

S. C. Nunes · V. de Zea Bermudez · M. M. Silva
M. J. Smith · E. Morales · L. D. Carlos
R. A. Sá Ferreira · J. Rocha

Sol-gel derived Li⁺-doped poly(ϵ -caprolactone)/siloxane biohybrid electrolytes

Revised: 11 October 2004 / Accepted: 21 December 2004 / Published online: 15 June 2005
© Springer-Verlag 2005

Abstract Electrolytes based on a poly(ϵ -caprolactone) (PCL)/siloxane organic/inorganic host framework doped with lithium triflate (LiCF₃SO₃) were synthesised through the sol-gel process. In this biohybrid matrix short PCL chains are covalently bonded via urethane linkages to the siliceous network. Samples with salt composition n (molar ratio of PCL repeat units per Li⁺ ion) ranging from ∞ to 0.5 were investigated. All the ormolyte materials analyzed are amorphous. Xerogels with $n > 0.5$ are thermally stable up to about 300°C. The most conducting ormolyte of the series is that with $n = 0.5$ (1.6×10^{-7} and $3.2 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ at 25 and 100°C, respectively). This sample is electrochemically stable between -1 and 6 V versus Li⁺.

Keywords Sol-gel · Poly(ϵ -caprolactone)/siloxane hybrid · Ionic conductivity

Introduction

Owing to their technological impact in the domain of solid state electrochemistry, in particular for the fabrication of advanced batteries, sensors and electrochromic and photoelectrochemical devices [1], polymer electrolytes [2] have attracted much interest in the past two decades.

Conventional polymer electrolytes are obtained through the dissolution of an ionic salt in a poly(oxyethylene) (POE)-type host polymer. Recently, the sol-gel process [3] emerged as a standard method for preparing improved polymer/siloxane electrolytes, since the organic/inorganic hybrid concept [4] allows to combine in a single material the amorphous character, the good mechanical resistance and the excellent thermal/chemical stability provided by the silica backbone, with the flexibility and solvating ability imparted by the POE chains. In addition, these modified host polymer systems withstand the addition of significantly higher amounts of guest salt than those usually permitted in the classical systems. Another advantage of this strategy is that the materials may be readily processed under mild conditions into thin films. Numerous Li⁺-doped ormolyte systems have been investigated in the last few years [5–13].

In the present work we introduce a new family of diurethane cross-linked siloxane-based hybrid electrolytes incorporating poly(ϵ -caprolactone) (PCL) segments (average molecular weight of 530 gmol^{-1}) and lithium triflate (LiCF₃SO₃) (Scheme 1). The structure, morphology, thermal properties and ionic conductivity of a series of samples with a wide salt concentration range have been investigated. To our knowledge, this is the first time that PCL is used for the purpose of developing ion conducting materials.

PCL is a linear, aliphatic thermoplastic, biocompatible, permeable, hydrophobic and biodegradable poly(ester), non-toxic for living organisms, that is resorbed after a certain period of implantation time.

S. C. Nunes · V. de Zea Bermudez (✉)
Departamento de Química and CQ-VR,
Universidade de Trás-os-Montes e Alto Douro,
5000-911 Vila Real, Portugal
E-mail: vbermude@utad.pt
Fax: +00-351-259-350480

M. M. Silva · M. J. Smith
Departamento de Química,
Universidade do Minho,
Gualtar, 4710-057, Braga, Portugal

E. Morales
Instituto de Ciencia y Tecnología de Polímeros (CSIC),
Calle Juan de la Cierva 3, 28006 Madrid, Spain

L. D. Carlos · R. A. Sá Ferreira
Departamento de Física and CICECO,
Universidade de Aveiro, 3810-193 Aveiro, Portugal

J. Rocha
Departamento de Química and CICECO,
Universidade de Aveiro, 3810-193 Aveiro, Portugal

Because of this unique set of properties, this biopolymer and its copolymers have found widespread application in the field of medicine, as biodegradable suture, artificial skin, resorbable prostheses and containers for sustained drug delivery [14–16]. In this context, PCL-based hybrid structures have been also developed. For instance, Tian et al. [17] produced PCL/silica ceramers that may find use as degradable bioglasses, as coating materials for bone implants and prosthetic devices and as supports for enzyme immobilization. A bioactive and degradable PCL/silica hybrid, with application as bone substitute, was also proposed by S-H. Rhee et al. [18]. In both cases the average molecular weight of the PCL molecule employed was 2000 g mol^{-1} .

The presence of $(\text{CH}_2\text{CH}_2\text{O})$ segments in amorphous polymeric networks is in many cases a sufficient condition for the materials to dissolve and transport ionic species. The objective of the present study was to use the sol-gel method to produce amorphous hybrid structures which combine high levels of conductivity with biodegradability. Such materials may be expected to have lower environmental impact than that of the electrolytes currently used in commercial cells.

Experimental

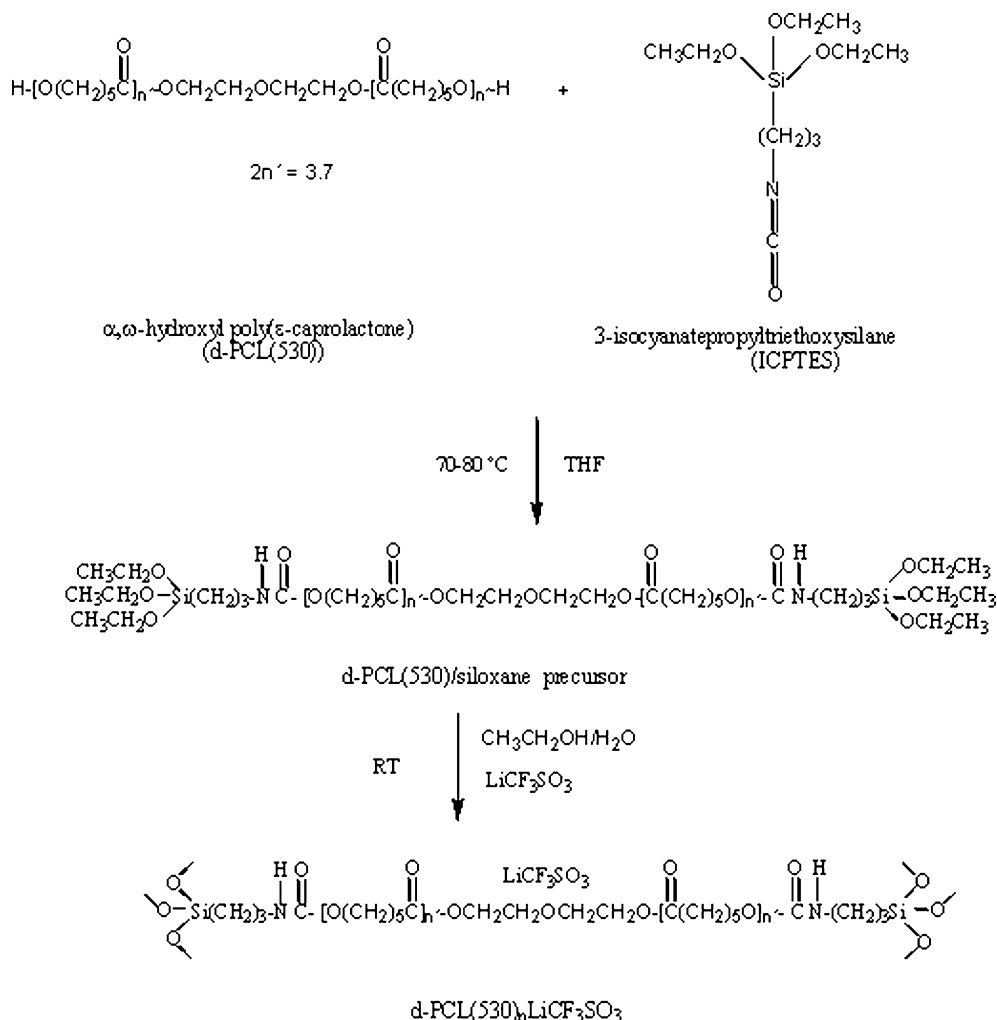
Materials

Lithium trifluoromethanesulfonate (LiCF_3SO_3 , Aldrich) was dried under vacuum at 25°C for several days prior to being used. α , ω -hydroxyl poly(ϵ -caprolactone) (PCL(530), Fluka, average molecular weight 530 g/mol) and 3-isocyanatepropyltriethoxysilane (ICPTES, Fluka) were used as received. Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, Merck) and tetrahydrofuran (THF, Merck) were stored over molecular sieves. High purity distilled water (H_2O) was used in all experiments.

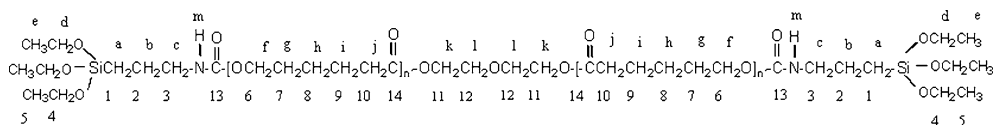
Synthesis of the d-PCL(530)/siloxane biohybrids (Schemes 1 and 2)

The preliminary stage of the preparation of the LiCF_3SO_3 -doped d-PCL(530)/siloxane hybrids (where d stands for di) involved the formation of a urethane cross-link between the hydroxyl ($-\text{OH}$) end groups of the PCL

Scheme 1 Synthetic procedure of the $\text{d-PCL}(530)_n\text{LiCF}_3\text{SO}_3/\text{siloxane}$ hybrids.



Scheme 2 Structure of the d-PCL(530)_nLiCF₃SO₃/siloxane hybrid precursor



chains and the isocyanate ($-N=C=O$) group of ICP-TES to yield the organic-inorganic hybrid precursor designated d-PCL(530)/siloxane precursor.

In the second stage of the synthetic procedure, a mixture of CH_3CH_2OH and H_2O was added to the d-PCL(530)/siloxane precursor to promote the hydrolysis and condensation reactions characteristic of the sol-gel process. In the case of the preparation of the doped biohybrids, $LiCF_3SO_3$ was added to the CH_3CH_2OH/H_2O solution.

A typical synthetic procedure follows:

Step 1 - Synthesis of the d-PCL(530)/siloxane precursor A mass of 2.000 g (3.774 mmol) of PCL(530) was dissolved in 10 ml of THF by stirring. A volume of 1.863 ml (7.548 mmol) of ICPTES was added to this solution with stirring in a fume cupboard. The flask was then sealed and the solution was stirred for approximately 24 h at 60–70°C. The grafting process was infrared monitored. During the formation of the urethane groups, the intensity of the strong and sharp band characteristic of the stretching vibration of the $-N=C=O$ group of ICPTES, typically located at 2273 cm^{-1} , was progressively reduced, until it disappeared upon completion of the reaction. In parallel, a series of new bands, associated with the vibrations of the urethane group, appeared in the $1800\text{--}1500\text{ cm}^{-1}$ spectral region. The d-PCL(530)/siloxane precursor was obtained as a yellowish transparent oil. Its structure, represented in Scheme 2, was confirmed by ^{13}C NMR ($CDCl_3$, 100.62 MHz) [13, 19–22] and 1H NMR ($CDCl_3$, 400.13 MHz) [13, 20–25] (Table 1).

Step 2 - Synthesis of the PCL(530)/siloxane biohybrid A volume of 1.761 ml (30.192 mmol) of CH_3CH_2OH , 204 μ l (11.32 mmol) of H_2O and an appropriate mass of $LiCF_3SO_3$ were added to the THF solution of the d-PCL(530)/siloxane precursor obtained in the previous step. The mixture was stirred in a sealed flask for 30 min and then cast into a Teflon mould, which was covered with Parafilm and left in a fume cupboard for 24 h. The mould was transferred to an oven at 50°C and the sample was aged for a period of 4 weeks. The materials were obtained as transparent, flexible monoliths with a yellowish hue. The ormolytes were identified using the notation d-PCL(530)_nLiCF₃SO₃, where n (salt composition) indicates the number of $(C(=O)(CH_2)_5O)$ PCL repeat units per Li^+ ion. Samples with $n = \infty, 200, 93, 19, 40, 2.3, 1, 0.5$ and 0.28 were produced. Some relevant details of the synthetic procedure are given in Table 2.

Characterisation

^{13}C and 1H NMR spectra were recorded on a Bruker ARX400 NMR spectrometer (100.62 MHz and 400.13 MHz, respectively) in $CDCl_3$ at CACTI - Universidade de Vigo (Spain). Chemical shifts, δ are quoted in ppm from tetramethylsilane (TMS). ^{29}Si magic-angle spinning (MAS) and ^{13}C cross-polarization (CP) MAS NMR spectra were performed using a Bruker Avance 400 (9.4 T) spectrometer at 79.49 and 100.62 MHz, respectively. ^{29}Si MAS NMR spectra were recorded with

Table 1 1H and ^{13}C NMR of d-PCL(530)/siloxane precursor and ^{13}C CP/MAS data of selected d-PCL(530)_nLiCF₃SO₃/siloxane hybrids

1H NMR d-PCL(530)/siloxane precursor	Attribution [13, 20–25]	^{13}C NMR d-PCL(530)/ siloxane precursor	^{13}C CP/MAS NMR d-PCL(530) _n LiCF ₃ SO ₃			Attribution [13, 19–22]		
			∞	93	2.3			
5.20–5.10	s, b	2H	H^m	173.11–172.91	173.39	173.38	175.20	C^{14}
4.20–4.00	m	4H	H^k	156.40	157.30	157.32	158.00	C^{13}
4.00–3.80	m	$\cong 7.4H$	H^f	68.65–68.61	69.00	68.93	69.00	C^{12}
3.67–3.61	q	12H	H^d	63.94–63.67	64.06	64.03	64.91	C^6
3.53–3.43	m	4H	H^l	62.95–62.87	61.51	62.32	62.00	C^{11}
3.05–2.97	m	4H	H^c	57.98	55.90	–	57.76	C^4
2.19–2.11	m	$\cong 7.4H$	H^j	43.06–42.99	43.03	44.20	44.60	C^3
1.53–1.42	m	$\cong 19.4H$	H^b, H^i, H^g	33.71–33.57	33.92	33.86	34.00	C^{10}
1.25–1.20	m	$\cong 7.4H$	H^h	28.3	28.47	28.44	28.04	C^7
1.06–1.03	t	18 H	H^e	25.12–25.08	25.40	25.46	25.15	C^9
0.47–0.43	t	4H	H^a	24.23–24.07	24.81	24.71	23.80	C^8
				22.89	20.38	20.96	20.30	C^2
				17.93–17.86	18.17	–	17.83	C^5
				7.23	14.85	14.63	14.30	C^1
					9.99	10.83		

s - singlet, t - triplet, q - quartet, m - multiplet, b - broad

Table 2 Details of the synthetic procedure of the d-PCL(530)_nLiCF₃SO₃/siloxane hybrids

n = [C(=O)(CH ₂) ₅ O]/Li ⁺ (molmol ⁻¹)	m(LiCF ₃ SO ₃) (g)	Si/Li ⁺ (molmol ⁻¹)	Si/Li ⁺ (gg ⁻¹)
∞	–	–	–
200	0.0109	107.527	170.491
93	0.0235	50.0000	79.2781
40	0.0547	21.5054	34.0981
19	0.1153	10.2150	16.1966
2.3	0.9523	1.2365	1.9606
1.0	2.1903	0.5376	0.8524
0.5	4.3805	0.2688	0.4262
0.28	7.8224	0.1505	0.2387

2 μs (equivalent to 30°) rf pulses, a recycle delay of 60 s and at a 5.0 kHz spinning rate. ¹³C CP/MAS NMR spectra were recorded with 4 μs ¹H 90° pulse, 2 ms contact time, a recycle delay of 4 s and at a spinning rate of 8 kHz. Chemical shifts (δ) are quoted in ppm from TMS.

The X-ray diffraction (XRD) measurements were carried out at room temperature (RT) with a Rigaku Geigerflex D/max-c diffractometer system using monochromated CuK_α radiation (λ = 1.54 Å) over the 2θ range of between 4 and 80° at a resolution of 0.05°. The xerogel samples, analysed as solids, were not submitted to any thermal pre-treatment.

A DSC131 Setaram Differential Scanning Calorimeter (DSC) was used to determine the thermal characteristics of the ormolytes. Disk sections with masses of approximately 25 mg were removed from the d-PCL(530)/Siloxane film, placed in 40 μl aluminium cans and stored in a dessicator over phosphorous pentoxide (P₂O₅) for one week at RT under vacuum. After this drying treatment the cans were hermetically sealed and the thermograms were recorded. Each sample was heated from 25 to 300°C at 10°C min⁻¹. The purge gas used in both experiments was high purity nitrogen supplied at a constant 35 cm³ min⁻¹ flow rate.

Samples for thermogravimetric analysis (TGA) were transferred to open platinum crucibles and analysed using a Mettler TGA/SDTA 851 thermobalance at a heating rate of 10° min⁻¹ using dry nitrogen as purging gas (20 cm³/min). Prior to measurement, the xerogels were vacuum-dried at 80°C for about 48 h and stored in an argon-filled glove box.

Prior to characterisation of conductivity behaviour, the d-PCL(530)/Siloxane ormolytes were vacuum-dried at 80°C for about 48 h and stored in a high-integrity, argon-filled glove box. For bulk conductivity measurements, an ormolyte disk was placed between two 10 mm diameter ion-blocking gold electrodes (Goodfellow, > 99.9%). The electrode/ormolyte/electrode assembly was secured in a suitable constant-volume support [26] which was installed in a Buchi TO 51 tube oven. A calibrated type K thermocouple, placed close to the ormolyte disk, was used to measure the sample temperature with a precision of about ± 0.2°C and samples were characterised over a temperature range of between 25 and 100°C. Bulk conductivities of the samples were obtained

during heating cycles using the complex plane impedance technique (Schlumberger Solartron 1250 frequency response analyser and 1286 electrochemical interface) over a frequency range of 65 kHz to 0.5 Hz. The electrolyte behaviour was found to be almost ideal and bulk conductivities were extracted in the conventional manner from impedance data by using an equivalent circuit composed of R_b in parallel with C_g, where R_b is the electrical resistance of the electrolyte and C_g is its geometric capacity. The circuit element corresponding to the blocking electrode interface was simulated by a series C_{dl} element, where C_{dl} is the double layer capacity. The experimental spectra showed a single high frequency semicircle with a low frequency vertical spike. Reproducibility of measurements was better than 5%.

The redox stability domain of the most conducting sample was studied by means of cyclic voltammetry using an Autolab PGSTAT30 potentiostat/galvanostat equipment. The ormolyte was sandwiched between two nickel foil ion-blocking electrodes, with lithium foil counter and reference electrodes, and located inside a PTFE sealed cell. The assembly of the cell was performed in an argon-filled dry-box, with a humidity level lower than 2 ppm. Prior to characterisation the xerogel (6 mm diameter) was dried under vacuum at 80°C for about 48 h. Experiments were run at 80°C at a sweep rate of 20 mV min⁻¹.

Results and Discussion

Structure and Morphology

The ¹³C CP/MAS and ²⁹Si MAS NMR spectra of selected d-PCL(530)_nLiCF₃SO₃/siloxane hybrids are reproduced in Figs. 1 and 2, respectively. The position and attribution of the resonance peaks [19–25] are listed in Tables 1 and 3, respectively.

The ¹³C CP/MAS NMR spectra of the urethane cross-linked d-PCL(530)/siloxane xerogels with n = ∞, 93 and 2.3 is dominated by a series of peaks attributed to the resonance of the methylene carbon atoms of the PCL repeat units (see carbon atoms C⁶ to C¹⁰ in Scheme 2, Table 1 and Fig. 1). The peaks associated with the carbonyl carbon atoms of the ester (C(=O)OCH₂) and urethane (NHC(=O)O) groups are ill-defined and weak

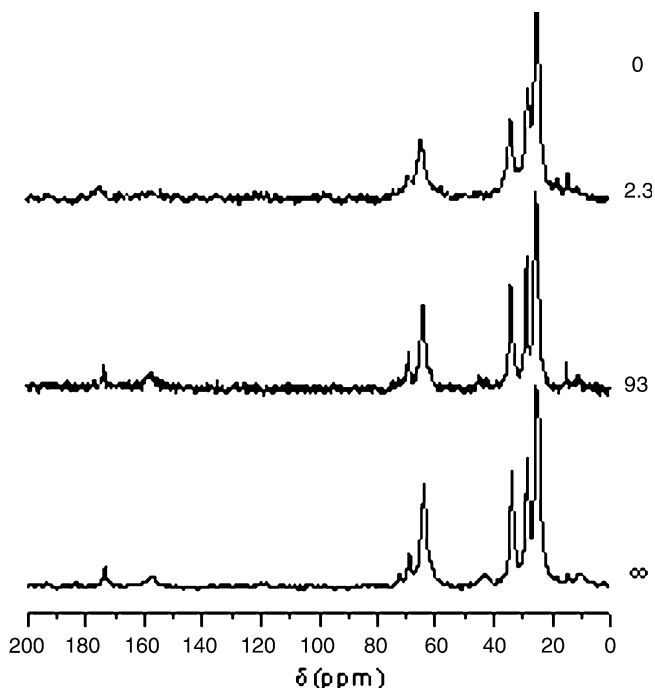


Fig. 1 ^{13}C CP/MAS NMR spectra of selected d-PCL(530) $_n$ LiCF $_3$ SO $_3$ /siloxane hybrids

(see carbons C 14 and C 13 in Table 1 respectively, Scheme 2 and Fig.1). The characteristic peaks of the propyl carbon atoms of the -Si-(CH $_2$) $_3$ -N moieties are present in the ^{13}C CP/MAS NMR spectra of all the three samples (see carbons C 1 , C 2 and C 3 in Scheme 2, Table 1 and Fig. 1), an evidence that the grafting reaction was not accompanied by the rupture of bonds in the Si-propyl segments. The absence in the ^{13}C CP/MAS NMR spectrum of the hybrid material with $n = 93$ of the peaks due to the ethoxy carbon atoms (see carbons C 4 and C 5 in Table 1 and Fig. 1) provides confirmation that the hydrolysis reaction went to completion.

It may be inferred from Fig. 2 that the ^{29}Si MAS NMR spectra of the d-PCL(530)-based xerogels with $n = \infty$, 93 and 2.3 display peaks at approximately -50,

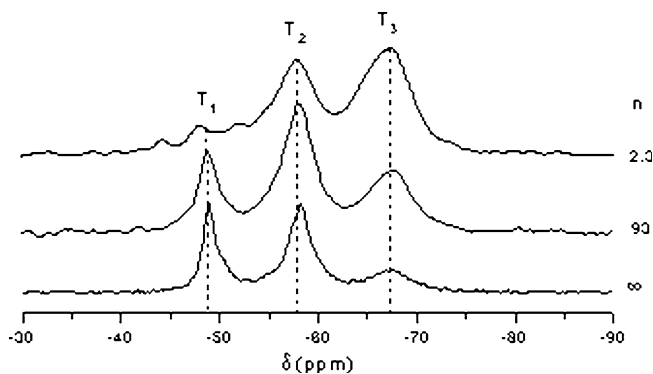


Fig. 2 ^{29}Si MAS NMR spectra of selected d-PCL(530) $_n$ LiCF $_3$ SO $_3$ /siloxane hybrids

-58 and -66 ppm (Table 3). These signals are assigned to T $_1$ (CH $_2$ -Si(OR) $_2$ (OSi)), T $_2$ (CH $_2$ -Si(OR)(OSi) $_2$) and T $_3$ (CH $_2$ -Si(OSi) $_3$) sites, respectively (Note: according to the conventional T $_m$ silicon (Si) notation $m = 1, 2, 3$ is the number of Si atoms bonded to O-Si units. The classical notation T $_n$ has been changed to T $_m$, to avoid any confusion with the notation n used for salt composition throughout the text). The polycondensation rates c (where $c = 1/3 (\%T_1 + 2\%T_2 + 3\%T_3)$) calculated for the d-PCL(530)/siloxane doped materials are significantly higher than that of the non-doped framework and suffer an increase with the increase of salt concentration. The empirical formula deduced for the three samples examined is given in Table 3. Based on the conclusions retrieved from the analysis of the ^{13}C CP/MAS NMR spectrum of the xerogel d-PCL(530) $_{93}$ LiCF $_3$ SO $_3$, we associate the residual OR groups in the T $_1$ and T $_2$ site formula indicated above to non-reacted -OH groups (Table 3), a clear indication that the final material contains residual silanol groups (-Si-OH).

The XRD patterns and the DSC thermograms of the d-PCL(530) $_n$ LiCF $_3$ SO $_3$ samples illustrated in Figs. 3 and 4, respectively, indicate that the materials investigated are entirely amorphous. The broad band, Gaussian in shape, centered at approximately 21.98° in the diffractograms of all the biohybrids is associated with the coherent diffracting domains of the siliceous backbone [27]. The weak band distinguished at approximately 44° in the diffractogram of the samples with $n \geq 1$ is tentatively associated with the second-order of the peak centred near 21.98°.

The TGA curves of representative urethane cross-linked d-PCL(530) $_n$ LiCF $_3$ SO $_3$ composites are depicted in Fig. 5. These data demonstrate that the thermal decomposition of the doped materials with $n > 0.5$ is initiated at temperatures higher than 300°C. The presence of the guest salt appears to destabilise the hybrid host structure in a non-oxidising atmosphere. In the case of the less concentrated d-PCL(530) $_n$ LiCF $_3$ SO $_3$ samples with $n = 200$ and 93, a unique mass loss (gradual) is detected in the curves (onset at approximately 300°C). In contrast, in the hybrids with $n = 19, 2.3$ and 0.5 we observe a degradation process with a three separate mass loss steps.

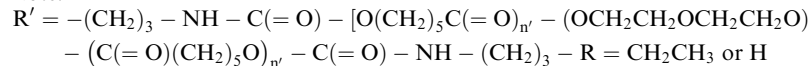
Ionic conductivity

The results of this study of the conductivity behaviour of doped d-PCL(530) $_n$ LiCF $_3$ SO $_3$ xerogels illustrated in Fig. 6(a) confirm that the most conducting ormolyte composition over the temperature range characterised is d-PCL(530) $_{0.5}$ LiCF $_3$ SO $_3$. Although the conductivity levels observed with this composition are modest (4.0×10^{-6} , 1.0×10^{-6} and $6.7 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ at 35, 50 and 104°C, respectively), relative to state-of-the-art solid polymer electrolytes described by other authors [28], they should be considered to be reference values which

Table 3 ^{29}Si MAS/NMR data of selected d-PCL(530) $_n$ LiCF $_3$ SO $_3$ /siloxane hybrids

^{29}Si MAS NMR					
n	T $_1$ (CH $_2$ -Si(OSi)(OR) $_2$) (%)	T $_2$ (CH $_2$ -Si(OSi) $_2$ (OR)) (%)	T $_3$ (CH $_2$ -Si(OSi) $_3$) (%)	c (%)	Empirical formula
∞	-49.1 (33.5)	-58.1 (52.9)	-66.6 (13.6)	60	R' $_{0.5}$ Si (OR) $_{0.9}$ (O) $_{1.2}$
93	-48.9 (20.0)	-58.0 (56.1)	-66.0 (23.0)	67	R' $_{0.5}$ Si (OH) $_{1.0}$ (O) $_{1.0}$
2.3	-51.2 (11.9)	-57.4 (35.6)	-66.9 (52.5)	80	R' $_{0.5}$ Si (OR) $_{0.6}$ (O) $_{1.2}$

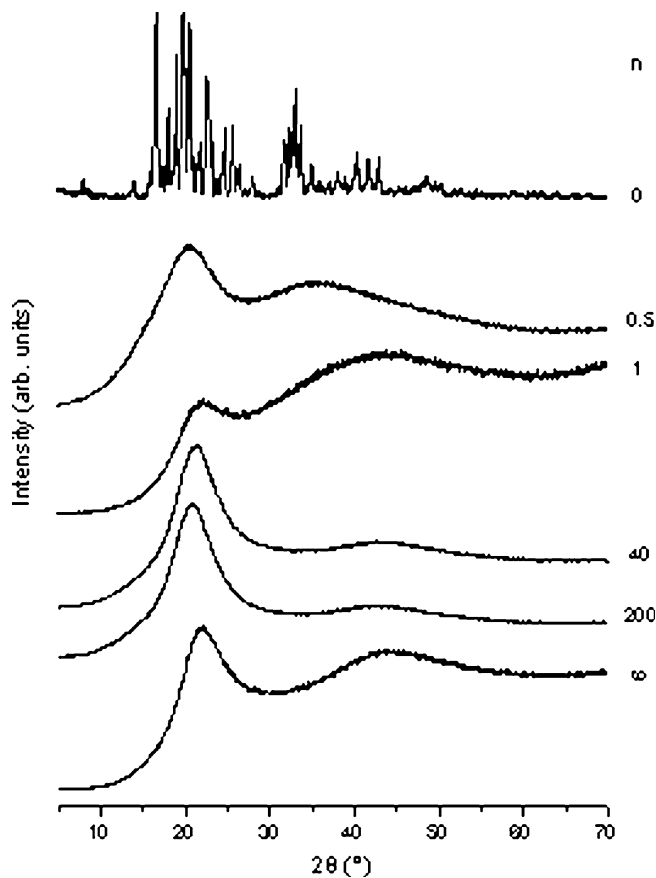
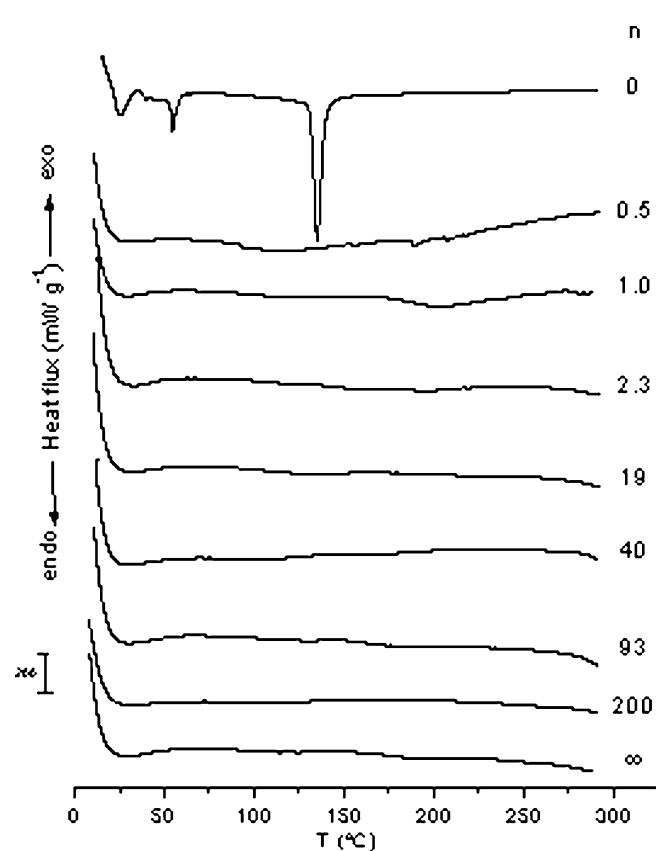
Note:



establish the existence of ionic mobility in these materials. This electrolyte already demonstrates excellent mechanical stability over the normal cell operating temperature range, and significant improvement in conductivity may be expected as a result of optimisation of the nature and concentration of guest salt and chain segment extension [29].

The variation of the conductivity of solid polymer electrolytes with composition, illustrated in the conductivity isotherms included in Fig. 6(b), clearly shows the presence of a local conductivity maximum at $n = 0.5$. The influence of salt composition on the total ionic conductivity of conducting polymeric media is often

extremely complex and in certain cases may be explained by the presence of crystalline phases, transitions between phases or the changing composition of ion aggregates in a medium of low dielectric constant. The amorphous nature of the d-PCL(530) $_n$ LiCF $_3$ SO $_3$ xerogels, demonstrated by X-ray, DSC and thermal studies, excludes the possible influence of crystalline phases and consequently the authors attribute the observed behaviour to alterations in the number and mobility of charge carriers present in the electrolyte. The low conductivity of electrolyte compositions with high values of n , or low salt content, are intuitively explained by the low concentration of mobile species within the electrolyte. As the salt content of electrolyte is increased, and values of n decrease, the total ionic conductivity of the electrolyte

**Fig. 3** XRD patterns of selected d-PCL(530) $_n$ LiCF $_3$ SO $_3$ /siloxane hybrids**Fig. 4** DSC curves of the d-PCL(530) $_n$ LiCF $_3$ SO $_3$ /siloxane hybrids

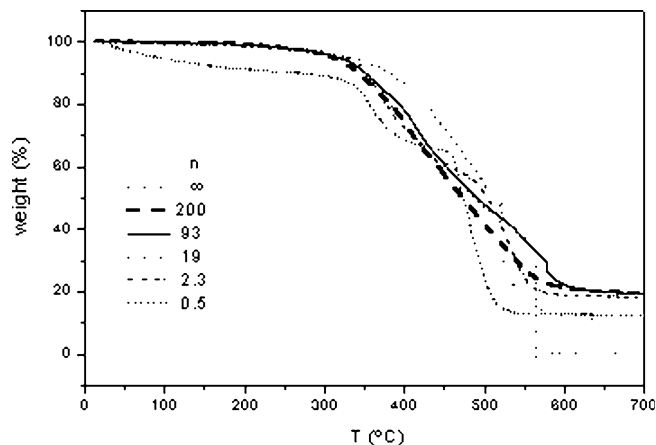


Fig. 5 TGA curves of selected d-PCL(530)_nLiCF₃SO₃/siloxane hybrids

system rises. Polyethers, or indeed any polymeric matrices with polyether segments, are known to behave as solvents with low dielectric constants. Consequently as the salt composition increases the salt begins to become poorly dissociated and ion aggregates form. This behavior has already been reported and discussed in terms of ion associations by Gray [1] and other authors. The practical result is that the number and mobility of charged species present in the electrolyte system is lower at higher salt content and the electrolyte conductivity is often seen to decrease. The complex ion-aggregate interactions which occur may lead to alterations in the charge transport mechanism and cause the variations in conductivity observed in Fig. 6(b). In common with previously characterised electrolytes, the presence of even higher salt concentrations may lead to a further decrease in ionic conductivity, either because of ion-ion interactions inhibiting transport or through polymer-ion-polymer attractions creating transient cross-links between polymer chain segments. The existence of these cross-links would be expected to inhibit polymer chain segment mobility necessary for ion transport. A sample of electrolyte with a higher concentration of salt ($n = 0.28$) was prepared in order to determine whether a further increase in salt concentration would result in a reduction or an increase in ionic conductivity. This new sample of electrolyte exhibited mechanical properties which were markedly different from those of more dilute samples. The d-PCL(530)_{0.28}LiCF₃SO₃ sample was not transparent and was considerably less flexible than electrolytes with less added salt. We are led to conclude that this composition marks the solubility limit of salt in this host matrix and that the optimal electrolyte formulation is indeed d-PCL(530)_{0.5}LiCF₃SO₃. Clearly the explanation of conductivity behaviour is complicated and further information regarding the precise nature of free ions, ion pair or mobile charged cluster formation, deduced from detailed infrared or Raman spectroscopic characterisation, may provide useful support.

The cyclic voltammogram of the sample with the highest conductivity of the series (d-PCL(530)_{0.5}LiCF₃-

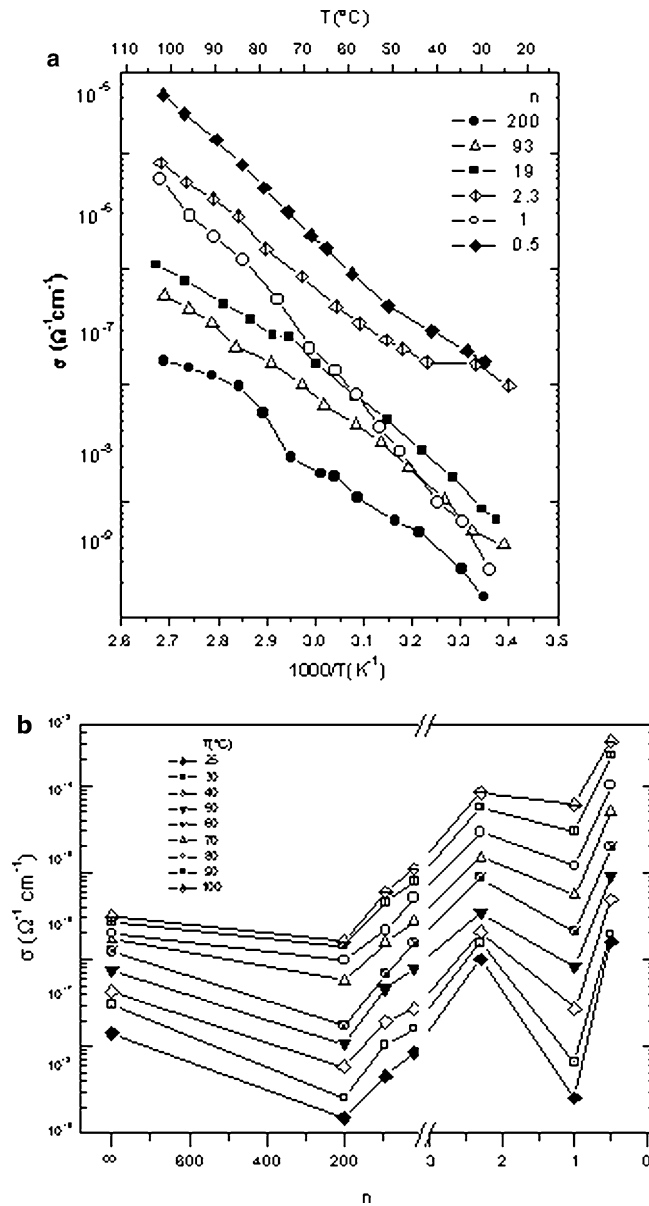


Fig. 6 Arrhenius conductivity plot (a) and isotherms of the ionic conductivity versus composition (b) of the d-PCL(530)_nLiCF₃SO₃/siloxane hybrids

SO₃) was obtained at 80°C so that the minimum conductivity (of the order of $10^{-5} \Omega^{-1} \text{cm}^{-1}$) that typically leads to growth of peaks of detectable intensity could be attained. Fig. 7 demonstrates that even under these conditions, no peaks are detected on the oxidation (formation of passivation layers due to the lithium deposition-dissolution process) and reduction (irreversible degradation of the anion) processes. This fact and the low values of the current density observed (of the order of $\mu\text{A}/\text{cm}^2$) suggest that the sample with $n = 0.5$ is electrochemically stable from a practical point of view over the voltage range examined (-1 to $+6$ V versus Li^+).

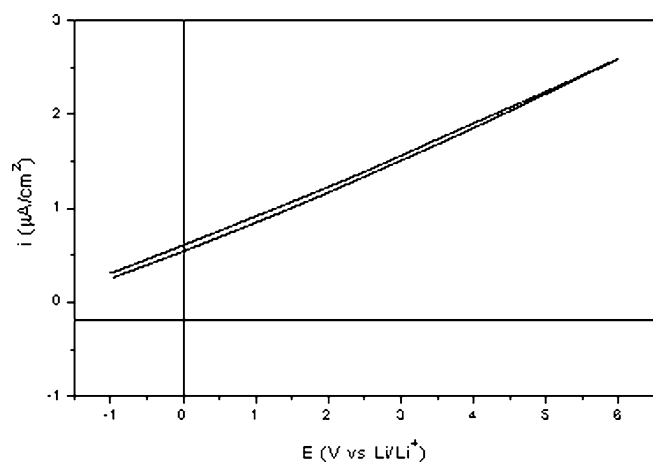


Fig. 7 Cyclic voltamogram of the d-PCL(530)_{0.5}LiCF₃SO₃ hybrid (sweep rate = 20 mV min⁻¹) obtained with a nickel working electrode and lithium counter and reference electrodes

Conclusions

LiCF₃SO₃-doped d-PCL(530)/siloxane biohybrid electrolytes were synthesised by the sol-gel process and samples with salt composition in the range $200 > n > 0.5$ were produced as thin amorphous, flexible monoliths with excellent thermal stability. The d-PCL(530)_{0.5}LiCF₃SO₃ compound displays the highest ionic conductivity over the range of temperatures analysed (approximately 4.0×10^{-6} and $6.7 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ at 35 and 104°C, respectively) and its electrochemical stability domain spans 7 V versus Li⁺. The encouraging results obtained suggest that further research on this type of system is worth pursuing.

In commercial devices the ionic conductivity is undeniably of crucial importance, however practical aspects of thermal, chemical and mechanical stabilities and electrode/electrolyte compatibility should not be ignored. While the levels of ionic conductivity measured with the optimal electrolyte composition are not comparable to those observed with some recently reported elastomeric electrolytes, the results nevertheless encourage further investment in the PCL/siloxane biohybrid systems.

Acknowledgements This work was supported by Fundação para a Ciência e Tecnologia (POCTI/P/CTM/42478/02, POCTI/P/CTM/46780/02 and SFRH/BD/13559/03). S. C. Nunes acknowledges Fundação para a Ciência e Tecnologia for a grant.

References

- Gray FM (1997) *Polymer Electrolytes*, RSC Materials Monographs. The Royal Society of Chemistry, London
- Armand M, Duclot MT, Chabagno JM (1978) In: *Proceedings of the Second International Meeting on Solid State Electrolytes*, St. Andrews, Scotland, Extended Abstract 6.5.
- Brinker CJ, Scherer GW (1990) *Sol-gel Science: The Physics and Chemistry of Sol-Gel Processing*. Academic Press, San Diego CA
- Gomez-Romero P, Sanchez C (eds) (2003) *Functional Hybrid Materials*. Wiley Interscience, New York
- Ravaine D, Seminel A, Charbouillot Y, Vincens M (1986) *J Non-Cryst Solids* 82:210
- Popall M, Andrei M, Kappel J, Kron J, Olma K, Olsowski B (1998) *Electrochim Acta* 43(10–11):1155
- Judeinstein P, Titman J, Stamm M, Schmidt H, (1994) *Chem Mater* 6:127
- Dahmouche K, Atik M, Mello NC, Bonagamba TJ, Panepucci H, Aegerter MA, Judeinstein P (1997) *J Sol-Gel Sci Technol* 8:711
- de Zea Bermudez V, Alcácer L, Acosta JL, Morales E (1999) *Solid State Ionics* 116:197
- Wang C, Wei Y, Ferment GR, Li W, Li T (1999) *Mater Lett* 39:206
- MacCallum JR, Seth S (2000) *Eur Polym J* 36:2337
- Nishio K, Tsuchiya T (2001) *Sol Energy Mater Sol Cells* 68:295
- Nunes SC, de Zea Bermudez V, Ostrovskii D, Silva MM, Barros S, Smith MJ, Carlos LD, Rocha J (2005) *J Electrochem Soc* 152(2):A429
- Pak J, Ford JL, Rostron C, Walters V (1985) *Pharm Acta Helv* 60:160
- Grijpma DW, Zondervan GJ, Penning AJ (1991) *J Polym Bull* 25:327
- Coombes AGA, Rizzi SC, Williamson M, Barralet JE, Downes S, Wallace WA (2004) *Biomaterials* 25:315
- Tian D, Dubois Ph, Jérôme R (1996) *Polymer* 37(17):3983
- Rhee S-H, Choi J-J, Kim HM (2002) *Biomaterials* 23:4915
- De Kesel C, Lefèvre C, Nagy JB, David C (1999) *Polymer* 40:1969
- Armelin E, Franco L, Rodríguez-Galán A, Puiggali J (2002) *Macromol Chem Phys* 203(1):48
- Armelin E, Paracuellos N, Rodríguez-Galán A, Puiggali J (2001) *Polymer* 42:7923
- Gonçalves MC, de Zea Bermudez V, Sá Ferreira RA, Carlos LD, Ostrovskii D, Rocha J (2004) *Chem Mater* 16(13):2530
- Messori M, Toselli M, Pilati F, Mascia L, Toneli C (2002) *Eur Polym J* 38:1129
- Wu C-S (2003) *Polym Degrad and Stab* 80:127
- Seretoudi G, Bikiaris D, Panayiotou C (2002) *Polym* 43:5405
- Silva CJR, Smith MJ (1995) *Electrochim Acta* 40:2389
- Carlos LD, de Zea Bermudez V, Sá Ferreira RA, Marques L, Assunção M (1999) *Chem Mater* 11(3):581
- Pennarun PY, Jannasch P, Papaefthimiou S, Yianoulis P (2004) *Extended abstracts 9th International Symposium on Polymer Electrolytes*. Mragowo, Poland, pp 157
- Silva MM, de Zea Bermudez V, Carlos LD, Smith MJ (2000) *Electrochim Acta* 45:1467