



Design, synthesis and photo-cross-linking of a new photosensitive macromonomer from tetra-branched poly(ethylene oxide)s

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ABSTRACT

A general procedure to increase the amount of photoreactive chromophore groups per oligoether chain is presented. In this work, a photoreactive macromonomer with four functionalities was synthesized by a four-step synthetic pathway with high yield. The photochemical behavior of this compound was studied with a view to obtaining polymeric networks. The significant advantage in this strategy is that the preparation of this material has as last operation, the obtaining and processing of polymer as thin film. In this way, the synthetic strategy based on assembling: (i) the polyether chains, (ii) a film forming backbone, and (iii) a photoactive moiety to be used for cross-linking, seems a viable solution to the problem of the continuous processing of materials.

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1. Introduction

The growing interest in polymer electrolytes stems from their essential role in high-end technological applications such as solid-state batteries [1] and super-capacitors [2]. The essential features that must be displayed by these materials are [3]: (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 flow in the event of an

unforeseen temperature rise. These requirements have been progressively optimized in various laboratories by a systematic approach covering a wide variety of structures and thorough inspection of thermal, dynamic-mechanical, transport and electrochemical properties [3]. One of the most suitable materials complying with these requirements consists of short poly(ethylene oxide) chains (low T_g solvating moieties) assembled into a network [4], e.g. through epoxy resins chemistry [5], and containing ca. 1 M concentrations of LiClO_4 .

On the other hand, polymers bearing photo-reactive polymerizable sites capable of self-coupling through photochemical activation [6] have been known and used for several decades, particularly in the realms of photography [7], printing [7] and microlithography [8]. The most rational approach involves a bimolecular reaction of excited species with its ground-state counterpart without intervention of free radicals, which usually give rise to undesired side reaction [9]. Thus, for example, cinnamic moieties attached to polymer backbones have been

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exploited successfully for around 60 years, albeit in different structures, according to the specific application required [8].

Much work has shown that 5-methyl-furfural can be readily oligomerized by nucleophilic self-condensations to give oligo(2,5-furylene vinylene)s with the general structure shown in Scheme 1, and that this process can be adapted to the synthesis of specific individual species with $n = 1, 2$ and 3 [9–11].

The photochemical behavior of the dimer (di-2,5-furylene vinylene, DFV, Scheme 1 where $n = 1$) was extensively studied [12]. When irradiated with UV light at approximately 260 nm, this molecule undergoes self-coupling through the alkenyl moieties between the two furan heterocycles, yielding the corresponding cyclobutane-based product (presented in Scheme 2). Moreover, the presence of an aldehyde function at one end of this dimer is a significant feature of its synthesis, as further chemical modification can occur, such as the preparation of Schiff-bases with different amines leading to interesting oligomeric products. These have been further explored in the context of photochemical derivatization [10,12].

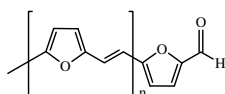
Recent studies have concentrated on improving such features as the processing of thin films with good mechanical properties and the possibility of inducing the cross-linking only at the final stage of the material production [10,12,13].

The present investigation describes a synthetic pathway to increase the amount of photoreactive chromophore groups per oligoether chain following a dendritic approach [14,15]. This method presents the advantage of an increased number of cross-linking points per mol of oligoether, allowing for the use of short poly(ethylene oxide). In this work, an oligoether bearing amine end-groups was derivatized to incorporate four photoactive furan-based chromophores, in order to prepare materials bearing (i) a low T_g solvating moieties, (ii) a film forming macromolecular backbone, and (iii) latent sites to be exploited in the final photochemical cross-linking. The photo-cross-linking reaction was also studied and the resultant network was characterized.

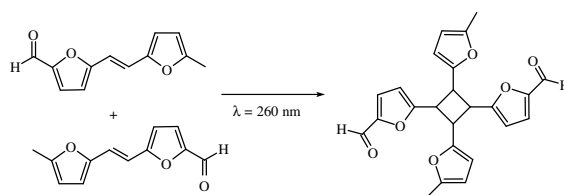
2. Experimental

2.1. Materials

4,7,10-Trioxa-1,13-tridecanediamine (Aldrich, 97%), 3,5-dinitrobenzoyl chloride (Fluka, 98%), thionylchloride (Aldrich) and 10% palladium-carbon (Pd-C) (Aldrich), were used as received. 3,5-diaminobenzoic acid was purified by recrystallization from water. Solvents such as chloroform (Ciccarelli), ethanol (Porta), and methylene chloride (CH_2Cl_2) (Ciccarelli) were used without purification. *N,N*-dimethylacetamide (DMAc) (Tedia), and dimethylformam-



Scheme 1. General structure of oligo(2,5-furylene vinylene)s.



Scheme 2. Self-coupling of di-2,5-furylene vinylene (DFV).

ide (DMF) (J.T. Baker) were distilled after drying under a bed of calcium hydride. 5-Methylfurfural (Aldrich, 97%) was purified by fractional distillation.

2.2. Analytical techniques

Characterizations by FTIR were performed using a Nicolet 5-SXC spectrometer on KBr discs or NaCl plates. ^1H NMR spectra were recorded using a Bruker AC200 in deuterated dichloromethane, chloroform, water and DMSO solutions. UV-Vis spectra were recorded using a Thermo-Spectronic UNICAMUV 500 and using spectrophotometric grade solvents. Irradiations were carried out under nitrogen atmosphere using a 500 W medium-pressure mercury arc equipped with a Pyrex filter to limit the excitation to wavelengths higher than 290 nm. DSC experiments were carried out with a TA Instrument DSC Q100 using ca. 2 mg of the studied material in sealed aluminium capsules. The samples were analyzed by heating-cooling cycles between -150 and 170 °C, at a rate of 10 °C min^{-1} . Measurements were carried out under a nitrogen flow (20 mL min^{-1}). An empty pan was used as a reference.

2.3. Synthesis of the photoreactive macromonomer

2.3.1. Synthesis of tetranitro (compound 2)

3,5-dinitrobenzoyl chloride (20.0 mmol) and DMAc (40 mL) were placed into a flask equipped with a magnetic stirrer and a nitrogen inlet. The solution was cooled to -5 °C and then 4,7,10-trioxa-1,13-tridecanediamine (**1**) (9.1 mmol) was added, under a stream of nitrogen. The solution was stirred for 12 h. The reaction mixture was then poured into diluted hydrochloric acid (1.5 N). The crude was dissolved in CH_2Cl_2 , washed with sodium bicarbonate and finally with water. Then, it was dried with anhydrous CaCl_2 , and concentrated under vacuum to obtain the tetranitro compound **2**. The yield was 76%. ^1H NMR (CDCl_3) δ : 9.08 (t, 2H,Ar), 9.03 (d, 4H,Ar); 8.07 (t, 2H,CONH); 3.65–3.33 (m,16H, $\text{CH}_2\text{CH}_2\text{O}$ and $\text{CH}_2\text{CH}_2\text{N}$); 1.85 (q, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$). FTIR (cm^{-1}): 1102, 1344, 1541, 1659, 2871, 2920, 3098, 3260.

2.3.2. Synthesis of tetra-amine (compound 3)

A stirred suspension of compound **2** (2.0 mmol), and 10% Pd-C (0.42 g) in ethanol was degassed and purged with hydrogen several times and then stirred at 60 psi of H_2 at 25 °C for 24 h in a Parr hydrogenator. The mixture was filtered using Celite-545. The solution was concentrated and dried at room temperature under vacuum. Compound **3** was obtained with a yield of 84%. ^1H NMR (D_2O) δ : 6.58

(d, 4H, Ar), 6.43 (t, 2H, Ar), 3.75–3.50 (m, 12H, CH₂CH₂O), 3.43 (t, 4H, CH₂CH₂N), 1.88 (q, 4H, CH₂CH₂CH₂). FTIR (cm⁻¹): 1449, 1543, 1624, 1688, 1717.

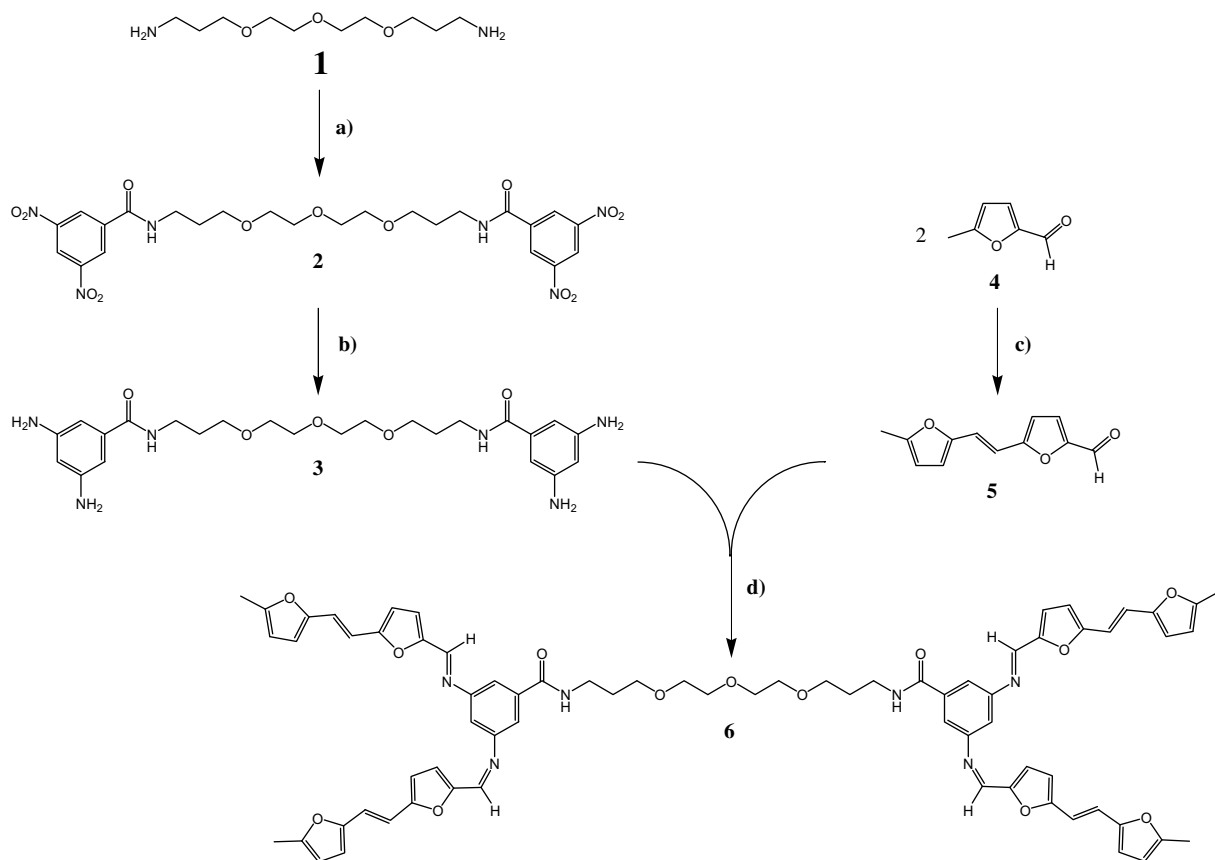
2.3.3. Synthesis of chromophore (compound 5 or DFV)

Compound 5 was prepared by mixing 20 mL of 5-methylfurfural (5-MF) (4) with 30 mL of water and 15 mL of methanol. Then, 1.2 g of NaOH was added under magnetic stirring and a stream of nitrogen. The resulting mixture was refluxed for 3 h. The purified dimer (DFV, 5) was obtained in ca. 40% yield by distillation under vacuum. ¹H NMR (CD₂Cl₂) δ: 9.53 (s, 1H); 7.23 (d, 1H); 7.04 (d, 1H); 6.76 (d, 1H); 6.48 (d, 1H); 6.40 (d, 1H); 6.07 (m, 1H);

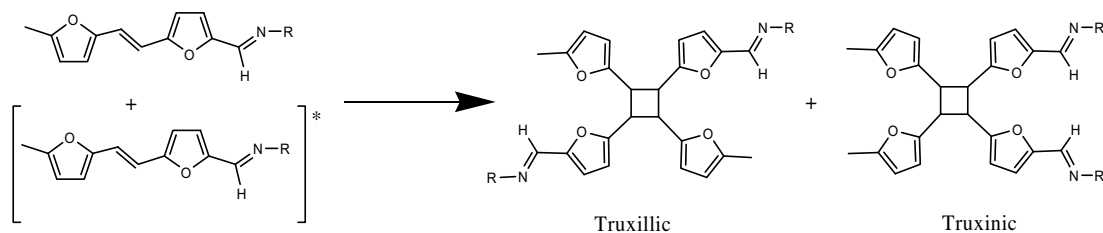
2.33 (s, 3H). FTIR (cm⁻¹): 958, 1018, 1625, 1660, 2946, 3113. Melting point: 86–87 °C.

2.3.4. Synthesis of Schiff-tetrabase (compound 6)

Compound 5 (4.4 mmol) and tetraamine 3 (1.0 mmol) were dissolved in 30 mL of methanol into a flask equipped with a magnetic stirrer and nitrogen inlet. The solution was stirred at room temperature for 1 h, and then concentrated using a rotary evaporator and finally dried under vacuum. The reaction mixture was stirred and heated at 90 °C for 96 h under vacuum. The progress of the reaction was performed by FTIR spectroscopy as follow: at different reaction times a certain quantity of the reagent media was



Scheme 3. The synthetic pathways followed to obtain compound 6. Conditions: (a) 3,5-dinitrobenzoyl chloride, DMAc, 12 h, yield: 76%; (b) 10% P/C, EtOH, H₂ (60 psi), 24 h, yield: 84%; (c) water/MeOH, NaOH, 3 h reflux, yield: 40%; (d) 90 °C, 96 h under vacuum, yield: 83%.



Scheme 4. Intermolecular coupling of Schiff-base oligoethers bearing di-2,5-furylene units.

dissolved in CH_2Cl_2 and deposited on a NaCl plate, after evaporation of the solvent FTIR spectra were recorded. The reaction was allowed to continue until the decrease of the band corresponding to aldehyde function at $\approx 1670\text{ cm}^{-1}$ remained constant. The volatile residual DFV was removed using a secondary ramp of vacuum. The conversion of the initial monomers reached 91%, as calculated from ^1H NMR spectrum. The yield of this reaction was 83%. ^1H NMR (DMSO- d_6) δ : 8.15–8.05 (m, 3.7H, Schiff's base); 8.03–7.85 (m, 3.9H, ortho-imine and ortho-amide); 7.40–6.10 (m, 23.5H, Ar); 3.70–3.25 (m, 12H, $\text{CH}_2\text{CH}_2\text{O}$); 2.92–2.77 (m, 4H, $\text{CH}_2\text{CH}_2\text{N}$); 2.39 (br., 10.95H, CH_3); 1.91–1.83 (m, 3.8H, $\text{CH}_2\text{CH}_2\text{CH}_2$). FTIR (cm^{-1}): 954, 1024, 1118, 1565, 1641. T_g (DSC) = $44\text{ }^\circ\text{C}$. UV-Vis (CH_2Cl_2): $\lambda = 295\text{ nm}$ and $\lambda_{\text{max}} = 410\text{ nm}$.

2.3.5. Photo-cross-linking of the compound 6

Samples for irradiations were prepared as follows: solutions of the macromonomer **6** in methylene chloride were deposited on NaCl plates and slowly dried in order to form thin films. The films presented an average thickness of about $18\text{ }\mu\text{m}$. Irradiations were carried out under nitrogen atmosphere using a Pyrex filter to limit the excitation to wavelengths higher than 290 nm . The same procedure was followed to form films inside of the DSC pans. These films also presented an average thickness of about $18\text{ }\mu\text{m}$ and an average mass of about 2 mg .

3. Results and discussion

3.1. Synthesis of the photoreactive macromonomer

The pathway for the synthesis of the tetra-amine **3** from compound **1** (4,7,10-trioxa-1,13-tridecanediamine) is an adaptation of the Kakimoto's method for the preparation of dendrimers [14,15]. Compound **5** (DFV) was chosen as photoreactive chromophore and was synthesized and purified following the procedure previously developed by Coutterez and Gandini [10]. The synthetic pathways followed to obtain the compounds **2–6** is briefly presented below (Scheme 3).

3.2. Photochemistry

Recent photochemical studies of various Schiff-base oligoethers [13,16] suggest that the near-UV irradiation of macromonomers induce inter-macromolecular couplings between an excited and a ground-state furan chromophore, eventually leading to the formation of a polymeric network (Scheme 4). In other words, compound **6** was expected to react through the same coupling mechanism.

Evidence supportive of this mechanism was obtained by following the irradiation of **6** by FTIR spectroscopy. Fig. 1 shows that the most relevant change was, as expected, the progressive decrease of the alkenyl $\text{C}=\text{C}$ band at 1640 cm^{-1} , which was accompanied by the appearance of new bands corresponding to the cyclobutane ring, near to 1210 cm^{-1} , CH bending modes around 735 cm^{-1} , and other modes associated with the ring deformation. Understandably, these spectral changes were quantitatively much less

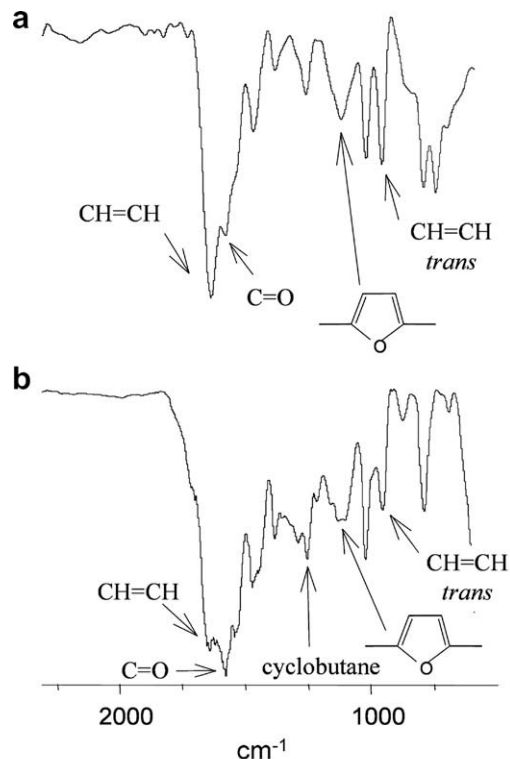


Fig. 1. FTIR spectra of compound **6**: (a) before and (b) after 7.5 h of irradiation between two NaCl plates.

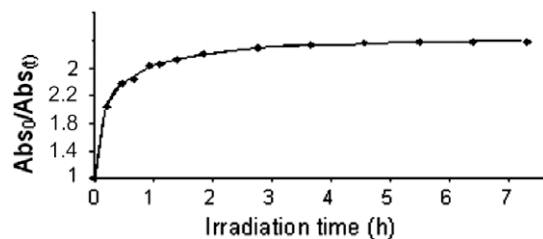


Fig. 2. Kinetic of photo-cross-linking reaction of compound **6**. The plot shows the relative absorbance of the band at 954 cm^{-1} as a function of reaction time ($\text{Abs}_0/\text{Abs}_t$).

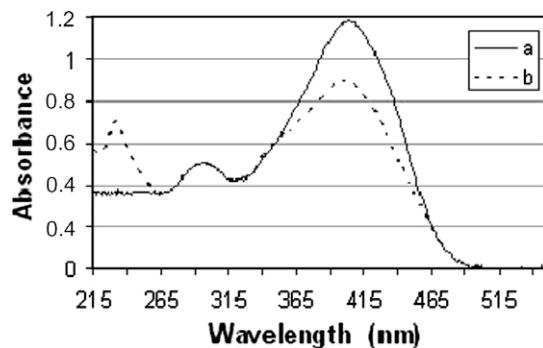


Fig. 3. UV-Vis spectra of compound **6**: (a) before and (b) after 7.5 h of irradiation.

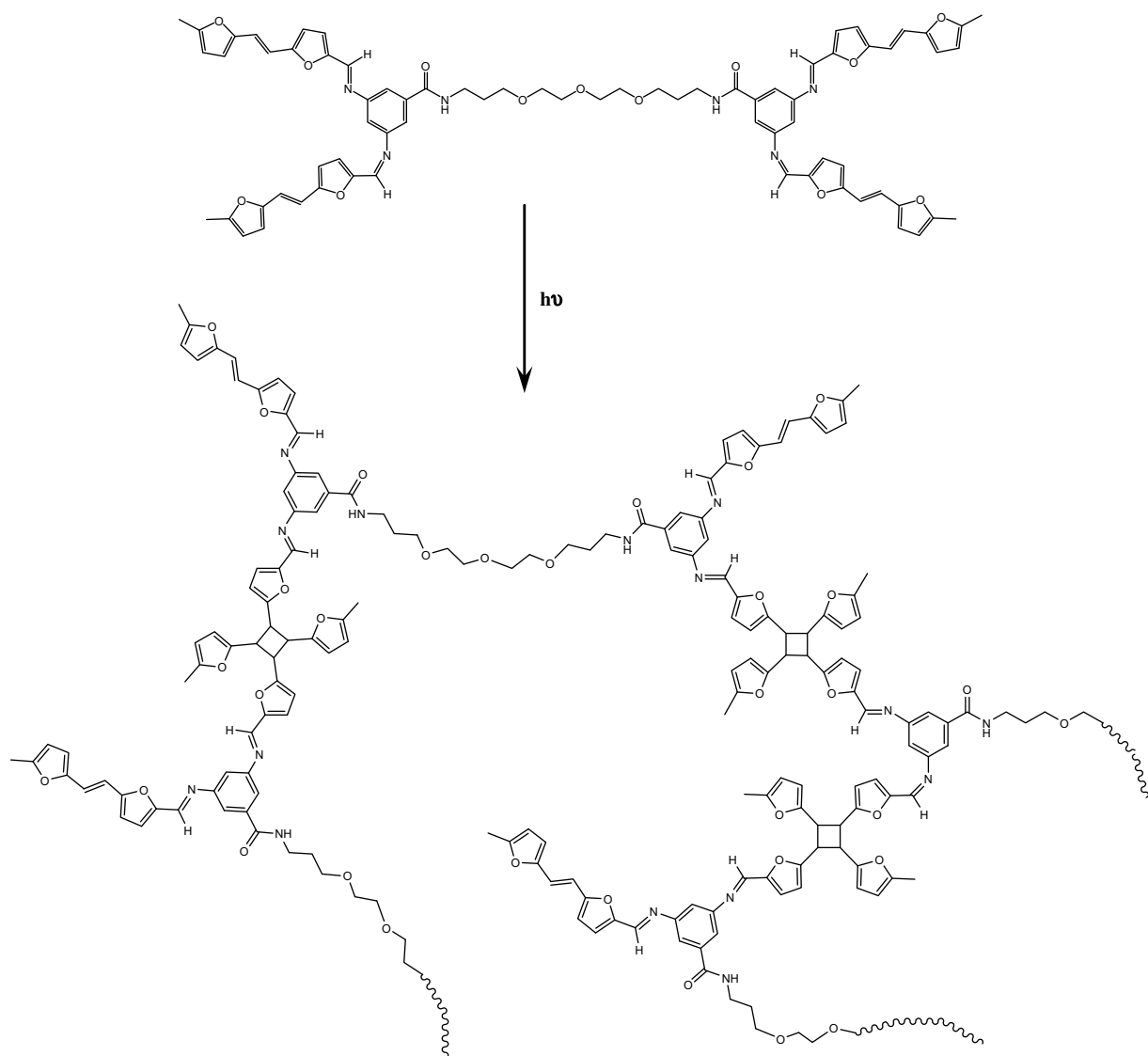
important than those observed with pure DFV [16], because of the lower probability of binary chromophore encounters, compared with DFV itself. Such a feature can be rationalized by: (i) the low concentration of photoreactive alkenyl in the macromonomer and (ii) the lower mobility of the furan chromophores. It took approximately 5.5 h to reach the plateau in the extent of coupling, suggesting the formation of networks where chain mobility is restricted.

The kinetic of photo-cross-linking was also examined. The plot is shown in relative absorbance of the band at 954 cm^{-1} as a function of reaction time ($Abs_{(0)}/Abs_{(t)}$), as illustrated in Fig. 2.

UV-Vis spectroscopy also provides further corroborating evidence for the $[\pi2 + \pi2]$ cycloaddition mechanism, demonstrating the favourability of intermolecular coupling between alkenyl moieties through a decrease in λ_{max} at

410 nm for the Schiff-tetrabase and the appearance of a new signal at 232 nm after irradiation because of the significant loss of conjugation associated with the disappearance of unsaturated moieties between the two furan heterocycles (Fig. 3). From the obtained results, coupling between terminal chromophores seemed to occur as shown in Scheme 5, for photoactive macromonomer 6.

No other significant changes were observed, suggesting that the photochemistry followed, predominantly, one molecular process and that the contributions from the free radicals reactions can be neglected. This was confirmed by carrying out identical experiments in the presence of a free radical trap. The result associated to this set of experiments displayed the same features as those described above. Moreover, the introduction of lithium perchlorate in the macromonomer 6 (equimolar mixture) did not change the photochemical behavior of 6 and allowed the



Scheme 5. Photo-cross-linking of compound 6.

preparation of PEO-based cross-linked polymer, probably excellent candidates for conducting materials through a very simple operation. This result makes this material an interesting candidate for application in lithium based batteries [17].

3.3. Characterization of polymeric network

In the FTIR spectra of the macromonomer **6** and cross-linked product (Fig. 1) the relative intensity of the bands (at 954 cm^{-1}) was small. In other words, after irradiation of the compound **6**, there is still an intense band corresponding to $\text{HC}=\text{CH}$ at 954 cm^{-1} , indicating that few unsaturations had been involved in the network formation. However, the extent of cross-linking of the films after irradiation for 7.5 h was found to be 100% for the compound **6**. This reaction yield was determined by the mass balance after soxhlet solvent extractions with dichloromethane.

It is known that ionic conductivity is related to the thermal properties of polymer networks [18] since lithium ion transport is strongly coupled to the segmental motion of PEO chains. Then, the thermal behavior of the resulting network was also studied by DSC, showing a T_g value of $50\text{ }^\circ\text{C}$. It is worth to mention that the T_g of the initial macromonomer was $44\text{ }^\circ\text{C}$. The relatively low increase in the T_g could be attributed to a low cross-linking density, which in turn is probably due to the stiffness of the macromonomer **6** and the location of the photoreactive groups. Thus, the encounter between two alkenyl moieties on different molecules is relatively hindered in these structures. Although the studied polymer has a T_g value of $50\text{ }^\circ\text{C}$, which is about $100\text{ }^\circ\text{C}$ higher than an electrolyte that would have a high conductivity, the strategy seems to be adequate since it can be made with much longer PEO units. These longer PEO segments would induce lower T_g values in both macromonomer and networks without modifying the photochemical behavior.

4. Conclusions

A simple, general procedure that increases the amount of chromophore groups per oligoether chain was established. A new photoreactive macromonomer (compound **6**) bearing four functional groups was synthesized, following a four-step synthetic pathway with relatively high yield. The photochemical behavior of **6** was investigated and the obtained polymeric network studied. It is impor-

tant to emphasize that the T_g value of the resulting material has been only slightly larger than that of the macromonomer, indicating only a small decrease in the mobility of the oligoether chains.

Finally, the synthetic strategy based on assembling: (i) the polyether chains indispensable for ionic solvation and transport, (ii) a film forming backbone, and (iii) a photoreactive moiety to be used for cross-linking, seems a viable solution to solve the problem of the continuous processing of materials.

Work is in progress to develop a greater understanding of these novel materials (macromonomer and polymeric network) and specifically to evaluate the electrochemical behavior of the lithium salts in these systems.

Acknowledgments

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