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LETTER TO THE EDITOR

A study of the recrystallisation dynamics in solid, mixed-salt, polyether electrolytes, $P(\text{EO})_4(\text{LiCF}_3\text{SO}_3)_{0.5}(\text{NaI})_{0.5}$ and $P(\text{EO})_8(\text{LiCF}_3\text{SO}_3)_{0.5}(\text{NaI})_{0.5}$

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Abstract. The dynamics of the crystallisation process in a mixed salt/polyethylene oxide (PEO) solid ionic conductor is investigated, using nuclear magnetic resonance techniques. The formation of the crystalline complex and the formation of the PEO crystals from 100% amorphous samples (obtained by a quenching technique) are observed, by ¹H NMR, to occur with time constants sufficiently different to permit easy identification of the components of the inhomogeneous samples at equilibrium at 313 K. ¹⁹F NMR then shows in which component of the sample the anions reside. The evidence is that the anion/cation pairs of a particular salt do not in general reside in the same component of the samples.

We have performed some quenching experiments on a solid, high molecular weight, polyethylene oxide doped with equal mixtures of lithium triflate, LiCF_3SO_3 , and sodium iodide, NaI. The fast ionic conductor so formed is potentially a solid electrolyte material for battery application. The results clarify a residual problem concerning the location of the anions in the different phases of these heterogeneous materials. These experiments were undertaken, using nuclear magnetic resonance, on samples of $P(\text{EO})_4(\text{LiCF}_3\text{SO}_3)_{0.5}(\text{NaI})_{0.5}$ and $P(\text{EO})_8(\text{LiCF}_3\text{SO}_3)_{0.5}(\text{NaI})_{0.5}$; the fabrication techniques of the samples are described in an earlier paper (Tunstall *et al* 1988, subsequently referred to as TTMV).

The experiments involved the heating of samples in an oven to ~ 475 K (i.e. above the liquidus temperature as determined by differential scanning calorimetry to give a homogeneous amorphous phase), then quenching to 77 K in liquid nitrogen to 'freeze' the amorphous state, giving a short T_2 (¹H ($\sim 10 \mu\text{s}$) or ¹⁹F ($\sim 30 \mu\text{s}$)) signal (TTMV). Upon rapid heating to 313 K the amorphous state passed through the glass transition temperature T_g to give a longer T_2 signal, whereupon the growth of the crystalline fraction (i.e. the growth of a short T_2 signal) was monitored as a function of time. (The heating rate was about 10 K min^{-1} . T_g for the mixed salt samples, detected as a lengthening of the short T_2 free induction decays, was found to be about 298 K for the 4/1 sample and about 283 K for the 8/1 sample, showing the expected viscosity effect on T_g of salt content.)

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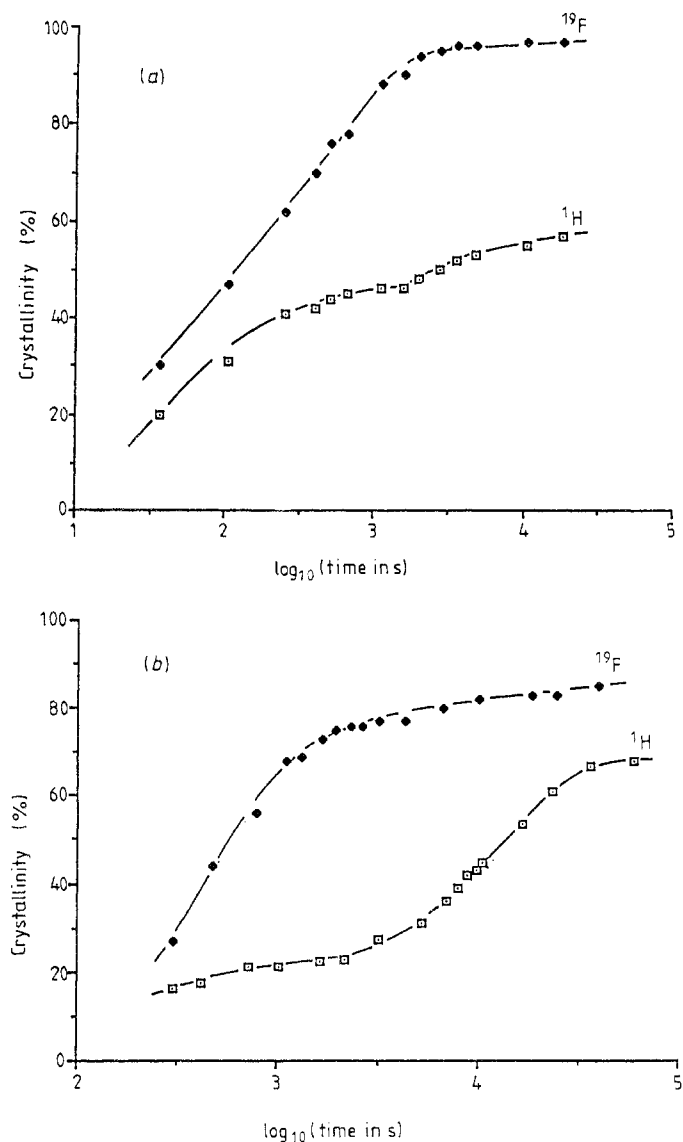


Figure 1. The growth of the crystalline components as measured by the NMR free induction decays (crystalline and amorphous components have easily separable decay constant). Two different samples have been studied, with different PEO: total salt ratios: (a) 4: 1, (b) 8: 1.

Figures 1(a) and 1(b) show relevant plots for the ¹H and ¹⁹F nuclei in the respective mixed salt samples. Here crystallinity (%) indicates the amount of crystalline fraction obtained from the usual two-component free induction decay (FID) (see TMV) analysis. (⁷Li was not studied because its T_1 was long, of the order of seconds, and noise levels required signal averaging (~ 36 FIDs), during which time the observed FID would be changing due to the recrystallisation process.)

The ¹H data in the high-density sample, figure 1(a), shows that at 313 K there was a rapid initial recrystallisation, taking roughly six minutes, with about 46% of the protons

losing their motion in the process. This value remained constant for about $\frac{3}{4}$ h until a second, slow loss of proton motion was noted, taking about 5 h to reach the equilibrium fraction at 313 K of the heating cycle experiment. It is also interesting to note that the 46% of the electrolyte which initially recrystallised under isothermal conditions corresponds to the 46% of the electrolyte remaining above 333 K in the heating cycle, which was assigned to the high melting temperature crystalline complex (Tunstall *et al* 1989, figure 4). It is not unreasonable, therefore, to assume that the initial recrystallisation observed here is that of the high melting temperature phase, the so-called crystalline complex.

No two-step process is apparent in the fluorine data, which indicates that the CF_3SO_3 anion continually lost motion until at about $\frac{3}{4}$ h it had attained the equilibrium value of crystallinity obtained on the heating cycle ($\sim 95\%$). If the initial processes ($0-\frac{3}{4}$ h) for the polymer chain and the process for the CF_3SO_3 anion occurred in the same phase, then the interesting conclusion emerges that nearly all the triflate is in the crystalline complex phase with the approximate stoichiometry $\text{EO}/\text{CF}_3\text{SO}_3^- \approx 4/1$. In its turn this implies that the predominant anionic species in the mixed salt amorphous (conducting) phase is iodide. Earlier work (Tunstall *et al* 1989) has established that, in the mixed salt solid electrolyte, the magnetic environment of the lithium ions becomes time varying, and hence averages to zero, at much lower temperatures than does that of the triflate ions. The present work seems to provide an answer; the triflate ions must be buried deep in the spherulites (Neat *et al* 1985) of the crystalline complex whilst the lithium ions are nearer the surface, where they more easily dissolve into the amorphous phase, and where polymer motion may be active enough to average the magnetic environment anyway.

In the less dense 8/1 sample, recrystallisation profiles and timescales similar to those of the 4/1 were found, figure 1(b), but, as would be expected for the electrolyte of lower overall salt content, the fraction of crystalline complex was smaller. The ^1H data again show what could be described as a two-stage process; a fast initial recrystallisation period taking about $\frac{3}{4}$ h, with about 24% of the protons losing their motion, followed by a slow loss of proton motion to the equilibrium value noted in the heating cycle experiment ($\sim 70\%$). That there is a slower second process is probably in qualitative agreement with the accepted view that following the initial recrystallisation of the crystalline complex the remaining material is still too concentrated in salt to allow immediate formation of crystalline PEO-type material. Hence, time is required for the diffusion of remaining ionic species and the reorganisation of PEO chains.

The plateau at 24% in figure 1(b) is in agreement with the high-temperature (>333 K) plateau observed in our thermal equilibrium measurements (Tunstall *et al* 1989), just as in the earlier discussion of the 4/1 sample. This fraction is therefore associated, as before, with the crystalline complex.

This time the ^{19}F data was also two-stage, with a change of the recrystallisation rate occurring at the same time as for the protons ($\sim \frac{3}{4}$ h). If the initial processes occur in the same phase, then about 80% of the CF_3SO_3 content is in the crystalline complex with the approximate stoichiometry $\text{EO}/\text{CF}_3\text{SO}_3 \approx 5/1$. This then allows for a small amount of iodide anion to be present in the high melting temperature complex to maintain the 4:1 stoichiometry of the crystalline complex. The remaining iodide fraction must again be the predominant anionic species in the mixed-salt amorphous phase.

We conclude therefore that the two-step process of recrystallisation following these quenching procedures indicates that in solid electrolytes involving high-density mixtures of lithium triflate and sodium iodide there is a marked tendency for the triflate ions to

migrate to strongly crystalline regions of the spherulite and for the lithium ions to exist on the less crystalline, outer, regions, and in the amorphous state. We assume that the sodium ions must therefore tend to link with the triflate, and the iodide ions with the lithium.

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