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Furan–polyether-modified chitosans as photosensitive polymer electrolytes

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Abstract

This study describes a comprehensive approach to the preparation of novel polymer electrolytes comprising (i) oligo(ethylene oxide) solvating chains and conjugated furan chromophores, both grafted onto a film-forming chitosan backbone and (ii) lithium perchlorate as the ionic conductor. The combination of these four elements was conceived in order to optimize both the electrochemical and mechanical properties of the materials and to maintain their thermoplastic character until the last step of the process, since their photoinduced cross-linking takes place only after the dissolution of the salt and the formation of a thin film.

Keywords: Chitosan; Polyethers; Polymer electrolytes

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1. Introduction

The growing interest in elastomeric polymer electrolytes stems from their essential role in such high technology applications as solid state batteries, electrochromic devices and supercapacitors [1]. The essential features which must be displayed by these materials are: (i) a low T_g associated with a correspondingly high segmental mobility; (ii) a good solvating power of the polymer structure in terms of its capability to dissolve high concentrations of ionic species (mostly lithium salts of strong acids); (iii) a predominantly amorphous character to optimize charge mobility and (iv) a cross-linked architecture to avoid any flow in the event of an unforeseen temperature rise. These requirements have been progressively optimized in various laboratories thanks to a systematic approach covering a wide variety of structures and a thorough inspection of thermal, dynamic-mechanical, transport and electrochemical properties. One of the most suitable materials complying with these requirements consists of short poly(ethylene oxide) chains (the low-T_g solvating moieties) assembled into a network, e.g. through polyurethane chemistry, and containing ca. 1 M concentrations of $LiClO_4$ or $LiN(CF_3SO_2)_2$. The ionic mobility mimics the segmental motions through a free-volume WLF behavior, and conductivities above 10^{-5} S cm^{-1} are attained at room temperature [1].

Recent studies have concentrated on improving such features as the processing of thin films with good mechanical properties and the possibility of inducing the cross-linking only at the final stage of the production of the material. The contribution of our laboratory to this research effort has consisted in coupling the polyether chains with film-forming macromolecules based on natural polymers like cellulose derivatives and oxypropylated chitosan [1–3] or in appending photosensitive moieties to branched polyether chains to achieve the final formation of the network through ultraviolet irradiation [4].

The present investigation describes a strategy which applies both these aspects, by calling upon two structural features derived from renewable resources. For this, chitosan was grafted with both oligoether chains and furan chromophores in order to prepare thermoplastic materials bearing (i) the low-T_g solvating moieties, (ii) the film forming macromolecular backbone and (iii) the latent sites to be exploited for the final photochemical cross-linking.

Chitosan had been used previously as a host macromolecule in polymer electrolytes, as described in a series of papers by Arof et al. [5], but only in its unmodified conventional form, i.e. as a film cast from diluted aqueous acetic acid solutions.

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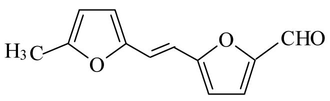
2. Experimental section

2.1. Reagents

Commercial β-D-glucosamine hydrochloride (Aldrich) was used as received. Furfural and 5-methylfurfural (Aldrich) were purified by fractional distillation. 5-[2-(5-Methyl furylene vinylene)]furancarboxyaldehyde (**MFVF**) was synthesized and purified following the procedure previously developed in our laboratory [6].



MFVF

The commercial α-methoxy-ω-hydroxy oligo(ethylene oxide)s (**PEO-OH**), of $M_n = 350$ (**PEO-OH-350**, $T_g = -70$ °C, $T_m = 0$ °C) and 750 (**PEO-OH-750**, $T_g = -70$ °C, $T_f = 30$ °C), respectively (Aldrich), were dried in vacuo at 150 °C for 24 h and kept thereafter under dry nitrogen. The commercial chitosan used in this investigation (Fluka) was purified by dissolving it in a 2% aqueous acetic acid solution. This solution was filtered and neutralized with a diluted NaOH solution under vigorous stirring. The ensuing precipitate was filtered, washed several times, first with distilled water, then with ethanol, and finally vacuum dried to constant weight. The characterisation of the purified commercial chitosan required first that its deacetylation degree (DAD) be determined, which was done by both FTIR [7] and ^{1}H NMR spectroscopy [8]. The results were in good agreement and gave DAD = 76 ± 1%. Its molecular weight was determined viscosimetrically in an aqueous solution of acetic acid (0.3 M) and sodium acetate (0.2 M) at 25 °C [9] and was found to be 167,000.

All other reagents, solvents and catalysts were high-purity commercial products.

2.2. Characterization

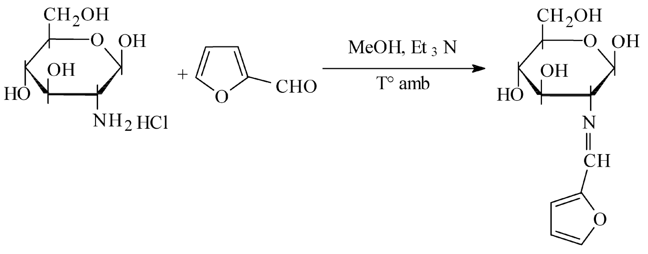
The products and materials obtained were submitted to a thorough characterization in terms of their structure and properties. FTIR spectra (Perkin–Elmer Paragon-1000) were taken by placing the samples between two NaCl plates (liquids) or in KBr pellets (solids). ^{1}H and ^{13}C NMR spectra (Brucker AC 300 or 200 MHz) were run from solutions in the appropriate deuterated solvents. UV–visible spectra (Beckman DU-64) were taken from spectroscopic grade CH_2Cl_2 solutions. DSC thermograms (Setaram DSC-92) were run in a nitrogen atmosphere with a heating rate of 10 °C min^{-1}. The ionic conductivities were derived from the corresponding complex impedance diagrams obtained with a Schlumberger-1272 impedance meter: samples in the form of thin films were pressed between stainless steel electrodes, evacuated and brought to the desired temperature before carrying out the measurements.

3. Results and discussion

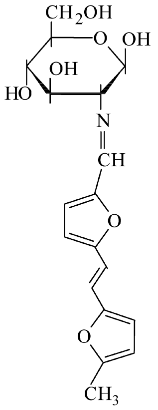
The choice of chitosan as the film-promoting macromolecular structure stemmed from two considerations, namely, on the one hand, the fact that previous work had shown the very good aptitude of this modified polysaccharide to give strong thin membranes [3] and, on the other hand, the presence of primary amino groups in most of its repeat units. The latter feature seemed particularly appropriate to achieve the grafting of the polyether chains and the furan chromophores through the same type of condensation reaction, viz. the formation of Schiff bases between the NH_2 functions of chitosan and the aldehyde function borne by both structures to be appended. It was therefore deemed necessary to study these reactions first with model compounds.

3.1. Model compounds and reactions related to furans + chitosan

The reaction of furfural with β-D-glucosamine hydrochloride at room temperature in MeOH or DMSO, in the presence of an excess of triethylamine (to generate the unprotected glucosamine in situ), gave the expected Schiff base **I** (see structure below), as shown by FTIR, UV and NMR spectroscopy and elemental analysis. The same experimental conditions were therefore applied to **MFVF** and the corresponding Schiff base **II** (see structure below) was obtained and also characterized spectroscopically and by elemental analysis. Thus, the possibility of attaching furanic aldehydes to the basic monomeric structure of chitosan proved viable.



I



II

Table 1
Structural characterisation of model compounds **I** and **II**

	Model Schiff base **I**					Model Schiff base **II**			
^{1}H NMR (ppm)	$\delta\ (H_{2\beta}) = 2.75$ (1H, t, $J = 8.76$ Hz) $\delta\ (H_{4\beta}) = 3.11–3.16$ (1H, m) $\delta\ (H_{5\beta}) = 3.21–3.28$ (1H, m) $\delta\ (H_{3\beta}) = 3.38–3.42$ (1H, m) $\delta\ (H_{6''\beta}) = 3.46–3.51$ (1H,m) $\delta\ (H_{6'\beta}) = 3.70–3.74$ (1H, m) $\delta\ (OH_6) = 4.45$ (1H, t, $J = 5.6$ Hz) $\delta\ (H_{1\beta}) = 4.65$ (1H, t, $J = 7$ Hz) $\delta\ (OH_3) = 4.76$ (1H,d, $J = 5.67$ Hz) $\delta\ (OH_4) = 4.83$ (1H, d, $J = 5.1$ Hz) $\delta\ (OH_1) = 6.47$ (1H, d, $J = 6.75$ Hz) $\delta\ (H_{10}) = 6.58$ (1H, q, $J = 3.12$ Hz) $\delta\ (H_9) = 6.9$ (1H, d, $J = 3.3$ Hz) $\delta\ (H_8) = 7.76$ (1H, s) $\delta\ (H_7) = 7.99$ (1H, s)					$\delta\ (H_{2\beta}) = 2.75$ (1H, t, $J = 8.4$ Hz) $\delta\ (H_{4\beta}) = 3.12–3.17$ (1H, m) $\delta\ (H_{5\beta}) = 3.21–3.28$ (1H, m) $\delta\ (H_{3\beta}) = 3.37–3.43$ (1H, m) $\delta\ (H_{6''\beta}) = 3.46–3.51$ (1H,m) $\delta\ (H_{6'\beta}) = 3.7–3.74$ (1H, m) $\delta\ (OH_6) = 4.49$ (1H, t, $J = 5.67$ Hz) $\delta\ (H_{1\beta}) = 4.68$ (1H, t, $J = 7.2$ Hz) $\delta\ (OH_3) = 4.76$ (1H, d, $J = 5.67$ Hz) $\delta\ (OH_4) = 4.83$ (1H, d, $J = 5{,}1$ Hz) $\delta\ (H_{13}) = 6.16$ (1H, d, $J = 2.4$ Hz) $\delta\ (OH_1, H_{12}) = 6.50$-$6.53$ (2H, t) $\delta\ (H_9) = 6.64$ (1H, d, $J = 3.5$ Hz) $\delta\ (H_{11}) = 6.74$ (1H, d, $J = 16$ Hz) $\delta\ (H_{10}) = 6{,}90$ (1H, d, $J = 16$ Hz) $\delta\ (H_8) = 6.95$ (1H, d, $J = 2.5$ Hz) $\delta\ (H_7) = 7.94$ (1H, s)			
FTIR (cm^{-1})	ν (CH=N) = 1647 ν (O–H) = 3440 ν (Fu) = 3146, 990, 931, 760 ν (C–H) = 2850 ν (CH$_2$) = 2960 ν (C–OH) = 1080 ν (C–O–C) = 1034					ν (O-H) = 3465 ν (C-H) = 2847 ν (CH$_2$) = 2965, 2880 ν (CH=N) = 1641 ν (CH=CH) = 1626, 955 (*trans*) ν (CH=CH Fu) = 1592 ν (C–O–C glucide) = 1070 ν (Fu) = 3198, 1020, 988, 783 ν (CH$_3$) = 2913			
UV (nm)	$\lambda_{max} = 280$; $\epsilon = 1.4 \times 10^4$ l mol^{-1} cm^{-1}					$\lambda_{max} = 365$; $\epsilon = 4.3 \times 10^4$ l mol^{-1} cm^{-1}			
Elemental analysis	%	C	H	N	O	C	H	N	O
	Calc.	51.38	5.83	5.45	37.34	59.52	5.78	3.85	30.84
	Found	51.60	5.95	5.47	37.39	59.11	5.97	3.85	30.79
DSC	$T_m = 155$ °C					$T_m = 168$ °C			

Table 1 gives the data obtained from the characterization of **I** and **II**.

3.2. Oxidation of PEO-OH

In order to graft the oligoether chains onto the chitosan backbone it was first necessary to oxidize the primary OH groups at one end of the two commercial **PEO-OH** samples into aldehyde functions, i.e. to prepare the corresponding aldehyde-terminated oligomers **PEO-CHOs**. This oxidation reaction was carried out with each **PEO-OH** sample, following a published procedure [10] based on the combined use of DMSO and oxalyl chloride in methylene chloride at low temperature. The reaction did take place, but in both cases we were unable to achieve yields higher than about 80%. The comparison between the infrared spectrum of the initial **PEO-OH-750** and that of the oxidized product, shown in Fig. 1, provided evidence for the formation of the aldehyde moieties through the strong decrease in the OH band around 3400 cm^{-1} and the concomitant appearance of the carbonyl peak at 1730 cm^{-1}. These results were confirmed by ^{1}H NMR spectroscopy, since the triplet of terminal hydroxy proton at 4.5 ppm was replaced by a singlet at 9.6 ppm attributed to the aldehyde counterpart, as shown in Fig. 2. The two oxidized products maintained the T_g and T_f of their precursors, viz. −70 and 0 °C for the **PEO-CHO-350** and −67 and 30 °C for the **PEO-CHO-750**. They were used as obtained for the subsequent grafting reactions, since the unmodified **PEO-OH** fraction did not interfere with their course and could be eliminated more easily after them.

3.3. Chitosan grafting reactions

The grafting reactions were first studied separately in a preliminary approach aimed at studying their feasibility. They were then carried out jointly to synthesize the desired solvating film-forming photosensitive material.

3.3.1. Chitosan-g-PEO

In the first tests on this coupling reaction we observed that the Schiff base was indeed obtained but that the imine function was very sensitive to hydrolysis, i.e. the reverse reaction. It was therefore decided to reduce these –CH=N–

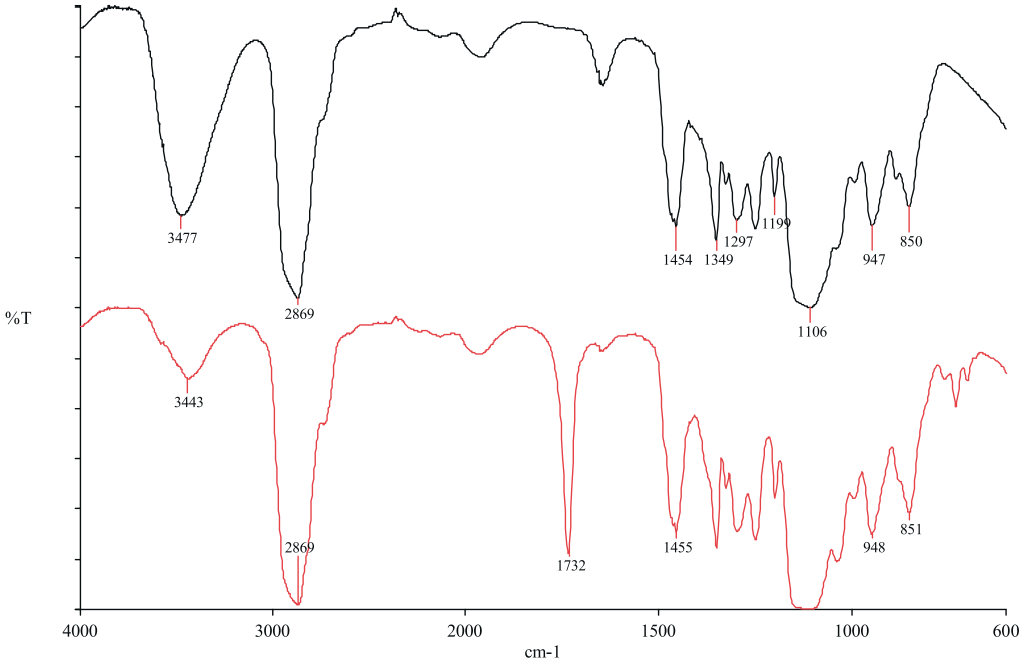


Fig. 1. FTIR spectra of PEO-OH-750 (upper tracing) and PEO-CHO-750 (lower tracing).

moieties in situ in order to stabilize the grafted PEO chains. The reaction of chitosan with each of the two **PEO-CHOs** was carried out in a mixture of acetic acid and methanol at pH 5 at room temperature. After 1 h, the solution was brought to pH 6.5 and an excess of $NaCNBH_3$ added dropwise for 25 min. After dialysis to remove all the salts, the acetic acid and the unreacted **PEO-CHO** and **PEO-OH**, the solution was lyophilised and the resulting solid washed with acetone and vacuum dried to constant weight. Scheme 1 summarises this procedure. Different $[NH_2]/[CHO]$ molar ratios and different amounts of the reducing agent (always in excess) were tested to optimise this double process.

The FTIR spectra of the products thus obtained indicated the presence of PEO chains and the absence of CH=N moieties. Their ^1H NMR spectra (solvent 1% CD_3COOD in D_2O, 80 °C) confirmed that both the $CHO + NH_2$ reaction and the reduction of the ensuing imine function had indeed taken place. A typical NMR spectrum is shown in Fig. 3,

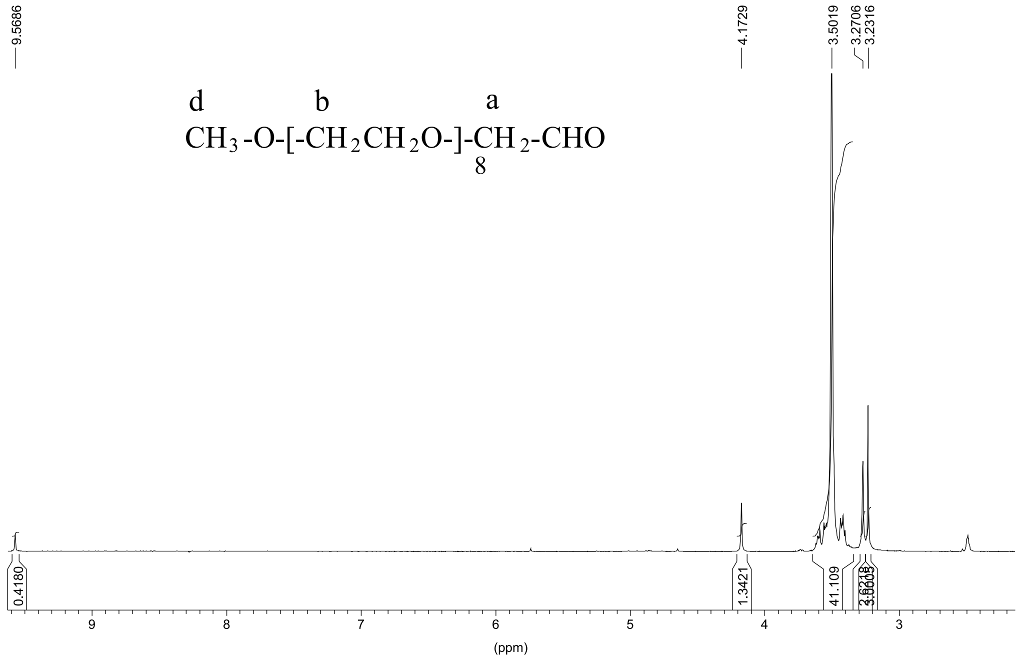
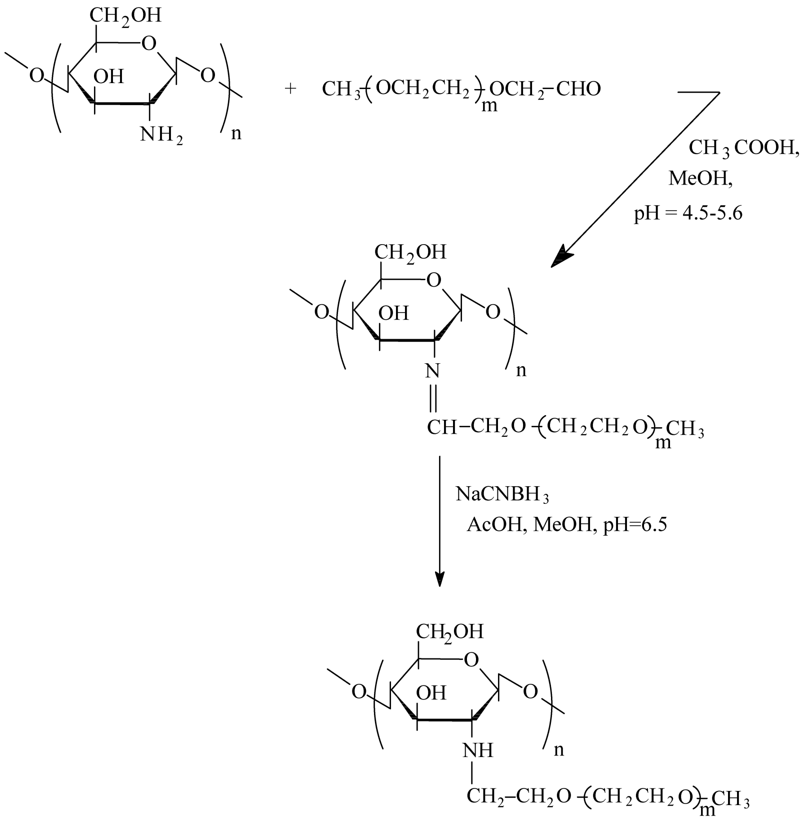


Fig. 2. 300 MHz ^1H NMR spectrum (CD_2Cl_2) of PEO-CHO-750.



Scheme 1.

together with the corresponding proton assignments. Thanks to these spectra, it was possible to carry out a quantitative analysis which provided the degree of substitution (DS) attained in each experiment, as given in Table 2. These results were corroborated by calculations based on the elemental analyses of the materials compared with that of the chitosan, which gave similar figures.

The T_g values of these grafted materials, also shown in

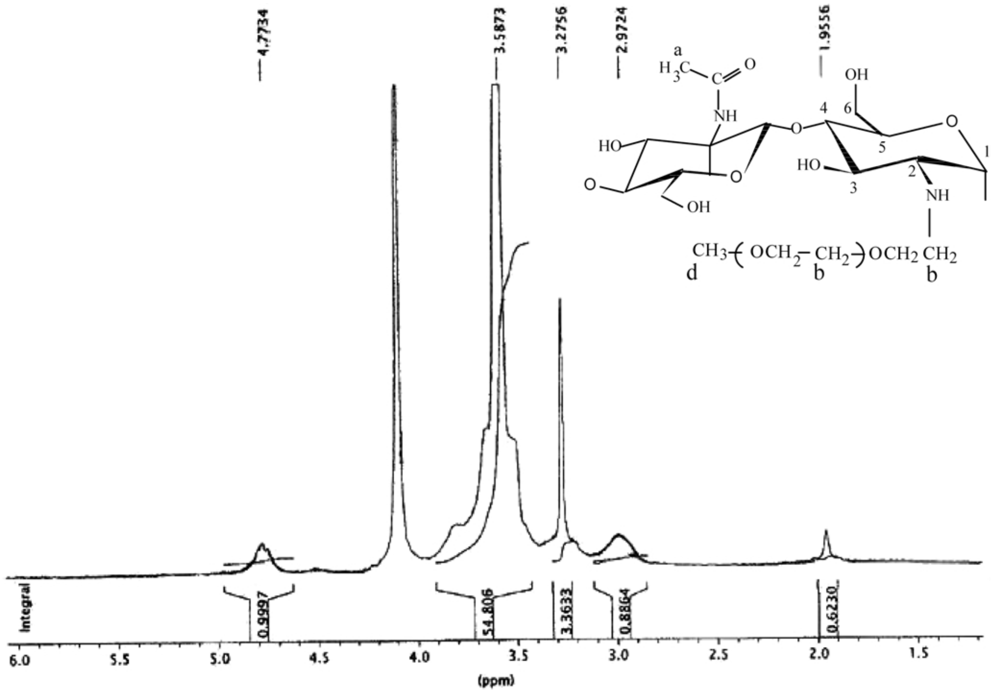


Fig. 3. 300 MHz ^1H NMR spectrum (1% CD_3COOD in D_2O) of Ch-PEO4 (see Table 2).

Table 2
Extent of grafting of PEO chains on chitosan

Reference	[CHO]/[NH$_2$]	DS (%)	T_g (°C)
Ch-POE 1[a]	0.29	22	−55
Ch-POE 2[a]	0.52	42	−57
Ch-POE 3[a]	1.0	70	−55
Ch-POE 4[a]	1.2	88	−63
Ch-POE 5[b]	1.2	87	−64

[a] PEO-CHO-350.

[b] PEO-CHO-750.

Table 2, were only modestly higher than those of the starting **PEO-CHOs**, i.e. the mobility of the oligoether segments remained very high. We had found a similar result in a previous study in which hydroxyethyl cellulose was grafted with oligoether monoisocyanates [2].

3.3.2. Chitosan-g-PEO-g-MFVF

The double grafting reactions were carried out following the procedure adopted for the chitosan–PEO experiments described under the preceding heading, the only difference being that now **PEO-CHO** and **MFVF** were added together to the chitosan solution. Two experiments were conducted using the same molar ratios among the reagents ([NH$_2$]/[CHO]/[MFVF] = 1/1.2/0.10), but with either **PEO-CHO-350** or **PEO-CHO-750**. Ninety percent of soluble product was isolated in each instance and characterized after purification and drying (see above).

Given the low content of furanic structures, the FTIR and ^{1}H NMR spectra revealed their presence, but did not allow their quantitative content in the materials to be assessed. For this to be done, we called upon the use of UV spectroscopy since the –Fu–CH=CH–Fu– moiety was the only conjugated structure in these polymers, absorbing in the near ultraviolet region of the spectrum, namely at 335 nm (the chitosans-*g*-PEO did not absorb above 250 nm).

From the reduction of model compound **II**, carried out with NaCNBH$_3$ as described above for the synthesis of chitosan-*g*-PEO, we obtained a model molecule with a chromophore simulating that appended onto the chitosan and determined its extinction coefficient ($\lambda_{max} = 335$ nm, $\epsilon = 4.3\ 10^{-4}\ \mathrm{l\ mol^{-1}\ cm^{-1}}$) in a 1% aqueous acetic acid solution. From the UV spectra of the chitosans-*g*-PEO-*g*-MFVF in the same solvent, it was thus possible to calculate the extent of grafted **MFVF**, which turned out to be 7 ± 1% for both materials, reflecting a yield of about 70% with respect to the MFVF used for the reactions.

The T_g of these two polymers were −64 °C (PEO-750) and −61 °C (PEO-350), indicating, as expected, that the presence of low amounts of pendant furan moieties did not alter the chain mobility of the polyether grafts.

3.4. Photocross-linking

The photochemical behaviour of the doubly grafted chitosans was studied by dissolving 10 mg of each product in 1 ml of a 1% aqueous acetic acid solution and irradiating the resulting solutions with a medium-pressure mercury arc. The exciting wavelengths were cut below 300 nm with a pyrex filter. The progress of the reaction was followed by UV spectroscopy between 0 and 60 nm, as shown in Fig. 4.

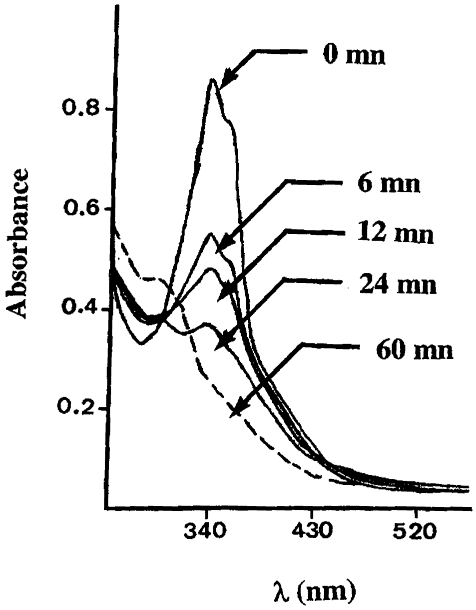


Fig. 4. Electronic spectrum of the doubly grafted chitosan dissolved in a 1% acetic acid aqueous solution, as a function of UV irradiation time.

The progressive decrease in intensity of the 335 nm band as a function of the irradiation time was accompanied by the concomitant precipitation of the polymer, suggesting that the photochemical reaction, responsible for both observations, was the same as that studied previously in our laboratory on poly(vinyl alcohol) grafted with MFVF [10], viz. a $\pi2 + \pi2$ cycloaddition reaction between an excited and a ground state moiety. This mechanism, applied to the present context, is shown in Scheme 2.

The precipitated polymer was filtered, washed with acetone and dried. It was insoluble in a variety of solvents of different polarity and displayed the typical features of a cross-linked elastomer (see below).

The strategy of attaching solvating and photosensitive grafts onto the chitosan backbone proved therefore successful in terms of both synthesis and photoreactivity. We thus moved to the preparation and characterisation of the corresponding polymer electrolyte.

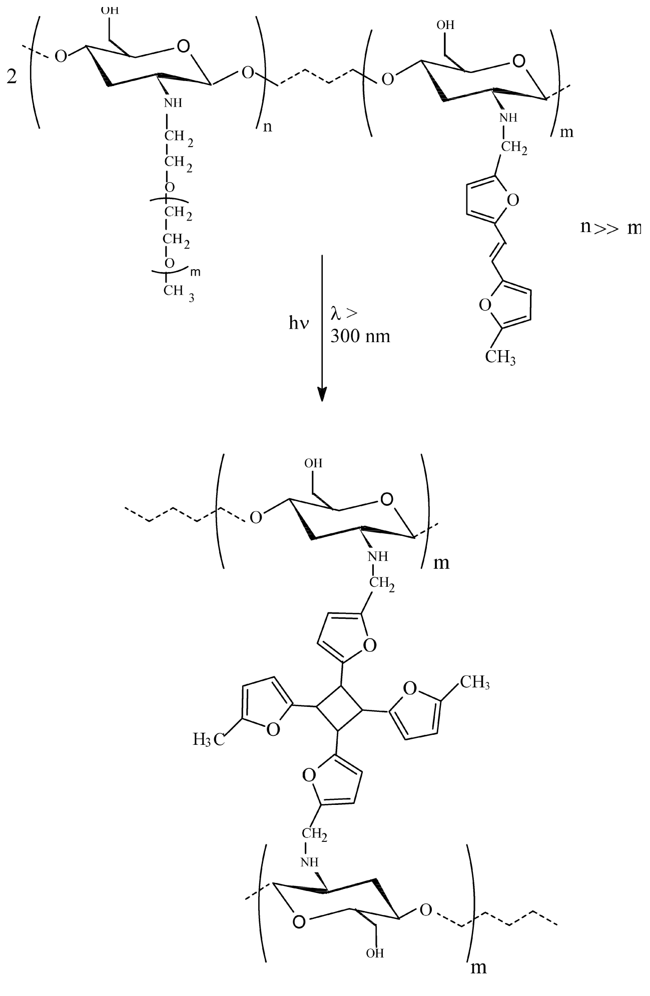
3.5. Conductivity measurements

Films of the photocross-linked chitosans were obtained by the double grafting process described above, followed by UV irradiation between two pyrex plates. Disks were cut from the ensuing elastomeric networks and placed in a LiClO$_4$/THF concentrated solution in order to induce the diffusion of $LiClO_4$ in the disk. The amount of salt incorporated into the network was monitored gravimetrically. Two salt concentrations were studied, namely those corresponding to [O]/[Li] values of 10 and 20, respectively, (here [O] indicates the molar concentration of oxygen atoms belonging to the PEO chains). It is well known [1] that the presence of salts in polyethers induces an increase of the polymer's T_g through physico-chemical cross-linking arising from the interaction of lithium cations with the electronic doublet on the oxygen atoms. In the present case, the T_g of the network based on **PEO-750** ($T_g = -64\,°C$) was raised to $-50\,°C$ with $[O]/[Li] = 20$ and to $-40\,°C$ with $[O]/[Li] = 10$, which does not represent a critical loss of chain mobility.

The ionic conductivity of these two systems was measured over a wide temperature range and the results were quite satisfactory, since the values obtained were similar to those of typical polyether-based networks [1]. Fig. 5 gives an Arrhenius-type plot applied to these data. Its non-linear trend, typical of ionic conductivity in polymer electrolytes [1], clearly indicates that the ionic transport did follow a classical activated process. A free volume model, based on the WLF treatment was therefore applied, viz.:

$$\log\left(\frac{\sigma_T}{\sigma_{T_r}}\right) = \frac{C_1^{T_r}(T - T_r)}{C_2^{T_r} + T - T_r}$$

and the corresponding plot gave the expected linear behavior, as shown in Fig. 6 for the film with $[O]/[Li] = 20$ and $T_r = 303$ K. From this plot, the calculation of the values of the 'universal' constants at T_g gave $C_1 = 19$ and $C_2 = 65$ K, which are in reasonable agreement with the theoretical values of 17.4 and 51.6 K, respectively.



Scheme 2.

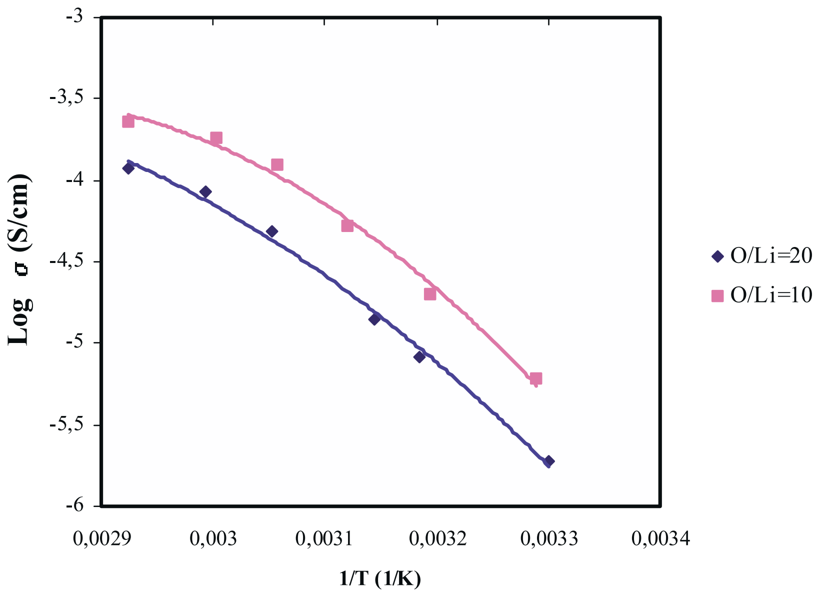


Fig. 5. Arrhenius plot related to the conductivity of the cross-linked chitosan–PEO membranes.

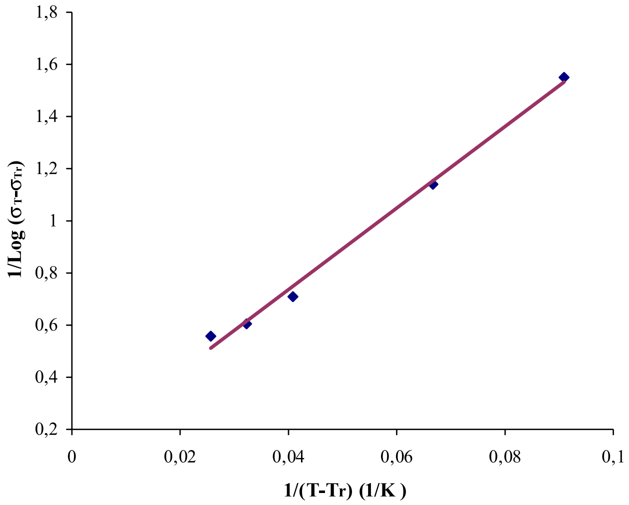


Fig. 6. WLF plot related to the conductivity of the cross-linked chitosan–PEO membranes.

4. Conclusions

The grafting strategy based on assembling (i) the polyether chains indispensable for ionic solvation and transport, (ii) a film forming backbone, (iii) and a photoactive moiety to be used for cross-linking seems a viable solution to the problem of the continuous processing of the material in its thermoplastic state. The addition of salt at this stage is thus simplified and the final network can thus be generated photochemically as the last step of the process. It is also important to emphasise that these novel materials were constructed using two components derived from renewable resources, viz. the chitosan backbone and the furan chromophore.

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