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Effects of composition and structure on the ionic conductivity of latex polymer electrolyte

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A series of poly(ethyl acrylate)/lithium salts were prepared. The ionic conductivity of latex films was compared with films prepared by solution polymerisation. By changing the composition of the latex and the lithium salt, we studied the influence of the latex surface composition, particle size, the lithium salt and its concentration on the conductivity of polymer electrolyte latex films. The results show that surface layer transport of ions plays an important role in increasing the ionic conductivity of polymer electrolytes.

Introduction

In recent years, the main focus of research on polymer electrolytes has been on the improvement of both mechanical properties and ionic conductivity. Much attention has been paid to multi-phase polymer electrolytes, in which ionic conductivity is increased by the mutual interaction between isophases. Initial results have been reported.[1–3] In this paper, the ionic conductivity and the conduction mechanism of poly(ethyl acrylate)/lithium dodecanesulfonate latex films were studied and compared with films of the same composition from solution polymerisation. Mobile lithium ions reside on the surface layer of the latex particles in the film. The transport of lithium ions occurs entirely at the surface. Therefore, the ionic transport is much less influenced by the segmental motion of the polymer chains and is less dependent on the polymer viscosity. The transport of free ions is favoured. As a result, the conductivity is higher than that in the solution-polymerisation complex film in which ionic transport is achieved by a segmental motion of the polymer chains.

The influence of composition and structure on the conduction of latex polymer electrolytes is discussed.

Experimental

Preparation of the materials

Preparation and purification of starting materials. The preparation of lithium methacrylate (MALi) was carried out according to a reported method.[4] Elemental analysis, calculated for $C_4H_5LiO_2$: C, 52.17%, H, 5.43%; found: C, 52.27%, H, 5.56%.

Preparation of lithium dodecanesulfonate (DSLi): Sodium dodecanesulfonate was passed through a $732^{\#}$ strong acid cationic exchange resin. The exchanged solution was neutralised by addition of saturated aqueous Li_2CO_3. The solvent was evaporated, and the solid material filtered, purified and then dried under an infrared light followed by vacuum drying. Elemental analysis, calculated for $C_{12}H_{25}LiO_3S$: C, 56.25%, H, 9.77%; found: C, 55.93%, H, 9.47%.

Methoxy oligo(oxyethylene) methacrylate (MEO_{12}, 12 oxyethylene units) was synthesised from oligo(oxyethylene) monomethyl ether and methacryloyl chloride in the presence of pyridine.

Lithium sulfohexyl methacrylate (SHMLi) was synthesised according to the published procedure.[5]

Ethyl acrylate (EA) was purified by distillation under reduced pressure. The plasticizers ethylene carbonate (EC), γ-butyrolactone (γ-BL), diethyl carbonate (DEC) and propyl carbonate (PC) were purified by distillation under reduced pressure before use. $LiClO_4$ was dried under vacuum at 175–185 °C for 24 h.

Emulsion polymerisation. The lithium salt was dissolved in either water or ethanol. The monomer and salt were combined under a nitrogen atmosphere. After the temperature was raised to 60 °C under a nitrogen atmosphere, the initiator $(NH_4)_2S_2O_8$ was added to the solution. Polymerisation was continued at this temperature for 5–6 h. Latex PEA/DSLi, P(EA-MALi) and P(EA-MEO_{12}-MALi) with a series of different compositions were obtained by polymerisation. The solid content of the emulsion was 20–30%, and the transfer ratio was 90–98%.

Solution polymerisation. The preparation of poly(ethyl acrylate) (PEA) was carried out according to a reported method.[6] The product was precipitated using anhydrous ethanol and then dried in a vacuum. The polymer was dissolved in tetrahydrofuran and the calculated amount of DSLi was added. The composition was the same as for the PEA/DSLi latex. The solid content was 2.27%.

Film preparation. Films were prepared using the solution casting method. The solvent was evaporated under a dried atmosphere and the film was finally dried for 24 h in vacuum at 60 °C.

Film plasticization. The films prepared above were dipped into an electrolyte solution until the desired content of electrolyte solution was obtained. The solid films including that with 70 wt% plasticizer show good mechanical properties and are of value for practical use.

Characterisation of the conductive properties

The films with and without plasticizers were cut into discs of 8 mm diameter. These were sandwiched between two stainless steel electrodes and the film conductivity was measured at 1100 Hz with a DDS-307 conductometer.

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Results and Discussion

Comparison of conductivity of the PEA/DSLi latex film with the PEA/DSLi film from solution polymerisation

The molar ratio of PEA/DSLi is 76.8 in both the PEA/DSLi latex films from emulsion polymerisation and the ordinary PEA/DSLi film from solution polymerisation. The carbonyl groups of the PEA in both complexes and the absorbed polar organic solvent promote dissociation of the salt to yield free ions. Consequently, all the films show ionic conductivity. The relationship between the plasticizer (EC:γ-BL = 3:2) content and the conductivity of both films is shown in Fig. 1. For the same concentration of plasticizer, the conductivity of the PEA/DSLi film from emulsion polymerisation is considerably higher than that of the film from solution polymerisation. This implies that the ionic conductivity is greatly affected by the internal structure of the films in addition to the same contributions made from the plasticizers. Therefore, the difference in conductivity arises from the different transport mechanisms in the two types of film. The transfer of free Li^+ ions in the polymer media of the film prepared by solution polymerisation is achieved by the segmental relaxation movement of the polymer. Therefore, it depends largely on the internal viscosity of the polymer media. However, the free Li^+ ions in latex films prepared by emulsion polymerisation are mainly dispersed on the surface layer of latex particles, and their transport occurs through a surface layer. This type of transport is much less hindered by polymer chain motion and is decoupled from the internal viscosity of polymer. As a result of this, the transport of ions is more favourable in the latex, giving rise to a complex with higher conductivity.

Influence of latex surface composition on the ionic conductivity

The relationship between the ionic conductivity of the latex film and the plasticizer (EC:γ-BL = 3:2) content is shown in Fig. 2 for P(EA-MALi) and P(EA-MEO_{12}-MALi). The latex film with the oligoether MEO_{12} content has the higher conductivity because the solvating effect of MEO_{12} promotes the dissociation of COOLi into Li^+ ions on the surface layer of the latex. As a result, the carrier number is increased with the introduction of the MEO_{12} monomer and the conductivity of the single ionic conductor P(EA-MEO_{12}-MALi) is increased considerably. Fig. 3 shows the conductivity of latex films of P(EA-MALi) and P(EA-MEO_{12}-MALi) containing 40 wt% electrolyte solution (EC:γ-BL)/$LiClO_4$ with different lithium perchlorate contents. For low salt concentrations, the conductivity of P(EA-MEO_{12}-MALi) film is slightly higher than that of the P(EA-MALi) film with the same amount of electrolyte solution. This dependence changes with increase in lithium salt content. The extra $LiClO_4$ in the latex of P(EA-MEO_{12}-MALi) forms a higher concentration of MEO_{12}-$LiClO_4$ complexes on the surface layers and reduces the segmental movement of MEO_{12} side chains. In this case, the ionic conductivity behaviour resembles that of the pure $PMEO_{12}$-$LiClO_4$ complex with a high salt content (Fig. 4). Consequently, for higher $LiClO_4$ contents the conductivity of latex films with MEO_{12} is lower than those without MEO_{12}.

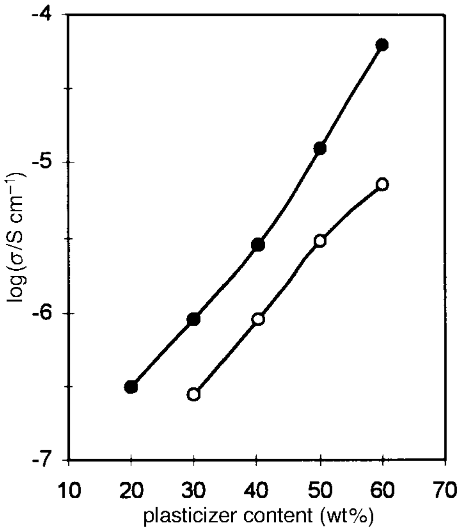

Fig. 1 Effect of plasticizer EC:γ-BL(3:2) on the ionic conductivity of PEA/DSLi films at 25 °C: (●) latex film and (○) solution polymerisation film

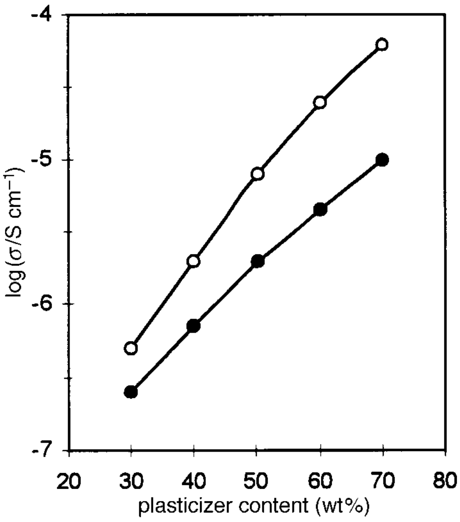

Fig. 2 Effect of plasticizer (EC:γ-BL = 3:2) content on ionic conductivity of latex films at 25 °C: (●) P(EA-MALi) and (○) P(EA-MEO_{12}-MALi)

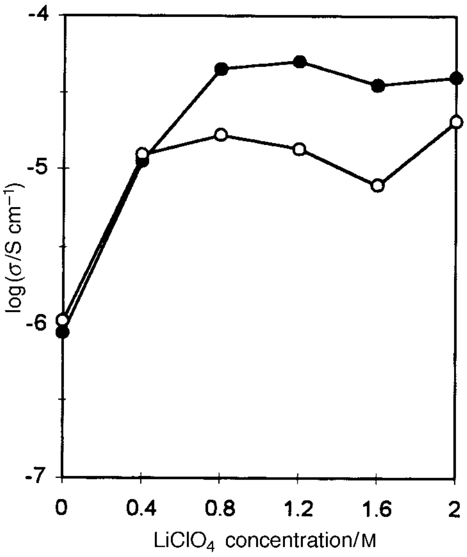

Fig. 3 Effect of $LiClO_4$ concentration in EC:γ-BL(3:2)/$LiClO_4$ solution on the ionic conductivity of latex polymer electrolyte at 25 °C. The content of electrolyte solution was 40 wt%. (●) P(EA-MALi) and (○) P(EA-MEO_{12}-MALi)

Effect of particle composition on the ionic conductivity of latex

When a vinyl acetate (VAc) component, which has a high solvating effect on alkali ions, was introduced into the latex particles, the conductivity of P(EA-VAc)/DSLi latex film plasticized by (EC + γ-BL) decreased over that of PEA/DSLi latex film plasticized in the same way, as shown in Table 1. This is because the VAc component stays inside the latex particles

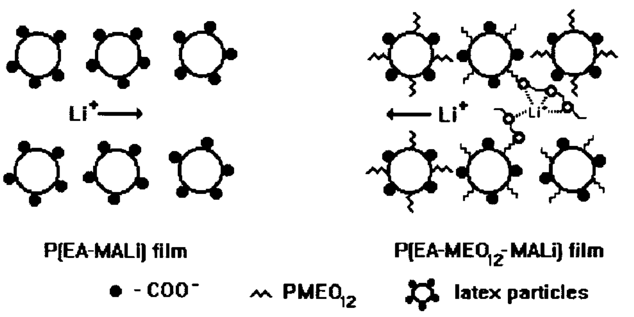

Fig. 4 Movement of Li$^+$ cation in latex films

and has little solvating effect on the Li$^+$ ions on the particle surface according to the mechanism of emulsion polymerisation. On the other hand, PVAc has a higher T_g, which makes the polymer segment stiffer, so the VAc component here causes a detrimental effect on the transport of ions. It is also shown in Table 1 that there is no significant change of conductivity of P(EA-VAc)/DSLi latex film plasticized by LiClO$_4$/PC over that of PEA/DSLi latex film plasticized in the same way, which indicates that the VAc component has a solvating effect on the LiClO$_4$ salt in electrolyte solution in addition to its detrimental effect on the transport of ions. At the lower part of the Table, a similar phenomenon is observed for the conductivity of P(EA-VAc-MALi) latex film with different contents of VAc component.

Effect of lithium salt content on the ionic conductivity of latex film

The conductivity of latex films increases with increasing lithium salt content. However, a maximum conductivity of latex films exists for both strong acid salts and weak acid salts (Fig. 5 and 6). The conductivity of substances can be represented by the following formula:[7]

$$\sigma = \Sigma n_i q_i \mu_i$$

where n_i is the carrier density, q_i is the carrier charge, μ_i is the carrier transference number, i is the carrier type. Carrier number per unit volume (n_i) increases as the salt concentration in the latex film increases, which has a favourable effect on the conductivity. On the other hand, the amount of associated salt also increases with increasing salt concentration. The salt mainly exists as ion pairs or ion clusters that hinder segmental motion by chelating the ether oxygen atoms, which results in a decrease in ionic mobility and hence conductivity, especially in the high concentration region. As a result of the effect of lithium salt concentration on carrier number and ionic mobility, there exists a maximum conductivity at a certain salt concentration.

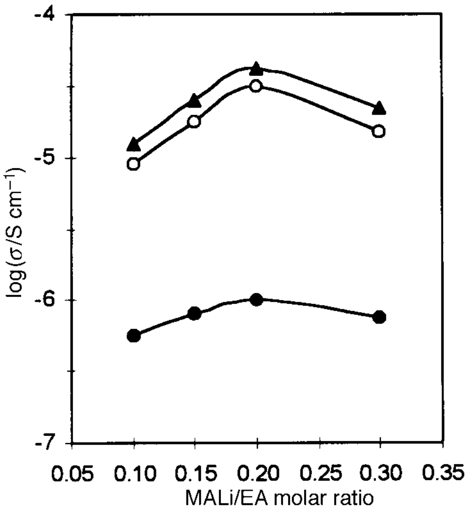

Fig. 5 Variation of conductivity at 25 °C of P(EA-MALi) latex film with different MALi contents, in which 40 wt% electrolyte solution EC:γ-BL(3:2)/LiClO$_4$ was added. LiClO$_4$ concentration in EC:γ-BL(3:2)/LiClO$_4$ solution: (●) 0, (▲) 0.4 and (○) 0.8 M.

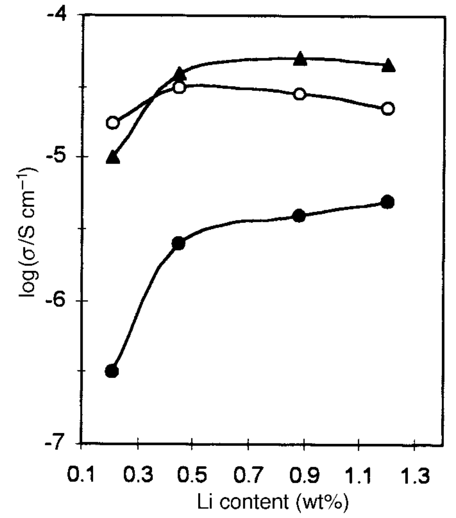

Fig. 6 Variation of the conductivity of P(EA-SHMLi) latex film at 25 °C with different SHMLi contents, in which 40 %wt electrolyte solution EC:γ-BL(3:2)/LiClO$_4$ was added. LiClO$_4$ concentration in EC:γ-BL(3:2)/LiClO$_4$ solution: (●) 0, (▲) 0.4 and (○) 0.8 M.

Effect of lithium salt dissociation degree in latex film on the ionic conductivity

The ionic conductivity of latex films prepared from strong organic acid lithium salt (SHMLi) is higher than that from weak organic acid lithium salt (MALi), as shown in Fig. 7.

Table 1 Ionic conductivity of plasticized latex polymer electrolytes (S cm^{-1}, 25 °C)

		Plasticizers			
		EC:γ-BL(3:2) (wt%)		LiClO$_4$/PC (1 M) (wt%)	
Polymer electrolytes	Monomer molar ratio	40	50	40	50
PEA/DSLi	—	2.23×10^{-6}	1.40×10^{-5}	6.98×10^{-5}	2.89×10^{-4}
P(EA-VAc)/DSLi	EA:VAc 60:40	4.31×10^{-7}	4.25×10^{-6}	1.69×10^{-4}	2.33×10^{-4}
P(EA-MALi)	MALi:EA 2:10	8.68×10^{-7}	2.20×10^{-6}	4.44×10^{-5}	2.30×10^{-4}
P(EA-VAc-MALi)	VAc:EA 20:80	2.43×10^{-6}	8.25×10^{-6}	1.49×10^{-4}	5.32×10^{-4}
	VAc:EA 40:60	6.57×10^{-7}	8.76×10^{-7}	3.76×10^{-5}	2.37×10^{-4}
[MALi:(EA+VAc) 2:10]	VAc:EA 60:40	3.44×10^{-7}	1.06×10^{-6}	1.25×10^{-4}	3.18×10^{-4}
	VAc:EA 80:20	5.80×10^{-7}	—	6.35×10^{-5}	—

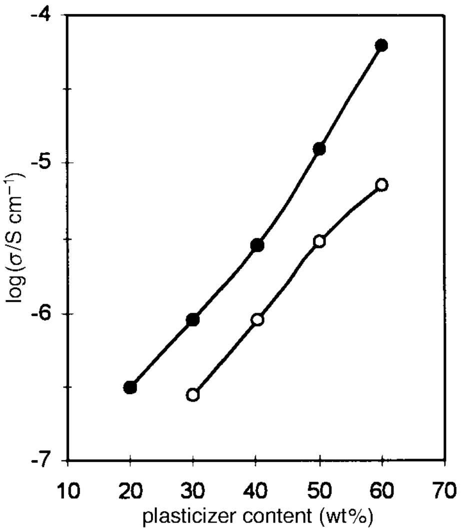

Fig. 7 Effect of plasticizer (EC:γ-BL = 3:2) content on the ionic conductivity of latex films at 25 °C: (●) P(EA-MALi) and (○) P(EA-SHMLi)

This is because lithium salts of strong acids in the latex film are more readily dissociated than those in the case of weak organic acid, therefore there are more free ions in the former system.

Conclusions

Summarised from the above, the following conclusions can be made.

Ionic transfer in the surface layer of latex particles is an effective method of increasing the conductivity of polymer electrolytes.

Among the components which have solvating effects on the lithium salt in polymer electrolytes, only hydrophilic components can promote the dissociation of the lithium salt on the surface layer.

A maximum conductivity relationship exists between ionic conductivity and lithium salt concentration in the polymer electrolyte latex films.

The ionic conductivity of latex films with lithium salts of strong organic acids is higher than that of lithium salts of weak organic acids. In view of their practical usage, the latter may be beneficial.

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