FAST ION CONDUCTION IN COMB SHAPE POLYMERS

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ABSTRACT

Studies of fast ion conduction in solid amorphous polymer-salt mixtures have increased rapidly in the last decade since it was demonstrated that their application in dry battery manufacture was feasible.

The most successful type of polymer matrix found so far is poly(ethylene oxide) PEO which can dissolve a wide range of salts to form solid homogeneous solutions. A major drawback in these systems is that PEO tends to crystallise readily and as ionic conduction takes place in the amorphous regions of the polymer a reduction in the crystalline content of the host polymer is desirable, if reasonable conduction levels are to be attained at ambient temperatures.

One way of achieving this is to synthesise comb-shaped polymers with short side chains of poly(ethylene glycol) or poly(propylene glycol) (PPG) which do not crystallise but are long enough to coordinate with the metal cations of the added salt.

Structures with this architecture based on poly(methacrylic acid), poly(itaconic acid) and polyphosphazene backbones with either PEO or PPG side chains have been prepared by several groups of workers. These form amorphous solutions with a range of alkali metal salts and conductivity levels of up to $10^{-3}$ S cm$^{-1}$ have been recorded in several systems.

The factors influencing ionic conductivity in these comb branch systems such as salt selection, glass transition temperatures, and temperature of measurement, will be discussed with particular reference to the polymers based on poly(itaconic acid), and ethylene oxide macromers.

INTRODUCTION

One of the first major studies on the effect of mixing salts with a polymer was reported by Moacanin and Cuddihy [1]. They observed that LiClO$_4$ could be dissolved in poly(propylene oxide), PPO, to give homogeneous, amorphous, mixtures and that the glass transition temperature ($T_g$) rose as more salt was added to the mixture. It was later shown that several other polymers were capable of dissolving salts with a concomitant enhancement of $T_g$ [2].

Real interest in these polymer/salt solutions only developed after it was demonstrated by Wright et alia [3,4] that mixtures of poly(ethylene oxide), PEO, and various inorganic salts displayed conductivity levels which were sufficiently large to merit consideration for use as solid polymeric electrolytes in high energy density...
batteries. Subsequent investigations have shown that in addition to the polyalkyloxides there are several systems suitable for consideration, containing donor atoms, such as O, N and S, which are capable of complexing with the cations of inorganic salts. Among those studied so far are poly(ethylene succinate) [5,6], poly(β-propiolactone), [7], poly(ethylene adipate) [8], poly(ethylene imine) [9-11], poly(alkylene sulphides) [12] and poly(vinyl methyl ether) [13], but PEO still seems to be the best structure for solvating cations. This appears to be related to the favourable spacing between the ether oxygens and the tendency for the PEO chain to adopt a helical structure. It has been shown that PEO has a (ttg), conformation in two turns of a helix whose repeat distance is 19.25 Å. Papke et alia [14] have suggested that on complexing with metal cations PEO has a (ttg, ttg) conformation which forms a tighter helix. This also provides an oxygen lined cavity which can easily accommodate certain cations of a given size, e.g. Na⁺ can fit comfortably into such a cavity and coordinates with four oxygens in this geometry. This favourable conformation is most easily achieved with PEO. Construction of space filling models demonstrates that even PPO can only form a much more open helical structure because of steric hindrance and that this is probably a less efficient cation binding conformation. This difference in structure can be seen in Figures 1(a) and (b) for short segments of PEO and PPO attached as an ester unit to a

Figure 1(a): Molecular model of polyethylene oxide trimer. 
Figure 1(b): Molecular model of polypropylene glycol trimer.