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"THE EFFECT OF LOW MOLECULAR WEIGHT ADDITIVES ON THE PROPERTIES OF
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by

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The Effect of Low Molecular Weight Additives on the
Properties of Poly(ethylene oxide)-based Zn(II) and Li(I)
Electrolytes

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Abstract: The incorporation of low molecular weight additives significantly improves the conductivity of both PEO-based ZnBr₂ and LiClO₄ electrolytes from 0 to 100°C, particularly at room temperature and below. Apparently additives have two effects: (1) to increase the segmental mobility of the PEO chains in the amorphous conducting phase, and, therefore, increase the mobility of charge carriers; and (2) to increase the degree of salt dissociation in the amorphous conducting phase and thus increase the number of charge carriers. The effectiveness of additives in improving conductivity is greatly influenced by the type of salts involved.

[Revised 28 August 1991]

1. Introduction

Most solid polymer electrolytes have relatively low ionic conductivities, typically 10^{-7} to 10^{-9} S cm⁻¹ at room temperature. Approaches taken to increase their

conductivity include the synthesis of amorphous polymer matrices with very low glass transition temperatures and thus high segmental mobilities and the blending of a polymer with good solvating power, such as PEO, with various additives which enhance conductivity. The blending technique seems to provide an effective and practical approach, particularly for PEO-based electrolytes. By taking advantage of the outstanding solvating power of PEO and its good mechanical properties, various additives, such as low molecular weight polyethers and organic solvents with high dielectric constants and low viscosities, can be blended into PEO-based electrolytes to improve their room temperature conductivity. For example, conductivities of 10^{-5} to $10^{-3} \text{ S cm}^{-1}$ at room temperature have been reported for a few hybrid PEO-based lithium electrolytes [1,2].

As a general guide, a good additive should have (i) good miscibility with the polymer; (ii) low viscosity; (iii) high polarity (high dielectric constant); and (iv) low volatility. By optimizing these factors, it is possible to achieve high conductivity at room temperature. Shown in Table 1 [3] are physical data for some of the more popular additives; water is also listed as a reference.

Table 1 Physical data of additives [3]

Solvent		Dielectric Constant at 25°C	Viscosity cP
Dimethylformamide	DMF	36.7	0.80
	H ₂ O	78.5	1.00
γ -butyrolactone	γ -BL	39.1	1.75
Ethylene Carbonate	EC	89.6	1.90
Propylene Carbonate	PC	64.4	2.53
poly(ethylene glycol)	PEG ₄₀₀	5	3

Studies conducted by Watanabe et al. [4-6] on electrolytes of LiClO_4 dissolved in polyacrylonitrile (PAN) containing polar additives such as DMF, PC and EC showed that the trend in conductivity enhancement is $\text{DMF} > \text{PC} > \text{EC}$, i.e. increased conductivity correlates with decreased viscosity of the additive rather than a change in its dielectric constant. This result implies that it is the mobility rather than the charge carrier concentration that plays the most important role in determining total conductivity. Watanabe et al. also suggested that the role of the additives is to provide a pathway for the ion conduction, while the polymer only acts as a supporting system that offers structural stability as a matrix in a polymer electrolyte system with additives.

The goal of the present work was to explore the effect of additives on the physical and electrochemical properties of two PEO-based electrolyte systems: (i) a divalent ZnBr_2 system, and (ii) a monovalent LiClO_4 system. Low molecular weight poly(ethylene glycol) (PEG) and poly(ethylene glycol)dimethylether (PEGDME) with $\text{MW}=400$ and ethylene carbonate (EC) were chosen as additives for the following reasons. PEG, PEGDME, and PEO have the same repeat unit $(-\text{CH}_2-\text{CH}_2-\text{O})-$ and therefore can be expected to be mutually miscible. The obvious difference between PEG and PEGDME is in the end groups. PEG is terminated by hydroxyl groups, $-\text{OH}$, which may affect ion solvation through hydrogen bonding. The terminal methyl groups, $-\text{CH}_3$, in PEGDME, should have less effect on the solvation of ions. EC, on the other hand, has a lower viscosity and a much higher dielectric constant, as shown in Table 1, and is expected to improve ionic mobility as well as ion solvation, and therefore may increase both the number of charge carriers and their mobility in the electrolyte system.

2. Sample Preparation

All samples were prepared by a solution-casting technique using the starting materials listed in Table 2. Stoichiometric amounts of salts, PEO and additives were dissolved in acetonitrile or ethanol/acetonitrile mixtures and stirred at room temperature for about 24 hours to produce homogeneous solutions. The solutions were then cast in glass rings on silicone release paper and allowed to stand at room temperature for about 24 hours to allow solvent to evaporate. The glass rings, with polymer film attached, were transferred to a vacuum line and vacuum dried, first at room temperature for about 24 hours and then at 50-70°C for another 24 hours. Samples were stored in an argon-purged drybox until further study. Electrolytes with the compositions, $\text{ZnBr}_2[0.5\text{PEO}+0.5\text{A}]_{16}$ and $\text{LiClO}_4[0.5\text{PEO}+0.5\text{A}]_{20}$, where A=PEO, PEGDME, PEG and EC were prepared. Each formula repeat unit of PEO, PEGDME and PEG has one ether oxygen. Each EC molecule is considered to have only one coordinating oxygen, the oxygen in the carbonyl group.

3. Experimental

Thermogravimetry (TG) was used to study the thermal stability of the electrolytes. The measurements were performed on a DuPont 951 TGA with a DuPont 2100 controller. Samples, approximately 10 mg in weight, were heated under dry nitrogen atmosphere at 10°C/min.

DSC studies were carried out using a DuPont 910 DSC cell from -110 to 200°C and higher. Samples, approximately 10 mg in weight, were hermetically sealed in aluminium pans in an argon filled drybox. They were first heated at 10°C/min, held isothermally at 200°C for 20 minutes, then quenched with liquid nitrogen and reheated from -110 to 200°C (second heating). The glass transition temperature, T_g , of each composition studied, was taken as the onset of the transition, i.e. the point

Table 2 Starting materials for preparing PEO-based electrolytes with additives at which the extrapolated baseline intersects the extrapolated slope in the transition state.

Starting Materials	MW	Source	Pre-treatment
LiClO_4		Aldrich, anhydrous	Vacuum dried at 120°C
ZnBr_2		Aldrich, 99.999%	Used as received
Poly(ethylene oxide) PEO	5×10^6	Aldrich	Vacuum dried at 50°C
Poly(ethylene glycol) PEG	400	Polyscience	Molecular sieve dried
Poly(ethylene glycol dimethylether) PEGDME	400	Polyscience	Molecular sieve dried
Ethylene Carbonate EC	88	Aldrich, 98%	Vacuum dried at 50°C, purified by sublimation
Ethanol $\text{C}_2\text{H}_5\text{OH}$		Aldrich, anhydrous	Used as received
Acetonitrile CH_3CN		Aldrich, anhydrous	Used as received

Ionic conductivity was determined using complex ac impedance analysis with blocking platinum electrodes. Measurements were carried out over the temperature range 30 to 160°C and the frequency range 10^2 to 10^5 Hz using a Solartron 1174 frequency response analyzer under computer control. Samples were allowed to equilibrate at each temperature for 10 minutes before data collection.

4. Results and Discussion

4.1 Effect of additive concentration

Electrolyte compositions of $\text{ZnBr}_2[(1-x)\text{PEO}+x\text{PEGDME}]_{16}$, where $x = 0, 0.25, 0.50$ and 0.75 in mol%, were prepared to study the effect of PEGDME (MW = 400) on

conductivity. Electrolytes with 50 mol% PEGDME or less had good mechanical strength, but the composition with 75 mol% of PEGDME was rather sticky and mechanically weak.

Conductivities of the electrolytes was measured from 30 to 130°C. PEGDME increases the ionic conductivity over the entire temperature range, particularly below 60°C, as shown in Figure 1(a). The higher the mole fraction of PEGDME, the higher the conductivity of the electrolyte. Values of conductivity at 30°C increased from 10^{-9} S cm⁻¹ for an electrolyte without any additive to 3×10^{-6} S cm⁻¹ for the electrolyte with 50 mol% PEGDME.

< Insert Figure 1. >

The conductivity of a $\text{ZnBr}_2[0.5\text{PEO}+0.5\text{PEGDME}]_{16}$ sample was also measured in three temperature cycles between 30 to 130°C, and the results are shown in Figure 1(b). The conductivity of this sample remained at a nearly constant and high level throughout the thermal cycling, indicating that the electrolyte is stable in this temperature range. The small increase in conductivity observed during cycling is probably due to sample flow at high temperatures.

To summarize, the incorporation of 50 mol% PEGDME into a PEO-based ZnBr_2 electrolyte significantly improves its conductivity at temperatures below 60°C without significant degrading its mechanical strength. Therefore, a molar ratio of 50:50 of PEO/additive was chosen for the following studies.

4.2 Effects of different additives

A further study was carried out to investigate the effects of various additives on the physical and electrochemical properties of PEO-based ZnBr_2 electrolytes. In this case, a group of electrolytes of composition, $\text{ZnBr}_2[0.5\text{PEO}+0.5\text{A}]_{16}$, with A = PEO, PEGDME, PEG, and EC were prepared.

Striking differences in physical appearance and mechanical properties were observed among the three hybrid compositions. The sample containing PEG was a waxy film with little mechanical strength; the electrolyte with PEGDME retained good mechanical strength, similar to that of a pure PEO-based ZnBr_2 electrolyte, but the surface of the film was oily ("perspiring"); the sample with EC appeared transparent with a few crystalline spherulites dispersed on the very elastomeric matrix.

The thermal stability of these hybrid electrolytes was studied by TG in a dry nitrogen atmosphere, and the results are shown in Figure 2. A pure PEO-based Zn(II) sample was found to be stable up to a final, one-step decomposition around 345°C . A sample with 50 mol% of PEGDME started to lose weight at about 150°C and continued to 280°C , at which a increase in the rate of weight loss was observed. The final decomposition occurred around 335°C . The weight loss below 280°C is most certainly the result of the evaporation of PEGDME, however, less weight loss (25 wt%) was observed than would be expected based on the stoichiometry (38 wt%). A sample with 50 mol% of PEG showed a very similar decomposition pattern. However, in the sample containing 50 mol% EC, a clear two-step decomposition was observed. This sample started to loss weight at about 100°C and reached a plateau at about 250°C , by which all the EC had evaporated according to the stoichiometry (55 wt%). The rest of sample decomposed at about 350°C . The TG results indicate that all three electrolyte compositions studied are thermally stable up to 100°C and EC has a higher volatility in the electrolytes than either PEGDME or PEG.

< Insert Figure 2. >

DSC studies indicate that the incorporation of additives significantly reduces both the crystallinity and the glass transition temperature as shown in Figure 3. In general, the glass transition temperature of a polymer blend is a measure of the

effectiveness of the additive in plasticizing the polymer matrix. The glass transition temperatures of the hybrid electrolytes decreased in the following order: EC > PEGDME > PEG, as summarized in Table 3. EC is the most effective of the three in plasticizing the PEO matrix and increasing segmental mobility. In addition, while PEGDME and PEG reduced the melting temperature of the PEO crystalline phase slightly, the melting temperature in the composition containing EC was so much lower that the crystalline phase was most likely a eutectic rather than a pure PEO.

< Insert Figure 3. >

Table 3. T_g of amorphous phase in $\text{ZnBr}_2[0.5\text{PEO}+0.5\text{A}]_{16}$ electrolytes

$\text{ZnBr}_2[0.5\text{PEO}+0.5\text{A}]_{16}$	T_g (°C)
A = None	-16
A = PEG	-24
A = PEGDME	-47
A = EC	-62

The conductivities of $\text{ZnBr}_2[0.5\text{PEO}+0.5\text{A}]_{16}$ electrolytes are shown in Figure 4. A dramatic improvement in conductivity over the entire temperature range (30 to 100°C) was observed when additives were incorporated. The room temperature conductivity reached about $5 \times 10^{-4} \text{ S cm}^{-1}$ for the electrolyte containing 50 mol% EC. The trend in conductivity enhancement again followed EC > PEGDME > PEG. Clearly, incorporating additives greatly improved the mobility of the PEO matrix and, therefore, the mobility of charge carriers in these hybrid electrolytes, leading to

the dramatic improvement of conductivity. It is worthwhile to point out that an important difference between PEG and PEGDME, on the one hand, and EC, on the other, lies in the significantly higher dielectric constant of latter, as shown in Table 1. As a result, it is reasonable to expect a higher number of charge carriers in the electrolytes containing EC, which should increase the number of charge carriers at room temperature.

< Insert Figure 4. >

4.3 PEO-based LiClO_4 electrolytes with additives.

To explore further the effects of additives on different PEO/salt electrolyte systems, a parallel investigation was carried out on PEO-based lithium electrolytes of the composition, $\text{LiClO}_4 [0.5\text{PEO} + 0.5\text{A}]_{20}$, where A = PEO, PEGDME, PEG, and EC. Electrolytes containing PEG and PEGDME were mechanically stable but oily on the surface. The electrolyte with EC was a transparent elastomeric film.

Results of TG measurements on the $\text{LiClO}_4 [0.5\text{PEO} + 0.5\text{A}]_{20}$ electrolytes are shown in Figure 5. The pure PEO-based LiClO_4 sample was stable up to about 330°C and showed a sharp one-step decomposition. For the samples with PEG and PEGDME, the initial weight loss started at about 200°C and continued until the final decomposition at about 330°C. The sample with 50 mol% EC again showed a two-step weight loss. The first step started at about 100°C and reached a plateau at about 230°C, at which 20 wt% weight loss was observed due to the evaporation of EC, which is only one third of the value expected from the stoichiometry (60 wt%). The final decomposition was very similar to those of the other compositions. The results are quite similar to those obtained with hybrid PEO-based ZnBr_2 electrolytes. The only obvious difference is that EC appeared to be somewhat more strongly bound in the LiClO_4 electrolytes. As a result, it only partially evaporated before final decomposition occurred.

< Insert Figure 5. >

DSC was used to characterize the phase transition behavior of the electrolytes. As shown in Figure 6, all the additives reduced the glass transition temperature by about 20°C, which suggests that the additives are about equally effective in plasticizing the PEO matrix. In addition, electrolytes incorporating PEG or PEGDME contained significant amounts of pure PEO crystalline phase, identified by the large endothermic peak observed in the DSC. However, EC effectively suppressed the crystallization of the pure PEO phase, as indicated by the small endothermic observed in DSC.

< Insert Figure 6. >

The temperature dependence of the conductivity of each of the electrolytes is shown in Figure 7. Two main features can be seen: (i) all additives enhance the conductivity at temperatures below the melting point of PEO; and (ii) EC increases the conductivity over the full temperature range studied. A conductivity of $2 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C was achieved in the electrolyte containing EC.

< Insert Figure 7. >

The plasticizing effect produced by the additives is presumably the cause of the conductivity enhancement at low temperatures. Although EC is more effective in suppressing crystallinity at low temperatures, this factor cannot be principally responsible for the high temperature conductivity enhancement observed with EC. More likely, it is the high dielectric constant (89) of EC increases in the number of charge carriers over the entire temperature range and increases the conductivity.

5. Conclusions

EC, PEG, and PEGDME dramatically increase the conductivity of PEO electrolytes containing LiClO_4 and ZnBr_2 over the entire temperature studied, 0 to 100°C,

particularly at room temperature and below. It appears that the additives have at least two effects. (i) They significantly reduce the crystallinity of the PEO-based electrolytes as well as the glass transition temperature of the amorphous conducting phase (plasticizing effect). The effectiveness of the additives in plasticizing PEO depends on the type of salt involved. For ZnBr_2 electrolytes it follows the order $\text{EC} > \text{PEGDME} > \text{PEG}$, whereas for LiClO_4 electrolytes, these additives are equally effective in plasticizing PEO. Plasticizing increases the segmental mobility of the PEO chains and thus the mobility of charge carriers. It appears that the plasticizing effect is the primary reason for the conductivity enhancement in the hybrid PEO-based ZnBr_2 electrolytes. The conductivity enhancement is greatest with the most effective plasticizing agent: the hybrid electrolyte containing EC has the highest conductivity over the entire temperature studied, followed by the electrolyte with PEGDME, and then PEG. (ii) In addition to the plasticizing effect, an additive with a high dielectric constant, such as EC, may also increase ion dissociation in the PEO-based electrolytes. As a result, the number of charge carriers will increase, resulting in an additional conductivity enhancement in the hybrid electrolytes. In case of the hybrid PEO-based LiClO_4 electrolytes, all three additives, are equally effective in plasticizing the PEO, resulting in a significant increase of the conductivity at temperatures below 65°C . However, the electrolyte with EC has an even higher conductivity over the entire temperature range studied, which is believed due to an increase in the number of charge carriers.

6. Acknowledgements

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Figure Captions

- Figure 1. Conductivity of $\text{ZnBr}_2[(1-x)\text{PEO}+x\text{PEGDME}]_{16}$ electrolytes, x in mol%
- Figure 2. TG curves of $\text{ZnBr}_2[0.5\text{PEO}+0.5\text{A}]_{16}$ electrolytes: a. A = PEO,
b. A = PEGDME, and c. A = EC
- Figure 3. DSC curves of $\text{ZnBr}_2 [0.5\text{PEO}+0.5\text{A}]_{16}$ electrolytes
- Figure 4. Conductivity of $\text{ZnBr}_2[0.5\text{PEO}+0.5\text{A}]_{16}$ electrolytes
- Figure 5. TG curves of $\text{LiClO}_4 [0.5\text{PEO}+0.5\text{A}]_{20}$ electrolytes: a. A = PEO,
b. A = PEGDME, and c. A = EC
- Figure 6. DSC curves of $\text{LiClO}_4[0.5\text{PEO}+0.5\text{A}]_{20}$ electrolytes
- Figure 7. Conductivity of $\text{LiClO}_4 [0.5\text{PEO}+0.5\text{A}]_{20}$ electrolytes

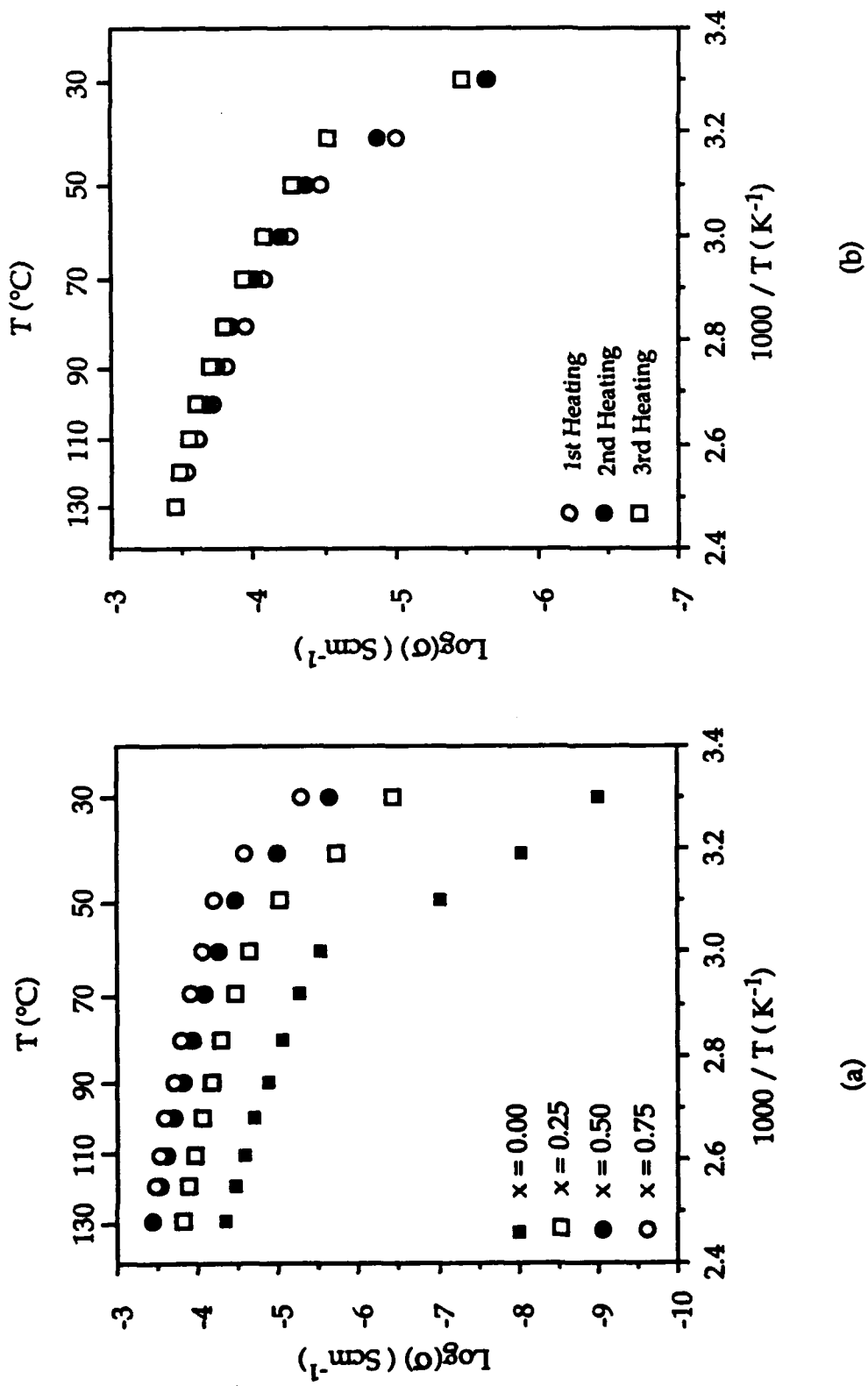


Figure 1 Conductivity of $\text{ZnBr}_2[(1-x)\text{PEO}+x\text{PEGDME}]_{16}$ electrolytes, x in mol%

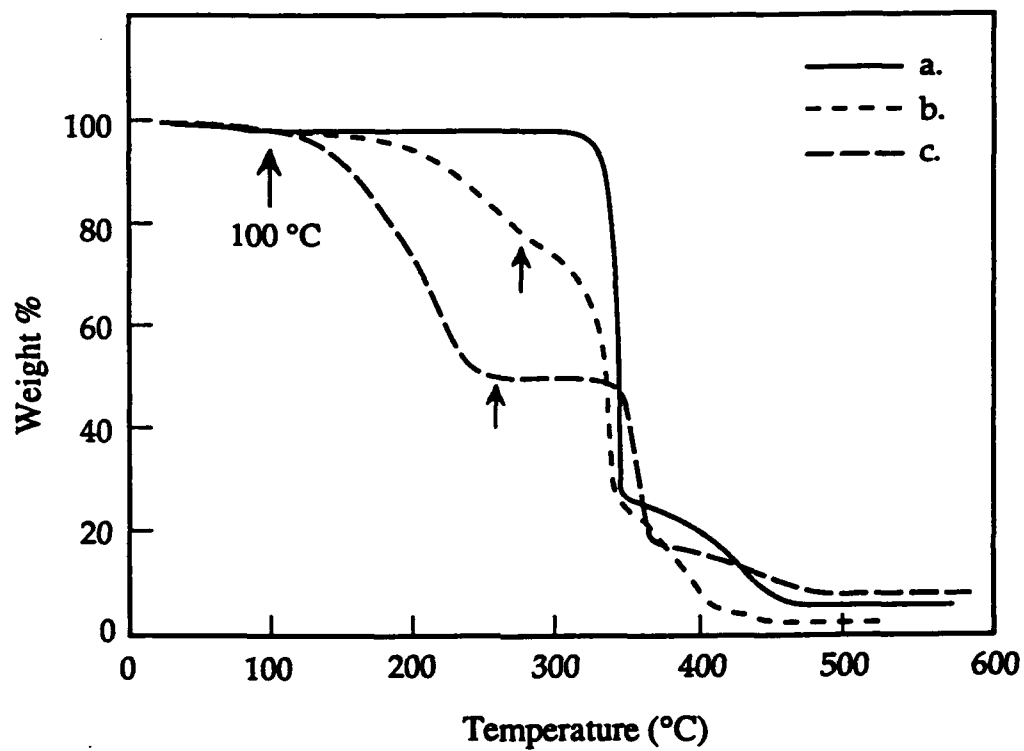


Figure 2 TG curves of ZnBr₂[0.5PEO+0.5A]₁₆ electrolytes
a. A = PEO, b. A = PEGDME, and c. A = EC

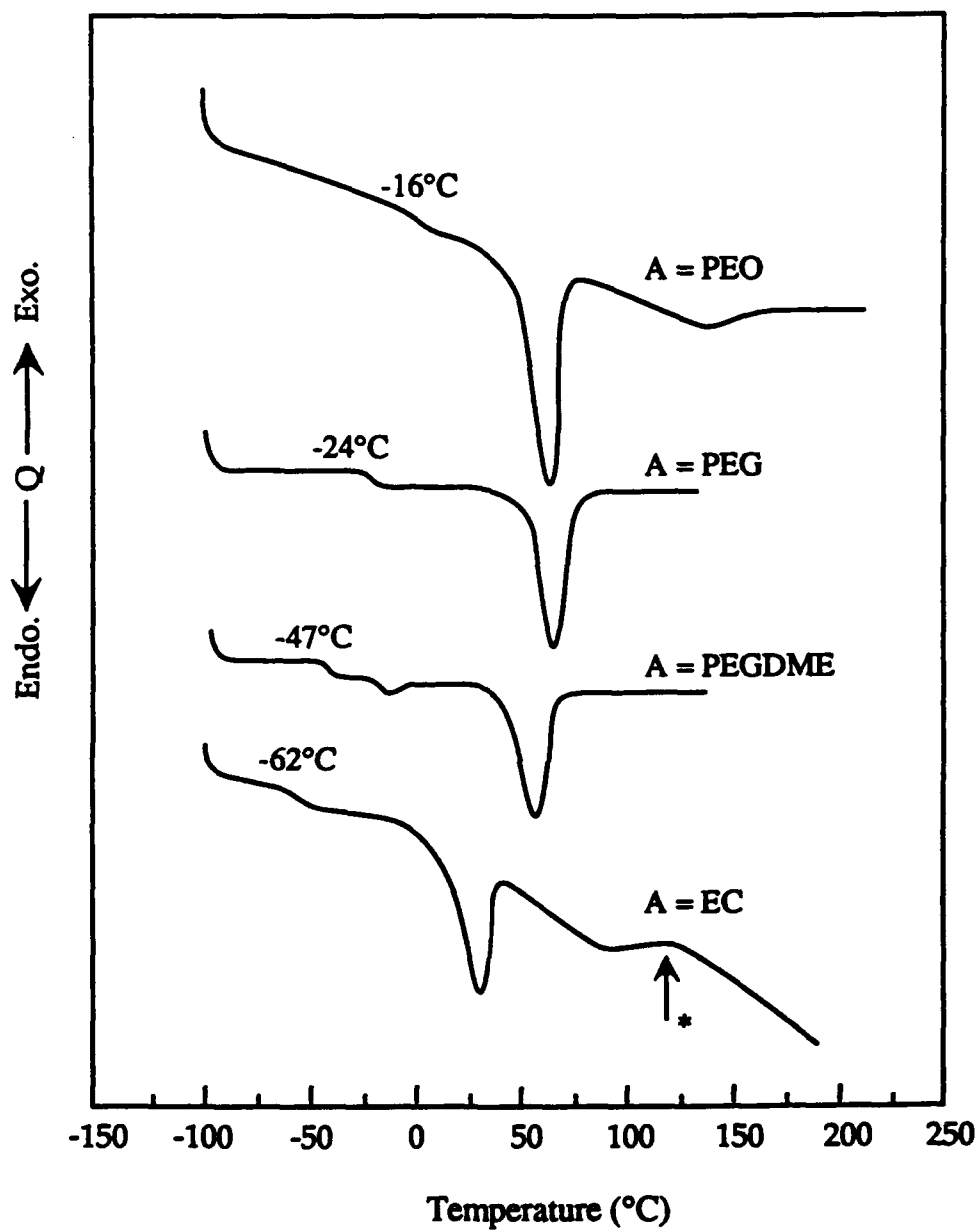


Figure 3 The DSC curves of ZnBr₂ [0.5PEO+0.5A]₁₆ electrolytes
* Temperature at which significant weight loss is observed in TG

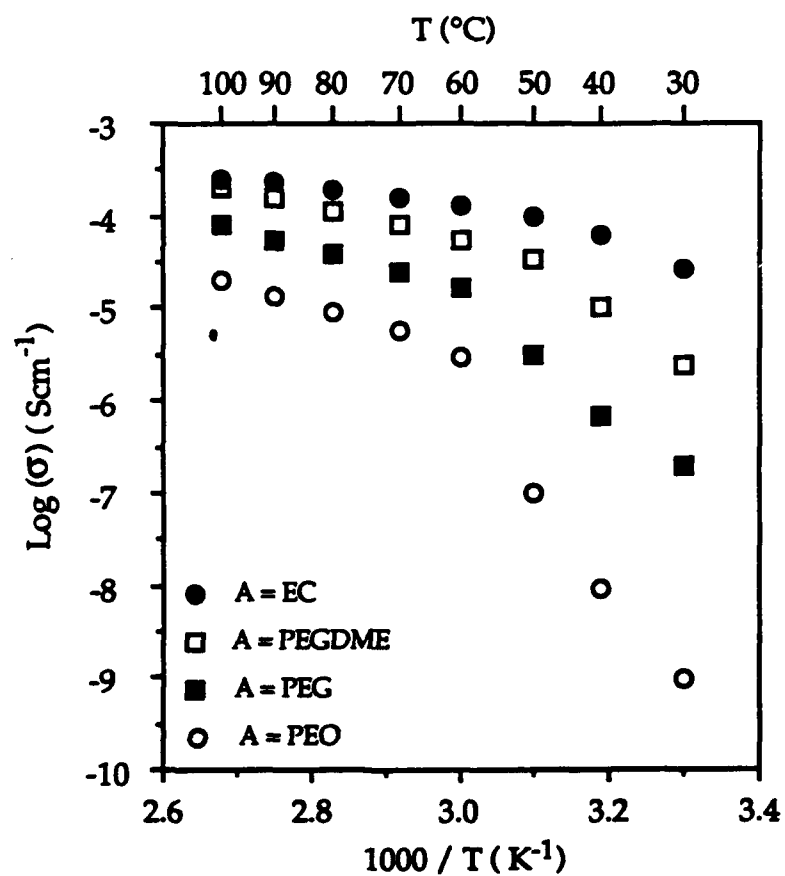


Figure 4 Conductivity of $\text{ZnBr}_2[0.5\text{PEO}+0.5\text{A}]_{16}$ electrolytes

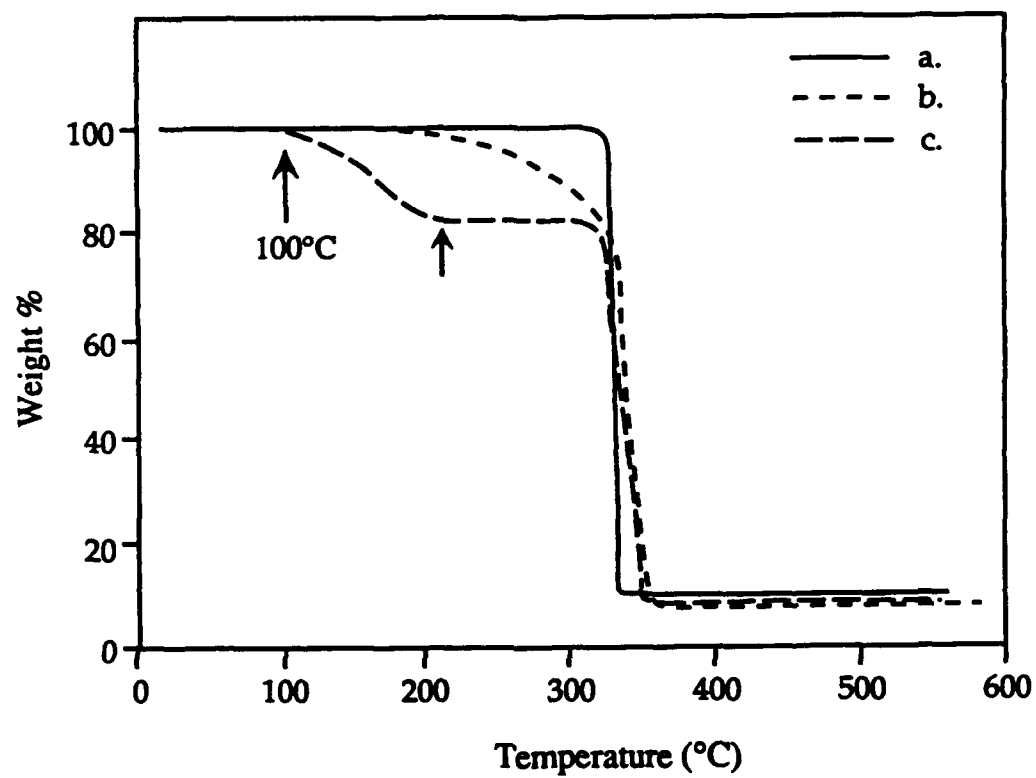


Figure 5 TG curves of LiClO_4 $[0.5\text{PEO}+0.5\text{A}]_{20}$ electrolytes
a. A = PEO, b. A = PEGDME, and c. A = EC

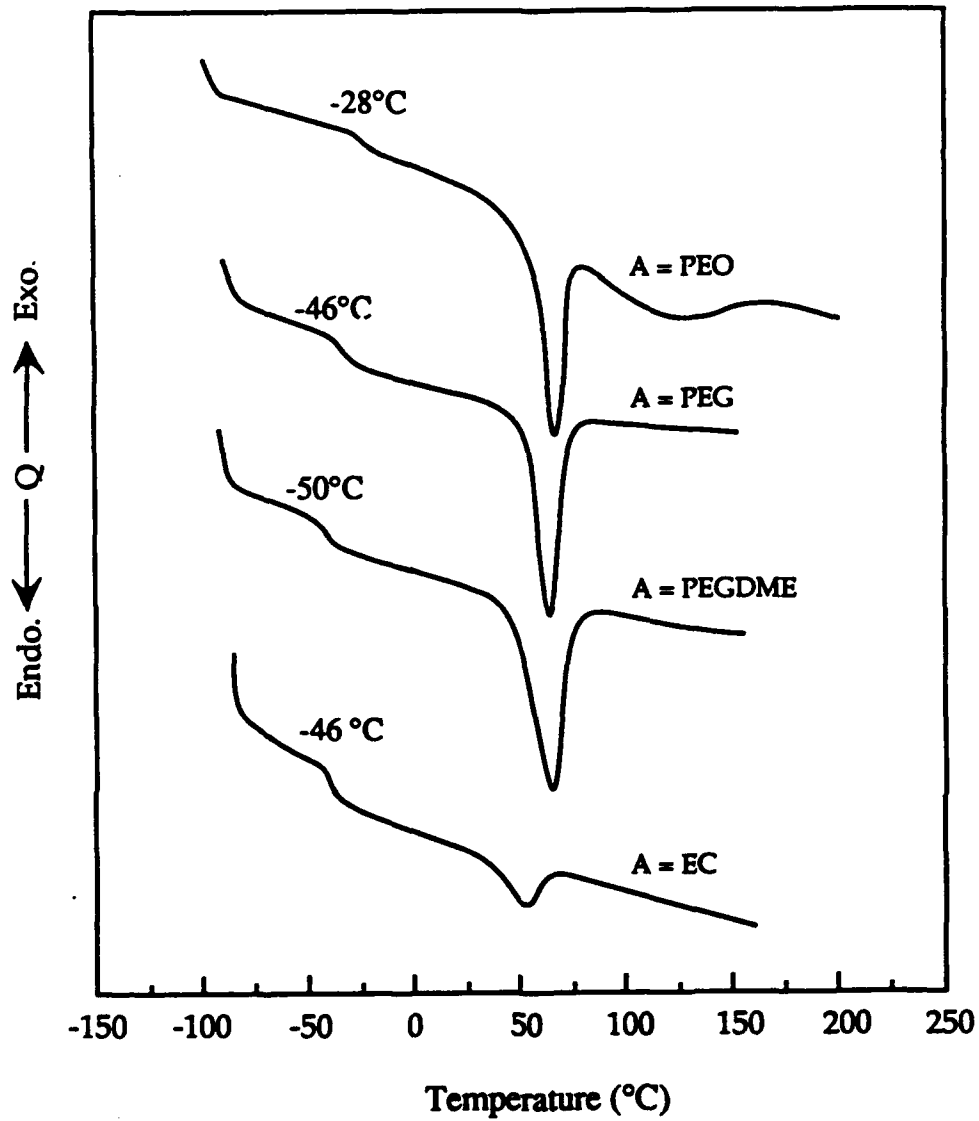


Figure 6 DSC curves of $\text{LiClO}_4[0.5\text{PEO}+0.5\text{A}]_{20}$ electrolytes

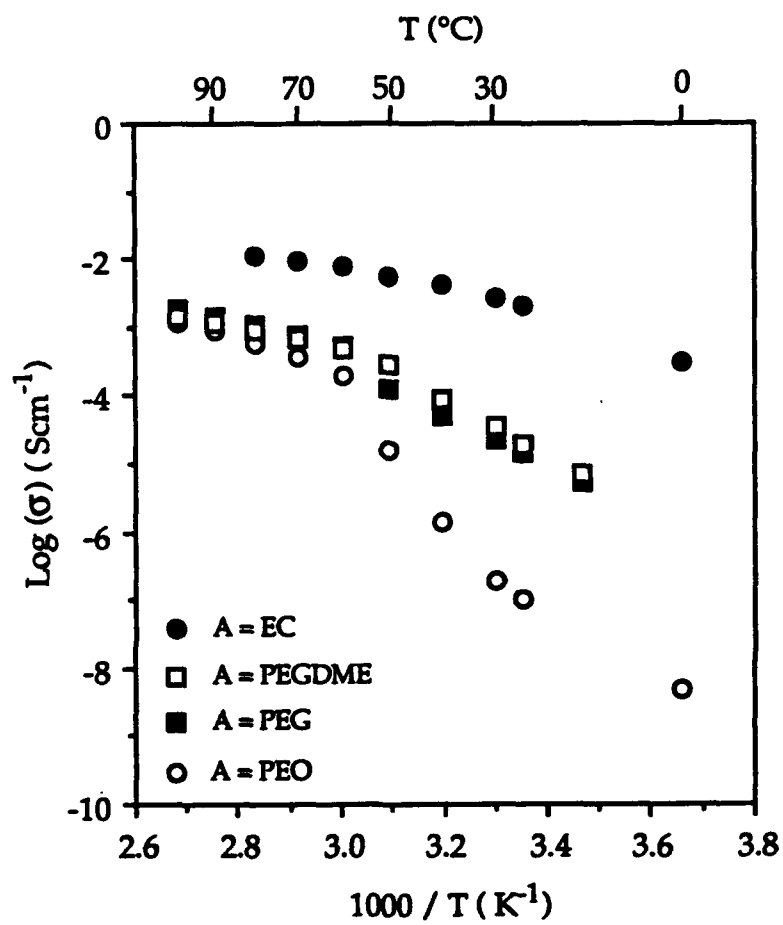


Figure 7 Conductivity of $\text{LiClO}_4 [0.5\text{PEO}+0.5\text{A}]_{20}$ electrolytes