Effect of Various Plasticizers on the Transport Properties of Hexanoyl Chitosan-Based Polymer Electrolyte

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ABSTRACT: Hexanoyl chitosan that exhibited solubility in tetrahydrofuran was prepared by acyl modification of chitosan. Films of hexanoyl chitosan-based polymer electrolyte were prepared by the technique of solution casting. Ethylene carbonate, propylene carbonate, and diethyl carbonate with different dielectric constants were employed as the plasticizing solvents and lithium trifluoromethanesulfonate ($LiCF_3SO_3$) was used as the salt. The importance of dielectric constant affecting conductivity and transport properties of hexanoyl chitosan:$LiCF_3SO_3$ electrolytes have been examined in the present study. An enhancement in the ionic conductivity has been found on plasticization, and the magnitude of conductivity increment strongly depended on the dielectric constant of the plasticizer. Transport properties such as activation energy and charge carrier concentration have been calculated to obtain information that may be used to elucidate the mechanism of conductance. In addition to conductivity studies, thermal studies and transference number measurements were performed to correlate the phase structure and diffusion phenomena to the conductivity behavior of hexanoyl chitosan-based polymer electrolyte. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4474–4479, 2006

Key words: hexanoyl chitosan; $LiCF_3SO_3$; plasticizer; diffusion; ionic conductivity

INTRODUCTION

Polymer electrolytes have emerged as the key object of academic and industrial interest. These materials have vast potential application in solid state batteries, fuel cells, and electrochromic devices. Ionic conduction is an important characteristic in determining the practical application of these materials. The solid polymer electrolytes display many advantages, such as satisfactory mechanical properties, ease of fabrication as thin-films of desirable sizes, and good contact with electrode materials. Various combinations of salts and polymers forming polymer–salt complexes have been investigated, with particular attention to lithium-based complexes.[1–4] A major drawback of these polymer–salt complexes, however, is the low ionic conductivity at ambient temperature, which is due to the high crystallinity.[5,6]

With the confirmation of the predominance of amorphous region on higher ionic mobilities and conductivities by Berthier et al.,[7] several strategies to suppress crystallinity in polymer systems have been developed. These strategies are copolymerization,[8–11] crosslinked polymer networks,[12–15] comb formation,[16,17] etc. In these cases, the conductivity enhancement is achieved by increasing the amorphous content of polymer electrolytes.

The most striking advancements in improving the conductivity of polymer electrolytes with minimal loss of their mechanical properties have been attained through plasticization. The roles of plasticizer as the conductivity enhancer[18–23] are as follows:

i lowers the glass transition temperature of the polymer
ii helps the dissociation of salt into ions
iii associates with the ionic carriers and allows them to move faster.

However, the mode of action of plasticizer is much more complicated.[24] The magnitude of conductivity enhancement is governed by the intrinsic nature of the plasticizer (dielectric constant, viscosity, etc).

The product that is able to dissolve in dilute acetic acid when chitin is deacetylated is generally referred to as chitosan. Chitosan is well known for its aptitude to generate thin films.[25] The oxygen and nitrogen atoms of chitosan, in particular, have lone pair electrons that can form complexes with inorganic salts. Plasticized chitosan-based polymer electrolytes showing ionic conductivity of $\sim 10^{-5}$ S cm^{-1} at room temperature have been reported by Arof and coworkers.[26,27] In these studies, due to the insolubility of chitosan in a large number of aprotic solvents, the chitosan films

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were prepared using dilute acetic acid as a solvent. The reactivity of water and acetic acid with lithium metal or lithium intercalation-type electrodes remains as a crucial problem for the successful application of chitosan-based polymer electrolytes in the rechargeable lithium batteries. One of the prospective ways of solving this problem is to improve solubility of chitosan in aprotic solvent.

To improve its solubility in aprotic solvents, acyl modification of chitosan (MW 6×10^{-5} g mol^{-1}) was carried out in the present study. Hexanoyl chitosan that is soluble in tetrahydrofuran (THF) was prepared by reacting the chitosan with hexanoyl chloride in a mixture of pyridine and THF. The detail synthetic procedures of hexanoyl chitosan were described in the literature.[28]

The objective of this study is to investigate the role of dielectric constant of the plasticizer on the transport properties of hexanoyl chitosan-based polymer electrolytes. Ethylene carbonate (EC), propylene carbonate (PC), and diethyl carbonate (DEC) of different dielectric constants have been used as the plasticizing solvents. Results from conductivity, thermal studies, and transference number measurements provide comparative information on the differences in the functionality of each plasticizer.

EXPERIMENTAL

Sample preparation

$LiCF_3SO_3$ with purity >96% obtained from Aldrich (Milwaukee, WI) was dried at 120°C for 24 h prior to use. EC and DEC with high purity (>99% and >99.5%, respectively) purchased from Fluka, PC with purity >99.7% from Aldrich, and THF with purity >99% from J.T. Baker were used as received. Films of hexanoyl chitosan-based polymer electrolytes were prepared by the technique of solution casting. The required amounts of hexanoyl chitosan and $LiCF_3SO_3$ were mixed evenly and dissolved in THF to prepare the hexanoyl chitosan–$LiCF_3SO_3$ system. To prepare the gel polymer electrolyte, the required amounts of EC, PC, or DEC were mixed with the hexanoyl chitosan and $LiCF_3SO_3$ dissolved in THF. The homogeneous solutions thus obtained were cast in glass petri dishes and allowed to evaporate slowly at room temperature to form films. The resulting polymer electrolyte films were labeled as follows:

HL: Hexanoyl chitosan + $LiCF_3SO_3$
HLEC: HL + 30 wt % EC
HLPC: HL + 30 wt % PC
HLDEC: HL + 30 wt % DEC

In this work, only the samples with highest room temperature conductivity were studied. Samples with other plasticizer compositions were considered for other characterization. This is because for application as electrolyte in batteries, the electrolyte must have sufficiently high conductivity. In the present study, the electrolyte containing 30 wt % of plasticizer has the highest conductivity.

Sample characterization

For the impedance measurements, the polymer electrolyte film was sandwiched between two stainless steel electrodes with diameter 1 cm, under spring pressure. Impedance of the films was measured using the HIOKI 3531 Z LCR Hi-tester impedance spectroscopy. Glass transition temperatures of hexanoyl chitosan-based polymer electrolytes were determined by means of differential scanning calorimetry (DSC) using a Mettler Toledo DSC822 at a scanning rate of 10°C/min. The cation transference numbers in the polymer electrolytes were measured using the direct current (dc) polarization method.[29,30] The dc is monitored as a function of time on application of a fixed dc voltage (1.5 V) across the sample sandwiched between two stainless steel electrodes.

RESULTS AND DISCUSSION

The ionic conductivity of the prepared hexanoyl chitosan-based polymer electrolytes was calculated from eq. (1)

$$\sigma = \frac{t}{R_b A} \tag{1}$$

where t is the thickness of the film and A is the film–electrode contact area. The bulk resistance, R_b of the electrolyte was obtained from the complex impedance plot.

The dependence of conductivity of hexanoyl chitosan-based polymer electrolytes on temperature is given in Figure 1. Within the temperature range investigated, the variation of log σ with $1/T$ is quite linear, indicating that the conductivities of the polymer electrolytes are thermally assisted and can be described by Arrhenius law:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \tag{2}$$

where σ_0 is the pre-exponential factor, E_a is the activation energy of ionic conduction, k is the Boltzmann constant, and T is the absolute temperature. The results of Figure 1 reveal that the order of the ionic conductivity was HL < HLDEC < HLPC < HLEC.

The variation of room temperature conductivity and E_a for the various electrolyte types is depicted in Fig-

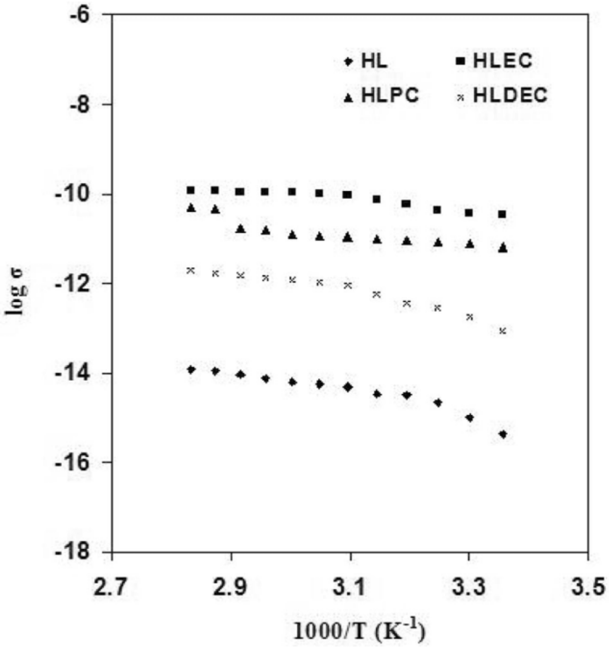

Figure 1 Ionic conductivity versus reciprocal temperature for the samples investigated.

ure 2. The plasticized electrolytes have a higher ionic conductivity and lower E_a than the nonplasticized electrolyte. The variation in E_a could be attributed to a variation in the polymer segmental movement. A decrease in E_a suggests an increase in mobility of conducting ions due to enhanced segmental motion of polymer chains. The addition of plasticizer to the polymer electrolyte increases the local chain flexibility as evidenced by a decrease in glass transition temperature of the polymer.

Figure 3 illustrates the DSC thermograms for the prepared polymer electrolytes at the second heating scan. Glass transition temperatures, T_g, estimated as the mean value between onset and endset temperatures of the process are summarized in Table I. According to Zong et al.,[28] the T_g of hexanoyl chitosan polymer is detected at −10°C using dynamic mechanical analyses. However, in the present study, from the DSC thermograms as shown in Figure 3, the T_g for hexanoyl chitosan was observed at −20°C. When complexed with $LiCF_3SO_3$, it increased to −10.2°C. Similar increase in the value of T_g when a polymer was complexed with an alkali metal salt has been reported by other researches.[31,32] Subsequent to the addition of a plasticizer at 30 wt % level, there was a decrease in T_g. Since T_g is concerned with the flexibility of polymer chains, and the ion transfer is greatly affected by such segmental motion, an electrolyte with lower value of T_g implies rapid ion conduction and hence higher conductivity.

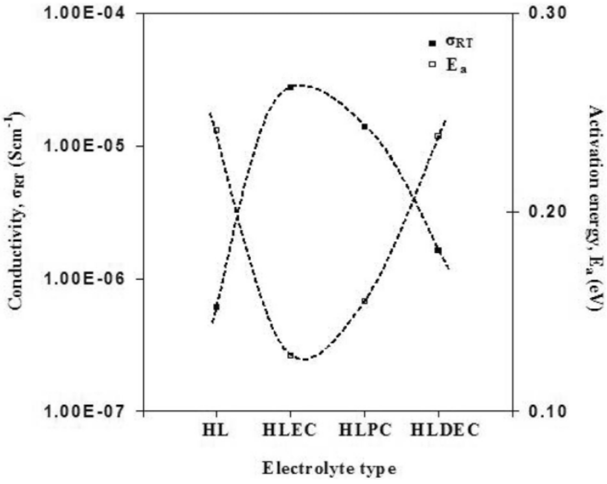

Figure 2 Plots of room temperature conductivity (filled symbols) and activation energy (open symbols) versus electrolyte type: HL, HLEC, HLPC, and HLDEC.

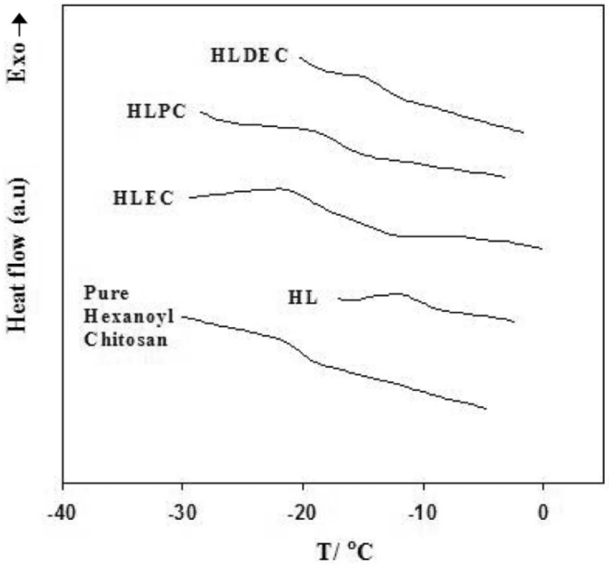

Figure 3 DSC curves at second heating scan.

The determination of the value of n permits a quantitative comparison of the ability of plasticizing solvents to enable dissociation of the lithium salt. The n values for various electrolyte types have been calculated based on the Rice and Roth model.[33] Figure 4

TABLE I
Glass Transition Temperatures Obtained from DSC Thermograms

Sample	Glass transition temperature, T_g (°C)
Pure hexanoyl chitosan	−20.0
HL	−10.2
HLEC	−16.1
HLPC	−15.3
HLDEC	−12.3

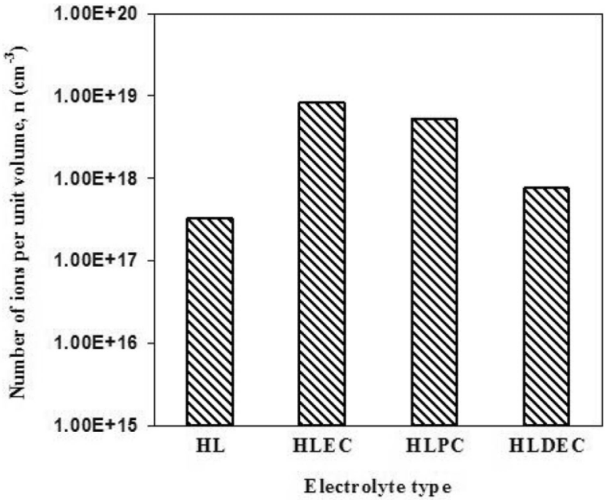

Figure 4 Concentration of charge carriers versus electrolyte type.

presents the variation of n for various electrolyte types. When the total concentration of $LiCF_3SO_3$ salt in the prepared electrolyte systems is the same, the variation in n should be ascribed to the permittivity effect of the plasticizer. The physical properties of EC, PC, and DEC are listed in Table II.[34,35] The plasticizer EC showed the highest value in dielectric constant, ε_r, followed by PC and DEC. The higher dielectric constant of EC ensures a higher degree of salt dissociation, which is reflected in the higher value of n. Although low viscosity should facilitate the ionic mobility, the low dielectric constant of DEC increases ion association, which reduces the effective number of charge carriers, thus giving lower value of conductivity. The above results can be summarized as follows:

ε_r: EC (89.6) $>$ PC (64.4) $>$ DEC (2.8)
n: HLEC $>$ HLPC $>$ HLDEC
σ: HLEC $>$ HLPC $>$ HLDEC

The cation transference numbers, t_+, determined by the dc polarization method are shown in Figure 5. Even if this method carries a certain degree of uncertainty,[36,37] reproducible values were obtained within an acceptable error range.

To further understand the effect of various types of plasticizers on the conduction mechanisms of the polymer electrolytes, the diffusion coefficients were calculated. The diffusion coefficients of cations and anions in each of the electrolyte systems can be calculated from the measured values of conductivity and t_+ according to the following equations[15,19,34,38]

$$\sigma = \frac{ne^2}{kT}(D_+ + D_-) \tag{3}$$

$$t_+ = \frac{D_+}{(D_+ + D_-)} \tag{4}$$

where D_+ (D_-) is the diffusion coefficient of cation (anion), respectively.

Combining eq. (3) with eq. (4), we obtain

$$D_+ = \left(\frac{\sigma kT}{ne^2}\right)t_+ \tag{5}$$

The calculated values of D_+ were then used to calculate the D_- using eq. (4).

The variations of D_+, D_- , and the total mass transport of salt, D_{salt}, as a function of electrolyte types are presented in Figure 6, where D_{salt} is the summation of D_+ and D_-. The diffusion data clearly shows that the $CF_3SO_3^-$ anion diffuses faster than the Li^+ cation in all the electrolyte systems. This is probably due to the differences in solvation between the Li^+ cation and the $CF_3SO_3^-$ anion.[39] From the value of n in Figure 4 and diffusion data in Figure 6, it can be inferred that the conductivity enhancement could be attributed not

TABLE II
Physical Properties of the Plasticizers Used

Plasticizer	Dielectric constant	Viscosity at 25°C (MPa s)
Ethylene carbonate (EC)	89.6	1.86
Propylene carbonate (PC)	64.4	2.53
Diethyl carbonate (DEC)	2.8	0.75

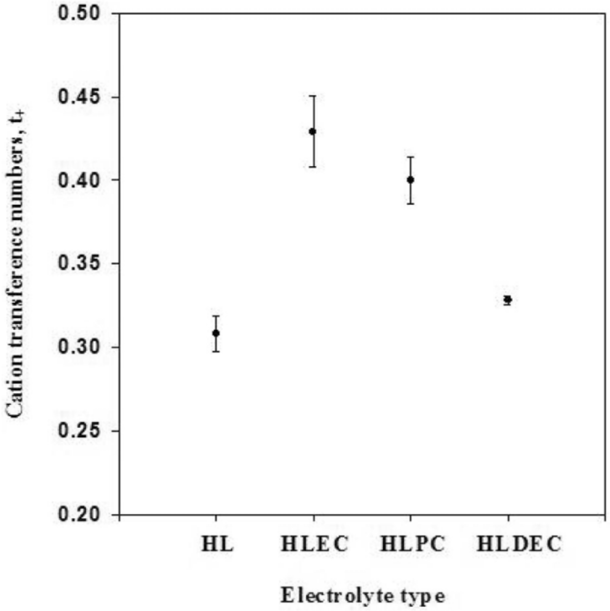

Figure 5 The transference numbers for hexanoyl chitosan-based polymer electrolytes at room temperature.

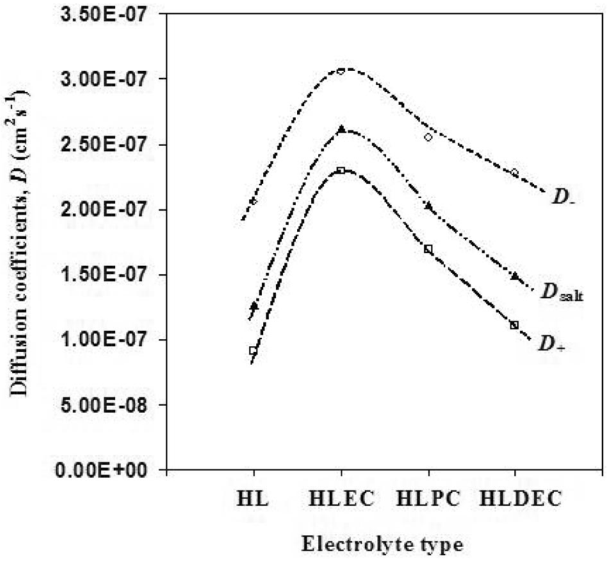

Figure 6 Diffusion coefficients at room temperature.

only to the increase in the number of ions, but also to the increase in the diffusivity of ions and *vice versa*.

n: HL $<$ HLDEC $<$ HLPC $<$ HLEC
D_{salt}: HL $<$ HLDEC $<$ HLPC $<$ HLEC
σ: HL $<$ HLDEC $<$ HLPC $<$ HLEC

The D_{salt} has the same trend as the conductivity data with HLEC, showing the highest value in both conductivity and D_{salt}, followed by HLPC $>$ HLDEC $>$ HL. The increase in ionic diffusivity upon the addition of plasticizer can be explained with the help of vibrational study. In our FTIR spectroscopic studies of hexanoyl chitosan-$LiCF_3SO_3$-EC/DEC,[40] we found that EC, for example, not only interacts with the Li^+ ions of $LiCF_3SO_3$, but also competes with the polymer on associating with Li^+ ions. The first kind of interaction yields "free" Li^+ ions while the second kind of interaction reduces the fraction of polymer–Li^+ complex, resulting in less restriction to the segmental mobility of polymer chains (reflected in the lower value of T_g). The first interaction coupled with the second interaction led to conductivity enhancement.

Figure 7 displays the increment percentage of D_+ and D_- in the presence of plasticizer (EC, PC, or DEC). Smaller increment of D_- (relative to the D_+) is observed in all the plasticized systems. For instance, the incorporation of EC to hexanoyl chitosan : $LiCF_3SO_3$, dry solid electrolyte (HL), increases the D_+ by 60% and D_- by only 32%. The difference in the increment percentage of D_+ and D_- may be discussed in the following manner.

In the plasticized system, the plasticizer extracts conducting Li^+ ions from the hexanoyl chitosan–Li^+ complex and forms separate domains, which serve as a pathway for Li^+ ions to diffuse. Because of the lower diffusion activation energy than hopping activation energy,[41] Li^+ diffuses rather than hops from one polymer chelation site to another. Thus, motion of Li^+ ions is greatly enhanced, which is reflected by greatly increased D_+. On the other hand, due to the noncoordination of anion to the polymer, the $CF_3SO_3^-$ remains solvated in the environment around the polymer and its motion is not affected by the segmental movement of polymer chains. The smaller increment of D_- with respect to D_+ is due to the release of anion from the columbic-trap with the cation in the presence of the plasticizer.

The low viscosity of DEC should facilitate ion diffusivity as mentioned earlier. However, the diffusion coefficients (both D_+ and D_-) of DEC-plasticized sample (HLDEC) are lower than those of HLEC and HLPC. To understand this phenomenon, it is important to make a distinction between the macroscopic and microscopic viscosities. The experimental measured viscosity of DEC as given in Table II is macroscopic whereas it should be the microscopic or local viscosity which is related to ion diffusivity.[42,43]

The low dielectric constant of DEC does not favor the complete dissociation of $LiCF_3SO_3$. Hence, presence of a large concentration of ion aggregates which do not take part in the conduction process lead to an increase in the local viscosity. An increase in local viscosity shall result in lower diffusivity.

CONCLUSIONS

The addition of plasticizer to hexanoyl chitosan: $LiCF_3SO_3$ polymer electrolytes has been found to result in an increase in conductivity, and the magnitude of increase is in accordance with the dielectric constant

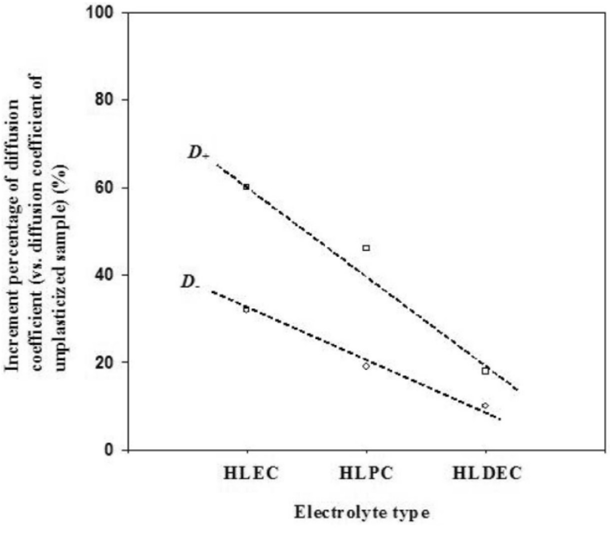

Figure 7 Permittivity effect of the plasticizer on diffusion phenomena.

of the plasticizer. The conductivity trend observed could be corroborated by results obtained from thermal studies and transference number measurements. The correlations between conductivity and diffusion phenomena were explored on the basis of Nernst-Einstein equation.

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