE II
Conductivities (σ) of PEO/TCNQ Complexes and PVP/TCNQ Complex at 25°C

TCNQ/EO (molar ratio)	TCNQ/VP (molar ratio)	σ (10^6) (S/cm)
0.025	–	0.34
0.033	–	0.46
0.05	–	1.54
0.10	–	0.33
–	0.5	0.09

TABLE III
Conductivities (σ)^a of PEO/PVP/LiClO₄/TCNQ blend system at 25°C

PEO/PVP (weight ratio)	Li/EO (molar ratio)	TCNQ/VP (molar ratio)	σ (10 ⁶) (S/cm)			
			σ_I	σ_E	σ_M	R
8/2	0.05	0.5	0.15	0.19	0.16	0.47
8/2	0.10	0.5	2.95	0.19	2.20	0.70
8/2	0.20	0.5	4.00	0.19	1.63	0.39
6/4	0.10	0.5	1.37	0.20	3.90	2.48
5/5	0.10	0.5	0.20	0.16	0.74	2.06
4/6	0.10	0.5	0.15	0.16	0.25	0.81
2/8	0.10	0.5	0.11	0.15	0.19	0.73

^a Here σ_I , σ_E , and σ_M are the ionic conductivities of PEO/PVP/LiClO₄ blend, electronic conductivity of PEO/PVP/TCNQ blend, and mixed conductivity of PEO/PVP/LiClO₄/TCNQ blend, respectively.

PEO/PVP/TCNQ blend system

As well known, TCNQ can form charge transfer complex with PVP, which shows electronic conductivity (σ_E). TCNQ can also form charge transfer complex with PEO, because the oxygen of PEO has lone pair electrons and acts as an electron donor. Figure 6 also indicates the Arrhenius plot of conductivity of PEO/TCNQ. The conductivity of PEO/TCNQ complex increases with increasing temperature. At temperature higher than 25°C, the conductivity increases more quickly than that lower than 25°C. This is caused by changing the crystalline PEO chains into amorphous PEO chains with increasing temperature.

Table II indicates that the conductivity of PEO/TCNQ reaches a maximum value at a TCNQ/EO molar ratio of 0.05 and decreases as the TCNQ content increases further. Also the conductivity of the PVP/TCNQ blend is lower than that of the PEO/TCNQ blends and hence the electronic conductivity of PEO/PVP/TCNQ blend is mainly contributed by PEO/TCNQ blend.

A maximum conductivity (σ) value of the PEO(80)/PVP(20)/TCNQ existed at a TCNQ/VP molar ratio of 1.0. Its Arrhenius plot is also shown in Figure 7.

TABLE IV
Glass transition temperature (T_g), melting temperature (T_m), and fusion heat (ΔH) of PEO, PEO(80)/PVP(20)/LiClO₄ or TCNQ blend

Li/EO (molar ratio)	TCNQ/VP (molar ratio)	T_g (°C)	T_m (°C)	ΔH (cal/g)
0	0	–	63.7	22.7
0.05	0	–46.1	58.7	13.4
0.10	0	–33.4		
0.20	0	–18.5		
0	0.2	–	59.3	20.4
0	0.5	–	59.9	16.5
PEO		–	69.3	34.4

PEO/PVP/LiClO₄/TCNQ blend system

When PEO/PVP blend is doped both with LiClO₄ and TCNQ, it will show a mixed (ionic–electronic) conductivity (σ_M). Table III shows that when the molar ratio of Li/EO and TCNQ/VP are 0.1 and 0.5 respectively, R [the ratio of $\sigma_M/(\sigma_I + \sigma_E)$] of PEO(60)/PVP(40) and PEO(50)/PVP(50) becomes greater than 1, indicating the existence of a synergistic effect in mixed (ionic–electronic) conductivity. The reason may be explained by the compatibility between PEO and PVP enhanced by LiClO₄ and PVP, as shown later by DSC and TGA.

Characterization with DSC and TGA

T_g , T_m , and fusion heat (ΔH) of PEO or PEO/PVP blend doped with LiClO₄ or TCNQ are listed in Table IV. For PEO or PEO/PVP blend without LiClO₄, T_g is unobserved in the temperature range studied. When LiClO₄ is added to the PEO(80)/PVP(20)

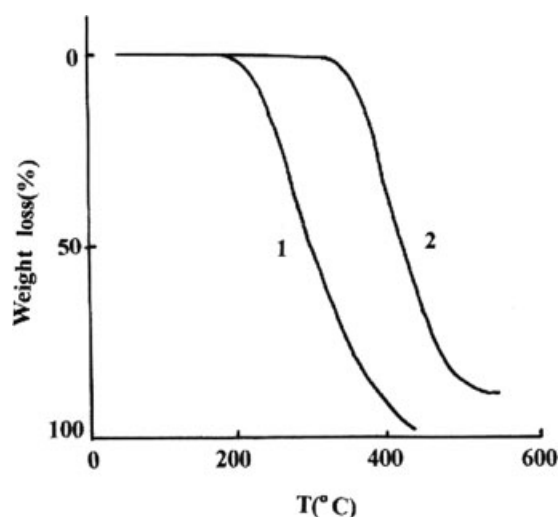


Figure 8 TGA curves of PEO (1) and PEO/TCNQ complex (2).

blend, its T_g increases with increasing Li/EO molar ratio, whereas T_m and ΔH decrease, but T_m and ΔH cannot be observed with Li/EO > 0.10, as shown in Table IV. It can be explained as follows: complexes are formed between PEO, PVP and lithium ions in the blend, and change the crystalline phase of PEO into amorphous phase of PEO. This fact indicates that LiClO₄ salt can compatibilize PEO and PVP.

Table IV also shows that T_m and ΔH of PEO/PVP/TCNQ blend at a TCNQ/VP molar ratio of 0.2 or 0.5 are lower than those of PEO or PEO/PVP blend. This may be attributed to the charge transfer complexes formed between TCNQ and PVP or between TCNQ and PEO, because TCNQ is a kind of strong electron acceptor, whereas PVP and PEO have nitrogen atoms and oxygen atoms with lone pair electrons, respectively. As a result, the crystalline phase of PEO is lowered.

Figure 8 shows the TGA curves of PEO and PEO/TCNQ blend with molar ratio of TCNQ/EO = 0.033 under nitrogen atmosphere. Weight loss of PEO begins at 190°C and ends at 450°C, whereas that of the blend begins to lose weight at 307°C and loses about 88 wt % at 497°C. Since weight percentage of PEO in the blend was 86.6 wt %, it can be suggested that the weight loss in the range of 307–497°C was attributed to that of PEO and the residue at 497°C was TCNQ. The fact that decomposition of PEO in the PEO/TCNQ blend is higher than that of pure PEO may imply that complexation of PEO with TCNQ in the blend really occurred.

CONCLUSIONS

High molecular weight PEO was synthesized by using a quaternary catalyst composed of triisobutyl aluminum, phosphoric acid, water, and *N,N*-dimethylaniline (DMA). The activity of polymerization mainly depends upon the composition of catalyst. The optimum composition for high activity is: i-Bu₃Al : H₃PO₄ : H₂O : DMA = 1 : 0.17 : 0.17 : 0.10–0.15 (molar ratio). The active centers of the catalyst was R₂Al—O—RAI—O—P(=O)—(O—AlR—O—AlR₂)₂, complexed with electron donor, DMA. The polymerization is

presumed to be of coordinated anionic type, similar to the Vandenberg catalyst composed of hydrolytic product of AlR₃ with acetylacetonate as electron donor. The molecular weight of the polyoxyethylene obtained can approach one million. The blends of polyoxyethylene with molecular weight of about 1,000,000 synthesized by this catalyst with poly(2-vinyl pyridine) (PVP) after doped with LiClO₄ and TCNQ were conductive elastomeric materials as the content of PEO is in the range of 50–80 wt %. When the weight ratio of PEO and PVP is 6/4 or 5/5 doped at a Li/EO molar ratio of 0.1 and a TCNQ/VP molar ratio of 0.5, the mixed conductivity of the blend of PEO/PVP/LiClO₄/TCNQ is higher than the sum of ionic conductivity of PEO/PVP/LiClO₄ and electronic conductivity of PEO/P2VP/TCNQ. This material may be used as the polymer electrode with the solid polymer electrolyte in the solid state battery. Differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), and the appearance of the blend showed that both TCNQ and LiClO₄ can complex with PEO and PVP, thus enhancing the compatibility between PEO and PVP.

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