

POLYMER ELECTROLYTES: POLY(ETHYLENE ADIPATE)- SODIUM IODIDE COMPLEXES

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(Received 19 June 1989)

ABSTRACT

Ionic conductances and thermal data are reported for a number of mixtures of sodium iodide with poly(ethylene adipate) samples of different molecular weights. Comparison of the thermal data and conductivity measurements indicates a close connection between the data and highlights the dominant importance of crystallinity on the bulk ion conductivity in the polymer system.

INTRODUCTION

The development of ionic conducting electrolytes has attracted considerable interest in the last ten years (1,2). The polymer should not only possess a high ionic conductivity but also should have good adhesion to the electrode as well as mechanical stability at the operational temperature. Poly(ethylene oxide) has been the best polymer for battery applications but it tends to creep at the operational temperature (120°C) and has poor adhesion to the electrodes. It has been shown recently (3) that incorporation of poly(ethylene oxide) into a urethane elastomer improves both adhesion and mechanical stability without any significant reduction in the ionic conductivity. Poly(ethylene adipate) is widely used as a soft block in many polyurethane elastomers and it therefore seems appropriate to explore the ionic conductivity of this system as a potential conducting medium for composite polymer electrolytes.

EXPERIMENTAL

Samples of poly(ethylene adipate) of different molecular weights were obtained from Briggs & Townsend (Manchester, U.K.). The molecular weights by gel permeation chromatography had number-average values of 900, 2000 and 4650; values of \bar{M}_w/\bar{M}_n were approximately three. The polymer was first dried at 333K in a vacuum oven and then placed in a vacuum desiccator to cool to room temperature. Sodium iodide was dried at 358K overnight and similarly cooled in a desiccator. Solutions of the polymer and the salt were made at room temperature in a dry box using acetone as solvent. The solvent was removed by distillation from the samples placed in Petri dishes in a vacuum chamber attached to a vacuum line. The samples were then dried in a vacuum oven overnight. The solid was then pressed into a 2mm thick disc using a hydraulic press operated at 343K.

Conductivity measurements were made using a Wayne Kerr bridge operating at 1kHz. Additional measurements were made over an extended frequency range (0.1Hz - 65kHz) using a Solartron swept frequency impedance bridge; they indicated that the conductivity found at 1kHz is the true ionic conductivity of the polymer electrolyte. The samples were also subjected to thermal analysis using a Du Pont 900 series differential scanning calorimeter.

RESULTS AND DISCUSSION

The relatively high ionic conductivity of poly(ethylene oxide) -alkali metal salt complexes has led to their use as electrolytes in solid batteries based on the concept of the rechargeable lithium battery (4). Many other systems have been studied including poly(vinyl acetate) (5), poly(ethylene imine) (6,7), poly(alkylene sulphide)s (8), polyepichlorhydrin (9), poly(ethylene succinate) (10,11), poly(ethylene sebacate) (12) and poly(β -propiolactone) (13). In this paper, we explore the potential of poly(ethylene adipate) as an ionic conductor.

Thermal Analysis Data. Before examining the conductivity data, those for thermal analysis are considered. DSC measurements on pure poly(ethylene adipate) (PEA), when quenched, show a strong glass transition at 213K, followed by a crystallization exotherm at 265K and a melting transition at 315K. Addition of NaI to PEA (\bar{M}_n , 960) produces rises in the temperatures for the transitions (see Table 1). This type of behaviour has been observed for other systems and can be attributed to interaction between the salt and the polymer. The change in T_g per mol % of NaI decreases with increasing salt concentration indicating a decrease in the effectiveness of the interaction between salt and polymer. The variation of T_g on addition of salt shows the ability of PEA to solvate the salt and to form free ions. It should be noted that there is no evidence from the thermal analysis of the separation of free salt, confirming that molecular solutions had in fact been produced. At low concentrations of added salt, a strong complex appears to be formed leading to an increased melting point. Further addition of salt to the polymer leads to a decrease in the melting temperature and a decrease in the crystallinity as calculated from the melt exotherm (Table 1). The decrease in crystallinity is so marked that no melt peak is observed for the 4:1 ratio doped sample. Similar observations have been made for LiClO_4 -doped poly(β -propiolactone).

Table 1. Summary of thermal data for PEA(960):NaI systems

Dopant concentration salt		glass transition	crystallization	melting	% crystallinity
		temperature	temperature	temperature	of ester phase
wt/%	ratio	T_g/K	T_c/K	T_m/K	
0		213	265	315	57
3	32:1	222	278	320	58
5.2	16:1	223	273	316	50
7.3	12:1	227	272	314	25
11.1	8:1	229		313	5.5
14.6	6:1	231		311	1.7
22.5	4:1	234		-	0

Conductivity Data. The variation of the conductivity with molecular weight at 300K (Figure 1) indicates that the conductivity decreases as the molecular weight of the polymer is increased. Increasing the molecular weight of the polymer causes T_g to rise and also increases the crystallinity, factors unfavourable for high ionic conductivity.

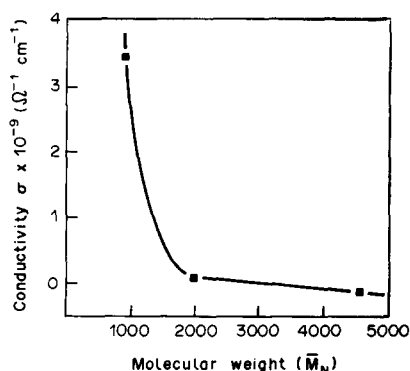


Figure 1. Variation of the conductivity at 300K with the molecular weight of the polymer.

The form of the conductivity plots as a function of temperature was independent of molecular weight (Figure 2); incorporation of salt leads to shifts in the transition temperatures and an increased level of conductivity but in general there is the same overall profile. The break in the variation of conductivity with temperature correlates well with the melting point of the doped system.

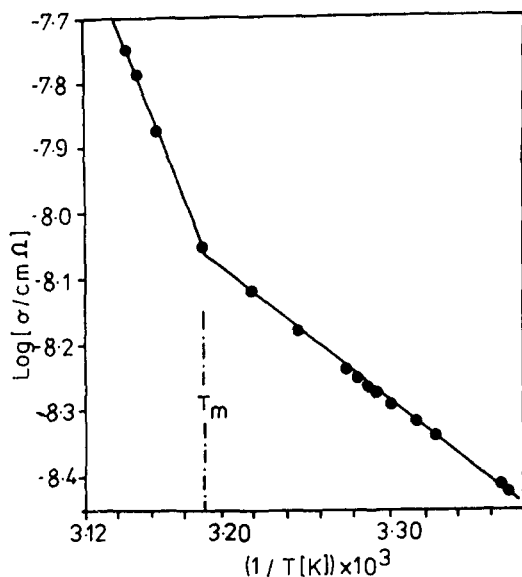


Figure 2. Variation of the conductivity with temperature.

The conductivity of the doped systems varies with the concentration of salt (Figure 3) and exhibits a maximum at a ratio of PEA:NaI of 32:1 for PEA of molecular weight 960. Similar

variations were found for the other samples of PEA, maximum values of 20×10^{-9} and 15×10^{-9} respectively being found for the polymers of molecular weights 2000 and 4650 with NaI; because of the low values, the data have been omitted from Figure 3.

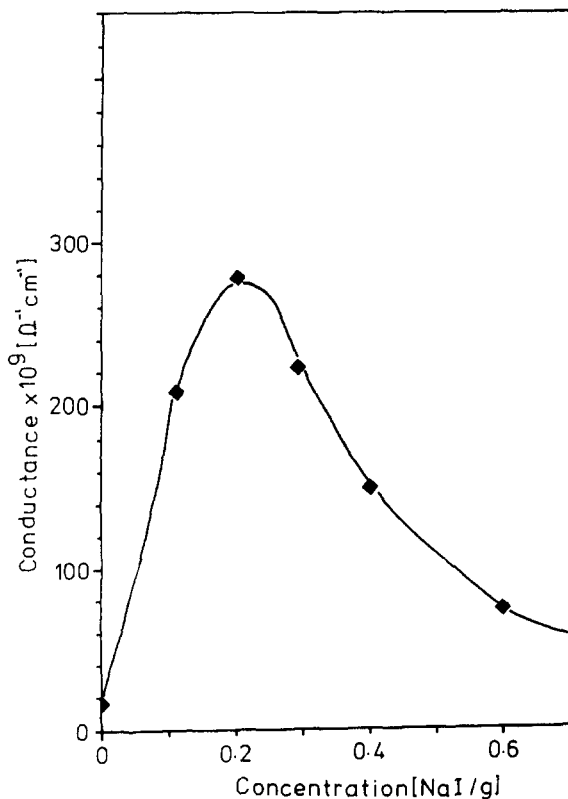


Figure 3. Variation of the conductivity with doping content.

The DSC measurements show that a complex is formed between the salt and the polymer at this ratio (32:1) leading to the suggestion that this is instrumental in raising the conductivity. The conductivities of these systems are however orders of magnitude lower than those in PEO complexes making further development of these systems unattractive. The low conductivity probably reflects the low degree of ionization of the salt and the combined effects of residual crystallinity of the polymer and complex formation on the mechanism of conduction.

Conclusion. The behaviour of poly(ethylene adipate) as a polymer electrolyte is similar to that of poly(ethylene oxide) but the higher crystallinity of the polymer and the poorer solvation of the ions lead to low levels of ionic conductivity.

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