AD-A254 818 N PAGE

Form Approved
OMB No. 0704-0188

2

hour per response, including the time for reviewing instructions, searching existing data sources,
ction of information. Send comments regarding this burden estimate or any other aspect of this
gton Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson
nent and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503

1. AG

June 12, 1992

3. REPORT TYPE AND DATES COVERED
Technical — 5/31/91 – 6/30/92

4. TITLE AND SUBTITLE
"STUDIES OF PLASTICIZED POLYMER ELECTROLYTES CONTAINING MIXED Zn(II) AND Li(I)"

5. FUNDING NUMBERS
G—N00014-90-J-1559

6. AUTHOR(S)
B.V.R. Chowdari, R. Huq and G.C. Farrington

DTIC
ELECTE
SEP 0 1 1992
S B D

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Pennsylvania
Department of Chemistry
Philadelphia, PA 19104-6323

8. PERFORMING ORGANIZATION REPORT NUMBER
1992-21

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Sponsoring Agency:	Monitoring Agency:
DARPA 3701 N. Fairfax Drive Arlington, VA 22203-1714	ONR 800 N. Quincy Street Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Distribution Unlimited

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Thin solid films of mixtures of PEGDME and PEO containing various ratios of $ZnBr_2$ and LiBr have been prepared. Equal parts of PEGDME and PEO were used, and the ether oxygen to total metal ratio was kept constant at 16. TG data have shown that the thermal stability of the polymer electrolytes is affected more so by the zinc salt than the lithium salt. DSC data show that these electrolytes are inhomogeneous mixtures of amorphous regions and crystalline PEO and PEO/salt complexes. Conductivity data did not show a mixed-cation effect.

92-23983

92 8 28 085

14. SUBJECT TERMS
poly(ethylene glycol) (PEG), poly(ethylene glycol dimethyl ether) (PEGDME), electrolytes, zinc salt, lithium salt, amorphous regions, mixed-cation effect

15. NUMBER OF PAGES
9

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL

OFFICE OF NAVAL RESEARCH

GRANT NO.: N00014-90-J-1559

R & T CODE NO.: A400004DF3

TECHNICAL REPORT NO.: 1992-21

"STUDIES OF PLASTICIZED-POLYMER ELECTRILYTES CONTAINING MIXED Zn(II) AND Li(I)"

by

B.V.R. Chowdari, R. Huq and G.C. Farrington

Accepted for Publication in
J. Interfac. Electrochem. (1991)

University of Pennsylvania
Department of Chemistry
Philadelphia, PA 19104-6323

June 12, 1992

Studies of Plasticized-Polymer Electrolytes Containing Mixed Zn(II) and Li(I)

B.V.R.Chowdari*, Rokeya Huq and Gregory C. Farrington
Department of Materials Science and Engineering
University of Pennsylvania
Philadelphia, Pa 19104, USA

Abstract

Thin solid films of mixtures of PEGDME and PEO containing various ratios of $ZnBr_2$ and LiBr have been prepared. Equal parts of PEGDME and PEO were used, and the ether oxygen to total metal ratio was kept constant at 16. TG data have shown that the thermal stability of the polymer electrolytes is affected moreso by the zinc salt than the lithium salt. DSC data show that these electrolytes are inhomogeneous mixtures of amorphous regions and crystalline PEO and PEO/salt complexes. Conductivity data did not show a mixed-cation effect.

1. Introduction

A variety of high conductivity polymeric electrolytes have been developed over the past 10-15 years. Most commonly, they consist of polymers such as polyethylene oxide (PEO) or polypropylene oxide (PPO) in which ionic salts are dissolved. Initial investigations were focused, for the most part, on lithium ion conducting electrolytes, but recent years have seen a growth of interest directed towards the synthesis and characterization of other ion conducting polymer electrolytes including those formed by dissolving salts of divalent and trivalent cations (1,2).

Several approaches have been taken to improve the conductivity of polymer electrolytes, including the addition of plasticizers, among them poly(ethylene glycol) (PEG) and poly(ethylene glycol dimethyl ether) (PEGDME). The addition of salts to either PEO or plasticized-PEO strongly influences the conducting properties, thermal stability, melting and glass transition temperatures of the electrolytes (3,4). Studies on glasses (5), beta/beta"- aluminas (6), and a polymer electrolyte of composition, $[0.5Ca(CF_3SO_3)_2 + 0.5Mg(CF_3SO_3)_2][PEO]_{15}$, (7) have shown that the presence of two different cations produces nonlinear deviations in such physical properties as conductivity, dielectric loss and internal friction. The maxima or minima usually observed in these data as a function of the mole fraction of cations have been referred to as the "mixed-cation effect".

---

*Permanent Address: Department of Physics, National University of Singapore, Singapore-0511.

Recent studies on different compositions of $ZnBr_2[xPEGDME+(1-x)PEO]_n$, in which n is the mole ratio of ether oxygens to the metal ions, have shown that the specific composition with n=16 and x=0.5 has an exceptionally high conductivity and good mechanical properties (8). Furthermore, studies of $[xZnBr_2+(1-x)LiBr][PEO]_{16}$ have shown that the conductivity of the mixed-salt electrolytes is higher than that of either pure salt electrolyte (8). Similar studies on $[xMgBr_2+(1-x)LiBr][PEO]_{16}$ and $[xKSCN+(1-x)NaSCN][PPO]_{9.6}$ have shown no mixed-cation effect (8,9). In this paper we present the results of thermal and electrical characterization of solid polymer films of $[xZnBr_2+(1-x)LiBr][0.5PEGDME + 0.5PEO]_{16}$ with x ranging from 0.0 to 1.0.

2. Experimental Procedures

PEO (Aldrich, av. mol.wt.=5×10^6), PEGDME (Polyscience, av. mol.wt.=400), $ZnBr_2$ and LiBr (Aldrich, ultrapure) were used as starting materials. Acetonitrile (Aldrich) was added to PEO which had been dried for ~48 h at ~55°C under dynamic vacuum, and the mixture was stirred for 24 h to form a homogeneous solution. This solution was combined with PEGDME of the same weight as that of PEO and stirred for a further 6 h. To this resulting solution, stoichiometric amounts of $ZnBr_2$ and LiBr which had been earlier dissolved in anhydrous ethanol (Aldrich) were added and stirred for an additional ~18 h to ensure complete dissolution. The solution was then cast in a large glass ring on low-adhesion silicon paper and the solvent evaporated for ~48 h in an open atmosphere. The resulting films were heated at ~60°C for ~48 h under dynamic vacuum to remove residual solvent.

For bulk conductivity measurements, polymer samples of 10 mm diameter and approximately 0.25 mm thickness were placed between two spring loaded stainless steel electrodes. Complex ac impedance analysis was carried out using a Solartron 1250 Frequency Response Analyzer and 1286 Electrochemical Interface controlled by a Hewlett-Packard 9122 microcomputer. To ensure better contact between the electrodes and electrolyte and eliminate residual solvent, all samples except the one for which x=0.0 were first heated to 100°C in a flowing argon atmosphere and then allowed to cool to room temperature. The data reported here were obtained during a second heating cycle after the samples had remained at room temperature overnight under flowing argon.

A DuPont 910 differential scanning calorimeter (DSC) was used to determine the glass transition temperatures, melting temperatures, and other thermal characteristics of the electrolytes. Hermetically sealed samples were used. Thermograms were recorded at a rate of 10°C/min under a nitrogen atmosphere. Each sample was first heated from -120°C to 100°C and then allowed to cool to room temperature. Only those data obtained in a second heating cycle carried out from -120°C to 250°C after a sample had remained overnight at room temperature are reported here. The thermal stability of the samples was studied by heating them in a nitrogen atmosphere at the rate of 10°C/min using a DuPont 951 Thermogravimetric Analyzer.

3. Results and Discussion

3.1 Thermal Studies

Thermogravimetric (TG) studies carried out on the films of various compositions have shown that they decompose in a complicated way. All the films exhibited a relatively small weight loss, <3% , in the temperature range 50 to 100°C, presumably due to the evaporation of residual solvent or moisture absorbed when the samples were loaded. Above 100°C, i.e after complete dehydration, no further weight loss was detected until irreversible decomposition began around 150°C. A typical TG trace, e.g. for $x=0.4$ shown in Fig. 1 (curve a), exhibits the weight loss due to decomposition at three different temperatures, 273, 316 and 368°C, with the maximum weight loss at 368°C(seen clearly in Fig.1 curve b which is a derivative of heat flow with respect to time). Similar observations were made on all other samples with salt compositions in which the value of x ranged from 0 to 1.

In order to understand the origin of the various weight losses, TG experiments had also been carried out on pure PEGDME and PEO with PEGDME taken in equal ratio and the corresponding traces are given in Fig. 1 (curves c and d) for comparison. Curve c shows that the PEGDME begins to volatilize around 150°C with the maximum rate of loss being at 261°C. Curve d shows that the weight loss in PEO with PEGDME taken in equal ratio begins around 200°C instead of 150°C and three distinct weight losses, two minor ones at 305 and 350°C and a major one at 412°C. A comparison of all these data indicates that the first weight loss occurring at 261°C in PEGDME, or at 305°C in PEGDME- plasticized PEO, or at 273°C in PEGDME-plasticized PEO with salt present can be attributed to the loss of PEGDME. The weight loss occuring at about 412°C in PEGDME-plasticized PEO (curve d) appears to be due to the decomposition of PEO itself, as the pure PEO is known to decompose at about 420°C. These results indicate that the thermal stability of PEGDME increases when mixed with PEO, but adding salt to the mixture decreases the thermal stability of the mixture somewhat, just as adding salt to PEO decreases the stability of PEO. Observation of an distinct weight loss which could be attributed to the loss of PEGDME in both PEGDME-plasticized PEO and PEGDME-plasticized PEO with salt suggests that at least a fraction of the PEGDME present in these samples is not as miscible in PEO as normally believed. The weight loss due to the volatilization of PEGDME and the final decomposition temperature (T_d) of PEO were found to depend on salt concentration. T_d varied from 385 to 335°C as the zinc content was increased from 0 to 100%. Thus the overall thermal stability of PEO is more affected by the concentration of the zinc salt than the lithium salt. The source of the decomposition occurring at 350°C in PEGDME-plasticized PEO or at 316°C in the $x=0.4$ composition is not clear.

Detailed DSC studies carried out in the temperature range of -120 to 250°C have shown that all the samples exhibited a glass transition (T_g) at around -45°C and an endothermic peak (T_m) at around 60°C that is attributable to the melting of crystalline PEO. The actual values of T_g and T_m varied with composition. Since the heat of melting for T_m is always less than 156 J/g, the value for crystalline PEO, it would appear that not all of the PEO present in the samples was crystalline. The DSC data for samples of all compositions that had been left at room temperature under vacuum for about 2 to 3 weeks are summarized in Table 1. In addition to T_g and T_m, all lithium-rich samples corresponding to $x < 0.5$ showed an intense broad endothermic peak (T_{m1}) at around 200°C and a small endothermic peak (T_{m2}) at around ±5°C. T_{m1} was noticeable even in those samples in which Zn content is not very high ($x < 0.6$). Since an endothermic peak at about 5°C had been observed in pure PEGDME also, T_{m2} could be attributed to the melting of immiscible PEGDME. The observation of T_{m2} in Li-rich samples alone imply that the effect of PEGDME as plasticizer may become less and less relevant as the concentration of Li-salt is progressively increased. T_{m1} can be attributed to the melting of crystalline PEO/salt complexes, the formation of which depend on the nature of metal ion, its bonding, and kinetics. The absence of T_{m1} in zinc-rich samples, particularly in those for for which $x > 0.6$, clearly shows that the complexation in these samples is relatively slow as compared to that in lithium-rich samples. Furthermore, in the first heating

Table 1: DSC data for $[xZnBr_2 + (1-x)LiBr][0.5PEGDME + 0.5PEO]_{16}$

x	T_g (°C)	T_{m2} (°C)	T_{m3}(°C)	T_m (°C)	T_{m1} (°C)
0.0	-44.0	4.6		63.1	197.8
0.2	-55.3	-7.9		61.6	182.8
0.4	-42.6	-5.7		64.3	208.5
0.5	-48.3		50.9	59.5	232.8
0.6	-44.0		46.0	58.4	191.8
0.8	-32.5		57.1	62.6	
1.0	-42.8		48.0	53.6	

cycle all the zinc-rich samples exhibited a small endothermic peak ($T_{m3} \sim 50^\circ C$) close to that attributed to the melting of crystalline PEO. Since this peak disappeared after the first heating cycle, it may be attributed to the eutectic phase of PEO and PEO/salt complex. This might account for the absence of a high temperature T_{m1} in zinc-rich samples. It also suggests that the dissociation of $ZnBr_2$ may be less-complete compared to that of LiBr in PEGDME-plasticized PEO. All these data imply that the polymer electrolytes studied in the present investigation are inhomogeneous mixtures of amorphous regions, crystalline PEO, and PEO/salt complexes. Although T_g is expected to depend on the salt concentration in the amorphous phase, the presence of crystalline PEO/salt complex phase or eutectic phase of PEO and PEO/salt complex prevents us from making any correlation between the T_g values and salt concentration. Thus the absence of any systematic variation in T_g with salt concentration is not surprising.

3.2 Conductivity Studies

Fig. 2 shows plots of log(σ) vs. 1000/T for various electrolyte samples. The sample with x=0.0, i.e $LiBr[0.5PEGDME + 0.5PEO]_{16}$, has the highest conductivity (3.1×10^{-4} S/cm at 80°C) over the entire temperature range studied, 30 to 80°C, as compared to that (6.0×10^{-5} S/cm at 80°C) for x=1.0, i.e $ZnBr_2[0.5PEGDME + 0.5PEO]_{16}$. While conductivity values for the compositions 0.0<x<0.5 at temperature beyond the melting temperature of PEO are nearly same, for all other compositions the values lie between the above given limits. No mixed-cation effect is observed. The increase in conductivity observed for all the samples at ~60°C corresponds to the melting of crystalline PEO. As was evident from DSC studies, Li-rich samples contain more of immiscible PEGDME and hence less of plasticizing effect. This fact may have great bearing on the lack of observation of mixed-cation effect. The sample for which x=0.0, i.e in which no zinc salt was present, exhibited a decrease in conductivity above 80°C, which may be due to an irreversible decomposition. For this very reason these samples were heated up to 80°C only in the first heating cycle. The addition of zinc salt appears to increase the electrolyte stability.

Reconsidering the DSC data for the composition range $0.7<x<1.0$, the absence of a crystalline PEO/salt complex melting transition and the presence of eutectic phase of PEO and PEO/salt complex melting at ~50°C suggests that any temperature increase above 65°C should release more salt into the amorphous conducting phase. Such a situation should create more effective charge carriers to contribute to the total conductivity if the $ZnBr_2$ is completely dissociated. However, the conductivity showed little change at T~65°C, which suggests that most of the $ZnBr_2$ exists as ion pairs and clusters.

Acknowledgements

This research was supported by the Defense Advanced Research Projects Agency through a contract monitored by the Office of Naval Research. Additional support from the NSF-MRL program under grant no. DMR88-19885 is gratefully acknowledged. One of the authors(BVRC) would like to thank the authorities of the National University of Singapore for granting him sabbatical leave.

References

1. G.C.Farrington and R.G.Linford, *Polymer Electrolyte Reviews II*, J.R. MacCallum and C.A.Vincent, eds., (Elsevier Appl. Sci., New York, 1989)p. 255.
2. P.G.Bruce, J.Nowinski, F.M.Gray and C.A.Vincent, *Solid State Ionics*, 38, 231 (1990).
3. I.E.Kelly, J.R.Owen and B.C.H.Steele, *J.Power Sources*, *14*, 13(1985).
4. H.Yang, R.Huq and G.C.Farrington, *Solid State Ionics*, 40/41, 663(1990).
5. M.D.Ingram, *Phys. and Chem. of Glasses*, *28*,215(1987).
6. P.K.Davies, *J. Solid State Chem.*, *66*, 350(1987).
7. A.Moryoussef, M.Bonnat, M.Fouletier and P.Hichter, *Proc. of the 6th RISO Int. Symposium on Metallurgy and Materials Science*, Roskilde, p. 335(1985).
8. Hong Yang, *Ph. D Thesis*, University of Pennsylvania, Philadelphia, USA (1991).
9. D.Teeters and J.C.Norton, *Solid State Ionics*, 40/41, 648(1990).

Figure Captions

Fig.1. Thermograms of different polymers. (a) for $[xZnBr_2 + (1\text{-}x)LiBr][0.5PEGDME + 0.5PEO]_{16}$ with x=0.4, (b) derivative of curve a with respect to time, (c) for PEGDME, and (d) for PEO+PEGDME taken in equal ratio.

Fig.2. Plots of log(σ) vs. 1000/T for various electrolyte samples in the $[xZnBr_2+(1\text{-}x)LiBr][0.5PEGDME + 0.5PEO]_{16}$ system with x ranging from 0.0 to 1.0.

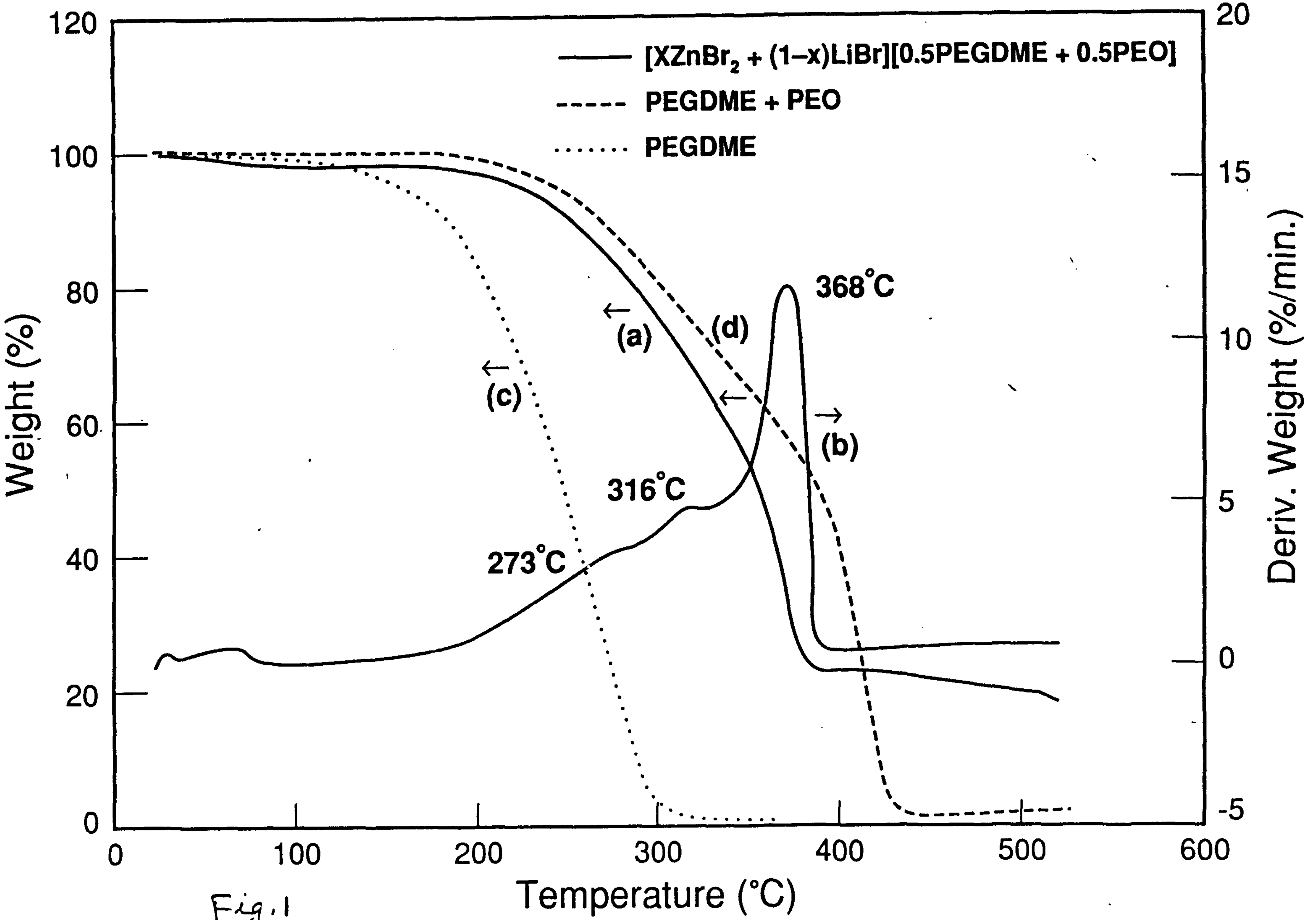
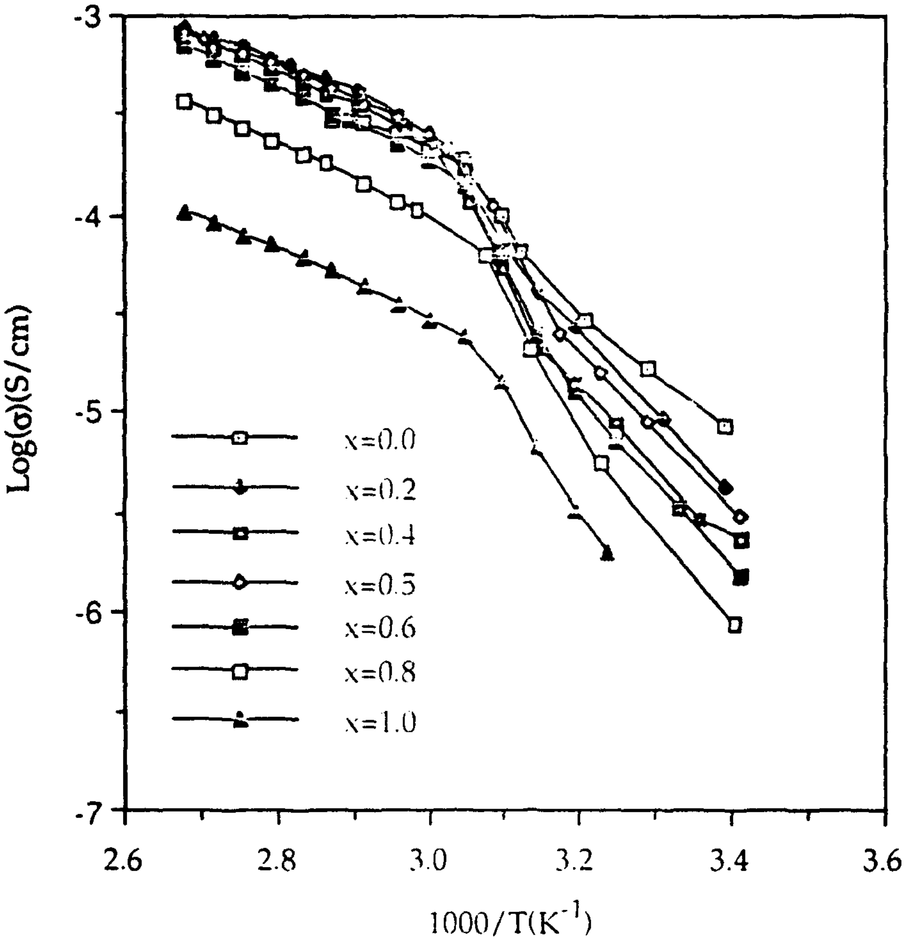

[XZnBr$_2$ + (1−x)LiBr][0.5PEGDME + 0.5PEO]
PEGDME + PEO
PEGDME
Weight (%)
Deriv. Weight (%/min.)
Temperature (°C)
368°C
316°C
273°C
(a)
(b)
(c)
(d)
0
20
40
60
80
100
120
-5
0
5
10
15
20
0
100
200
300
400
500
600

Fig. 1


Log(σ)(S/cm)
-3
-4
-5
-6
-7
2.6
2.8
3.0
3.2
3.4
3.6
1000/T(K^{-1})
x=0.0
x=0.2
x=0.4
x=0.5
x=0.6
x=0.8
x=1.0