

Vibrational analysis of d-PCL(530)/siloxane based hybrids doped with two lithium salts

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Abstract

The present study has been focused on environmentally friendly sol-gel derived electrolytes based on a di-urethane cross-linked d-PCL(530)/siloxane network (where d represents di, PCL identifies the poly(ϵ -caprolactone) biopolymer and 530 is the average molecular weight in $\text{g}\cdot\text{mol}^{-1}$) doped with a wide range of concentration of lithium perchlorate (LiClO_4) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). Fourier Transform Infrared and Raman (FT-IR and FT-Raman, respectively) spectroscopies have been applied to evaluate the extent of ionic association. Characteristic bands of the PCL(530) segments, of the urethane cross-links and of the anions have been examined to gain insight into the cation/biopolymer, cation/anion and cation/cross-link interactions. In both electrolyte systems “free” ions and contact ions have been identified. The addition of salt modifies the hydrogen-bonded array of the host matrix, causing the destruction/formation of the urethane/urethane aggregates.

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1. Introduction

Polymer electrolytes (PEs), composed of a host macromolecule and a guest salt, have been widely studied in the field of solid state electrochemistry, because of commercial interest in their application in the domains of advanced batteries, sensors and electrochromic devices (ECDs) [1].

In this context, the most extensively studied host polymer has been poly(oxyethylene) (POE), a hard polybasic macromolecule which exhibits an extraordinary capacity to solvate ionic salts. However, POE has several major disadvantages that have severely restricted practical applications: (1) The materials show a marked tendency to crystallize, a process that leads a significant reduction in the room temperature ionic conductivity. (2) At high salt concentration the solubility limit is exceeded and salting-out is often observed. (3) Under these circumstances the mechanical properties of the materials are rather poor. Among the strategies that have been proposed to overcome these drawbacks the combination of the sol-gel method [2] with the hybrid concept [3] and the development of modified electrolytes is considered to be a very attractive approach. The resulting POE/siloxane hybrid materials are essentially amorphous ormolytes (organically modified silicate electrolytes). Typically these materials exhibit good processability, high thermal, mechanical and chemical stability and are able to solubilize significantly higher guest salt concentrations than conventional PEs.

Over the last few years many ormolyte systems have been developed using the hybrid approach [4-22]. To elucidate the relationship between ionic conductivity and ionic association, Fourier Transform Infrared and Raman (FT-IR and FT-Raman) spectroscopic analyses were performed on some of these hybrid electrolytes [23-25].

From the research carried out in this field, a series of particularly attractive sol-gel derived “low environmental impact” electrolytes have been developed based on the diurethane cross-linked d-PCL(530)/siloxane network (where d represents di, PCL identifies the poly(ϵ -caprolactone) biopolymer and 530 is the average molecular weight in $\text{g}\cdot\text{mol}^{-1}$). Electrolytes with this framework, doped with lithium triflate (LiCF_3SO_3) [17], magnesium triflate [18], potassium triflate [19], lithium tetrafluoroborate (LiBF_4) [26], lithium perchlorate (LiClO_4) [21,26], lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) [26] and a mixture of LiCF_3SO_3 and europium triflate have been prepared. Some of these systems were characterized in depth by FT-IR and FT-Raman spectroscopies [19, 20, 27]. Optimized ormolyte compositions were successfully tested in prototype ECDs [19-21, 26].

The present study is devoted to the characterization of the interactions that occur in d-PCL(530)/siloxane systems doped with LiClO_4 and LiTFSI for which no information exists at present. This study is of particular interest, as the electrolytes incorporating these salts display the highest conductivity values of all the analogue ormolytes (Table 1).

2. Experimental section

2.1. Synthesis

Lithium perchlorate (LiClO_4 , Aldrich, 99,99%), and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI , Aldrich, 99,95 %) were dried under vacuum at 25°C for several days prior to being used. α,ω -hydroxylpoly(ϵ -caprolactone) (PCL (530), Fluka, average molecular weight = $530\text{ g}\cdot\text{mol}^{-1}$ and 3-isocyanatepropyltriethoxysilane (ICPTES, Aldrich, 95%) 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.

The d-PCL(530)/siloxane-based hybrid electrolytes were prepared according to the procedure described in detail elsewhere [26]. The two series of materials were identified by the notation d-PCL(530)/siloxane_nLiX, where n corresponds to the number of $\text{O}(\text{CH}_2)_5\text{C}=\text{O}$ repeat units of PCL(530) per Li^+ ion and X is ClO_4^- and TFSI^- .

2.2. Characterization

FT-IR spectra were acquired at room temperature using a Unicam FT-IR spectrometer. The spectra were collected over the $4000\text{-}500\text{ cm}^{-1}$ range by averaging 64 scans at a spectral resolution of 4 cm^{-1} . About 1 mg of each solid sample was finely ground and mixed with approximately 100 mg of dry potassium bromide (Merck, spectroscopic grade) and pressed into pellets. FT-Raman spectra were recorded at room temperature with a Bruker IFS-66 spectrometer equipped with a FRA-106 Raman module and a near-infrared YAG laser with wavelength of 1064 cm^{-1} . The spectra were collected over the $4000\text{-}400\text{ cm}^{-1}$ range by averaging 200 scans at a spectral resolution of 4 cm^{-1} . To deconvolute complex band envelopes, the non-linear curve-fitting procedure available with PeakFit software (Version 4, Jandel Corporation, 2591 Rerner Boulevard, San Rafael, CA 94901, U.S.A.) was employed. The residuals procedure was used to place hidden peaks. This procedure identifies possible peak locations by detecting local maxima in a smoothed data stream. Hidden peaks may subsequently be added where peak locations are detected in the residuals. The best fit of the experimental data was obtained by varying the parameters of the bands (i.e., wavenumber, width and intensity) and by using Gaussian functions. A linear baseline

correction with a tolerance of 3% was employed. The standard error of the curve-fitting procedure was less than 0.00006.

Polarized Optical Microscopy (POM) images were recorded using an OPTIKA B-600POL microscope equipped with an 8 megapixel digital camera. The images were analyzed using the OPTIKA Vision Pro software.

3. Results and discussion

In the d-PCL(530)/siloxane hybrid medium guest cations may coordinate to the functional groups of the host hybrid framework through the ether -C-O-C-oxygen atoms, the ester C=O oxygen atoms of the PCL chains and the urethane C=O oxygen atoms of the cross-links. The guest cations may also coordinate to the guest anions present in the electrolyte.

3.1. Hydrogen bonding interactions

After being incorporated into the host hybrid, the guest Li^+ ions may bond to “free” urethane/ester C=O groups or to C=O groups present in hydrogen-bonded aggregates. In the latter case, the hydrogen bonds of these aggregates are necessarily disrupted. It is useful to evaluate the $\text{Li}^+ \cdots \text{O}=\text{C}$ interactions and, as a consequence, the hydrogen bonding interactions occurring in the two ormolyte families characterized.

To assess the strength and nature of the hydrogen bonding interactions the spectral region characteristic of the stretching mode of the C=O oxygen atoms of the urethane cross-links and of the ester groups of the PCL(530) segments was analyzed. This region, which includes the “amide I” band [28], ranges from 1800 to 1600 cm^{-1} . In this wavenumber interval the FT-IR spectrum of the non-doped PCL(530)/siloxane matrix exhibits four components situated at about 1762, 1736, 1720 and 1691 cm^{-1} [29]. The

1762 cm^{-1} feature is due to the presence of “free” C=O groups of the urethane cross-links (A1) [29, 30]. The 1736 cm^{-1} component is characteristic of ester C=O groups of amorphous PCL (530) chains (B1) [29, 31, 32]. The 1720 cm^{-1} band is associated with oxyethylene/urethane hydrogen-bonded aggregates (C1) [29, 30], whereas the 1692 cm^{-1} feature was ascribed to the absorption of C=O groups belonging to considerably more ordered hydrogen-bonded aggregates (ester/urethane [29] and urethane/urethane [30] aggregates) (D1).

The global profiles of the “amide I” envelopes of the undoped and LiClO_4^- and LiTFSI-doped d-PCL(530)/siloxane samples are practically the same, with intensity maxima close to 1740 cm^{-1} (Fig. 1). This result suggests that, regardless of salt composition, the addition of Li^+ ions to the d-PCL(530)/siloxane framework does not globally influence the extent of hydrogen bonding in the materials. The data of Fig. 2 lead us to conclude that in the most dilute sample ($n = 200$) of the two families of ormolytes, the amount of “free” ester C=O groups (B1) and those of the ester/urethane and/or urethane/urethane aggregates (D1) increases with respect to the situation encountered in the non-doped matrix. Moreover, the fraction of oxyethylene/urethane hydrogen-bonded aggregates (C1) and “free” urethane C=O groups (A1) are reduced. These variations strongly suggest that in electrolytes with low guest salt concentration more urethane/urethane aggregates are formed at the expense of the breakdown of oxyethylene/urethane and ester/urethane aggregates. At the composition $n = 35$ the proportion of “free” ester C=O groups (B1) is drastically reduced, whereas those of the “free” urethane C=O groups (A1), the oxyethylene/urethane hydrogen-bonded aggregates (C1), and the ester/urethane and/or urethane/urethane aggregates (D1) are increased. These variations indicate that the “free” ester C=O groups are involved in the formation of more ester/urethane aggregates. At $n = 25$ the proportion of “free” ester

C=O groups (B1), and those of the ester/urethane and urethane/urethane aggregates (D1) decreases, while at the same time, the fraction of “free” urethane C=O groups increases slightly and that of the oxyethylene/urethane hydrogen-bonded aggregates is increased. In the salt-rich d-PCL(530)/siloxane_{2.5}LiTFSI electrolyte (Fig. 2(b)) the same trend continues. In contrast, in d-PCL(530)/siloxane_{4.4}LiClO₄ no significant changes were apparent (Fig. 2(a)).

3.2. Li^+ -anion interactions

LiClO₄-doped materials: The “free” ClO₄⁻ ions adopts a tetrahedral symmetry (T_d) and their nine vibrational degrees of freedom are distributed between four normal Raman active modes: ν_1 (A₁), ν_2 (E₂), ν_3 (T₂) and ν_4 (T₂). Of these, ν_1 (A₁) and ν_2 (E₂) modes are infrared inactive. Cation coordination lowers the local symmetry around ClO₄⁻. This effect is manifest in the spectra through band splitting of the degenerate vibrations and through the activation of infrared-forbidden ν_1 (A₁) and ν_2 (E) modes. The magnitude of both the band separation and the frequency shift depend on the strength of ion association. An association of one or three of the oxygen atoms of ClO₄⁻ with a cation (in mono- or tridentate coordination, respectively) lowers the symmetry of the anion to C_{3v}. Mono- or tridentate configurations are identified through the splitting of the three-fold degenerate ν_3 and ν_4 vibrations into two components (A₁ and E), both in the infrared and Raman spectra. On the other hand, the association of a cation with two of the oxygen atoms of ClO₄ (in bidentate coordination) reduces the symmetry to C_{2v}. The bidentate configuration of the ClO₄⁻ and ions may be recognized by the splitting of the two-fold degenerate ν_2 vibration into two bands (A₁ and A₂) in the Raman spectrum and by the splitting of the three-fold degenerate ν_3 and ν_4 vibrations

into three components (A1, B1 and B2) in the infrared and Raman spectra. On the basis of the individual infrared values observed in different solvents, the following average wavenumbers were deduced for “free” ClO_4^- : ν_3 (T2), ν_1 (A1) and ν_4 (T2) modes appear at 1100, 931 and 624 cm^{-1} , respectively. An average wavenumber of 458 cm^{-1} was derived for ν_2 (E) from Raman values [33, 34]. It is widely accepted that the ClO_4^- symmetry is lowered to C_{3v} when this anion forms contact ion pairs with Li^+ ($\text{Li}^+\cdots\text{ClO}_4^-$) and C_{2v} in the so-called dimerized state $\text{Li}_2(\text{ClO}_4)_2$ [33-35].

Fig. 3 shows that the FT-Raman spectra of selected d-PCL(530)/siloxane_nLiClO₄ samples in the $\nu_3\text{ClO}_4$ region exhibit a single component at 931 cm^{-1} , assigned to “free” ClO_4^- ions [33, 36-40]. Fig. 4 represents the FT-Raman spectrum of d-PCL(530)/siloxane_{2.2}LiClO₄ xerogel in the $\nu_2\text{ClO}_4$ region (Note: the other samples showed ill-defined behavior in this region). The band envelope was decomposed into four components at 474, 464, 459 and 451 cm^{-1} . The 459 cm^{-1} feature of this band is associated with the occurrence of “free” ClO_4^- ions [41-43]. The origin of the 474 cm^{-1} component is uncertain. The observation of bands at 464 and 451 cm^{-1} , attributed to the ν_2 (A1) and ν_2 (A2) modes, respectively, supports the formation of C_{2v} symmetry and thus bidentate contact association between Li^+ and ClO_4^- [33,44]. Fig. 5(a) reproduces the FT-IR spectra of selected d-PCL(530)/siloxane samples in the $\nu_4\text{ClO}_4$ region. The curve-fitting results depicted in Fig. 5(b) show three components at 634, 626 and 623 cm^{-1} . These spectral events are attributed to ClO_4^- ions in a bidentate configuration, suggesting that the local symmetry around ClO_4^- must be C_{2v} [33]. The 626 cm^{-1} band is common to “free” and bidentate coordinated ClO_4^- ions [33]. The features at 634 and 619 cm^{-1} correspond to $^{37}\text{ClO}_4$ isotopomers [33]. The component at 637 cm^{-1} , and the shoulder at 640 cm^{-1} , are very probably produced by monodentate bonded ClO_4^- ions [33, 39].

LiTFSI-doped materials: In the 810-770 cm^{-1} FT-IR spectral range three typical vibration bands of TFSI are observed: the asymmetric stretching mode of the SNS group (ν_{aSNS}), the asymmetric deformation mode of the CF_3 group (δ_{aCF_3}) and the $\delta_{\text{sCF}_3}/\nu_{\text{sSNS}}$ mode. The FT-IR spectra of the d-PCL(530)/siloxane_nLiTFSI samples with $n \geq 35$ demonstrate the same behavior in this range of wavenumbers regardless of salt composition. A broad band centered at 789 cm^{-1} is visible in all the samples (Fig. 6(a)). This band was resolved into four components at 805, 798, 789 and 783 cm^{-1} (Fig. 6(b)). The spectral feature detected at 790 cm^{-1} is tentatively attributed to the presence of contact ion pairs [45, 46]. The 783 cm^{-1} band is associated with the existence of “free” TFSI ions.

The POM images of LiTFSI and LiClO₄ doped electrolytes illustrated in Fig. 7 demonstrate that both samples with $n = 25$ are birefringent. The anisotropy of these electrolytes suggests that crystalline phases are formed in d-PCL(530)/siloxane₂₅LiTFSI and d-PCL(530)/siloxane₂₅LiClO₄. However this sub-micrometer order does not give rise to any melting peaks in the DSC curves [26].

4. Conclusions

Sol-gel derived di-urethane cross-linked d-PCL(530)/siloxane hybrids doped with LiBF₄, LiClO₄ and LiTFSI were investigated by infrared and Raman spectroscopies to elucidate the Li⁺/urethane cross-link, Li⁺/ester polymer, Li⁺/anion and hydrogen bonding interactions.

The spectral data obtained support the suggestion that Li⁺ coordination is accompanied by the breakdown or formation of urethane/urethane hydrogen-bonded aggregates and, at the same time, the breakdown or formation of the oxyethylene/urethane hydrogen-bonded aggregates. In the d-PCL(530)/siloxane_nLiClO₄

system associated species are formed, which include the ClO_4^- ions in monodentate and bidentate coordination, as well as “free” ClO_4^- ions. Both “free” TFSI ions and contact ions pairs have been detected in d-PCL(530)/siloxane_nLiTFSI electrolytes. In previous studies “free” anions have also been detected in the LiCF_3SO_3 based electrolyte system [27].

Yi TF, Xie Y, Shu J, Wang ZH, Yue CB, Zhu RS, Qiao HB (2011) *J Electrochem Soc* 158:A266–A274

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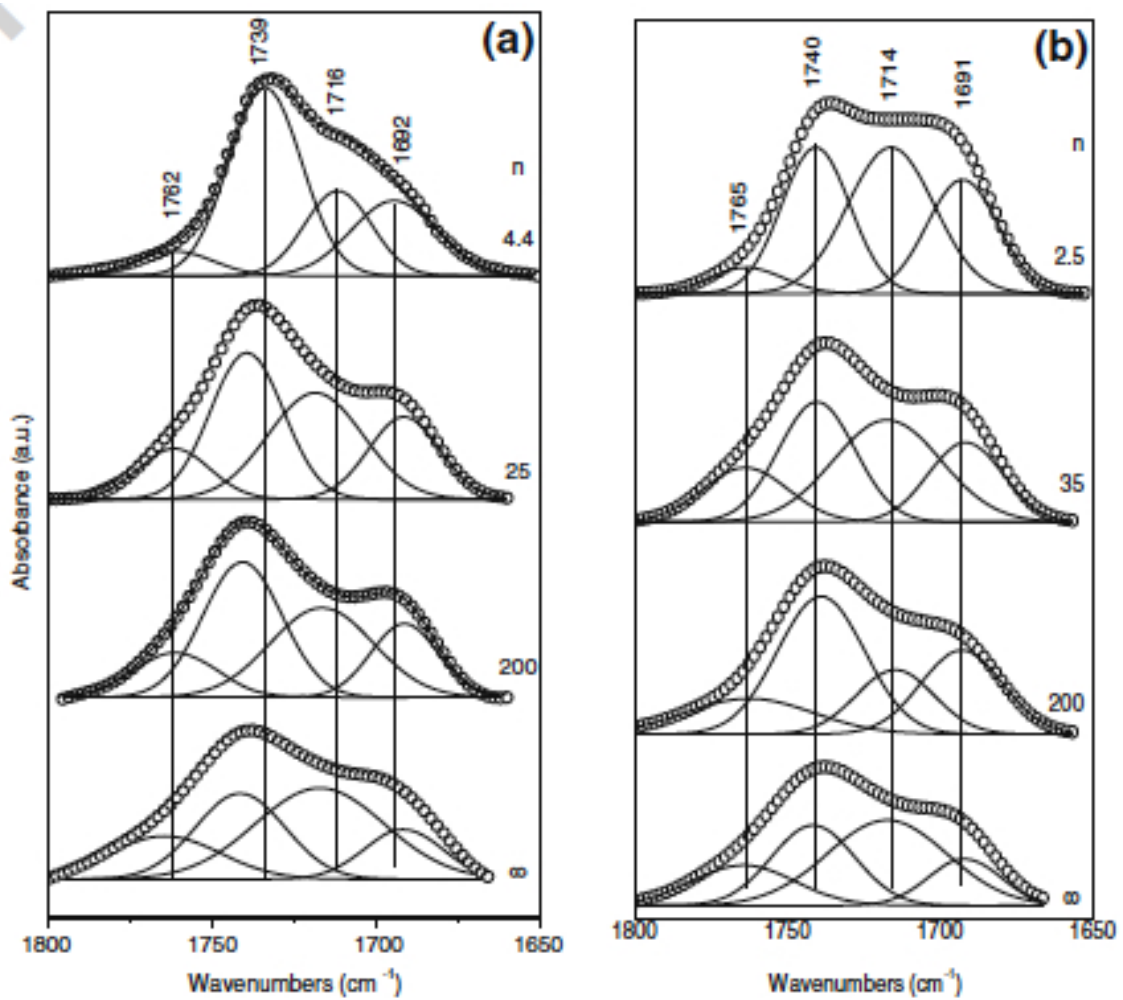
Acknowledgements

MEC, FEDER, Fundação para a Ciência e a Tecnologia (FCT) and COMPETE are thanked for financial support (contracts PTDC/CTM/101324/2008 and Pest-

C/CTM/LA0011/2011). B. C. Ferreira and M. Fernandes thank FCT for grants (BIC/PEst-C/QUI/UI0616/2011 and SFRH/BPD/78919/2011, respectively).

Table 1. Conductivity maxima of d-PCL(530)/siloxanenLiX ormolytes

MX	<i>n</i>	σ (S cm ⁻¹)			Reference
		36 °C	66 °C	98 °C	
LiBF ₄	2.5	1.74×10^{-8}	9.88×10^{-8}	2.50×10^{-7}	[26]
LiClO ₄	4.4	2.23×10^{-5}	1.00×10^{-4}	3.21×10^{-4}	[21]
LiTFSI	10	4.41×10^{-6}	4.85×10^{-5}	3.35×10^{-4}	[26]
LiCF ₃ SO ₃	0.5	4.00×10^{-6}	1.00×10^{-6}	6.70×10^{-5}	[17]
LiX/MX					
LiCF ₃ SO ₃ /Eu(CF ₃ SO ₃) ₃	6.1	3.00×10^{-6}	1.00×10^{-5}	1.60×10^{-4}	[20]

**Fig. 1.** Curve fitting of the “amide I” region of selected d-PCL(530)/siloxane-based samples doped with LiClO₄ (a) and LiTFSI (b)

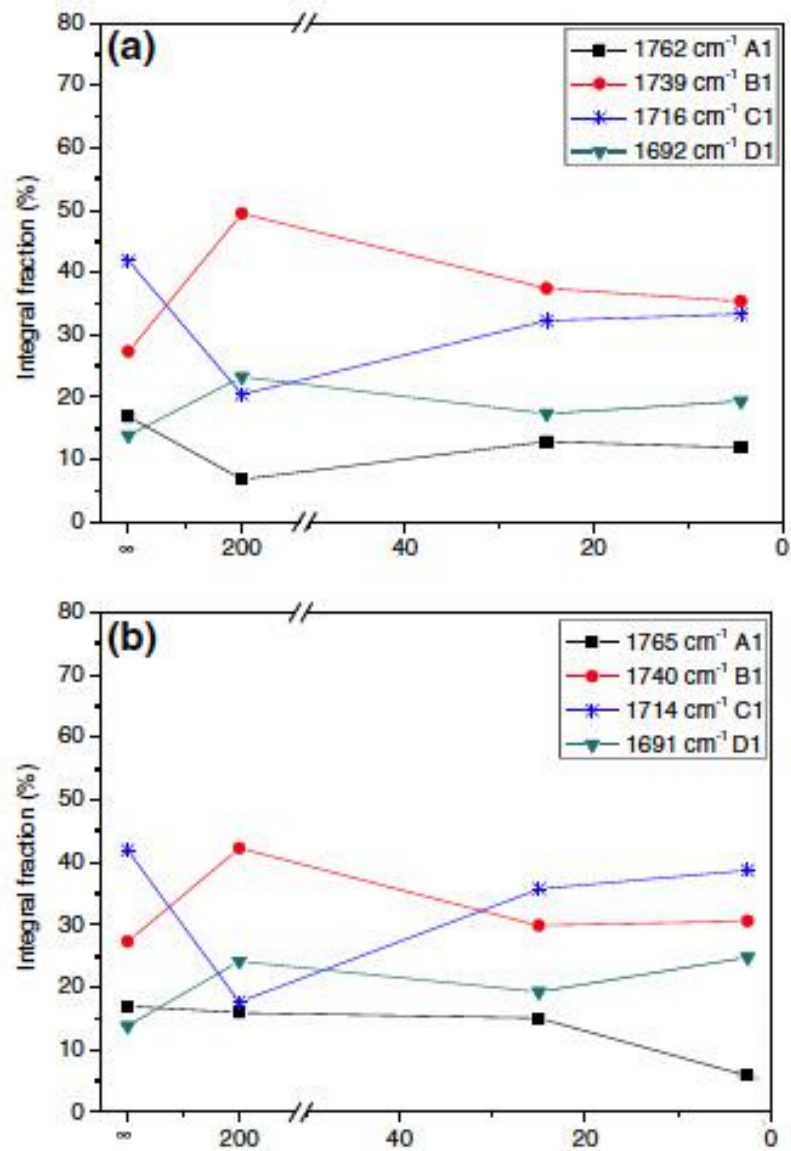


Fig. 2. Salt concentration dependence of the integral fraction of the resolved bands of the “amide I” region of selected d-PCL(530)/siloxane-based samples doped with LiClO₄ **(a)** and LiTFSI **(b)**. A1 “free” urethane C=O groups of the cross-links; B1 “free” ester C=O groups of amorphous PCL(530) chains; C1 C=O groups of oxyethylene/urethane hydrogen-bonded aggregates; D1 C=O groups of ester/urethane aggregates

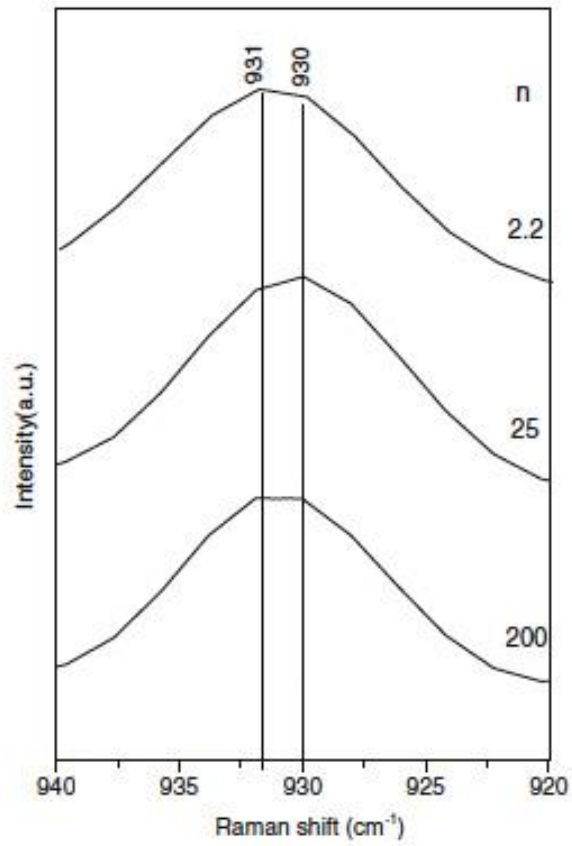


Fig. 3. FT-Raman spectra of selected d-PCL(530)/siloxane_n LiClO₄ samples in the ν_1 ClO₄ region

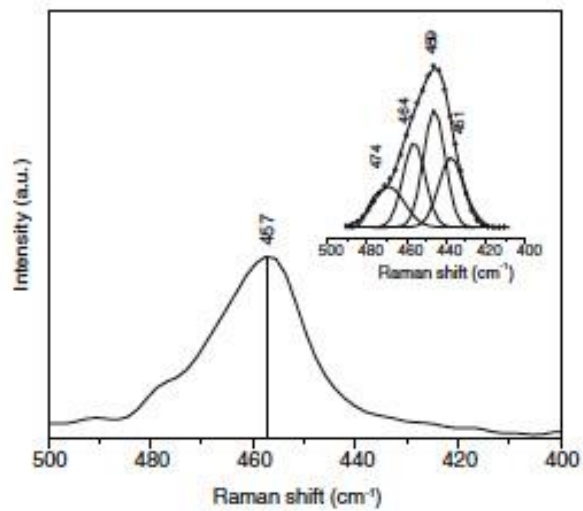


Fig. 4. FT-Raman spectra of the d-PCL(530)/siloxane_{2.2} LiClO₄ sample in the ν_2 ClO₄ region. Inset: curve-fitting results

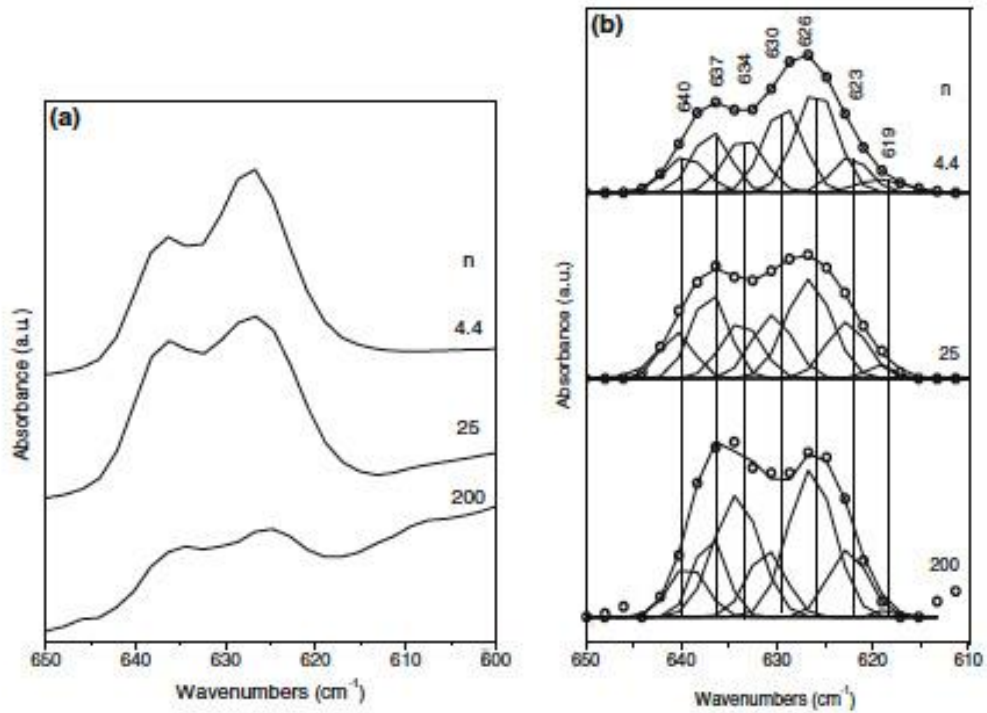


Fig. 5. FT-IR spectra of selected d-PCL(530)/siloxane_n LiClO₄ samples (a) and curve-fitting in the ν_4 ClO₄ region

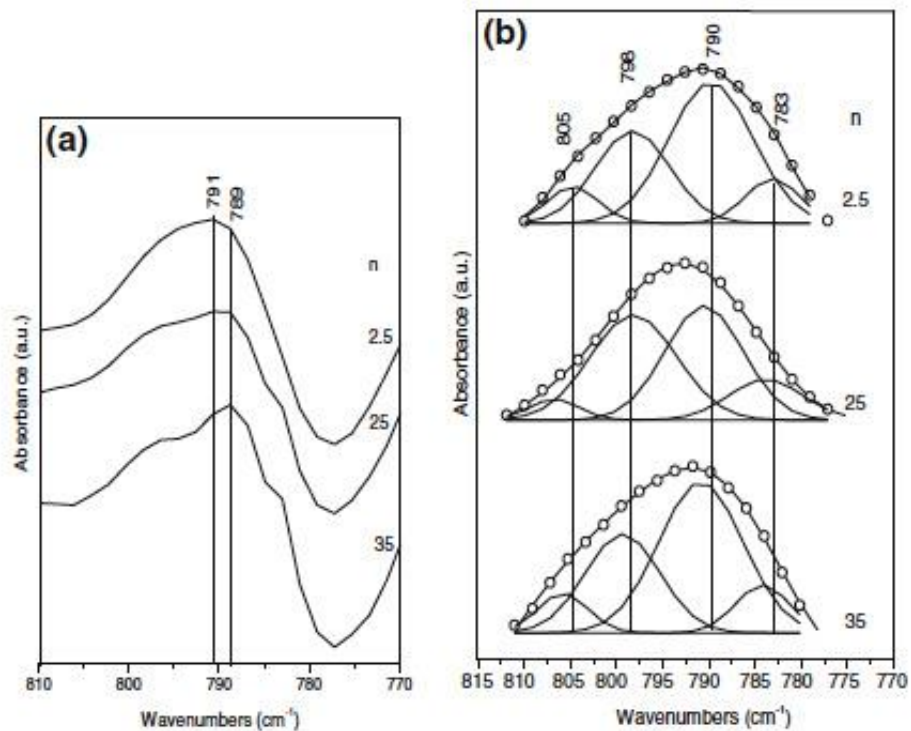


Fig. 6. FT-IR spectra of selected d-PCL(530)/siloxane in the δ_S CF₃/ ν_S SNS region (a) and curve fitting results (b)