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NONLINEAR EFFECTS ON THE IONIC CONDUCTIVITY OF POLY(ETHYLENE OXIDE)/LITHIUM PERCHLORATE COMPLEXES CAUSED BY THE BLENDING OF POLY(VINYL ACETATE)

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ABSTRACT

Poly(ethylene oxide) (PEO)/$LiClO_4$/poly(vinyl acetate) (PVAc) and PEO/$LiClO_4$/poly(vinyl pyrrolidone) (PVP) complexes were prepared with various weight ratios of PVAc and PVP to PEO. The conductivity (σ) of the PEO/$LiClO_4$ complex was increased in a nonlinear fashion by the presence of up to 60 wt% PVAc. PEO/$LiClO_4$/PVAc complexes with weight percents of PVAc greater than 60 had σ's less than that of PEO/$LiClO_4$. The σ of PEO/$LiClO_4$ was decreased by the presence of any PVP.

INTRODUCTION

Recently, polymer/inorganic salt complexes have been actively investigated as a result of the work of Wright et al. on the solid-state ionic conductivity of the PEO/isothiocyanate salt [1] mixture. Additional studies on the applications of these materials for batteries [2–4], electrochromic devices [5], moisture or gas sensors [6], and of the source of their conductivity have increased in number year by year [7]. Studies have centered on increasing the ionic conductivity of the complexes with an aim to developing materials with commercial applications.

It has been found that the ionic conductivity is larger in the amorphous phase of matrix polymers than that found for crystalline polymers [2, 4, 8]. These results suggest the possibility for development of a polymer blend that, when mixed with an inorganic salt, may have increased conductivity when compared to previous nonblended/salt complexes. The effect of a polymer blend on ionic conductivity has been investigated previously, but noteworthy results were not obtained [9, 10]. However, in this report an interesting relationship between conductivity and the poly(vinyl acetate) (PVAc) to poly(ethylene oxide) (PEO)/$LiClO_4$ blend ratio will be described.

EXPERIMENTAL

The PEO (Seitetsu Chemical Co.) had a molecular weight of 15 to 40 × 10^4 and was used as received. PVAc (Kanto Chemical Co.) had an uncertain average molecular weight, and poly(vinyl pyrrolidone) (PVP, Kishida Chemical Co.) had an average molecular weight of 120 × 10^4. Both PVAc and PVP were purified by the usual precipitation and filtration procedures. $LiClO_4$ (anhydrous special grade, Kanto Chemical Co.) was used as received. The water used in these studies was ion exchanged and distilled after microfiltration.

In order to prepare the complexes, the polymers and $LiClO_4$ were individually dissolved in water/isopropanol (1/2). The PEO solutions were then mixed with $LiClO_4$ (12 wt%). Various ratios of PEO to PVP and PVAc were used. Films of the complexes were obtained by casting the solution, followed by drying in vacuum at 60°C for several days. The thickness of the films was $\sim$30 μm.

Au comb electrodes were deposited onto the surface of the films by means of an ion coater. Conductivity (σ) measurements were made in a dry box at 20 to 25°C by using an impedance analyzer.

RESULTS AND DISCUSSION

Figures 1, 2, and 3 show the variation in the crystallinity of the spherulites formed from PEO, PEO/$LiClO_4$, PEO/$LiClO_4$/PVAc, and PEO/$LiClO_4$/PVP. All results were obtained by using a polarizing microscope with crossed Nicols. PEO, as seen in Fig. 1, grows in almost perfect

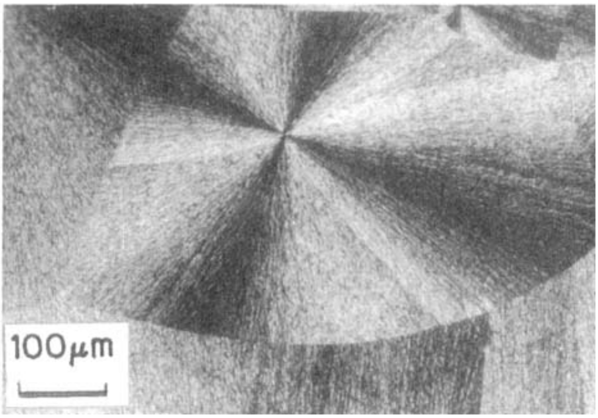

FIG. 1. Spherulitic patterns of PEO film by polarizing microscope.

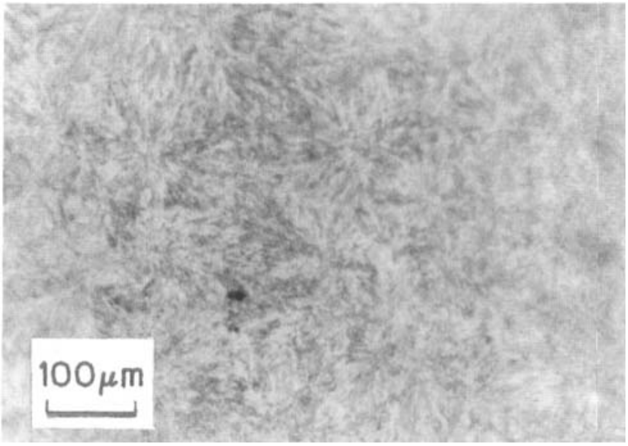

FIG. 2. Spherulitic patterns of PEO in the complex film of PEO/$LiClO_4$ by polarizing microscope.

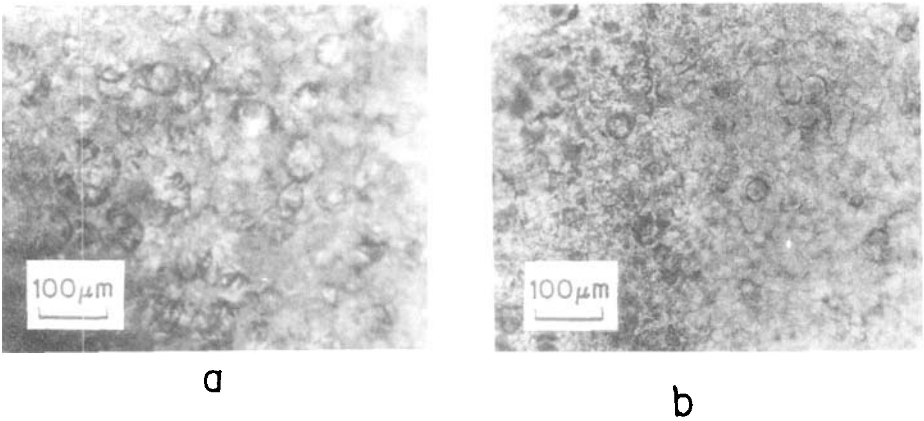

FIG. 3. Spherulitic patterns of PEO in the complex film of PEO/PVAc (50/50)/$LiClO_4$ (a) and PEO/PVAc (50/50)/$LiClO_4$ (b) by polarizing microscope.

crystalline forms. Figure 2 indicates that the regularity of the PEO spherulite is somewhat disrupted by inclusion of $LiClO_4$. Furthermore, from Fig. 3 it is clear that the blending of the noncrystalline polymers PVAc and PVP (seen in a and b, respectively) reduces the crystallinity of the PEO matrix.

Figures 4(a) and (b) show the ac frequency dependence of σ on the blend ratio of PVAc to PEO. σ increases with ac frequency up to a saturation level of about 10 to 100 kHz. These results are similar to those found for the conductivity of poly(2-(4-carboxyhexafluoro-butanoyl-oxy)-ethyl methacrylate–Li salt)/PEO complex [10]. Since σ at a relatively low frequency would be influenced by contact resistance at the electrodes, σ at 10 kHz was plotted for each blend ratio of PEO and PVAc (Fig. 5).

In complexes with a blend of PVAc to PEO of less than 6 to 1, the conductivities for complexes are higher than those for pure PEO/Li salt complexes even though the σ for the PVAc/Li salt complexes is much lower. This nonlinear relationship between σ and polymer blend composition has not been found previously and indicates that these materials would be interesting candidates for studying ion migration or ionization in solid polymeric electrolytes.

Figure 6 shows the relationship between σ and the ratio of PVP to PEO. A linear decrease in σ occurs as the amount of PVP is increased.

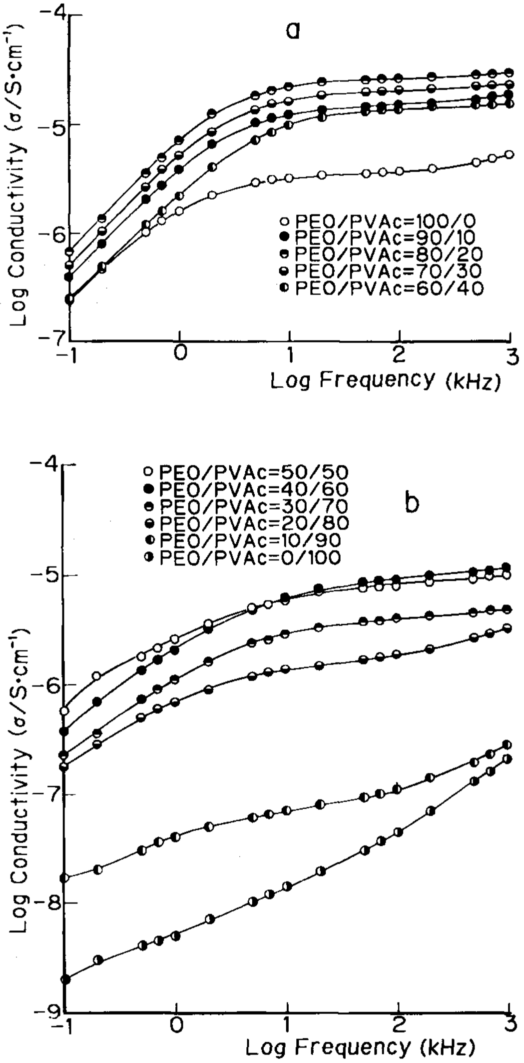

FIG. 4. Log frequency dependence versus log conductivity for PEO/PVAc/$LiClO_4$ complex films. Blend ratio of PVAc: (a) 0–40 wt%, (b) 50–100 wt%.

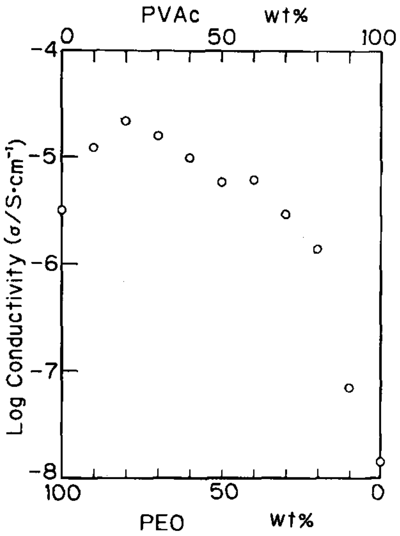

FIG. 5. Dependence of the log conductivity of the PEO/PVAc/$LiClO_4$ complex film at 10 kHz upon the PVAc weight percent in the blend.

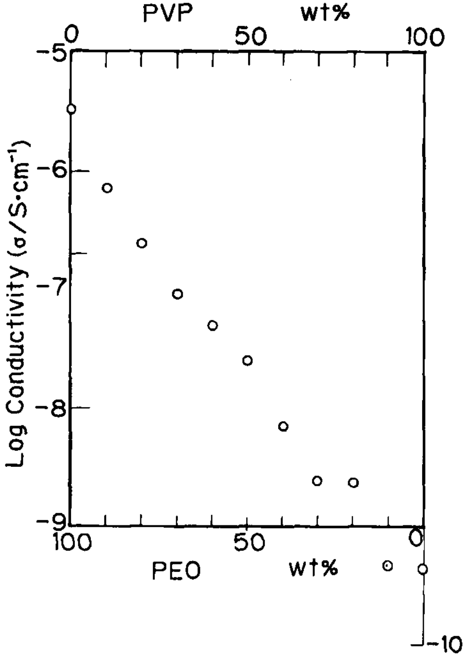

FIG. 6. Dependence of the log conductivity of the PEO/PVP/$LiClO_4$ complex films at 10 kHz upon the PVP weight percent.

Since PVP is much more hydrophilic than PVAc, moisture as a cause for the increase in σ noted for PVAc can be discounted.

By comparison of Figs. 5 and 6, the σ phenomena noted for PEO/Li/PVAc salt mixtures seems to be due to a particular interaction between each component in addition to the disruption of crystallization.

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