

Effect of Poly(vinylidene fluoride) on the Ionic Conductivity and Morphology of PEO-Salt Polymer Electrolytes

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SYNOPSIS

The high dielectric constant polymer poly(vinylidene fluoride) (PVDF) was blended with PEO-salt polymer electrolytes to improve their ionic conductivity. PVDF did improve the room-temperature ionic conductivity of the polymer electrolytes PEO-LiCF₃CO₂ and PEO-LiBF₄, and the ionic conductivity at room temperature went up one order of magnitude with 10⁻⁵S/cm for LIB4M-PF4 being the most prominent. PVDF exhibited strong effects on the ionic conductivity and morphology of the polymer electrolytes, such as weakening the association of poly(ethylene oxide) (PEO) with the salt, hindering the formation of the PEO-salt complex, enlarging the crystalline PEO phase in LIA_nM-PF_m polymer electrolytes, and reducing the crystalline PEO phase in LIB_nM-PF_m polymer electrolytes. Both LIA4M-PF4 and LIB4M-PF4 polymer electrolytes formed a new PEO-PVDF-salt complex. The new complex in the former was crystalline, but that in the latter was amorphous. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Since the discovery of high ionic conductivity from blending PEO with potassium salts by Fenton et al.,¹ polymer electrolytes have attracted a lot of interest, especially in thin film batteries. Polymer electrolytes consist of polar polymers and ionizable salts. The Li⁺ ion is the smallest metal ion, and lithium salts are among the most favored salts in polymer electrolytes. PEO is the most popular polymer used, due to its high solvating power with metal ions, good processability, and mechanical properties.²⁻⁶ Although the ionic conductivity of the PEO-salt polymer electrolytes at 100°C can be up to 10⁻⁴ ~ 10⁻³S/cm, the conductivity at room temperature is poor, usually hardly higher than 10⁻⁶S/cm. Therefore, much effort has been devoted to improving the ambient ionic conductivity of the polymer electrolytes by improving the cation's migration in the amorphous domain or in the helical structure of the crystalline. Since ions primarily

transport in the amorphous phase, many investigations aimed at improving ionic conductivity have focused on increasing the amorphous phase of the material. The ambient ionic conductivity can also be improved by introducing flexible chains into the copolymer main chain⁷ or by adding ceramic powder.⁸

Munshi⁹ and Rietman¹⁰ reported that the anions of the salts strongly influenced the conductivity behavior of the polymer electrolytes with the formation of ion-pairs resulting in a decrease of conductivity at high salt concentration. Also the energy required to separate the ion-pair was inversely proportional to the dielectric constant of the medium, which can be as low as 5 in the PEO-salt polymer electrolyte system. When the salt concentration exceeded the threshold point, the ionic conductivity began to decrease with salt concentration, due to the formation of ion-pairs. PVDF, a polymer with the high dielectric constant $\epsilon' = 8 - 13$, has been used to prepare polymer electrolytes.¹¹⁻¹² The ionic conductivity of PVDF-salt polymer electrolytes was somewhat lower than that of PEO-salt polymer electrolytes. We surmise that the stronger bonding of the metal ion to the fluorine atom than to the oxygen atom

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reduced the metal ion mobility in PVDF-salt polymer electrolyte, resulting in less conductivity than expected.

In this study, PVDF was blended as a minor component with PEO and salt to improve the ionic conductivity of the polymer electrolytes. The salts described in this paper include an organic salt and an inorganic salt. Both PVDF and PEO are polar polymers and have some compatibility with each other. We expected that the blending of PVDF with PEO might increase the amorphous phase and the dielectric constant of the medium, keeping the PEO contribution to the ionic conductivity.

EXPERIMENTAL

The polymer electrolyte films containing lithium salts were prepared by casting the polymer electrolyte solutions on surface-treated glass plates. The lithium salts LiCF_3CO_2 and LiBF_4 , acetonitrile, and PEO (molecular weight 200,000) were commercially available from Aldrich. PVDF was obtained from Dynamit Nobel. Before preparing polymer electrolytes, the lithium salts were dried in a vacuum oven at 90°C for 24 hours, and the polymers PEO and PVDF were also vacuum-dried at a temperature below the melting point of the polymers for 24 hours. Both the polymers and the salts were weighed in a nitrogen dry box at the desired molar ratios, denoted as "n," of monomeric units of both PEO and PVDF to that of the salts. The "n" values were equal to 16 and 4 in this study. Acetonitrile was used as a solvent. The polymer electrolyte solutions were stirred for 48 hours to make them homogeneous. The molar ratios of the monomeric units of PEO to that of PVDF, denoted as "m," were 4, 9, 15, 24, and 49. In this paper the polymer electrolytes are denoted as follows:

Polymer Electrolyte	Abbreviation
PEO- LiCF_3CO_2	LIA _n M, n = 16 or 4
PEO/PVDF- LiCF_3CO_2	LIA _n M-PF _m , m = 4, 9, 15, 24, 49
PEO- LiBF_4	LIB _n M
PEO/PVDF- LiBF_4	LIB _n M-PF _m

in which LIA_nM and LIB_nM represent the polymer electrolytes composed of polymer matrix PEO and salt LiCF_3CO_2 , and of PEO and LiBF_4 , respectively; and PF represents the incorporation of the second polymer matrix PVDF.

After casting on the glass plates, the samples were vacuum-dried at room temperature for 24 hours and

then at 70°C for 30 hours. Dry air was used to release the vacuum and the samples were immediately covered and stored in an electronic desiccator until tested. The sample preparation was handled with care in the dry box to exclude interference from water in air. The balance was also placed in the dry box for weighing. The dry box was first evacuated and then refilled with dry air, the operation was repeated several times, and finally the box was further dried with P_2O_5 powder.

The thermal transitions of the polymer electrolyte films were measured with a Seiko differential scanning calorimeter (DSC) at $10^\circ\text{C}/\text{min}$. in a dry nitrogen stream of 50 cc/min. The samples were preheated in the DSC cell at 120°C for 5 minutes in the dry nitrogen stream to evaporate any condensed water on site and then cooled to 0°C for DSC measurement. The dynamic ionic conductivity measurements of the solid polymer electrolytes were performed on a DuPont 2970 dielectric analyzer at 300KHz. This test was scanned at $3^\circ\text{C}/\text{min}$. under a dry nitrogen flow of 500 cc/min. It is generally accepted that the high-frequency response of the polymer electrolytes in an alternating electrical field reveals information on the electrical properties of the electrolytes themselves. The X-ray diffraction spectra were measured using a Siemens D5000 X-ray diffractometer. The X-ray sample chamber was first dried with P_2O_5 powder overnight before a sample was inserted for measurement.

RESULTS AND DISCUSSION

The ionic conductivities of PEO-salt polymer electrolytes with or without PVDF at room temperature are listed in Table I. The addition of PVDF to PEO-salt polymer electrolytes improved the room temperature ionic conductivity by a factor of 2 to 9, depending on the types and the concentration of salts. LIB4M-PF4 exhibited the highest conductivity of $10^{-5}\text{S}/\text{cm}$ (at 25°C) among the tested samples.

Table I The Ionic Conductivity of Polymer Electrolytes

Polymer Electrolytes	σ , S/cm 25°C	Polymer Electrolytes	σ , S/cm 25°C
LIA-16M	1.1×10^{-7}	LIB16M	2.0×10^{-6}
LIA16M-PF15	1.1×10^{-6}	LIB16M-PF24	5.9×10^{-6}
LIA4-M	8.0×10^{-8}	LIB4M	1.2×10^{-6}
LIA4M-PF24	4.7×10^{-7}	LIB4M-PF4	1.0×10^{-5}

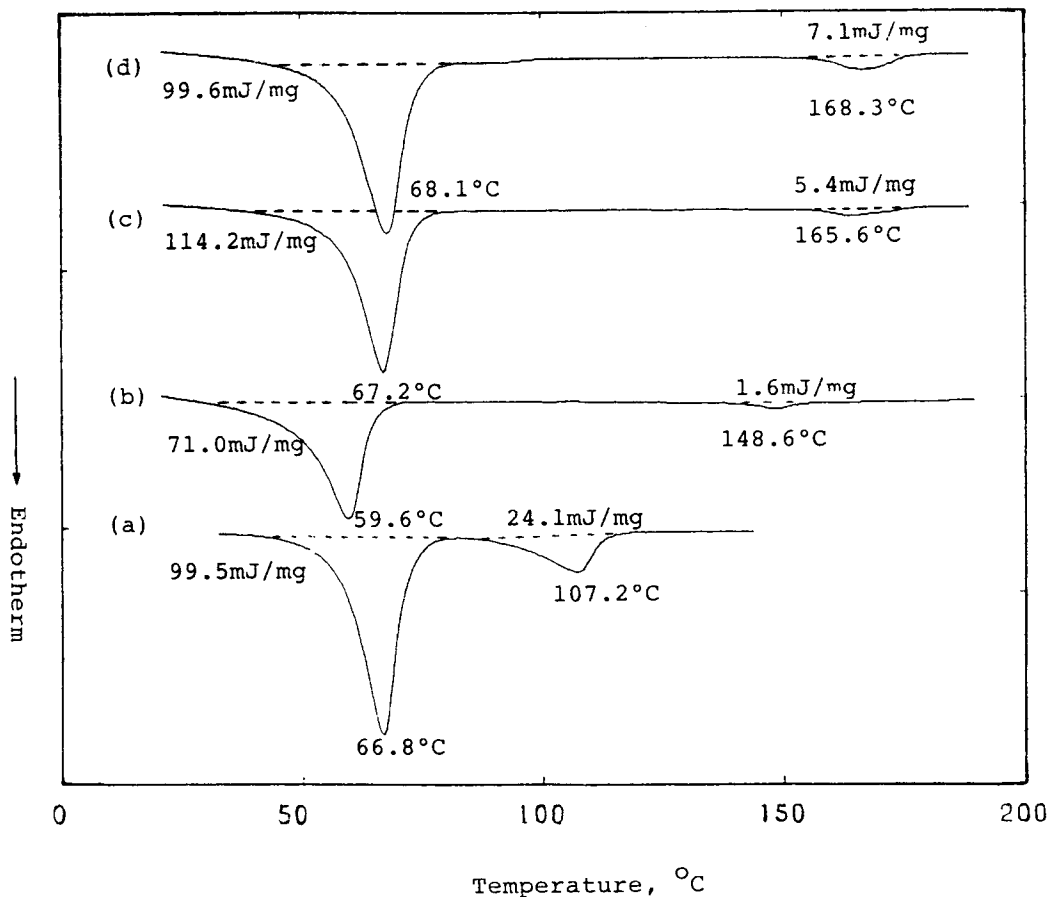


Figure 1 DSC thermograms of polymer electrolytes (a) LIA16M, (b) LIA16M-PF24, (c) LIA16M-PF15, and (d) LIA16M-PF9.

The cast sample of LIB4M is solid and non-sticky, but that of the LIB4M-PF4 films is soft and sticky even after drying in a vacuum oven for several days. No solvent loss was found on this sample by TGA. As PVDF is a semicrystalline polymer melting above 150°C, the softening of LIB4M-PF4 is not due to the inherent character of PVDF. It might be believed that PVDF exhibited strong interaction with PEO and LiBF₄ and caused a strong effect on the morphology of the polymer electrolytes, which in turn affected the ionic conductivity.

The Thermal Transitions of PEO-salt Electrolytes

The DSC thermograms and data in Figures 1, 2, 4, and 5 display three different thermal transitions in the polymer electrolytes. The lowest melting point (near 55-70°C) was from the crystalline PEO phase, the second melting point (near 105-130°C) was from the crystalline PEO-Li⁺ complex phase, and the third melting point (near 150-170°C) was from the crystalline PVDF phase. The addition of PVDF to

LIA16M polymer electrolyte resulted in the disappearance of crystalline PEO-LiCF₃CO₂ complex (in Fig. 1), demonstrating that PVDF reduced the association of PEO with the organic salt LiCF₃CO₂ and disintegrated the crystalline phase in LIA16M. In these LIA16M-PFm polymer electrolytes the crystalline PVDF phase increases with the PVDF concentration, but the effect of PVDF on the crystalline PEO phase is complicated and concentration-dependent. The PEO crystalline phase in LIA16M-PF24 was less than that in LIA16M. More crystalline PEO phase was present in LIA16M-PF15 than in LIA16M-PF24 or even in LIA16M. The crystalline PEO phase in LIA16M-PF9 was more than that in LIA16M-PF24 but less than that in LIA16M-PF15. We postulate that the blending of PVDF in LIA16M-PFm leads to two competitive effects: (1) the disintegration of the original crystalline PEO phase by introducing PVDF into the polymer electrolyte, and (2) the formation of new PEO phase (both crystalline and amorphous) due to weakening the association of the PEO-salt complex (amor-

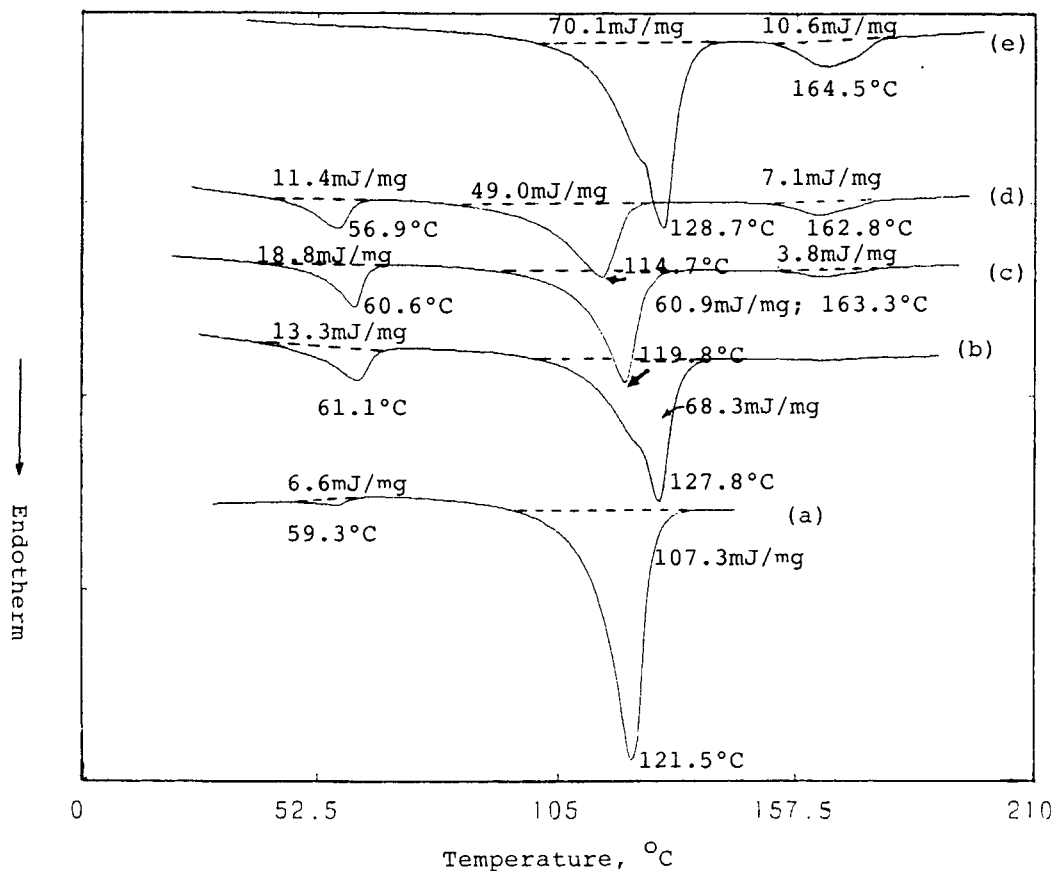


Figure 2 DSC thermograms of polymer electrolytes (a) LIA4M, (b) LIA4M-PF49, (c) LIA4M-PF24, and (d) LIA4M-PF15, and (e) LIA4M-PF4.

phous phase only; no crystalline phase was found in LIA16M-PFm) by increasing the dielectric constant of the polymer electrolytes with PVDF concentration. This complication was also revealed in the series of LIA4M-PF49, LIA4M-PF24, and LIA4M-PF15. According to Fedors¹³, one can estimate the solubility parameters of polymers by means of the group contributions to the cohesive energy and the molar volume: it is found that the solubility parameters of PEO and PVDF are close to each other with $19.17 \text{ (J/cm}^3)^{1/2}$ for PEO and $19.15 \text{ (J/cm}^3)^{1/2}$ for PVDF; and that the molar volumes of these two polymers are also close, with $36.0 \text{ cm}^3/\text{mole}$ for PEO and $36.9 \text{ cm}^3/\text{mole}$ for PVDF. This means that PEO and PVDF have excellent miscibility and good space fitting with each other. When PVDF was incorporated into the PEO-salt polymer electrolytes, both the excellent polymeric miscibility and good space fitting of these two polymers easily caused the destruction of the PEO crystallinity and the enhancement of the dielectric constant to weaken the association of PEO-salt complex and to raise the conductivity.

Thermal characteristics of LIA4M-PFm polymer electrolytes are shown in Figure 2. The crystalline PVDF phase increased with the PVDF content but the crystalline PEO-LiCF₃CO₂ complex phase first decreased, with PVDF content changing from PF49 to PF15 and then increasing at PF4. However, the crystalline PEO phase of LIA4M-PFm went up to a maximum at PF24 and then vanished at PF4. The abnormal ΔH_m of LIA4M-PF4 (melting peak at 128.7°C) might be due to the melting of a new crystalline PEO/PVDF/LiCF₃CO₂ complex, which has been confirmed by X-ray diffraction spectra in Figure 3. The peaks at $2\theta = 19.4^\circ - 20.0^\circ$ were the characteristic peaks of the crystalline PVDF phase. The X-ray spectrum of LIA4M-PF4 showed two new peaks at 29.23° and 41.20° , which did not appear in the spectrum of LIA4M-PF49. The X-ray spectrum of LIA4M-PF4 was quite different from that of LIA4M-PF49 except for the crystalline PVDF peaks. This might mean that there was a new crystalline complex in LIA4M-PF4.

The DSC thermogram data on the thermal transitions of LIB16M-PFm and LIB4M-PFm are

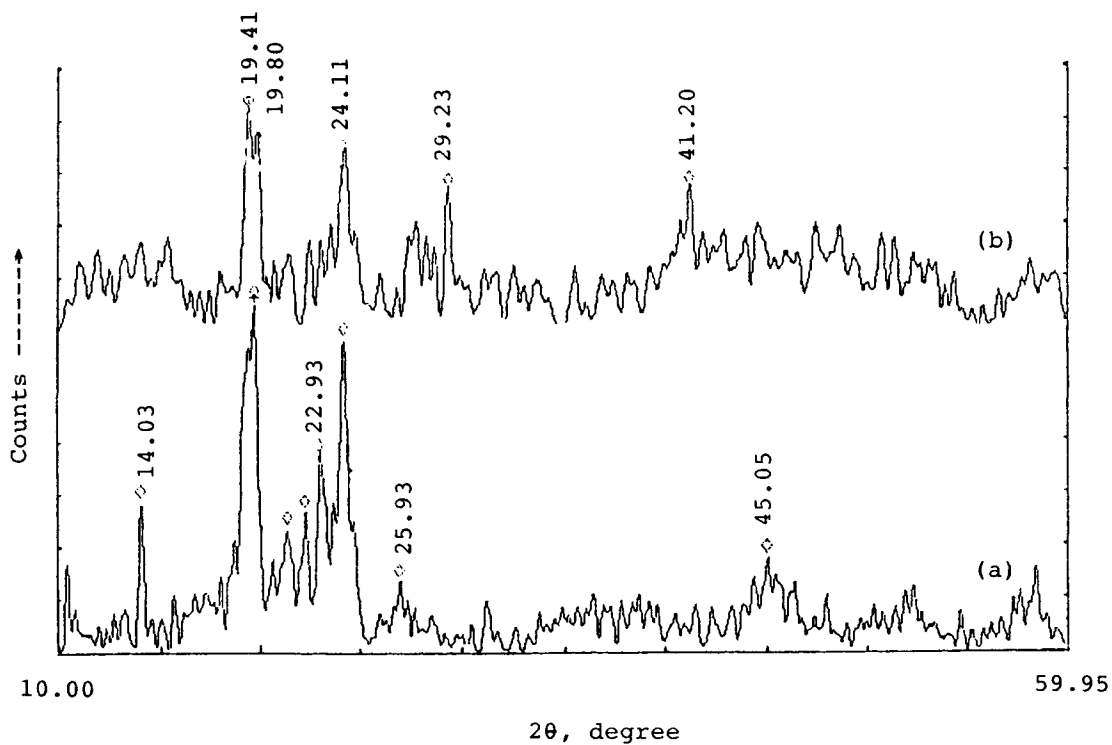


Figure 3 X-ray diffraction spectra of the polymer electrolytes (a) LIA4M-PF49 and (b) LIA4M-PF4.

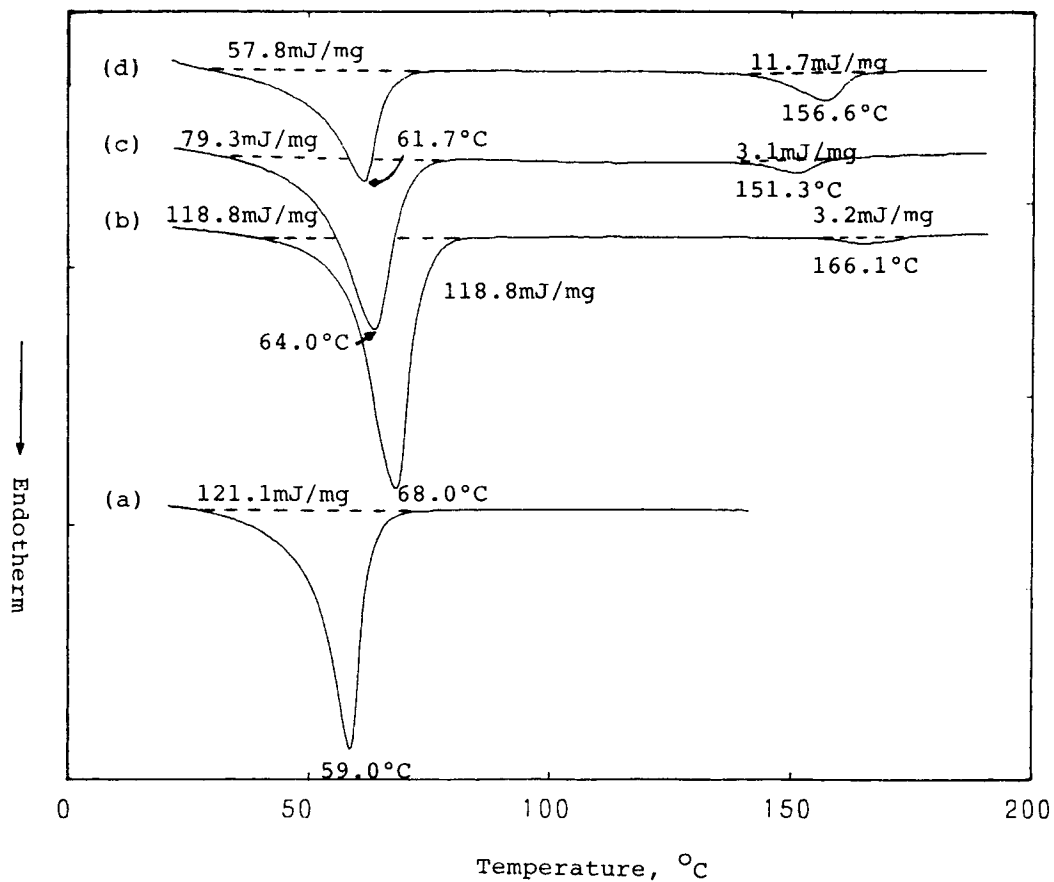


Figure 4 DSC thermograms of polymer electrolytes (a) LIB16M, (b) LIB16M-PF24, (c) LIB16M-PF15, and (d) LIB16M-PF4.

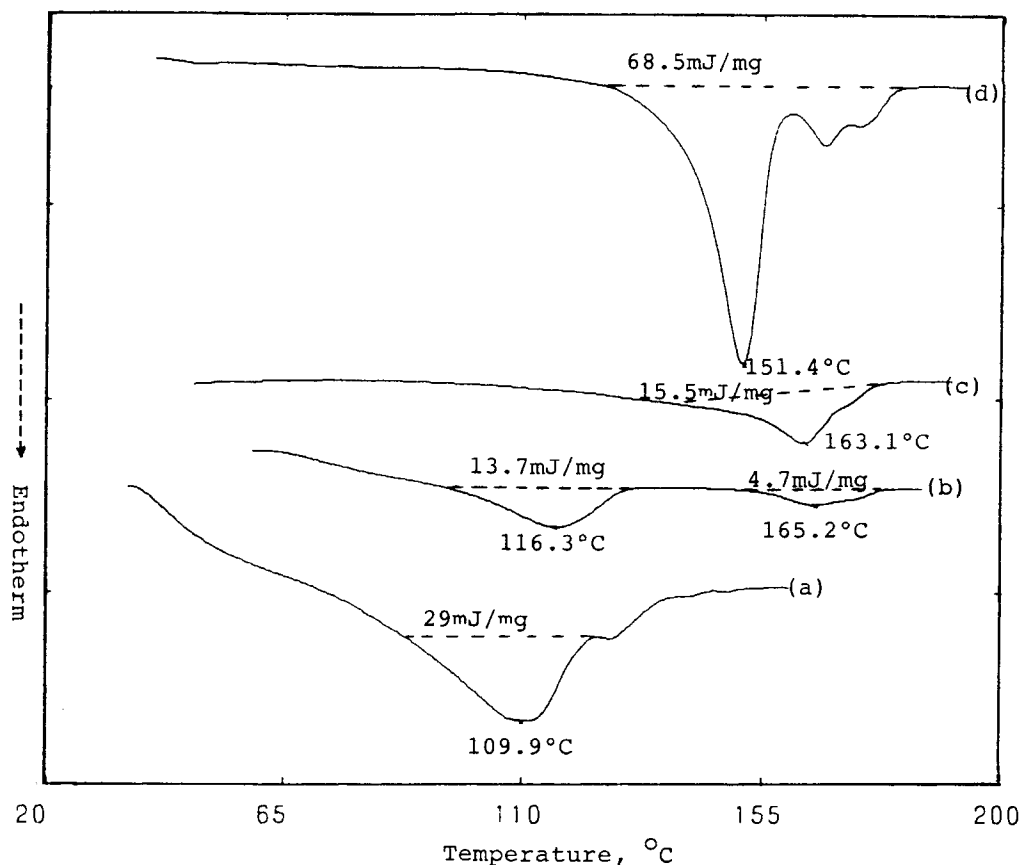


Figure 5 DSC thermograms of polymer electrolytes (a) LIB4M, (b) LIB4M-PF24, (c) LIB4M-PF15, and (d) LIB4M-PF4.

shown in Figures 4 and 5, respectively. No PEO-LiBF₄ crystalline complex phase was found in LIB16M, but a trace amount was found in LIB4M. A major peak for the crystalline PEO phase was found in LIB16M, but not in LIB4M. A higher PVDF content in the LIB16M-PFm series led to a reduction in the crystalline PEO major peak and an increase in the crystalline PVDF minor peak, with a crystalline complex peak absent. In the LIB4M-PFm series, the crystalline PEO-LiBF₄ complex phase of LIB4M-PF24 was much less than that of LIB4M; this phase was not found in LIB4M-PF15 or LIB4M-PF4 polymer electrolyte. No crystalline PEO phase was found in the three LIB4M-PFm, either. The peak associated with the crystalline PVDF phase in LIB4M-PFm series increased with the PVDF content. The peak at 151 °C in LIB4M-PF4 was much larger. It revealed that the introduction of PVDF into LIB4M resulted in the disintegration of the crystalline PEO-salt complex and finally led to the formation of a new PEO-PVDF-salt complex in LIB4M-PF4, which is sticky. As we

have mentioned elsewhere,¹⁴ the association of PEO with LiBF₄ was much weaker than with LiCF₃CO₂ and the PEO-LiBF₄ complex was much less than the PEO-LiCF₃CO₂ complex in the polymer electrolytes. The formation of the new PEO phase, due to the dissociation of the PEO-salt complex of the electrolytes by introducing PVDF, became much less important in LIBnM-PFm than in LIAnM-PFm. Therefore, the introduction of PVDF in LIB16M and LIB4M led to a reduction in the crystalline PEO phase and the crystalline PEO-salt complex phase.

The sticky characteristic of LIB4M-PF4 is quite peculiar. LIB4M is a solid polymer electrolyte. PEO is highly crystalline with a melting point of 65 °C and a glass transition temperature of -60 °C. PVDF is semicrystalline with a melting point higher than 150 °C and a glass transition temperature of -40 °C. Both polymers have high crystallizability. All the blends of PEO and PVDF (at various ratios) exhibited two melting peaks: one corresponded to the melting of the crystalline PEO phase and the other corresponded to the melting of the crystalline PVDF

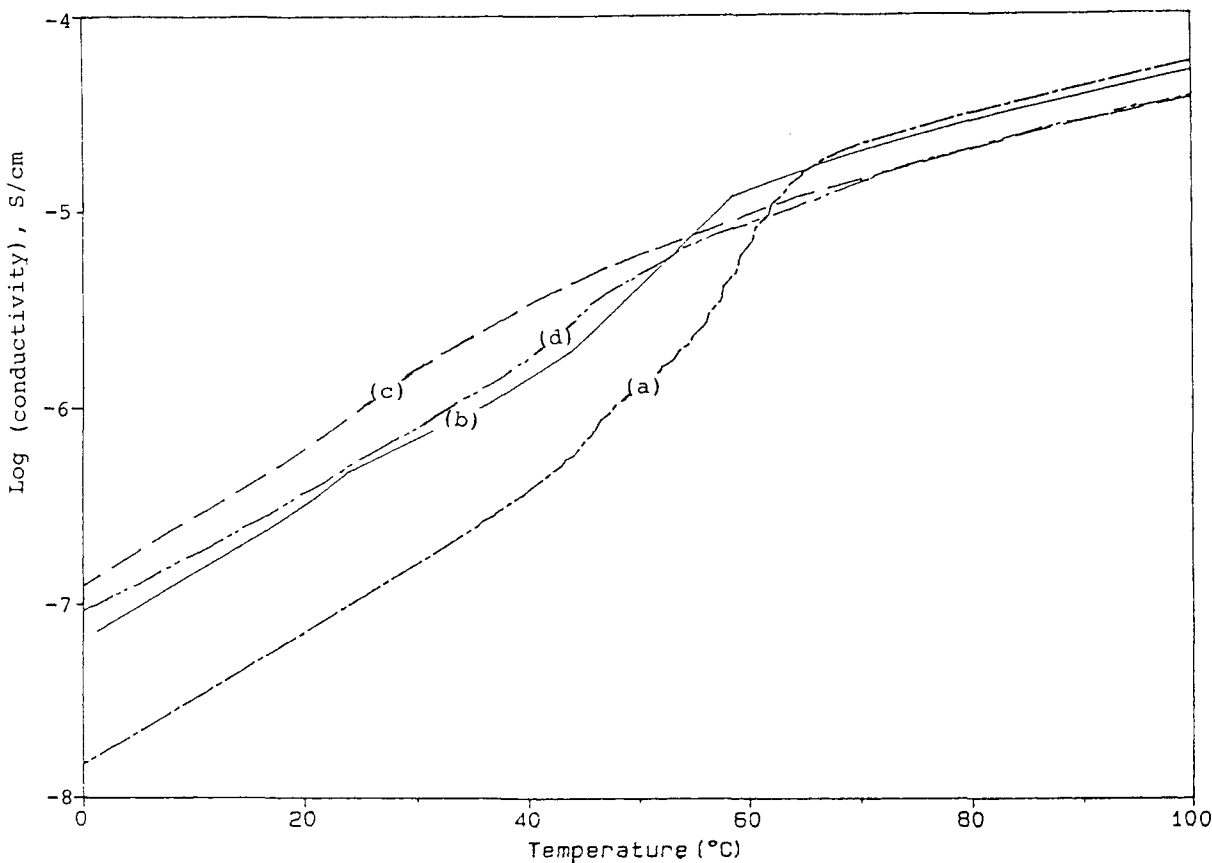


Figure 6 Ionic conductivities of polymer electrolytes (a) LIA16M (— · —), (b) LIA16M-PF24 (—), (c) LIA16M-PF15 (— — —), and (d) LIA16M-PF9 (— · · —).

phase. It is clear that the salt LiBF_4 in the polymer electrolyte LIB4M-PF4 assisted the PVDF polymer in disintegrating the crystalline PEO phase and the crystalline PEO-salt complex into amorphous phases, and that sufficient PVDF could make the disintegration complete. In the LIA16M-PFm and LIA4M-PFm series, only LIA4M-PF4 formed a new complex phase. This showed that sufficient amounts of PVDF and salt were required to completely disintegrate the crystalline PEO and complex in the polymer electrolytes to form a new complex. With the aid of the salt LiBF_4 to hinder the crystallization of these two polymers in LIB4M-PF4, the amorphous PEO phase which was miscible with the amorphous PVDF phase easily mixed to form a new complex phase with the salt. The complex phase was amorphous. The sticky characteristic of LIB4M-PF4 was due to the amorphous PEO and the amorphous PVDF being in the rubbery state at room temperature. The endothermic peak in the DSC curve of LIB4M-PF4 was attributed to the thermal dissociation between the polymer matrix and the salt in the new complex.

Ionic Conductivity

The effect of PVDF on the ionic conductivity of LIA n M-PF m series is shown in Figures 6–9. At low temperatures, all the polymer electrolytes containing PVDF displayed a higher ionic conductivity than the corresponding polymer electrolytes without PVDF. The definition of “low temperature” depended on the polymer electrolytes: 55°C for LIA16M-PFm, 75°C for LIA4M-PFm, 35°C for LIB16M-PFm, > 100°C for LIB4M-PFm. At temperatures higher than 65°C for LIA16M-PFm and 85°C for LIA4M-PFm, the effect of PVDF on the ionic conductivity for these two types of polymer electrolytes became negligible. The low-temperature ionic conductivity of LIA16M-PFm polymer electrolytes followed this order: LIA16M-PF15 > LIA16M-PF9 > LIA16M-PF24. In the meantime, the fraction of the crystalline PEO phase in the electrolytes followed the same order. The room-temperature ionic conductivities of LIA4M-PFm followed the same order as the fraction of their crystalline PEO phase: LIA4M-PF24 > LIA4M-

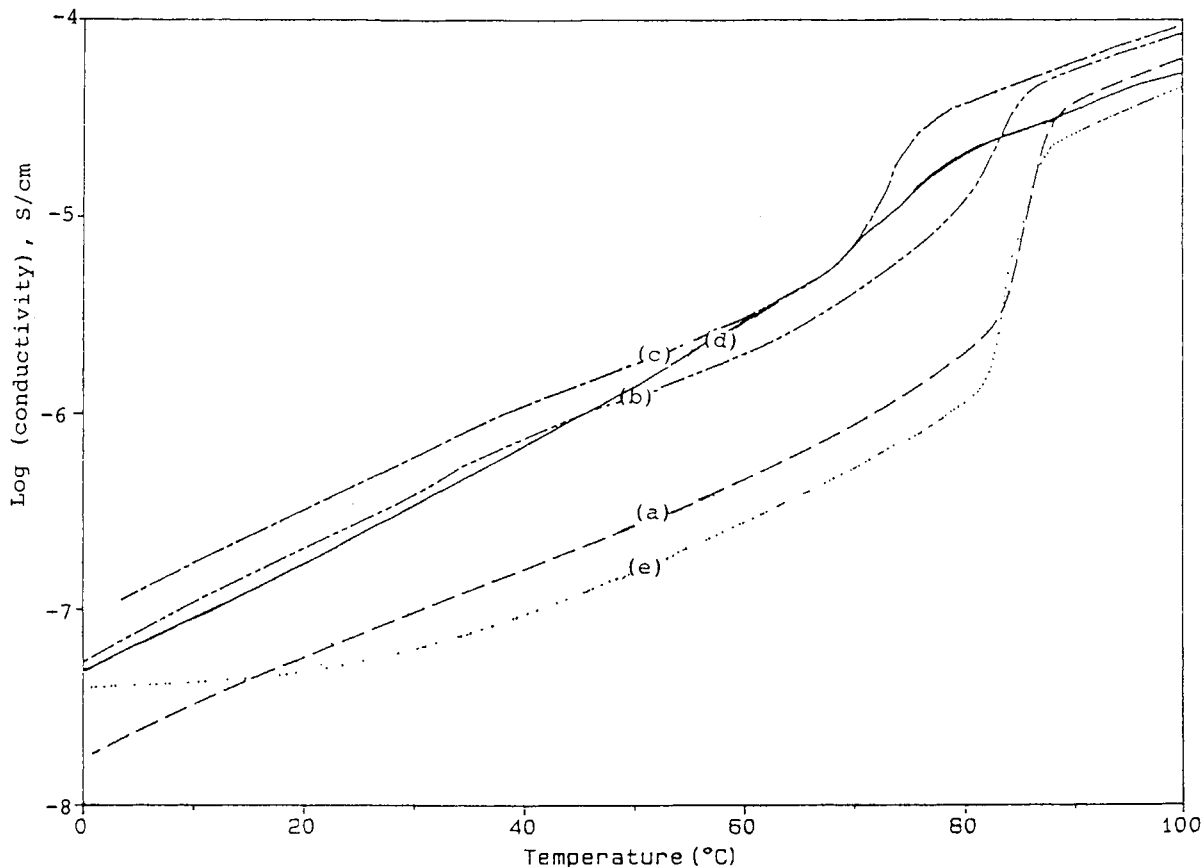


Figure 7 Ionic conductivities of polymer electrolytes (a) LIA4M (---), (b) LIA4M-PF49 (-·-·-), (c) LIA4M-PF24 (---), (d) LIA4M-PF15 (-), and (e) LIA4M-PF4 (····).

PF49 > LIA4M-PF15 > LIA4M-PF4. The high dielectric constant PVDF can increase the dielectric constant of LIA_nM-PF_m polymer electrolytes and weaken the association of the PEO-LiCF₃CO₂ complex. The reduction of the PEO-salt association in the polymer electrolytes may have caused the formation of some new PEO phase released from the PEO-LiCF₃CO₂ complex and higher ionic conductivity. The fraction of PEO phase might also be used as an indicator of the strength of PEO-salt association in LIA_nM-PF_m. The greater the fraction of the PEO phase, the lower the strength of the PEO-salt association and the higher the ionic conductivity.

The effect of PVDF on the ionic conductivities of LIB16M-PF_m polymer electrolytes was complicated. At low temperature the conductivities followed this order: LIB16M-PF4 ~ LIB16M-PF24 > LIB16M; but at high temperature (> 40°C) the conductivities followed the same order as the fraction of the PEO crystalline phase in the polymer electrolytes: LIB16M-PF4 < LIB16M-PF24 < LIB16M.

The addition of PVDF to LIB16M polymer electrolyte improved the low-temperature ionic conductivity, possibly due to an increase in the dielectric constant of the matrix and a reduction in the association of PEO with the salt. However, the ionic association in LIB_nM polymer electrolytes was much weaker than that in the corresponding LIA_nM polymer electrolytes, making them insensitive to the presence of more PVDF within the homologous series. This explains why the low-temperature ionic conductivities of LIB16M-PF24 and LIB16M-PF4 are similar. At temperatures higher than 45°C the crystalline PEO phase melted and changed to amorphous phase, but PVDF did not melt until above 150°C. Therefore the polymer electrolyte having the more amorphous PEO phase gave higher ionic conductivity: LIB16M > LIB16M-PF24 > LIB16M-PF4.

In LIB4M-PF_m homologues, all the polymer electrolytes containing PVDF exhibited higher ionic conductivity than LIB4M (shown in Figure 9), which did not contain PVDF, in the testing temperature range of 0°C to 100°C. It was found that

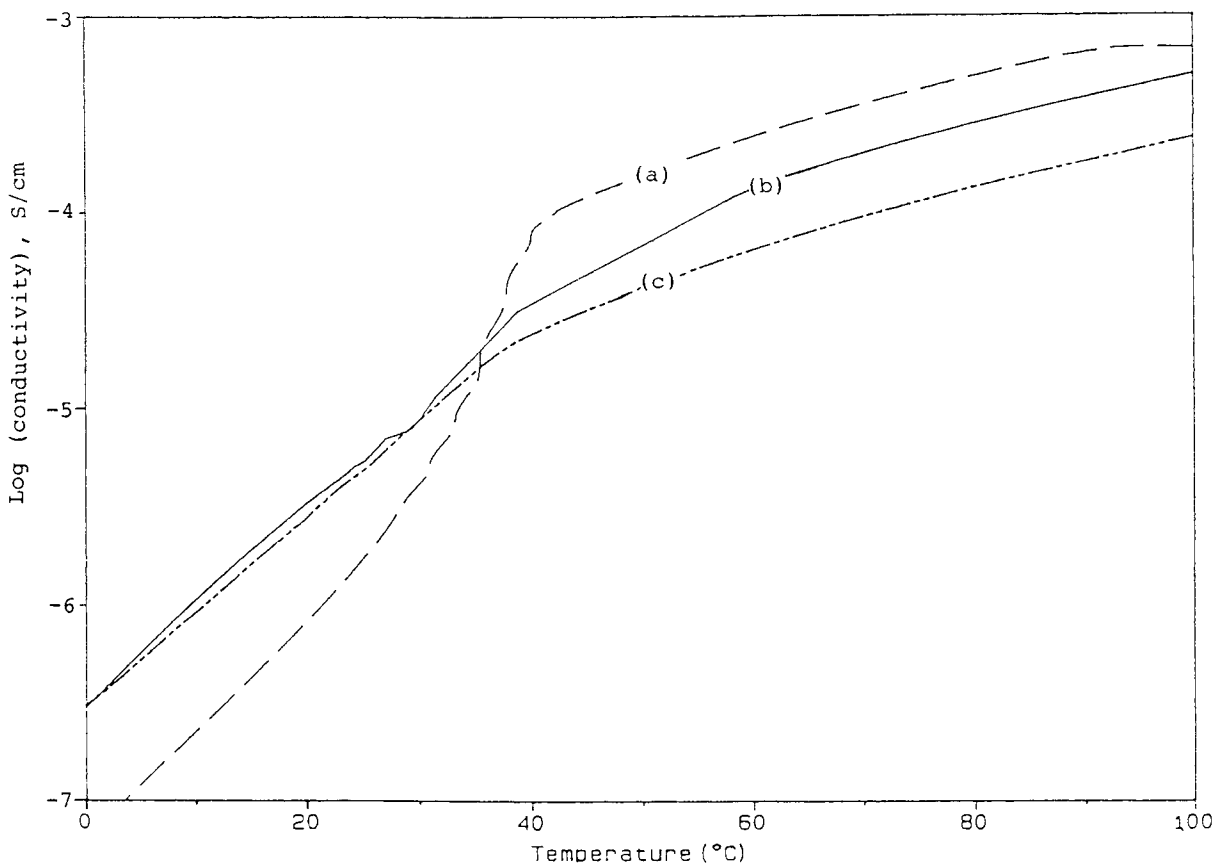


Figure 8 Ionic conductivities of polymer electrolytes (a) LIB16M (---), (b) LIB16M-PF24 (-), and (c) LIB16M-PF4 (-·-·-·-).

the ionic conductivity of LIB4M-PF_m polymer electrolytes increased with the PVDF concentration at temperatures from 0°C to 100°C except at temperatures higher than 80°C, where the ionic conductivity of LIB4M-PF24 polymer electrolyte crossed a bit over that of the LIB4M-PF15 sample. As shown in Figure 5, the crystalline PEO-salt complex was found in LIB4M, but it disappeared in LIB4M-PF15 and LIB4M-PF4. PVDF promoted the dielectric constant of LIB4M-PF_m polymer electrolytes and reduced the association of PEO-salt complex; therefore, the ionic conductivity of LIB4M-PF_m increased with the PVDF concentration. LIB4M-PF4 even became amorphous and sticky. Owing to its peculiar and favorable morphology, LIB4M-PF4 exhibited the best room temperature ionic conductivity of 10^{-5} S/cm.

CONCLUSION

PEO and PVDF have excellent miscibility and good space fitting with each other. When PVDF was in-

corporated into the PEO-salt polymer electrolytes, both the excellent polymeric miscibility and good space fitting of these two polymers easily caused the destruction of the PEO crystallinity and the enhancement of the dielectric constant to weaken the association of PEO-salt complex and to raise its conductivity. The addition of PVDF to PEO-salt polymer electrolytes significantly improved the room temperature ionic conductivity by a factor of 2 to 9. The highest conductivity was 10^{-5} S/cm for LIB4M-PF4. The association of PEO with LiBF₄ was much weaker than with LiCF₃CO₂, and PEO-LiBF₄ complex was much less than PEO-LiCF₃CO₂ complex in the polymer electrolytes. The formation of the new PEO phase due to the dissociation of PEO-salt complex of the electrolytes by introducing PVDF became much less important in LIB_nM-PF_m than in LIAnM-PF_m. Therefore, the introduction of PVDF in LIB16M and LIB4M led to a reduction in the crystalline PEO phase and the crystalline PEO-salt complex phase, but in the LIAnM-PF_m series the effect of PVDF on the crystalline PEO phase was more complicated.

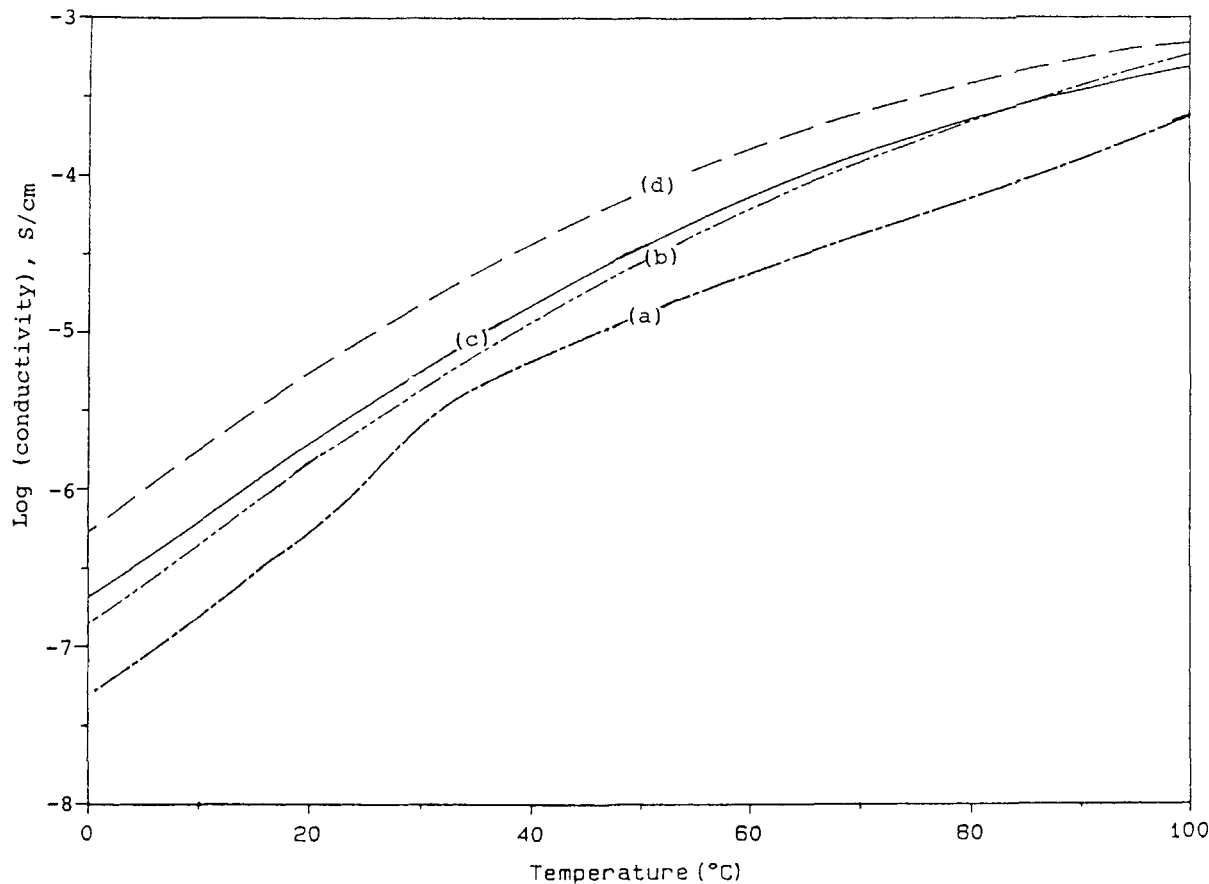


Figure 9 Ionic conductivities of polymer electrolytes (a) LIB4M (-·-), (b) LIB4M-PF24 (-··-), (c) LIB4M-PF15 (-), and LIB4M-PF4 (- - -).

Both the LIA_nM-PF_m and LIB_nM-PF_m series with a sufficient amount of PVDF (PF4) and salt (4M) formed a new complex. The new complex of LIA4M-PF4 was crystalline, but that of LIB4M-PF4 was amorphous and sticky. In addition to the effect of blending on reducing the crystallization of the polymer matrices, LiBF₄ salt might also assist in hindering the crystallization of these two polymer matrices. At room temperature the amorphous PEO and PVDF are in the rubbery state. The amorphous PEO is miscible with the amorphous PVDF and the two easily mixed with each other to form one new complex with the salt. LiCF₃CO₂ interacted with the polymer matrices more strongly than LiBF₄, so it formed crystalline complexes with the polymer matrices more easily than LiBF₄. The high room-temperature conductivity of LIB4M-PF4 was related to its amorphous and sticky morphology.

The fraction of PEO phase could be used as an indicator of the strength of the PEO-salt association

in LIA_nM-PF_m. The lower the PEO-salt association, the higher the fraction of the PEO phase. The ionic conductivity of LIA_nM-PF_m increased with the fraction of the PEO phase. LIB_nM polymer electrolytes had much weaker association of PEO-salt than LIA_nM polymer electrolytes. The ionic conductivity of LIB16M-PF_m was less sensitive to the presence of more PVDF within the homologous series than that of LIA_nM-PF_m. At room temperature the ionic conductivity of LIB16M-PF24 was close to that of LIB16M-PF4. In the LIB4M-PF_m series, the ionic conductivity increased with the PVDF content. The high room-temperature conductivity of LIB4M-PF4 is related to its peculiar morphology.

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