

CONDUCTING BLENDS OF POLY(2-VINYL PYRIDINE) AND POLYETHYLENE OXIDE WITH HIGH MOLECULAR WEIGHT*

CUI Minhui (崔敏慧) GUO Junshi (过俊石) and XIE Hongquan (谢洪泉)

(*Department of Chemistry, Huazhong University of Sci. & Tech., Wuhan 430074*)

CHENG Donghua (陈栋华)

(*Department of Chemistry, South-Central College for Nationalities, Wuhan 430074*)

ABSTRACT

Ionic, electronic and mixed (ionic-electronic) conductivities of blends of poly(2-vinyl pyridine) (P2VP) and poly(ethylene oxide) (PEO) with high molecular weight after doped with LiClO_4 , TCNQ or LiClO_4 and TCNQ were investigated. Effects of LiClO_4 and TCNQ concentrations on the conductivity of PEO/P2VP/ LiClO_4 or TCNQ blend were studied. The ionic conductivity of PEO/P2VP/ LiClO_4 blend increases with increasing PEO content. At a Li/ethylene oxide molar ratio of 0.10 and a TCNQ/2-vinyl pyridine molar ratio of 0.5, the mixed conductivity of PEO/P2VP/ LiClO_4 /TCNQ is higher than the total of ionic conductivity of PEO/P2VP/ LiClO_4 and electronic conductivity of PEO/P2VP/TCNQ when the weight ratio of PEO and P2VP is 6/4 or 5/5. Scanning electron microscopy (SEM) on the broken cross-section of the PEO/P2VP/ LiClO_4 blend and differential scanning calorimetry (DSC) results show that LiClO_4 could act as a compatibilizer in the blend.

INTRODUCTION

The area of electroactive polymers has become one of the most challenging and fruitful fields within the past two decades. Both electronically conductive polymers and polymer electrolytes have been prepared and studied in many laboratories. But both of them are limited to either ion-conducting^[1] or electron-conducting^[2] polymers. The mixed (ion-electron) conducting 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 solid-state battery.

Minett et al. synthesized poly[N-(3, 6, 9-trioxadecyl) pyrrole]^[3] and Li et al. synthesized poly[(2, 5, 8, 11, 14, 17, 20, 23-octapentacosyl methacrylate)-block-poly(4-vinyl pyridine)]^[4] and poly[3-methyl thiophene-block- ω -methoxyocta(oxyethylene)

* Project supported by the National Natural Science Foundation of China.

Received May 5, 1995

methacrylate]^[5]. After doping, electron-conducting polypyrrole, poly(4-vinyl pyridine) and poly(3-methyl thiophene) backbones with short oligo(oxyethylene) side chains which can be complexed with alkali metal salts to get ionic conductivity were obtained respectively. We have reported the synthesis of poly(2-vinyl pyridine)-graft-poly(ethylene oxide)^[6] with well-defined structure and indicated that the graft copolymer, after doped with LiClO₄ and TCNQ, showed a mixed conductivity with a synergistic effect which reached $4.4 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at room temperature. But preparation of these polymers needs complicated synthesis and purification processes. So, it is of interest to develop easier method for preparing mixed (ion-electron) conducting polymers. Li and Khan^[7,8] examined PEO (*MW*600,000)/poly(2-vinyl pyridine) (P2VP) (*MW*200,000) or poly(4-vinyl pyridine) (*MW*50,000) blend system with LiClO₄. Only ionic conductivity was studied and it reached $1.0 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at 25°C for PEO (85%)/P2VP(15%)/LiClO₄ blend at a Li/EO molar ratio of 0.10.

This paper deals with the ionic, electronic and mixed (ionic-electronic) conductivities of the blend of P2VP and PEO with high molecular weight after doped with LiClO₄ or/and TCNQ because PEO with high molecular weight will offer better mechanical strength to the blend. Microstructure and DSC of PEO/P2VP blend doped with LiClO₄ or TCNQ were also studied.

EXPERIMENTAL

Preparation of blends

PEO(*MW* about 1,000,000) (Aldrich Chemical Co.) was used as received. P2VP was synthesized by anionic polymerization of purified 2-vinyl pyridine using potassium naphthalene as initiator and its molecular weight was determined to be 14,500 by Knauer VPO apparatus, using chloroform as solvent. 7, 7, 8, 8-Tetracyano-1,4-quinodimethane (TCNQ) was synthesized according to literature [9]. Blends of PEO, P2VP and LiClO₄ were prepared by dissolving PEO and P2VP in dichloromethane followed by addition of a methanolic or ethanolic solution of LiClO₄ with stirring for 3.5h at room temperature. Blends of PEO, P2VP and TCNQ were obtained by mixing PEO, P2VP and TCNQ in DMF and stirring for 5h with slight heating. Blends of PEO, P2VP, LiClO₄ and TCNQ were prepared by dissolving PEO/P2VP/LiClO₄ blends and TCNQ in DMF and stirring for 5h with slight heating. After evaporating the solvent all the blends were dried in a vacuum oven at 60°C thoroughly for 24h.

Measurement of conductivity

The blend sandwiched between two thin aluminium foils was hot-pressed in a die into a disc (about 2mm thick and 14mm diameter) at 110°C for the PEO/P2VP/LiClO₄ blend and the PEO/P2VP/LiClO₄/TCNQ blend, at 120–130°C for the

PEO/P2VP/TCNQ blend. Before measuring, all the discs were dried over fresh P_2O_5 thoroughly for at least 48h.

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

Microstruture of PEO/P2VP/LiClO₄ blend

SEM was obtained on Jeol JSM-350C SEM operating at 25kV. The specimen was prepared by coating a broken cross-section of the blend film with a thin layer of gold.

DSC

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 at a rate of 320°C/min 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.

RESULTS AND DISCUSSION

PEO/P2VP/LiClO₄ blend system

Table 1 Appearance of PEO/P2VP/LiClO₄ blend system

PEO/P2VP (weight ratio)	Li/EO (molar ratio)	Appearance of blend
8/2	0.05	partially phase-separated, opaque, non-elastomeric
8/2	0.067	semi-transparent, elastomeric
8/2	0.10	transparent, elastomeric
8/2	0.20	transparent, elastomeric
6/4	0.10	phase-separated, elastomeric
5/5	0.10	phase-separated, elastomeric
4/6	0.10	phase-separated, non-elastomeric
2/8	0.10	phase-separated, non-elastomeric

The appearances of PEO(80 wt%)/P2VP(20 wt%) blends, abbreviated to PEO(80)/P2VP(20), with different molar ratios of Li/EO are indicated in Table 1. When no LiClO₄ is added to this blend, it appears macrophase separation. After the addition of LiClO₄ salt, the blends show different appearance. The blend at a Li/EO molar ratio of 0.05 still shows a microphase separation and the blend film is not transparent. As the concentration of LiClO₄ salt increases, the blend changes into

a semi-transparent elastomer. When the molar ratio reaches 0.10 or 0.20, this blend becomes a transparent elastomer. These could be explained as follows: Lithium ions can interact with the oxygen atoms of PEO and the nitrogen atoms of P2VP due to the ion-dipole interactions. Due to the differences in the electronegativity between oxygen and nitrogen and in the steric hindrance of PEO and P2VP, the complexing ability of PEO is superior to that of P2VP. When the concentration of lithium salt is lower ($\text{Li}/\text{EO} = 0.05$), a lithium ion first interacts with the oxygen of PEO, hence PEO and P2VP exist as two separated phases resulting in an opaque and phase-separated appearance. Through the increase in the amount of lithium salt, a part of the lithium salt can act as a compatibilizer between PEO and P2VP, because lithium ion could interact with the oxygen of PEO and the nitrogen of P2VP simultaneously. Optical transparency is one of the important criteria^[10] to illustrate the compatibility of two phases. Here, the blend at a Li/EO molar ratio of 0.10 or 0.20 is a transparent elastomer. This indicates that PEO and P2VP are compatible in the presence of a certain amount of lithium salt. This will be proved by SEM and DSC results discussed later.

When the molar ratio of Li/EO is fixed at 0.10, the appearances of PEO/P2VP blends with different weight ratios of PEO/P2VP are also different. Table 1 shows that PEO(80)/P2VP(20) is transparent. When the content of PEO in the PEO/P2VP blend decreases, this blend becomes phase-separated. The reason is that the LiClO_4 salt used decreases with the decreasing content of PEO at fixed molar ratio of Li/EO . Hence, the phase separation is partially caused by deficiency in LiClO_4 salt. Table 1 also indicates that the PEO/P2VP blend is elastomeric as the content of PEO is higher, while the PEO/P2VP blend becomes non-elastomeric when the content of PEO is less than 50 wt%. After complexed with LiClO_4 , crystalline phase of PEO changes into amorphous and PEO behaves as an elastomer. When the content of PEO is higher than that of P2VP, this blend looks like a reinforced rubber. But when the content of PEO is lower than that of P2VP, the PEO/P2VP blend behaves as a toughened plastics.

PEO/P2VP/ LiClO_4 blend can show ionic conductivity. The logarithmic conductivities of PEO(80)/P2VP(20) blends with different molar ratios of Li/EO are shown in Fig.1. In the range of LiClO_4 concentration studied, the room temperature conductivity increases with increasing LiClO_4 concentration, and the room temperature ionic conductivity of PEO(80)/P2VP(20)/ LiClO_4 blend at a Li/EO molar ratio of 0.20 is $4.0 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$. In addition, we have found that this molar ratio of Li/EO is higher than that in the general PEO/ LiClO_4 system in which the optimum Li/EO is 0.05. This is because in the PEO/P2VP/ LiClO_4 blend, pyridyl group could consume a part of LiClO_4 salt due to the ion-dipole interaction.

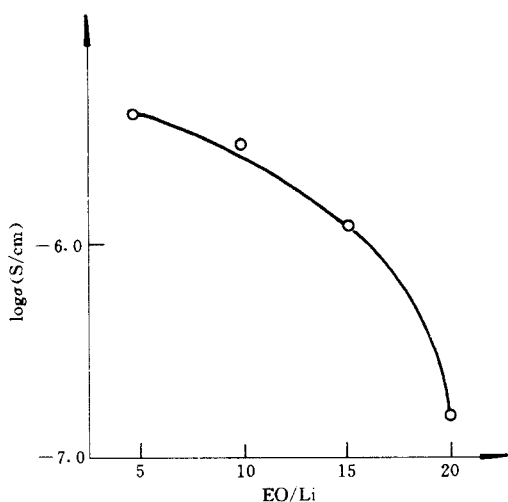


Fig.1 Logarithmic conductivity of PEO(80)/P2VP(20)/LiClO₄ blend at 25°C vs. molar ratio of EO/Li

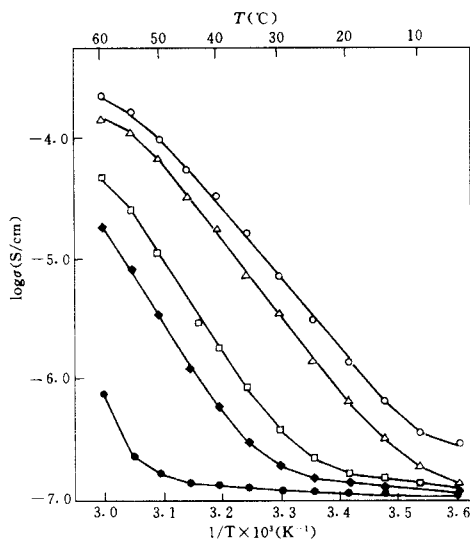


Fig.2 Arrhenius conductivity plots of PEO/P2VP/LiClO₄ blends (Li/EO=0.10): PEO/P2VP(w/w)=(○) 8/2; (△) 6/4; (□) 5/5; (◆) 4/6; (●) 2/8

When the molar ratio of Li/EO is 0.10, the conductivities of PEO/P2VP/LiClO₄ with different weight ratio of PEO/P2VP are shown in Fig.2. The conductivity of PEO/P2VP/LiClO₄ blend at a Li/EO molar ratio of 0.10 increases with increasing PEO content. Although the P2VP can also interact with lithium ion, its conductivity is much lower than that of PEO/LiClO₄ complex. (The conductivity of P2VP/LiClO₄ is shown in Fig.3.) The ionic conductivity of PEO/P2VP/LiClO₄ blend is mainly contributed by the PEO/LiClO₄ complex. Hence, the conductivity of PEO/P2VP/LiClO₄ at fixed molar ratio of Li/EO decreases with reducing PEO content. The room temperature conductivity of PEO(80)/P2VP(20)/LiClO₄ blend ($2.95 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$) at a Li/EO molar ratio of 0.10 is higher than that of PEO(20)/P2VP(80)/LiClO₄ blend ($1.10 \times 10^{-7} \text{ S}\cdot\text{cm}^{-1}$). Fig.2 also shows that when the PEO content is lower, the conductivity increases slowly at lower temperature. Since PEO is a dispersed phase in the PEO/P2VP blend with lower PEO content, the ionic conduction is difficult to take place. Only when the temperature is high enough, the ionic conduction is easy to carry on.

PEO/P2VP/TCNQ blend system

As well known, TCNQ can form charge transfer complex with P2VP which shows electronic conductivity. TCNQ can also form charge transfer complex with PEO because the oxygen of PEO has lone pair electrons and acts as an electron donor. So the electronic conductivity of PEO/P2VP/TCNQ blend is contributed by the com-

plexes of TCNQ with P2VP and with PEO. The appearances of PEO/P2VP/TCNQ blends are shown in Table 2. When the molar ratio of TCNQ/2VP is 0.2 or 0.5, the PEO(80)/P2VP(20)/TCNQ blend forms a glossy film; as the TCNQ concentration increases further, the PEO(80)/P2VP(20)/TCNQ blend can not form a good film. As the P2VP content in the PEO/P2VP/TCNQ blend increases, the blend gradually becomes phase separated and finally can not form a film at a TCNQ/2VP molar ratio of 0.5.

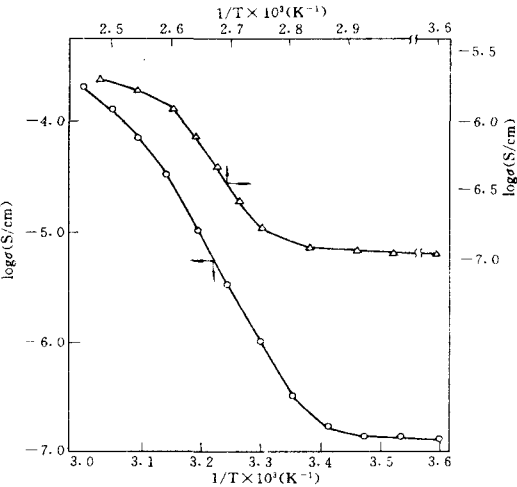


Fig.3 Arrhenius conductivity plots of PEO /TCNQ and P2VP/LiClO₄ complexes (○) TCNQ/EO= 0.10; (△) Li/2VP= 0.10

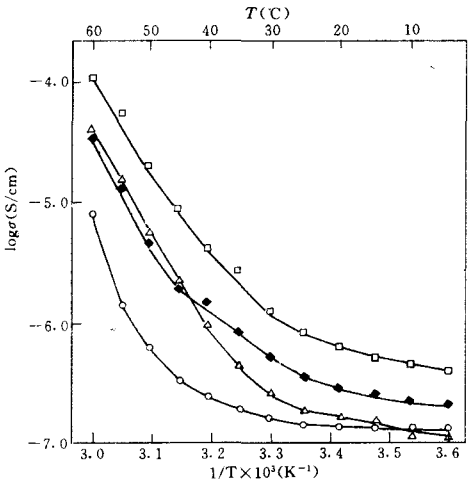


Fig.4 Arrhenius conductivity plots of PEO (80)/P2VP(20)/TCNQ blends TCNQ /2VP (molar ratio)=(○) 0.2; (△) 0.5; (□) 1.0; (◆) 1.3

Table 2 Appearance of PEO/P2VP/TCNQ blend system

PEO/P2VP (weight ratio)	TCNQ/2VP (molar ratio)	Appearance of blend
8/2	0.2	glossy film, better film-forming characteristics
8/2	0.5	glossy film, better film-forming characteristics
8/2	1.0	bad film-forming characteristics
8/2	1.3	bad film-forming characteristics
6/4	0.5	phase-separated, fragile film
5/5	0.5	phase-separated, fragile film
4/6	0.5	phase-separated, bad film-forming characteristics
2/8	0.5	phase-separated, bad film-forming characteristics

The Arrhenius plot of conductivity of PEO/TCNQ complex with TCNQ/EO molar ratio of 0.10 is also shown in Fig.3. 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. Maybe this is caused

by changing the crystalline PEO chains into amorphous PEO chains with increasing temperature. This indicates that hopping of carriers of PEO/TCNQ complex is connected with the mobility of PEO chain. The conductivity of PEO/TCNQ at 25°C is $3.30 \times 10^{-7} \text{ S}\cdot\text{cm}^{-1}$ and $2.05 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 60°C.

Table 3 Conductivities (σ) of PEO/TCNQ complexes and P2VP/TCNQ complex at 25°C

TCNQ/EO (molar ratio)	TCNQ/2VP (molar ratio)	$\sigma \times 10^6 \text{ (S}\cdot\text{cm}^{-1})$
0.025	—	0.34
0.033	—	0.46
0.05	—	1.54
0.10	—	0.33
—	0.5	0.09

Table 3 shows the conductivities of PEO/TCNQ blends at different molar ratios of TCNQ/EO. The conductivity of PEO/TCNQ increases with the increasing TCNQ content, and it reaches a maximum value at a TCNQ/EO molar ratio of 0.05 and decreases as the TCNQ content increases further. Table 3 also shows that the conductivity of P2VP/TCNQ complex at a TCNQ/2VP molar ratio of 0.5 is less than that of PEO/TCNQ blend when the molar ratio of TCNQ/EO is from 0.025 to 0.10.

The Arrhenius plots of electronic conductivities of PEO(80)/P2VP(20) blends with different molar ratios of TCNQ/2VP are shown in Fig.4. The maximum value appears at a TCNQ/2VP molar ratio of 1.0. The conductivity of PEO/P2VP/TCNQ blend is the sum of conductivity of PEO/TCNQ and that of P2VP/TCNQ. But the conductivity of P2VP/TCNQ is less than that of PEO/TCNQ, so the conductivity of PEO/P2VP/TCNQ blend is mainly contributed by PEO/TCNQ blend. The molar ratio of TCNQ/EO increases with the increasing TCNQ content, resulting in increasing conductivity. But further increase of TCNQ content in PEO/P2VP/TCNQ blend may cause decreasing conductivity. These cause a maximum value in the electronic conductivity of PEO/P2VP/TCNQ blend at a TCNQ/2VP molar ratio of 1.0.

The electronic conductivities of PEO/P2VP/TCNQ blend with different weight ratios of PEO/P2VP at 25°C are almost the same, which are equal to about $2.00 \times 10^{-7} \text{ S}\cdot\text{cm}^{-1}$, as shown in Table 4.

PEO/P2VP/LiClO₄/TCNQ blend system

PEO/P2VP can show ionic conductivity or electronic conductivity after doped with LiClO₄ or complexed with TCNQ. When PEO/P2VP blend is doped both with LiClO₄ and TCNQ, it will show a mixed (ionic-electronic) conductivity as illustrated in Table 4.

In Table 4, R (the ratio of $\sigma_M/(\sigma_I + \sigma_E)$) is smaller than 1 for PEO(80)/P2VP(20) with different molar ratio of Li/EO at a TCNQ/2VP molar ratio of 0.5. But when the molar ratio of Li/EO and TCNQ/2VP are 0.10 and 0.5 respectively, R of PEO(60)/P2VP(40) and PEO(50)/P2VP(50) become greater than 1, indicating the existence of a synergistic effect in mixed (ionic-electronic) conductivity. For PEO/P2VP blend, Table 4 shows that the mixed conductivity is not equal to the total of ionic and electronic conductivity. Under certain conditions, the mixed conductivity shows a synergistic effect, the reason of which is not yet explainable and needs further study. But we think that the synergistic effect may be caused by the changes of complexing ratios of Li/EO, Li/2VP, TCNQ/EO and TCNQ/2VP. After complexed with the second dopant (such as TCNQ), the complexing ratio of PEO or P2VP with the first dopant (such as LiClO₄) changes. If Li/EO, Li/2VP, TCNQ/EO and TCNQ/2VP are close to the optimum molar ratios, the mixed conductivity will be larger than the total of ionic and electronic conductivity, then the synergistic effect appears.

Table 4 Conductivities^{a)} of PEO/P2VP/LiClO₄/TCNQ blend system at 25°C

PEO/P2VP (weight ratio)	Li/EO (molar ratio)	TCNQ/2VP (molar ratio)	$\sigma \times 10^6$ (S·cm ⁻¹)			
			σ_I	σ_E	σ_M	R
8/2	0.05	0.5	0.15	0.19	0.16	0.47
8/2	0.067	0.5	1.18	0.19	0.46	0.34
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 conductivity of PEO/P2VP/LiClO₄ blend, electronic conductivity of PEO/P2VP/TCNQ blend and mixed conductivity of PEO/P2VP/LiClO₄/TCNQ blend, respectively

Microstructure of PEO/P2VP/LiClO₄ blend

In order to study the compatibilizing effect of LiClO₄ salt on PEO/P2VP blend, we examined the broken cross-section of PEO(80)/P2VP(20) blends with different LiClO₄ concentrations using SEM. Fig.5 is the SEM photographs of the broken cross-section of PEO/P2VP blends. The PEO/P2VP blend without LiClO₄ salt shows obvious phase separation (Fig.5a). When the PEO/P2VP is blended with LiClO₄ salt, the texture of the blend becomes more homogeneous with increasing LiClO₄ concentration. This result is consistent with the appearance of

PEO/P2VP blend with different LiClO_4 concentration and indicates that a certain amount of LiClO_4 can effectively improve the compatibility of PEO/P2VP blend because lithium ion not only complexes with the oxygen of PEO but also interacts with the nitrogen of P2VP through ion-dipole interaction.

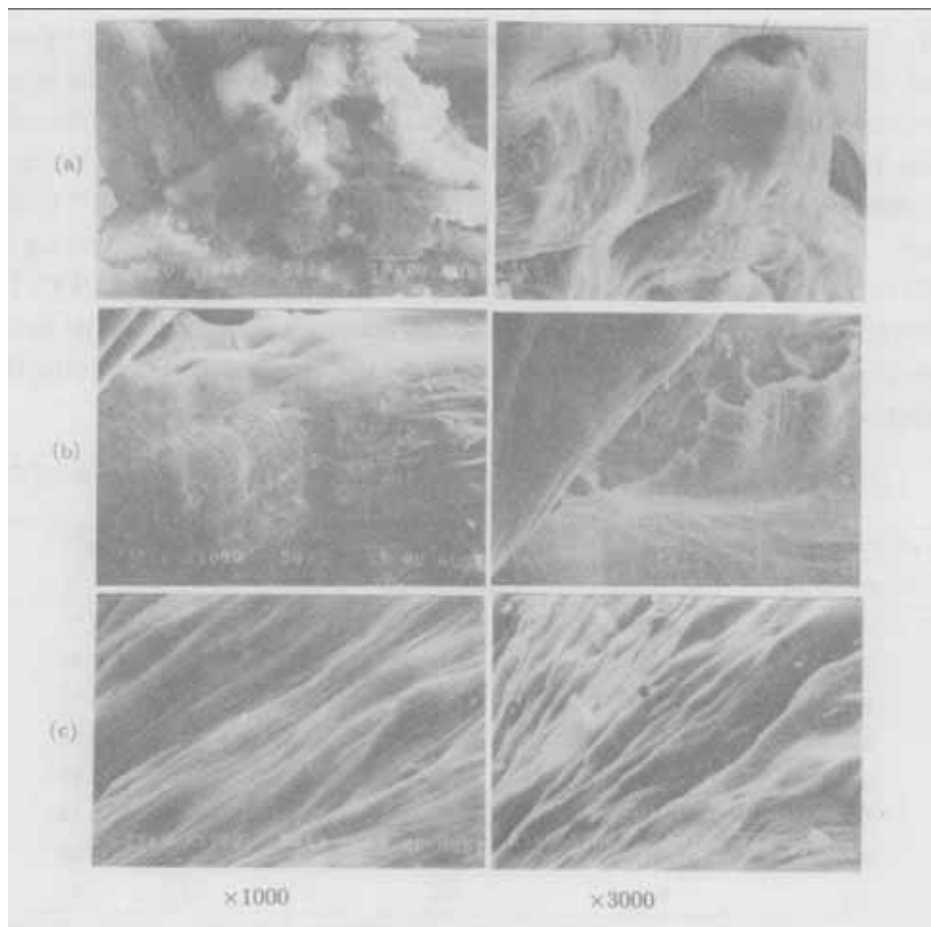


Fig.5 SEM microphotographs of PEO(80)/P2VP(20)/ LiClO_4 blends
(a) $\text{Li}/\text{EO}=0$; (b) $\text{Li}/\text{EO}=0.05$; (c) $\text{Li}/\text{EO}=0.10$

DSC

T_g , T_m and fusion heat (ΔH) of PEO and PEO/P2VP blend doped with LiClO_4 or TCNQ are listed in Table 5. For PEO or PEO/P2VP blend without LiClO_4 , T_g is unobserved in the temperature range studied. When LiClO_4 is added to the PEO(80)/P2VP(20) blend, its T_g increases with increasing Li/EO molar ratio but T_m and ΔH can not be observed with $\text{Li}/\text{EO} \geq 0.10$, as shown in Table 5. It can be explained as follows: more complexes are formed between PEO, P2VP and lithium ions in the blend, and the crystalline phase of PEO changes into amorphous phase

of PEO. T_m and ΔH of PEO/P2VP/LiClO₄ at a Li/EO molar ratio of 0.05 are also lower than those of PEO or PEO/P2VP blend, this indicates that LiClO₄ salt can compatibilize PEO and P2VP because T_m of the crystalline phase in the blend can show the miscibility between the two components in the blend.

Table 5 Glass transition temperature (T_g), melting temperature (T_m) and fusion heat (ΔH) of PEO, PEO(80)/P2VP(20)/LiClO₄ or TCNQ blend

Li/EO (molar ratio)	TCNQ/2VP (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

Table 5 also shows that T_m and ΔH of PEO/P2VP/TCNQ blend at a TCNQ/2VP molar ratio of 0.2 or 0.5 are lower than those of PEO or PEO/P2VP blend. This may be attributed to the charge transfer complexes formed between TCNQ and P2VP or between TCNQ and PEO because TCNQ is a kind of strong electron acceptor and P2VP or PEO has nitrogen atoms or oxygen atoms with lone pair electrons, respectively.

Keywords:

Poly(ethylene oxide); Poly(2-vinyl pyridine); Mixed (ionic-electronic) conductivity; Lithium perchlorate; Compatibilizing effect

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