Short-Chain Di-Ureasil Ormolytes Doped with Potassium Triflate: Phase Diagram and Conductivity Behavior

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Abstract. Di-urea cross-linked poly(oxyethylene)/siloxane hybrids, synthesized by the sol-gel process and containing a wide concentration range of potassium triflate, KCF_3SO_3 , have been analyzed by x-ray diffraction and differential scanning calorimetry. The pseudo-phase diagram proposed has been taken into account in the interpretation of the complex impedance measurements. The xerogels prepared are obtained as transparent, thin monoliths. At room temperature the highest conductivity found was $2 \times 10^{-6} \Omega^{-1}\text{cm}^{-1}$.

Keywords: di-ureasils, potassium triflate, phase diagram, ionic conductivity

1. Introduction

In the last 25 years researchers have been seeking polymer electrolyte systems with high ionic conductivity [1]. These studies have been essentially motivated by the potential use of such materials in solid state electrochemical devices, especially batteries.

Polymer electrolytes normally are composed of a high molecular weight polymer and a salt. The vast majority of work has concentrated on poly(oxyethylene), POE, as coordinating macromolecule, due to its remarkable capacity to solubilize salt species [1]. At room temperature, POE/salt mixtures are poor conductors with limited application. This disadvantage derives

from the fact that high molecular weight POE is highly crystalline. As a consequence, the corresponding salt-polymer complexes tend to contain crystalline POE and/or high melting complexes.

In the early 1980s, Berthier et al. [2] demonstrated that ionic conductivity in such semi-crystalline materials occurred predominantly through the amorphous phase. The construction of phase diagrams became necessary to determine the ranges of salt concentration and temperature in which conductivity was maximum [1]. Recently, Gadjourova et al. [3] have published original data that support the proposal that ionic conductivity in the crystalline phases of polymer/salt complexes can be greater than in the equivalent amorphous phases and that the transport process in the crystalline regions is exclusively controlled by the cations [3]. The latter aspect

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contrasts with the situation observed in the amorphous domains, where cations and anions contribute to the overall conductivity [1, 2]. In spite of the low levels of conductivity reported in Gadjourova et al. [3]'s work, it is clear that future investigation in this area must be directed towards the development of ordered structures containing available sites to be partially occupied by cations, a task that will obviously require significant effort in the next few years.

The study described here is devoted to the preparation and characterization of the morphological and conducting properties of polymer electrolytes containing K^+ ions with potencial interest for the fabrication of smart windows. To enhance the conductivity and to improve the mechanical and thermal stability of the proposed systems based on POE and potassium salts [4–7], we have produced ormolytes (acronym of organically-modified silicate electrolytes) through the incorporation of potassium triflate, KCF_3SO_3 , into a sol-gel derived POE/siloxane matrix. This host network, designated U(600), is the low molecular weight member of the di-ureasil family [8]. The main physical and chemical characteristics of this hybrid compound, in the non-doped [9] and doped (with Eu^{3+} [10], Er^{3+} [11] and Li^+ ions [12]) states have already been examined.

2. Experimental

3-isocyanatepropyl triethoxysilane (ICPTES, Fluka), O,O'-bis(2-aminopropyl)-polypropylene glycol (commercially designated as Jeffamine 600, Fluka, average molecular weight of 600) and potassium trifluoromethanesulfonate (KCF_3SO_3 , Aldrich) were used as received. Tetrahydrofuran (THF, Merck) and ethanol (CH_3CH_2OH , Merck) were stored over molecular sieves. Distilled water was used in all experiments.

The first stage of the preparation of the K^+ -doped di-ureasils involved the formation of a covalent urea bond between the terminal NH_2 groups of Jeffamine 600 and the $-N=C=O$ group of ICPTES. The second stage of the synthesis involved the addition of water and CH_3CH_2OH , to start the hydrolysis and condensation reactions characteristic of the sol-gel process. The nomenclature $U(600)_nKCF_3SO_3$ has been adopted to identify the final materials. Samples with $n = \infty, 400, 200, 100, 80, 60, 40, 20, 10, 5, 4, 3, 2, 1$ and 0.5 were obtained. The synthetic procedure of the $U(600)_nKCF_3SO_3$ ormolytes is identical to that of the $U(600)_nLiCF_3SO_3$ analogs described in detail else-

Table 1. Relevant details of the synthesis of the $U(600)_nKCF_3SO_3$ ormolytes.

$n = O/K^+$ (mol/mol)	$m(KCF_3SO_3)$ (g)	Si/K^+ (mol/mol)	Si/K^+ (g/g)
400	0.01	94.09	67.59
200	0.03	47.05	33.79
100	0.06	23.52	16.89
80	0.08	18.82	13.52
60	0.11	14.11	10.14
40	0.16	9.40	6.75
20	0.33	4.70	3.38
10	0.66	2.35	1.69
5	1.33	1.18	0.85
4	1.66	0.94	0.68
3	2.22	0.71	0.51
2	3.33	0.47	0.34
1	6.66	0.24	0.17
0.5	13.33	0.12	0.09

where [12]. The content of KCF_3SO_3 incorporated into each of the samples prepared is indicated in Table 1. The materials were obtained as transparent, flexible films.

A disk section with a mass of approximately 40 mg was removed from the mono-urethanesil film, placed in a 40 μl aluminium can and stored in a dessicator over phosphorous pentoxide for at least 12 h at room temperature. After this drying treatment the can was hermetically sealed and the thermogram of the sample was recorded with a DSC131 Setaram Differential Scanning Calorimeter. The purge gas used was high purity nitrogen supplied at a constant 35 $cm^3 min^{-1}$ flow rate. All the samples were subjected to a $10^\circ C min^{-1}$ heating rate and were characterized between 25 and $300^\circ C$.

The total ionic conductivity of the materials was determined by locating an electrolyte disk between two 10 mm diameter ion-blocking gold electrodes (Goodfellow, >99.9%). The electrolyte/electrode assembly was secured in a suitable constant volume support. The cell support was installed in a Buchi TO51 tube oven and a type K thermocouple placed close to the electrolyte disk measured the sample temperature. Bulk conductivities of electrolyte samples were obtained during heating cycles using the complex plane impedance technique (Schlumberger Solartron 1250 frequency response analyser and 1286 electrochemical interface) over a temperature range

of between 25 and 100°C and at approximately 7°C intervals.

X-ray diffraction (XRD) measurements were performed at room temperature with a Rigaku Geigerflex D/max-c diffractometer system using monochromated Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) over the 2θ range 4–80° at a resolution of 0.05°. The samples analyzed were not submitted to any thermal pre-treatment.

3. Results and Discussion

3.1. Morphological Aspects

We may immediately infer from the analysis of the XRD patterns of the $\text{U}(600)_n\text{KCF}_3\text{SO}_3$ electrolytes reproduced in Fig. 1(a) that samples with n greater than 5 are completely amorphous. The diffractograms of the more concentrated xerogels (i.e., those with n between

5 and 0.5) depicted in Fig. 1(b) clearly show that the introduction of increasing amounts of guest salt gives rise to important structural changes. At $n = 5$, a single, weak peak is distinctly observed at approximately 21.65° in the XRD pattern of this material (Fig. 1(b)). The magnitude of this event increases in the diffractogram of $\text{U}(600)_3\text{KCF}_3\text{SO}_3$. In the patterns of the diureasils with $n = 2$ and 1, the 21.65° peak becomes very sharp and strong (Fig. 1(b)). Another consequence of the incorporation of the potassium salt into the $\text{U}(600)$ host matrix at composition $n = 3$ is the appearance of three new medium intensity diffraction peaks located at about 8.95, 26.45 and 27.30° (Fig. 1(b)). The subsequent addition of KCF_3SO_3 leads to the production of a weak, distinct peak near 10.95° in the diffractogram of $\text{U}(600)_2\text{KCF}_3\text{SO}_3$ (Fig. 1(b)). Several new, weak diffraction peaks are also discerned in the latter XRD pattern between 30 and 40° (Fig. 1(b)). When the composition of the samples reaches $n = 0.5$, two important

Figure 1. X-ray diffraction patterns of the $\text{U}(600)_n\text{KCF}_3\text{SO}_3$ ormolytes: (a) n between ∞ and 10; (b) n between 5 and 0.

modifications occur (Fig. 1(b)): (1) The magnitude of the peaks at 8.95, 10.95, 21.65, 26.45 and 27.30° is considerably diminished; (2) A series of intense and sharp new peaks are detected (the main ones are located at 8.00, 15.80, 17.70, 19.75, 22.70, 27.55, 31.85 and 33.95°). It is essential to refer that the diffractogram of $\text{U(600)}_{0.5}\text{KCF}_3\text{SO}_3$ does not display any diffraction peak characteristic of the pure salt.

The set of peaks situated at 8.95, 10.95, 21.65, 26.45 and 27.30° in the XRD patterns of the xerogel samples with n ranging from 5 to 0.5 (Fig. 1(b)) may be unequivocally attributed to a crystalline POE/ KCF_3SO_3 complex with stoichiometry n between 2 and 1. This compound will be henceforth designated complex C1. The changes observed in the diffractogram of the most concentrated di-ureasil studied are indicative of the growth of a crystalline phase, as another (i.e., C1) disappears. We thus propose that a second crystalline POE/ KCF_3SO_3 complex (named C2) is formed at n lower than 0.5.

It is essential to mention that the study the $\text{POE}_n\text{KCF}_3\text{SO}_3$ system performed by Chintapalli et al. [7] provided conclusive evidence of the formation of a crystalline compound at $n = 1.2$ and the existence of free salt in samples with n lower than 1 [7].

The analysis of the thermograms of the $\text{U(600)}_n\text{KCF}_3\text{SO}_3$ materials given in Fig. 2 allows us to conclude that the samples with n ranging from 200 to 4 are totally amorphous. This finding is in perfect agreement with the XRD results discussed above, provided we exclude samples with $n = 4$ and 5. In fact, the diffractogram of $\text{U(600)}_5\text{KCF}_3\text{SO}_3$ indicated the presence of crystalline domains (Fig. 1(a)). This apparent inconsistency is common in morphological studies on polymer electrolytes, since these systems are often in a metastable state. As in the present work the XRD measurements were carried out prior to the DSC study, slow crystallization kinetics may account for the fact that the sample with $n = 5$, initially amorphous, presents crystalline domains after a certain period of time has elapsed.

The DSC trace of $\text{U(600)}_3\text{KCF}_3\text{SO}_3$ exhibits a broad, weak endothermic peak with onset at about 153°C (Fig. 2). Upon inclusion of more salt ($n = 2$), a very intense melting peak is produced (Fig. 2). The onset temperature of this thermal event is approximately 170°C. As still more salt is added ($n = 1$), the magnitude of this peak increases (Fig. 2). In addition, a new endotherm, with onset temperature near 209°C, is evident in the DSC curve of $\text{U(600)}_1\text{KCF}_3\text{SO}_3$ (Fig. 2).

Figure 2. DSC curves of the $\text{U(600)}_n\text{KCF}_3\text{SO}_3$ ormolytes.

In the thermogram of the most concentrated di-ureasil examined, the first melting peak becomes less intense, whereas the onset of the higher temperature event shifts to about 226°C (Fig. 2).

On the basis of the conclusions drawn from the XRD data, we ascribe the low temperature endothermic event (onset temperature at about 170°C) observed in the DSC traces of the salt-rich compounds with n between 2 and 0.5 to the melting of the crystalline complex C1. This peak is more intense at $n = 1$, suggesting that its stoichiometry is lower than $n = 2$. This explanation is supported by the fact that POE forms a crystalline complex with KCF_3SO_3 at $n = 1.2$ [5, 7]. In contrast with the results reported by Chintapalli et al. [7], our study indicates, not only that a second complex (C2) exists at very high salt concentration, but also that there are no traces of pure salt at $n = 0.5$.

The tentative pseudo-phase diagram constructed for the $\text{U(600)}_n\text{KCF}_3\text{SO}_3$ system is illustrated in Fig. 3. We

Figure 3. Tentative phase diagram of the $U(600)_n KCF_3SO_3$ system.

Figure 4. Variation of total ion conductivity versus inverse temperature for the $U(600)_n KCF_3SO_3$ ormolytes: (a) n between ∞ and 60; (b) n between 40 and 3.

Figure 5. Isotherms of the ionic conductivity versus composition in the $U(600)_n KCF_3SO_3$ ormolytes.

have located the C1 complex at $n = 2$, although its exact location is presumably at higher salt concentration.

3.2. Ion Conductivity

The Arrhenius conductivity plots of the $U(600)_n KCF_3SO_3$ ormolytes reproduced in Fig. 4 demonstrate that the most conducting sample at room temperature is $U(600)_{20} KCF_3SO_3$ ($2 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$) (Fig. 4(b)). According to the pseudo-phase diagram proposed (Fig. 3), at this temperature the sample exists in an amorphous region. Around 100°C , the latter xerogel and that with $n = 10$ lead to the highest conductivity value (around $1 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$) (Fig. 4(b)). As expected, the levels of conductivity in these di-ureasil hybrids are significantly lower than those observed with the POE-based analogs [7]. This aspect derives essentially from the fact that the POE chains of $U(600)$ are extremely short, meaning that their mobility, and therefore their capacity to transport ions is considerably more restricted than in high molecular weight POE chains.

The graph in Fig. 5 shows the conductivity isotherms of the xerogels. Two conductivity maxima occur at n between 100 and 80 and at n between 20 and 10. Spectroscopic studies are underway to characterize the cationic and anionic environments responsible for the location of the conductivity maxima at these two particular composition ranges.

4. Conclusions

A novel category of potassium triflate-based POE/siloxane ormolytes with good optical transparency over the entire range of salt concentration studied has been investigated. The initial results of the thermal analysis and conductivity characterization of these sol-gel processed materials encourage further studies of these compounds. A pseudo-phase diagram has been proposed for this system.

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