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Sol–gel processing and structural study of europium-doped hybrid materials

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The thermal, morphological and conducting properties of macromolecular organic–inorganic networks synthesized by the sol–gel process and containing a wide concentration range of europium trifluoromethanesulfonate, $Eu(CF_3SO_3)_3$, have been investigated. The hybrid matrix, U(2000), of these materials, classed as *ureasils*, includes a siliceous backbone and short polyether-based segments. The link between these components is made by urea bridges. The behaviour of the doped ureasils is significantly better than that of previously characterized electrolytes based on poly(ethylene oxide), PEO. The essentially amorphous character of the hybrid host contributes to an improved transparency and moderate conductivities of certain electrolytes at room temperature (*ca.* 5×10^{-6} Ω^{-1} cm^{-1}). DSC, XRD and FTIR measurements show that the formation of a high-melting crystalline complex results from the coordination of the Eu^{3+} ions by the ether oxygens of the organic moieties at composition $n = 5$ [where n represents the molar ratio of (OCH_2CH_2) units per Eu^{3+} ion]. The results obtained for samples with $n \geqslant 20$ suggest that in this range of composition the principal effect of the polyether chains is to exert a plasticizing influence, as the coordination of the cations by the urea linkages is favored.

Since the early studies of Wright and coworkers[1] in 1973 and the subsequent recognition of the technological potential of polymer electrolytes by Armand *et al.*,[2] a remarkable number of papers have been published describing examples of this subdomain of ionically conducting solids. The developments in the theoretical description of the mechanism of ion transport, and the preparation of improved polymer hosts, novel salts and additives which enhance the electrochemical or mechanical properties, have been extensively reviewed by several authors.[3] While most of the initial interest was directed toward the improvement of lithium salt based systems, motivated by the potential application of these materials in batteries, it soon became clear that salts based on multivalent cations were soluble in the polymeric host and that applications of these materials in sensors or electrochromic displays may also be of interest.[4] The incorporation of trivalent lanthanide cations into suitable polymer hosts has led to the extension of the list of possible applications to include flexible phosphors and solid-state lasers.[5–9]

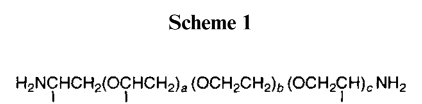
In recent years the sol–gel approach to the synthesis of a wide range of macromolecular structures has attracted interest from scientists working in a variety of domains. These materials take advantage of the rich chemistry of silicon-based networks to provide a relatively stable three-dimensional matrix, which can be readily tailored to obtain the desired chemical and physical properties. Highly transparent hybrid inorganic–organic structures with amorphous character, moderate thermal stability and a suitable capacity for dissolving guest species, are clearly of potential interest as the basis of fibre optic amplifiers, flexible phosphors and display matrices.[10]

This paper describes the preparation and characterization of ion-conducting ormosils (*or*ganically *mo*dified *sil*icate*s*), produced by the incorporation of $Eu(CF_3SO_3)_3$ into a macromolecular structure containing oligopolyoxyethylene chains grafted onto a siliceous network through urea bridges [–NHC(=O)NH–]. These materials have been classed as *ureasilicates*.[11] The undoped host matrix may be represented by the structure illustrated in Scheme 1.

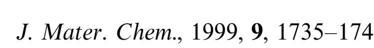
Three ureasil structures, containing 40.5, 15.5 and 8.5 oxyethylene units and designated as U(2000), U(900) and U(600), respectively, have been investigated very recently by IR[12] and photoluminescence[13] spectroscopies. These doped hybrids represent a new class of stable white light intrinsic phosphors which display broad visible photoluminescence between 14 K and room temperature.[13] The encapsulation of the europium ion by the inorganic–organic host seems to have the beneficial effect of partially shielding the luminescent centres, with a resulting reduction in their non-radiative energy losses, and providing a strong and narrow intra-$4f^6$ yellow–red contribution to the intrinsic ureasil network emission.[14] The encouraging results obtained with europium triflate, used as a model guest species, suggest that further improvements may be obtained with more suitable salt complexes.

Experimental

The diamine used in this study is available commercially as Jeffamine ED-2001® (with $a+c=2.5$ and $b=40.5$) with the structure illustrated in Scheme 2. Jeffamine ED-2001® (Fluka) was dried under vacuum for several days prior to use. $Eu(CF_3SO_3)_3$ was synthesized using a standard procedure.[15] Ethanol (Merck) and tetrahydrofuran (Merck) were stored



Scheme 1



$$H_2N\underset{CH_3}{C}HCH_2(O\underset{CH_3}{C}HCH_2)_a(OCH_2CH_2)_b(OCH_2\underset{CH_3}{C}H)_cNH_2$$

Scheme 2

over molecular sieves. 3-Isocyanatepropyltriethoxysilane (ICPTES, Fluka) was used as received. High purity distilled water was used in all experiments.

The preliminary step of the preparation of the ureasils involves the formation of urea linkages between the terminal amine groups of a doubly functional oligopolyoxyethylene segment [α,ω-diaminepoly(oxyethylene-co-propylene)] and the isocyanate group of an alkoxysilane precursor (ICPTES) in a tetrahydrofuran solution.[16] This grafting process was monitored by IR spectroscopy. As the reaction proceeds the very strong, narrow absorption band located at *ca.* 2274 cm^{-1}, assigned to the vibration of the isocyanate group of the ICPTES molecule, becomes progressively less intense, while the bands due to the presence of urea cross-links absorb more strongly.

$Eu(CF_3SO_3)_3$ was incorporated in the second step of the synthesis procedure. An appropriate amount of this salt was dissolved in a mixture of ethanol and water (molar ratio, 1 ICPTES : 4 EtOH : 1.5 H_2O), the solvents which start the hydrolysis and condensation reactions that lead to the formation of the xerogels. This solution was added to the polyether based urea cross-linked alkoxysilane precursor (designated as ureapropyltriethoxysilane, UPTES) prepared in the first stage. The mixture was stirred in a sealed flask at *ca.* 25 °C for 30 min and then cast into a Teflon® mold which was covered with Parafilm® and perforated with a syringe needle in order to ensure the slow evaporation of the solvents. The mold was left in a fume cupboard for 24 h. After a few hours gelation was already visible. The mold was maintained in an oven at 40 °C for a period of seven days and the sample was finally aged at *ca.* 80 °C for three weeks. A transparent, quite elastomeric xerogel with a yellow coloration was thus obtained.

The Eu^{3+} doped ureasils have been designated as $U(2000)_nEu(CF_3SO_3)_3$, where the letter U represents the urea linkage and 2000 indirectly indicates the length of the oligopolyoxyethylene chains. In the nomenclature adopted, *n* identifies the number of mol of (OCH_2CH_2) repeat units of the polymer chains per mol of $Eu(CF_3SO_3)_3$. Materials with 15 different compositions of *n* between 3 and 400 have been prepared.

Prior to thermal and electrical characterization, the samples were dried under vacuum for 48 h at 90 °C. All subsequent operations involving the manipulation of the ureasils and the preparation of samples for conductivity measurements and thermal analysis, were carried out under a dry argon atmosphere, within high-integrity gloveboxes.

The total ionic conductivity of the materials was determined by locating an electrolyte disk between two 10 mm diameter ion-blocking gold electrodes (Goodfellow, >99.95%). The electrolyte/electrode assembly was secured in a suitable constant volume support[17] and installed in a Buchi TO51 tube oven with a type K thermocouple placed close to the electrolyte disk to measure 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 *ca.* 7 °C intervals.

5 mm diameter ureasil disks were cut from films within the glovebox and transferred to open platinum cans which were used to support the samples during thermogravimetry (TG). These samples were transferred to the thermobalance with the shortest possible exposure to the laboratory atmosphere. Analysis took place under a flowing nitrogen atmosphere (30 cm^3 min^{-1}) at a heating rate of 10 °C min^{-1} using a Perkin Elmer TAC 7/DX controller with a TGA 7 furnace, operating at temperatures between 30 and 500 °C.

Disk sections with a mass of *ca.* 5 mg were removed from ureasil films and sealed within 40 μL aluminium differential scanning calorimeter (DSC) cans inside a preparative glovebox. The purge gas used in all the analyses was high purity argon supplied at a constant 35 cm^3 min^{-1} flow rate. Thermal analysis was carried out with a Mettler TC11 controller and a DSC 20 oven equipped with a cooling accessory. All samples were subjected to a 5 °C min^{-1} heating rate and were characterized between −40 and 350 °C.

X-Ray diffraction (XRD) measurements were performed at room temperature with a Rigaku Geigerflex D/max-c diffractometer system using monochromated Cu-Kα radiation ($\lambda = 1.54$ Å) in a 2θ range between 4 and 80°. The samples analyzed were not submitted to any thermal pre-treatment.

Mid-IR spectra were acquired at room temperature using a Unicam FT-IR system. The spectra were collected over the range 4000–400 cm^{-1} by averaging 60 scans at a maximum resolution of 1 cm^{-1}. Solid samples (2 mg) were finely ground and presented for analysis in the form of pressed disks by dispersing them in *ca.* 175 mg of dried spectroscopic grade potassium bromide (KBr, Merck). The disks were vacuum-dried at 90 °C to reduce the levels of solvent and adsorbed water in the samples prior to recording the spectra under ambient conditions. Consecutive spectra were recorded until reproducible results were obtained. The evaporation was monitored by IR in the OH region. A linear base line was assumed in all cases from 2000 to 400 cm^{-1}, in the wavenumber ranges where no significant absorbances were detected, and the intensities of the absorption bands in each spectrum were normalized relative to the most intense band. In order to evaluate complex band envelopes and to identify underlying component bands of the mid-IR spectra, the curve-fitting procedure in the ORIGIN computer software for IBM PC-compatible computers was used. Band shapes were described by Gaussian-type functions.

Results and discussion

Almost all electrolytes based on high molecular weight polymer hosts, which contain the CH_2CH_2O repeat unit are semicrystalline solids with complex microstructures.[3] The crystalline content of these materials is largely controlled by the structure of the polymer host, the interactions between the guest salt species and the host macromolecule, the composition of the electrolyte and the experimental conditions which are used to prepare the sample under study (*e.g.*, the choice and purity of casting solvent, the concentration of the casting solution and the thermal history of the sample). The use of commercial host polymers, such as poly(ethylene oxide), PEO, normally imposes limitations on the performance of the electrolyte as a direct consequence of the presence of crystalline domains within the material structure. In this study we have incorporated the CH_2CH_2O structural unit into an amorphous silicon-based network to produce homogeneous materials with optimized solubilization characteristics.

Ionic conductivity

Reference to Fig. 1 and 2, in which the variation of the total ionic conductivity as a function of electrolyte temperature and composition is shown, confirms that the conductivity of the electrolytes based on the U(2000) hybrid is almost independent of the salt content over a wide range of composition. In this respect the behavior found for the sol–gel derived materials is comparable to that reported in other oxyethylene-based polymer electrolytes[17] but very different from conventional aqueous or non-aqueous electrolytes and even that of classical solid electrolytes. The explanation generally proposed for this observation is that as the polymer environment is a medium of low dielectric constant, the dissociation of the guest salt depends on the salt concentration and increases as the concentration is reduced. Although the number of charged mobile species is less at higher values of *n*, the dissociation of the salt to form

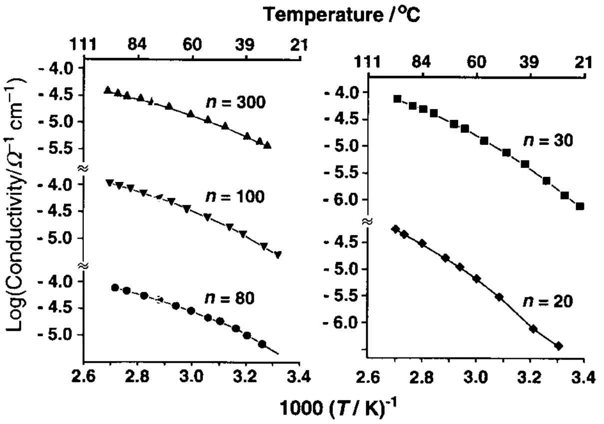


Fig. 1 Temperature dependence of ionic conductivity of selected U(2000)$_n$Eu(CF$_3$SO$_3$)$_3$ electrolytes.

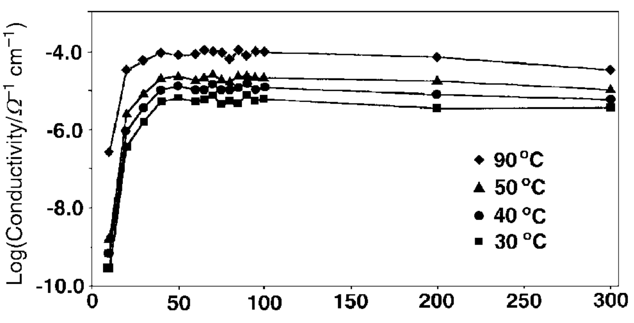


Fig. 2 Conductivity isotherms of selected U(2000)$_n$Eu(CF$_3$SO$_3$)$_3$ electrolytes.

charged species is greater, at least partially compensating for the effect of lower salt concentration. At high salt concentration, or low values of n, the salt dissociates to only a limited extent, forming ion pairs or higher ion aggregates with reduced ionic mobility.[18–20] The presence of relatively high concentrations of guest salt also results in the existence of a large number of sites where the attraction between the cation and the heteroatoms on the polymer segments acts as a transient structural pin between adjacent chains. These sites are designated as ionic cross-links and are thought to be responsible for the observed rapid decrease in electrolyte conductivity as they reduce the segmental mobility of the host polymer chains, thus leading to a sharp increase of the glass transition temperature, T_g. For instance, it has been reported[21] that in PEO-based electrolytes containing europium bromide, EuBr$_3$, the T_g of the host polymer (*ca.* −60 °C) undergoes a dramatic increase upon incorporation of the salt. A glass transition of 42–47 °C was found for PEO$_3$EuBr$_3$, a stoichiometry for which a salt-rich, high-melting point complex is formed.[21]

At room temperature the ionic conductivity of the ureasil with composition $n=80$ is *ca.* $5\times10^{-6}\ \Omega^{-1}\,\mathrm{cm}^{-1}$ (Fig. 1) and at $n=20$ is *ca.* $2\times10^{-7}\ \Omega^{-1}\,\mathrm{cm}^{-1}$. These conductivities are significantly higher than those observed with the electrolyte formed by the addition of the same salt to commercial PEO.[22] The most significant difference between the sol–gel derived electrolytes and commercial PEO-based materials is that the variation of ionic conductivity with temperature in the former materials is very much less. An explanation consistent with the observed results is that the sol–gel electrolytes are significantly more amorphous than the PEO-based materials, with a lower activation energy for ion transport. This aspect of their performance could make them more suitable for applications in devices designed to operate at ambient or moderate temperatures.

It should be noted at this stage that the complexation of the lanthanide ions in the ureasils also appears to be different from that normally found in the classical ion conducting polymers of the polyether type. The IR and photoluminescent spectral features of a series of recently studied Eu^{3+} doped ureasils with salt compositions ranging from $n=200$ to 20, provide conclusive evidence that the cations are preferentially coordinated by the carbonyl oxygens of the urea linkages rather than by the ether oxygens of the short polyether chains present in the materials.[23] This fact strongly suggests that the oxyethylene moieties may merely be playing the role of plasticizing agents in the hybrid xerogels with $200\geqslant n\geqslant20$.

Thermal studies

Further insight into the morphology of the polymer electrolyte formed by the addition of salt to the sol–gel processed host macromolecule, may be obtained from thermal analysis studies. Again a comparison of the novel electrolyte with PEO-based materials is useful. Compositions of the latter electrolytes with $n>30$ are increasingly crystalline, with a well-defined melting peak located at *ca.* 60 °C.[22] The results of thermal analysis of sol–gel processed samples indicate that electrolytes with values of n between 400 and 100 are much more amorphous than electrolytes prepared with PEO.[22]

The thermograms of some ureasils with low salt content (*e.g.*, $n=100$ and 85 in Fig. 3) show two fairly diffuse endothermic peaks in the temperature range where fusion of macromolecules containing CH$_2$CH$_2$O segments would be expected. Both thermal events have also been detected in the DSC thermogram of the undoped ureasil U(2000).[16] The presence of two melting peaks at this location suggests that there are two different, but closely related, polymer environments. Other authors[24] have ascribed the endotherms observed in the DSC traces of polymer mixtures to the hydrogen-bond disruption of structures detected by IR spectroscopic studies. The extensively hydrogen bonded polyurethane block copolymers, for example, belong to this category of materials. At the molecular level intimate mixing results from the formation of strong hydrogen bonds between alternating low glass transition soft segments (generally polyethers or polyesters) and more rigid, polar urethane [–HNC(=O)O–] hard segments formed from the extension of a diisocyanate (often aromatic) with low molecular weight diols. The donor sites are the N–H groups of the urethane linkages and the hydrogen bond acceptors may be either the hard urethane segments (the

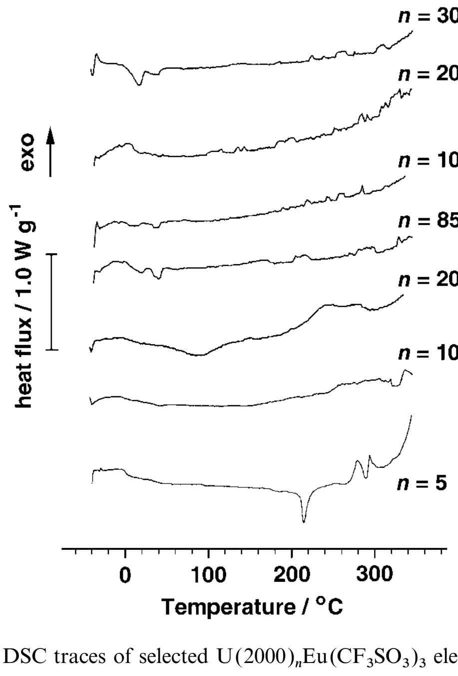


Fig. 3 DSC traces of selected U(2000)$_n$Eu(CF$_3$SO$_3$)$_3$ electrolytes.

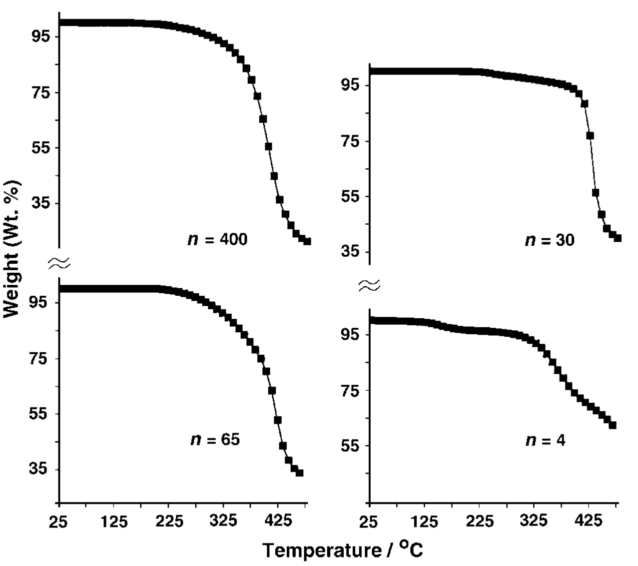


Fig. 4 Results of thermogravimetry of selected $U(2000)_nEu(CF_3SO_3)_3$ electrolytes.

carbonyl of the urethane groups) or the soft segments (ester carbonyls or ether oxygens). The ureasils are composed of flexible polyether chains trapped between rigid siliceous blocks by means of hard urea cross-links containing three active centers capable of participating in highly directional hydrogen bonds and they structurally resemble the polyurethane block polymers. Mid-IR spectroscopic studies[12] have confirmed that although most of the urea groups of the undoped ureasil U(2000) are 'free' (*i.e.*, completely devoid of any hydrogen bonding), two hydrogen-bonded urea–polyether structures are present in the material. The latter associations might be expected to arise in locations where the urea linkage is physically close to the chain segments. Recent data from gel permeation chromatography (GPC) studies and DSC analysis[25] of Jeffamine ED-2001® have allowed us to conclude that the parent diamine of U(2000) is composed of polyether chains with two different lengths. These results remove any doubts regarding the relationship between the two IR bands produced by the absorption of the hydrogen-bonded urea–polyether structures in U(2000)-based systems and the two melting peaks seen in Fig. 3 and confirm that their nature is clearly morphological.

At high salt concentration ($n=5$ in Fig. 3) no polymer segment fusion is observed but an endothermic peak is present at *ca.* 200 °C. This high temperature peak may be associated with the fusion of a salt–polymer complex, as reported in PEO-based systems with lanthanide salt guest species.[21] Within this range of compositions two exothermic events are also apparent at *ca.* 270 and 300 °C. Although further studies are necessary to determine the nature of this feature, deposition of salt from the polymer electrolyte might be expected to occur under these experimental conditions. A T_g of *ca.* -5 °C is also detected in the DSC trace of $U(2000)_5Eu(CF_3SO_3)_3$ (Fig. 3). As the T_g of the undoped material is *ca.* -53 °C[11b] these results confirm that the addition of significant amounts of salt results in a moderate variation of *ca.* 48 °C.

The stability limit of all the $U(2000)_nEu(CF_3SO_3)_3$ samples is located above 200 °C (Fig. 3). From this temperature a gradual but continuous loss of weight and an increasingly irregular heat flux was registered, characteristic of oxidative degradation of polymer molecules. Surprisingly, in view of the absence of thermal stabilizers or anti-oxidant additives in the host polymer, the materials were found to show moderate thermal stability. This conclusion is supported by data from thermogravimetry, included in Fig. 4, which suggest that the Eu^{3+} doped xerogels degrade, in various stages, to form silicate residues and small volatile organic fragments. We may also conclude from these studies that high $Eu(CF_3SO_3)_3$ contents destabilize the ureasils. Fig. 4 shows that weight loss begins at *ca.* 125 °C for the material with composition $n=4$.

X-Ray diffraction

Fig. 5 shows the XRD patterns of the undoped ureasil U(2000), that of Jeffamine ED-2001® and those of some $U(2000)_nEu(CF_3SO_3)_3$ compounds ($n=200$, 85, 55, 30, 10 and 5). The diffraction pattern of Jeffamine ED-2001® exhibits a series of several sharp Bragg peaks, with the principal peaks centered at 19.30, 23.45, 26.55, 36.15 and 39.4° (indicated in Fig. 5 as a, b, c, d and e, respectively). These peaks, identical to those produced by crystalline poly(ethylene glycol), PEG, a low molecular weight PEO, are therefore associated with the diffraction of the ordered short organic segments.[13] After inclusion of the diamine in the inorganic backbone, only the two more intense peaks (a and b) can be detected close to 19.15 and 23.25°. Apart from a slight shift (of 0.15–0.20°) towards smaller angles, there is an inversion of the relative intensity of both peaks (by approximately a factor of two). This intensity inversion is probably induced by the grafting procedure. The polymer chains lose their initial helical structure and gain segmental mobility, without reaching the liquid state, as suggested by IR analysis.[12]

The diffraction patterns of the doped ureasils, illustrated in Fig. 5, are consistent with the DSC thermal results discussed above. For low salt concentration hybrids (*e.g.*, $n=200$ and 85) the two main sharp peaks, characteristic of the crystalline polyether chains, are clearly observed at 19.3 and 23.50°, for $n=200$, and at 19.15 and 23.45°, for $n=85$. Although the position of the peaks is almost the same as that of the corresponding peaks in U(2000), there is an increase in the relative intensity of the second peak. This observation indicates that the incorporation of the europium salt in the hybrid host does not destroy the crystalline order of the polyether chains and strongly suggests that the Eu^{3+} ions are not coordinated by the ether oxygens of the short polyether chains present in the materials, in contrast with what has been observed for analogous PEO-based electrolytes. As previously suggested, the oxyethylene moieties may merely be playing the role of plasticizing agents in the hybrid xerogels.

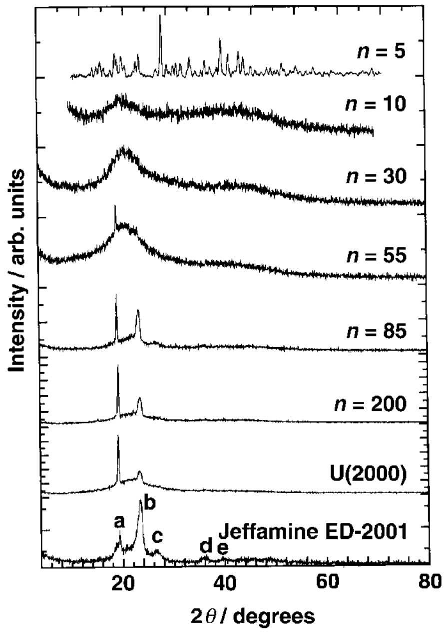


Fig. 5 XRD patterns of Jeffamine ED-2001®, of the undoped ureasil U(2000) and of the ureasils $U(2000)_nEu(CF_3SO_3)_3$ with $n=200$, 85, 55, 30, 10 and 5.

As the concentration of salt increases, the characteristic crystalline polyether peaks disappear and the XRD patterns show only the typical amorphous broad band associated with the coherent diffraction domains of the siliceous skeleton ($n=55$, 30 and 10 in Fig. 5).[13] This broad band, also detected in the diffraction patterns of Jeffamine ED-2001® and U(2000) at *ca.* 21.6°, has been discussed in detail elsewhere.[13]

The presence of a high-melting-point crystalline complex with a stoichiometry which appears to be close to an oxygen : Eu^{3+} ratio of 5 : 1, mentioned in the discussion of the DSC results, is clearly seen in the diffractogram of the $U(2000)_5Eu(CF_3SO_3)_3$ ureasil (Fig. 5). The series of sharp peaks observed between 14 and 50° [different from those observed in pure $Eu(CF_3SO_3)_3$[14,16]] certainly reflects the existence of this crystalline complex. A similar high-melting-point crystalline complex with a stoichiometry around 3 : 1 was previously reported for analogous PEO–$EuBr_3$ electrolytes.[21]

FTIR

The presence of the high-melting temperature complex detected by DSC and XRD is unequivocally demonstrated by IR spectroscopy. For the purpose of comparison Fig. 6 is included to show the room-temperature mid-IR spectra of the ureasils with $n=20$ and 5. Several features observed in the spectrum of $U(2000)_5Eu(CF_3SO_3)_3$, indicative of the coordination between the ether oxygens of the polyether segments of the hybrid matrix and the lanthanide ions, help to substantiate the formation of the complex.

Probably the most significant spectral evidence for the existence of this complex is the absence of the strong band attributed to the CO stretching vibration of non-coordinated polyether chains[26,27] from the spectrum of $U(2000)_5Eu(CF_3SO_3)_3$. This band, found at 1110 cm^{-1} in the spectrum of $U(2000)_{20}Eu(CF_3SO_3)_3$ (Fig. 6), is replaced by a strong band at 1056 cm^{-1} and a shoulder at 1069 cm^{-1} (Fig. 6). Shifts of the 1110 cm^{-1} band to *ca.* 1080, 1060 and 1075 cm^{-1} have been reported, respectively, by Wendsjö *et al.*[28] for the complex $PEO_9Pb(CF_3SO_3)_2$, by Twomey and Chen[29] for a PEO_nNdCl_3 crystalline compound and by Bernson and Lindgren[19] for PEO-based lanthanide triflate complexes. According to these authors, the downshift observed is caused by a change in the environment of the ether oxygens, probably produced by the coordination to metal ions, and its magnitude depends on the strength of the interaction. The origin of the shoulder observed in the spectrum of the ureasil with $n=5$ is unknown at this stage (Fig. 6). It is again stressed that no apparent changes in the environment of the ether oxygens which would result from the dissolution of $Eu(CF_3SO_3)_3$, were found in the spectra of a series of doped ureasils with $n \geqslant 20$.[23] The presence of two new distinct and intense bands at 1114 and 1105 cm^{-1} in the CO spectral region of the $U(2000)_5Eu(CF_3SO_3)_3$ compound (Fig. 6) is also noteworthy. A pair of bands at exactly the same location has been observed in the spectrum of the crystalline compound $PEO_1KCF_3SO_3$.[30]

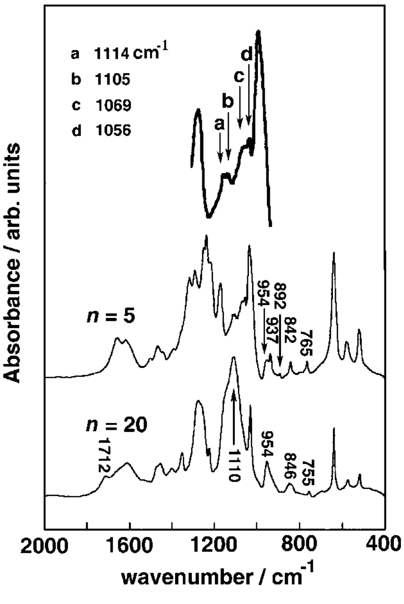


Fig. 6 Room-temperature mid-IR spectra of two selected $U(2000)_nEu(CF_3SO_3)_3$ ureasils in the 2000–400 cm^{-1} frequency range.

The spectral features described above suggest that all the ether oxygens are coordinated to Eu^{3+} ions for $n=5$ and are therefore in perfect agreement with the thermal behavior displayed by this ureasil. The Amide I region of the spectrum of $U(2000)_5Eu(CF_3SO_3)_3$ corroborates this claim. The Amide I band is produced by a very complex vibration which involves the contribution of the C=O stretching, the C–N stretching and the C–C–N deformation vibrations. It consists of several components reflecting C=O groups in different environments. Three components have been detected for U(2000) at 1750, 1716 and 1677 cm^{-1}.[12] The high frequency component, which has been tentatively assigned to the absorption of urea groups completely devoid of any hydrogen bonding,[12] disappears as the salt is incorporated.[23] The remaining two components have been associated with the vibration of NHC(=O)NH groups belonging to two urea–polyether structures. In the series of doped ureasils with $n \geqslant 20$ it was shown that the only component that remained was the medium intensity band at 1713 cm^{-1}.[23] In the spectrum of $U(2000)_5Eu(CF_3SO_3)_3$ this band is not visible (Fig. 6). This spectral observation is quite interesting as it suggests that for $n=5$ all the polyether chains are involved in the process of cation coordination and can thus no longer hydrogen bond to the N–H groups of the urea linkages, leaving them free.

The 1000–800 cm^{-1} spectral region, which includes absorption bands produced by a mixture of skeletal stretching and CH_2 rocking vibrational modes,[26,27] is also very sensitive to coordination effects arising from interactions between the ether oxygens of the polyether chains and metal cations. Changes in this range of frequencies reflect alterations ocurring in the local structure of the polymer backbone. It is immediately recognized that the spectra of the ureasils, depicted in Fig. 6, exhibit dramatic differences in this spectral region. While the dominating features in the spectrum of $U(2000)_{20}Eu(CF_3SO_3)_3$ are a medium intensity band located at 954 cm^{-1}, due to the coupled vibration of CC stretching and CH_2 rocking modes,[26,27] and a weak band found at 846 cm^{-1}, attributed to the coupled vibration of CO stretching and CH_2 rocking modes,[26,27] in the spectrum of $U(2000)_5Eu(CF_3SO_3)_3$ the strongest new band is an absorption situated at 937 cm^{-1}. Another new band, somewhat weaker, is detected at 892 cm^{-1} in the spectrum of $U(2000)_5Eu(CF_3SO_3)_3$ (Fig. 6). These two bands are associated with the presence of the complex. Similar observations have been reported by Chintapalli *et al.*[30] for a crystalline $PEO_nKCF_3SO_3$ compound with a 1 : 1 stoichiometry. Finally, it should be noted that the band observed at 846 cm^{-1} in the spectrum of $U(2000)_{20}Eu(CF_3SO_3)_3$ is downshifted to 842 cm^{-1} in the spectrum of $U(2000)_5Eu(CF_3SO_3)_3$, whereas the band located at 954 cm^{-1} remains unshifted.

It has been shown that the band assigned to the symmetric deformation of the CF_3 group, $\delta_s(CF_3)$, of the triflate ion is an extremely powerful tool for studying ionic association in polymer/salt systems.[31] In the spectrum of $U(2000)_{20}Eu(CF_3SO_3)_3$ a very weak band at 755 cm^{-1} and an even weaker shoulder at *ca.* 763 cm^{-1} are observed (Fig. 6). Curve-fitting has allowed us to conclude that $U(2000)_5Eu(CF_3SO_3)_3$ has three bands in this region. The shoulder at 763 cm^{-1} grows in intensity and becomes the dominating feature of this spectral region.

The intensity of the absorption at 755 cm^{-1} is drastically reduced for $n=5$ and the band is transformed into an almost insignificant shoulder located at 757 cm^{-1}. An additional shoulder, stronger than the latter, appears at 774 cm^{-1} in the spectrum of $U(2000)_5Eu(CF_3SO_3)_3$. We tentatively assign the band at 764 cm^{-1} and the shoulder at 774 cm^{-1} to the presence of the crystalline complex. In the system $PEO_nKCF_3SO_3$ the single peak detected at 765 cm^{-1} for stoichiometry 1 : 1 has also been associated with the existence of a crystalline compound.[30]

The ordered local structure of $U(2000)_5Eu(CF_3SO_3)_3$ is further confirmed by the breadth of its characteristic absorption bands which are markedly narrower than those of the spectrum of $U(2000)_{20}Eu(CF_3SO_3)_3$, a fact that underlines once more the crystalline character of the ureasil with $n=5$.

Conclusions

The conclusions of the preliminary characterization of the sol–gel processed materials described here suggest that these systems deserve more detailed study. The europium doped xerogels exhibit higher levels of total ionic conductivity than materials based on commercial PEO with similar salt concentration. The films were found to show good mechanical properties, were highly amorphous and, even without the addition of specific thermal stabilizers, were moderately stable. Their excellent optical transparency was maintained over a large range of salt concentration and even at high doping levels there was no indication of phase separation.

The structural data obtained from XRD studies were consistent with results of FTIR analysis and supported the proposal that at low europium concentrations the cation is coordinated to the carbonyl oxygens of the urea linkages rather than to the ether oxygens of the polyether chains. The increase in the number of cations with salt concentration results in a saturation of coordination sites and consequently the ether oxygens also become involved in europium coordination at higher salt doping levels.

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