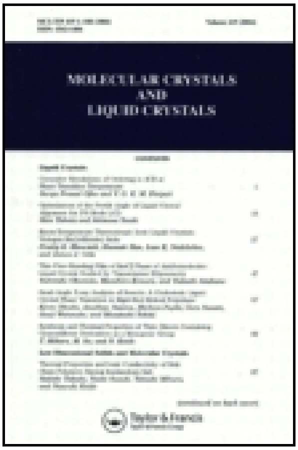

Molecular Crystals and Liquid Crystals

Solid Polymeric Electrolytes Based on Poly(vinylpyrrolidone-co-methacrylic acid) Blends

D. C. Dragunski [a] , A. P. Romani [a] , H. P. M. Oliveira [a] , M. H. Gehlen [a] & A. Pawlicka [a]

[a] Instituto de Química de São Carlos, Universidade de São Paulo, São, Carlos -SP, Brazil

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Solid Polymeric Electrolytes Based on Poly(vinylpyrrolidone-*co*-methacrylic acid) Blends

D. C. Dragunski
A. P. Romani
H. P. M. Oliveira
M. H. Gehlen
A. Pawlicka
Instituto de Química de São Carlos, Universidade de São Paulo,
São Carlos – SP, Brazil

Solid polymeric electrolytes based on poly(vinylpyrrolidone) plasticized with dioctylftalate and containing LiCl salt were obtained. The samples were prepared as membranes in the co-polymerization process of vinylpyrrolidone (VP) with methacrylic acid (20% in VP mass) and tetraethylene glycol diacrylate (10% in VP mass) as cross-linking agent. The ionic conductivity measurements as a function of plasticizant contents revealed that the best results were achieved with 20% (in VP mass) of dioctylftalate. The influence of lithium salt on the ionic conductivity measurements was also verified and the samples containing 20% of plasticizant and 8% (in VP mass) of LiCl showed conductivity of $3 \cdot 10^{-3}$ S/cm. From the measurements of ionic conductivity as a function of temperature an increase was observed in the conductivity values of one order of magnitude reaching 10^{-2} S/cm at 80°C. The activation energy value obtained from these measurements was 25 kJ/mol, which it was comparable with other solid polymeric electrolytes. These new SPEs based on poly(vinylpyrolidone) showed very good conductivity values at room temperature and are very good candidates to be applied in new devices.

Keywords: plasticization; poly(vinylpyrrolidone); solid polymeric electrolytes

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Address correspondence to A. Pawlicka, Departamento de Fisico-Quimica, Instituto de Química de São Carlos, Universidade de São Paulo, CP 780, CEP 13560-970 São Carlos – SP, Brazil. E-mail: Agnieszka@iqsc.usp.br

INTRODUCTION

Solid polymeric electrolytes (SPE) generally constituted by elastomeric materials that contain ions represent a promising alternative for the substitution of liquid electrolytes and inorganic crystals used in batteries, sensors, fuel cells and electrochromic devices [1]. These materials show excellent thermal and mechanical stability, flexibility and also processibility when compared with ceramic ionic conductors and liquid electrolytes [1].

There are many kinds of SPEs that are proposed by researchers to substitute pure poly(ethylene oxide) (PEO), which presents crystallization problems. Aiming to overcome these problems the new SPEs can be obtained by different ways. Among the various methods to produce SPEs are the insertion of ceramic fillers [2,3], promotion of polymer cross-linking [4,5] or plasticization process [6]. It can be also observed that new kinds of polymer electrolytes appear not always based on PEO. Among these new systems we can cite SPEs based on natural polymers, such as cellulose derivatives [4,5], starch [6,7], chitosan [8] and natural rubber [9]. These systems combine very good ionic conductivity of about $10^{-5}-10^{-4}$ S/cm with transparency, very good adherence to the glass and steel surface and low cost. The SPEs of glycerol plasticized starch tested in electrochromic device also show very promising performance [10,15].

Another kind of no-PEO SPEs are the polymer blends based on PVC/PMMA (poly(vinyl chloride)/poly(methylmethacrylate)) [11], PVC [12] or PVA/PMMA (poly(vinyl alcohol)/PMMA) [13,14]. These widely investigated systems also show very good ionic conductivity reaching the values of $10^{-4}-10^{-3}$ S/cm.

The present study show new solid polymeric electrolytes based on membranes of poly(vinylpyrrolidone-*co*-methacrylic acid) containing plasticizant and lithium salt. These new ionic conducting samples obtained by thermal polymerization were characterized by ionic conductivity measurements as a function of cross-linking agent, plasticizant and LiCl content. The structural measurements of the samples were also performed.

EXPERIMENTAL

The membranes were prepared by mass co-polymerization of 1-vinyl-2-pyrrolidone (VP, Aldrich) with methacrylic acid (Sigma, 20% in VP mass) and tetraethylene glycol diacrylate (5–50% of VP mass) as cross-linking agent. Hydrogen peroxide (Riedel-de Haen, 2.16% in VP mass) was used as the initiator, dioctylftalate (Scandiflex, 5–40% in vinylpyrrolidone mass) was the plasticizant and LiCl (Aldrich, 0.25–20%) was the salt for ionic conduction.

All the reagents were placed in a glass flask and subjected to magnetic agitation for a complete homogenization of the solution (5 min.). Next this viscous solution was dispersed in a Teflon plate and subjected to the polymerization process for 10 h at 75°C. The resulting membranes of 2 mm thickness were stored in a dry box to avoid the influence of humidity. The samples with small quantities of lithium salt (up to 8%) were transparent and with larger quantities, i.e., more than 8%, were opaque.

X-ray diffraction measurements were performed with membranes samples with different LiCl and dioctylftalate concentration with a URD-6, Carl Zeiss Jena instrument with CuK_α radiation.

Conductivity measurements were taken using an Eco Chemie-Autolab PGSTAT 30 with FRA2 module or Solartron 1260 in vacuum atmosphere. The frequency ranged from 10^6 to 10 Hz with amplitude of 5 mV.

RESULTS AND DISCUSSION

Aiming to obtain new ionic conductor samples, membranes based on poly(vinylpyrrolidone) *co*-polymerized with methacrylic acid (PVP-*co*-MA) and containing LiCl salt were subjected to the analysis of conductivity as a function of cross-linking agent tetraethylene glycol diacrylate (TGD). This TGD was added to 5–50% of vinylpyrrolidone mass sample and the ionic conductivity results are shown in Figure 1. In this figure it can be observed that the samples containing 1 and 8% of lithium salt show the same ionic conductivity behavior, i.e., for both samples the best conductivity values of $2.98 \cdot 10^{-3}$ and $2.82 \cdot 10^{-5}$ S/cm were for the samples containing 10% of cross-linking agent. The low value of TGD (5%) promotes a low ionic conductivity of both kinds of samples of one order of magnitude when compared with the sample with 10% of TGD. The same occurs for the sample with 10% of TGD where a drastic decrease is observed in the conductivity values of up to 10^{-5} and 10^{-6} S/cm for the sample with 8 and 1% of LiCl, respectively.

The next step was to verify the influence of plasticizant contents on the ionic conductivity of PVP-based membranes samples. The results of these investigations are shown in Figure 2, where one can observe that the increase of dioctylftalate promotes an increase in the ionic conductivity of the samples, reaching the best value of $5.59 \cdot 10^{-5}$ S/cm for 1% of lithium salt and 20% of plasticizant in the sample. Also this quantity of plasticizant was maximal due to the loss of film properties

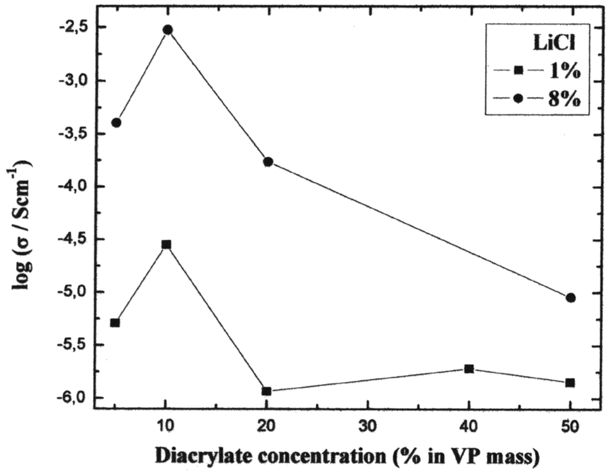

FIGURE 1 Ionic conductivity measurements as a function of tetraethylene glycol diacrylate content for the samples of PVP-*co*-MA with 1 and 8% of LiCl and 20% of dioctylftalate.

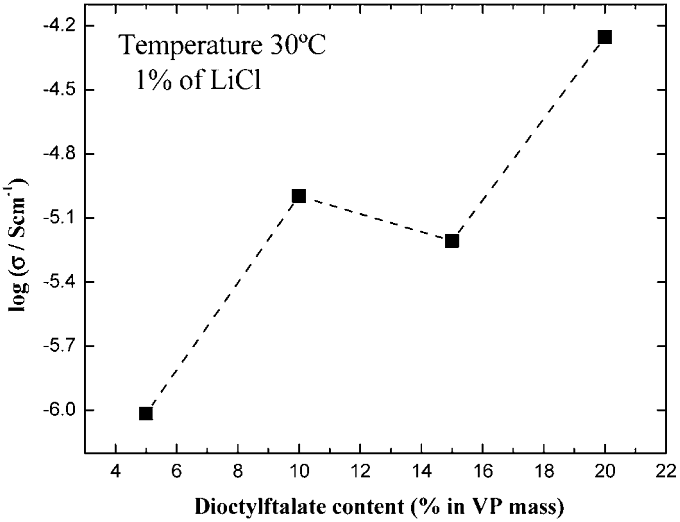

FIGURE 2 Ionic conductivity measurements as a function of dioctylftalate content for the samples of PVP-*co*-MA and containing 1% of LiCl, 10% of TGD.

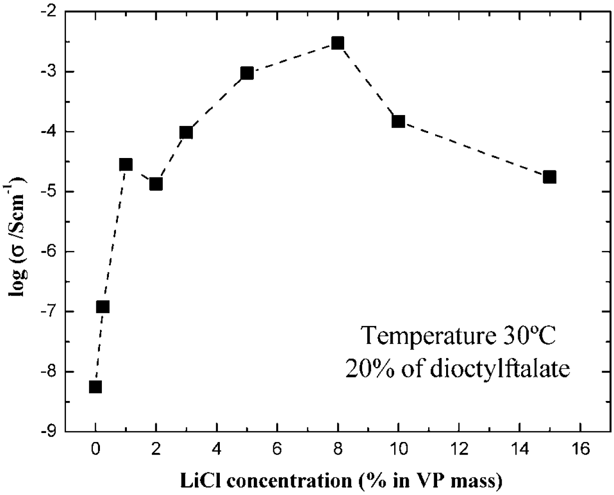

FIGURE 3 Ionic conductivity measurements as a function of LiCl concentration for the samples of PVP-*co*-MA plasticized with dioctylftalate.

for a larger dioctylftalate amount. These results are also very similar to the results obtained for other plasticized systems based on natural polymers, such as starch-based samples plasticized with 30% of glycerol and ethylene glycol [15] and hydroxyethyl cellulose-based samples plasticized with 48% of glycerol [16].

The influence of salt content on the ionic conductivity of the PVP-based samples and plasticized with 20% of dioctylftalate was verified. As it can be observed in Figure 3 there is an accentuated increase of about six orders of magnitude in the ionic conductivity, with the increase of LiCl content from 0 to 8%, where a maximum of ionic conductivity of $3 \cdot 10^{-3}$ S/cm is observed. Such value is comparable with starch-based SPE [6]. For larger salt quantity the ionic conductivity values slightly decrease to $1.75 \cdot 10^{-5}$ S/cm, which is also considered a very good value as well similar to the ionic conductivity values obtained for most of SPEs. At this point it should be also stated that 8% of lithium salt were the barrier when the samples became more opaque than transparent, probably due to a decrease in the salt dissolution properties. However, as can be seen in Figure 3, no crystalline peaks were observed in X-ray diffractograms.

The samples were subjected to structural measurements by X-ray diffractometry (Fig. 4), where a very large band centered at about 22° was observed. As it can be noted in Figure 4 this band was observed for all the samples, indicating their predominantly amorphous state.

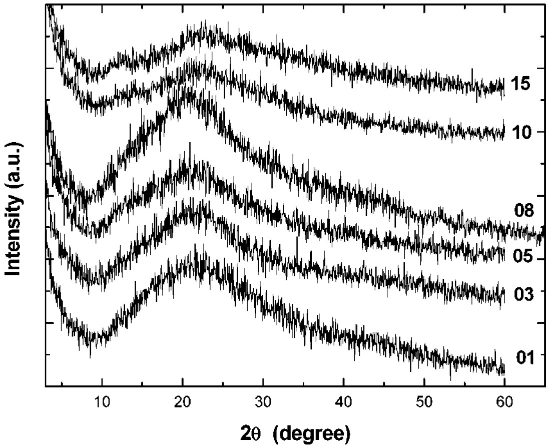

FIGURE 4 X-ray diffractograms for the samples of PVP-*co*-MA with 10% of TGD, 20% of dioctylftalate and different LiCl content.

Also the absence of lithium salt peaks indicates that all salt was very well dissolved. However the samples with larger salt amount, i.e., 10 and 15%, also showed a small band at 12°, which can be due to the formation of small polymeric crystalline regions because of the presence of salt. These results are also very similar to the results obtained for starch and HEC based solid polymeric electrolytes [5,6].

The measurements of ionic conductivity as a function of temperature for the samples with different lithium salt contents are shown in Figure 5. As it can be observed in this figure all the samples exhibit an increase in the conductivity values with the increase of temperature of about one order of magnitude in the temperature range from 20 to about 89°C. The ionic conductivity of the sample with 8% of LiCl increased from $2.1 \cdot 10^{-3}$ S/cm at 19°C to $1.8 \cdot 10^{-2}$ S/cm at 89°C. Also all the samples showed very good agreement with the Arrhenius conductivity model. From these measurements the activation energy values showed in Figure 6 were obtained.

Comparing Figures 3 and 6 it can be stated that the activation energy values decrease with the increase in the ionic conductivity of the PVP-based membranes samples. For the small LiCl quantity of 0.25% the Ea obtained was 68.7 kJ/mol and decreased to 21.4 kJ/mol for 5% of lithium salt. This is the lowest value observed for this kind of samples. However the highest ionic conductivity was observed for the sample containing 8% of LiCl (Ea = 27 kJ/mol). This small difference can be due to the experimental error, however as it can be observed in

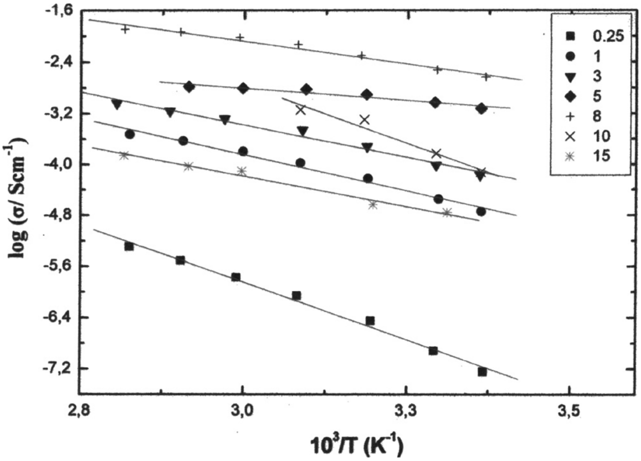

FIGURE 5 Ionic conductivity as a function of temperature for the samples of PVP-*co*-MA plasticized with 20% of dioctylftalate and containing different LiCl quantity.

Figure 5 the increase in the conductivity values as a function of temperature was smaller when compared with other samples. It seems that the conductivity values of this particular sample remained independent of temperature.

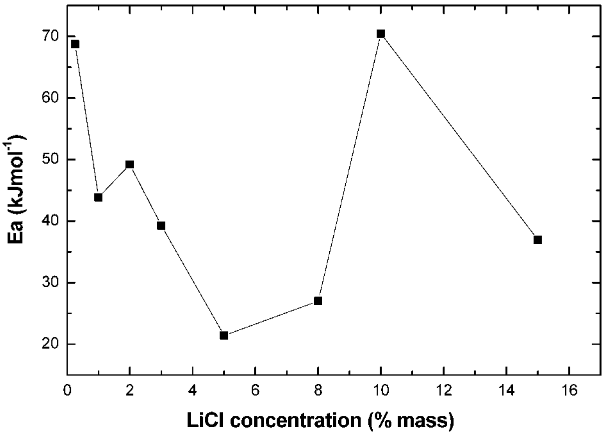

FIGURE 6 Activation energy as a function of LiCl concentration for the samples of PVP-*co*-MA plasticized with dioctylftalate.

CONCLUSION

This paper presented the preparation and characterization of new SPE based on membranes of PVP-*co*-MA plasticized with dioctylftalate. The obtained results revealed that the best ionic conductivity of $3 \cdot 10^{-3}$ S/cm was achieved for the samples with 20% (in VP mass) of dioctylftalate, 10% of TGD and 8% of LiCl. The measurements of ionic conductivity as a function of temperature showed an Arrhenius behavior increasing one order of magnitude from room temperature to 80°C. The ionic conductivity of the sample with 8% of LiCl increased from $2.1 \cdot 10^{-3}$ S/cm at 19°C to $1.8 \cdot 10^{-2}$ S/cm at 89°C. The activation energy value of this sample was 25 kJ/mol and was comparable with other solid polymeric electrolytes. Also the structural investigations of all the samples showed the predominance of the amorphous state.

All the presented results show that new solid polymeric electrolytes based on membranes of poly(vinylpyrrolidone-*co*-methacrylic acid) and containing plasticizant and lithium salt are very good candidates to be applied as solid polymeric electrolytes in different devices.

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