

A novel approach to crosslinked polymer electrolytes based on polyethers: network formation via photochemistry

Luca Albertin, Paola Stagnaro, Claire Coutterez, Jean-François Le Nest and Alessandro Gandini*

Matériaux Polymères, Ecole Française de Papeterie et des Industries Graphiques (INPG), BP 65, 38402 St. Martin d'Hères, France
 (Revised 9 January 1998)

This communication describes a novel approach to crosslinking functionalized oligoether chains based on the photochemical irradiation of their terminal chromophores bearing conjugated furan moieties. The interest of this study resides in the possibility of preparing polymer electrolytes which can be handled as thermoplastic materials and crosslinked only at the last stage of their processing, e.g. as thin films. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polymer electrolytes; conjugated furans; photochemical crosslinking)

Introduction

The growing interest in solid polymer electrolytes arises from their potential use in applications such as batteries, sensors and electrochromic devices. Our laboratory has been engaged for many years in investigations related to these materials in terms of both the synthesis of original structures and the characterization of their physical and working properties^{1,2}. This research has led to the formulation of elastomeric polyether-based networks with good overall performances, including a pronounced film-forming aptitude resulting from the presence of polysaccharide chains in the crosslinked architecture³. The introduction of the salt, which provides the ionic transport across the polymer membrane, is usually carried out by diffusion into the final network, a procedure which can be cumbersome. Also, the technical processing of thin films *before* crosslinking is a delicate task. We have therefore looked into the possibility of working with a thermoplastic or viscous precursor, which could be easily filled with salt and cast into thin films, leaving the crosslinking operation as the *very last stage* of the process.

The formation of the network by photochemical means appears to be a good approach since it would call upon a latent reactivity readily and rapidly exploited by a simple exposure to uv radiation. The present communication describes such an approach based on intermolecular photochemical coupling.

Results and discussion

The central feature to be maintained was the inevitable presence of oligoether chains, e.g. polyethylene oxide (PEO) or polypropylene oxide (PPO), which remain today the best structures found for polymer electrolytes thanks to their low T_g , good solvating power for lithium ions (i.e. the most frequently used cations) and lack of crystallinity at low chain lengths^{1,2}. The commercial availability of Jeffamines, i.e. linear and branched oligo(ethylene oxide)s and oligo(propylene oxide)s bearing one, two or three NH₂

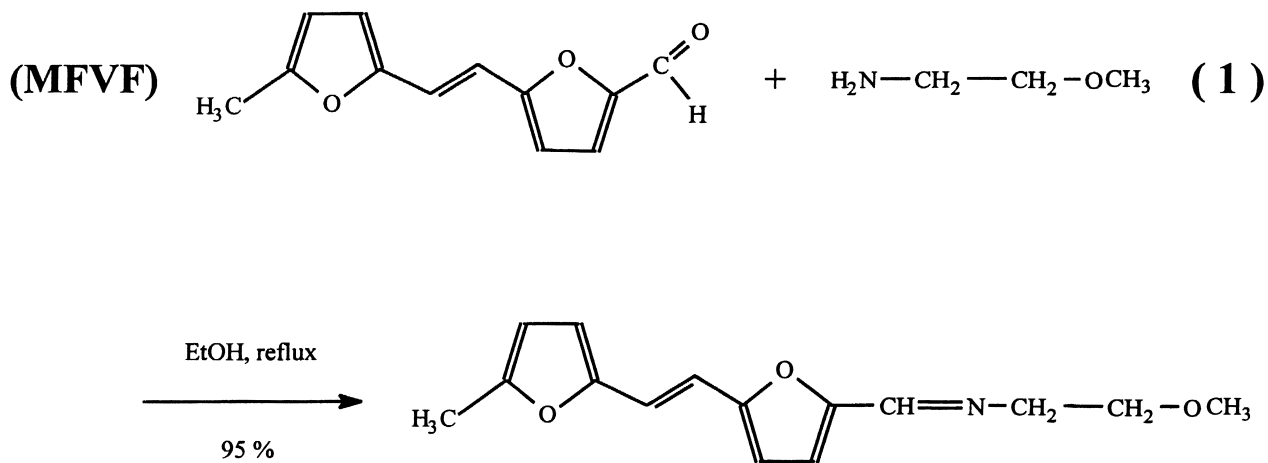
end-groups, was our first starting consideration for this investigation. The second, referred to a recent study in our laboratory⁴ which showed that bis-(2,5-furylene)vinylene moieties (among other conjugated heterocyclic structures) give a clean photochemical response when they are excited with wavelengths higher than 300 nm, namely a $[\pi 2 + \pi 2]$ cyclodimerization through the external unsaturation, without the intervention of any secondary free radical mechanism. Finally, our work in progress⁵ on conjugated furanic polymers and oligomers derived from 5-methyl-2-furancarboxyaldehyde (MF) provided a domestic source of photo-sensitive coupling agents for the Jeffamines.

The classical condensation reaction between a primary amine and an aldehyde function was therefore used to prepare the various Schiff-base oligoethers carrying the latent photoreactivity associated with the -2,5-Fu-CH=CH-2,5-Fu- moiety. The amino reagents included a model compound, viz. CH₃-O-CH₂-CH₂-NH₂ (**1**), and a selection of both PEO- and PPO-based linear and branched Jeffamines. The standard furanic reagent was the conjugated aldehyde 5-[2-(5-methyl-furyl vinylene)] furancarboxyaldehyde (MFVF) resulting from the selfcondensation of MF^{4,5} (see *Scheme 1*), but MF itself was also employed to prepare a model Schiff base deprived of vinylene moieties. *Scheme 1* illustrates this process applied to a monofunctional Jeffamine and MFVF.

All these compounds, obtained in high yields, were thoroughly characterized spectroscopically in order to confirm their expected structure. They were then submitted to irradiation with $\lambda > 300$ nm using various u.v. sources and a pyrex filter. Solid substances were pressed into KBr pellets (which enabled FTi.r. monitoring during irradiation), whereas the viscous oligomers were photolyzed as thin films deposited between NaCl or glass plates. The model derived from MF + **1** did not show any photosensitivity and was recovered unchanged after several hours of u.v. treatment. Thus, the imino function conjugated with a furan ring, i.e. -CH=N-2,5-Fu- was found to be photochemically inert following excitation with $\lambda > 300$ nm in the absence of an external -C=C- group.

Instead, all the Schiff bases obtained according to *Scheme 1* showed a clear-cut photochemical behaviour in

* To whom correspondence should be addressed



Scheme 1

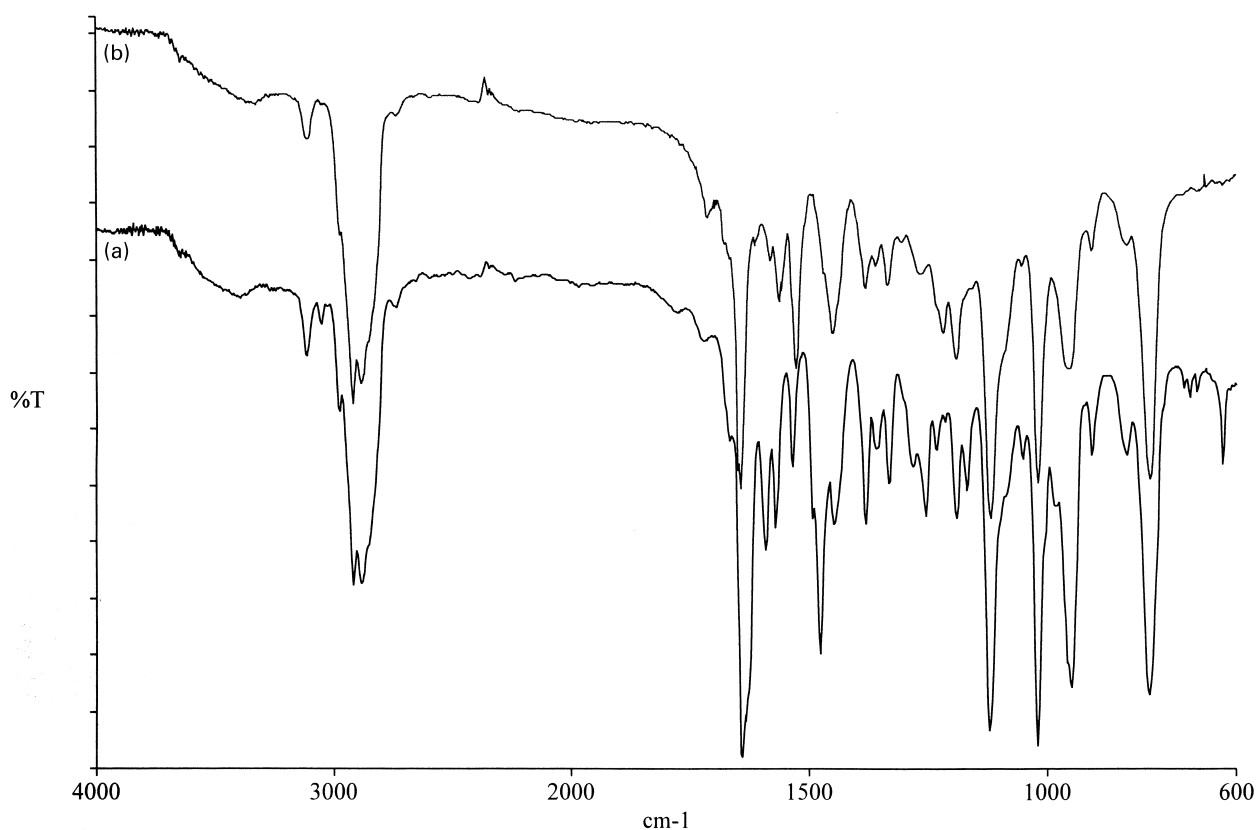
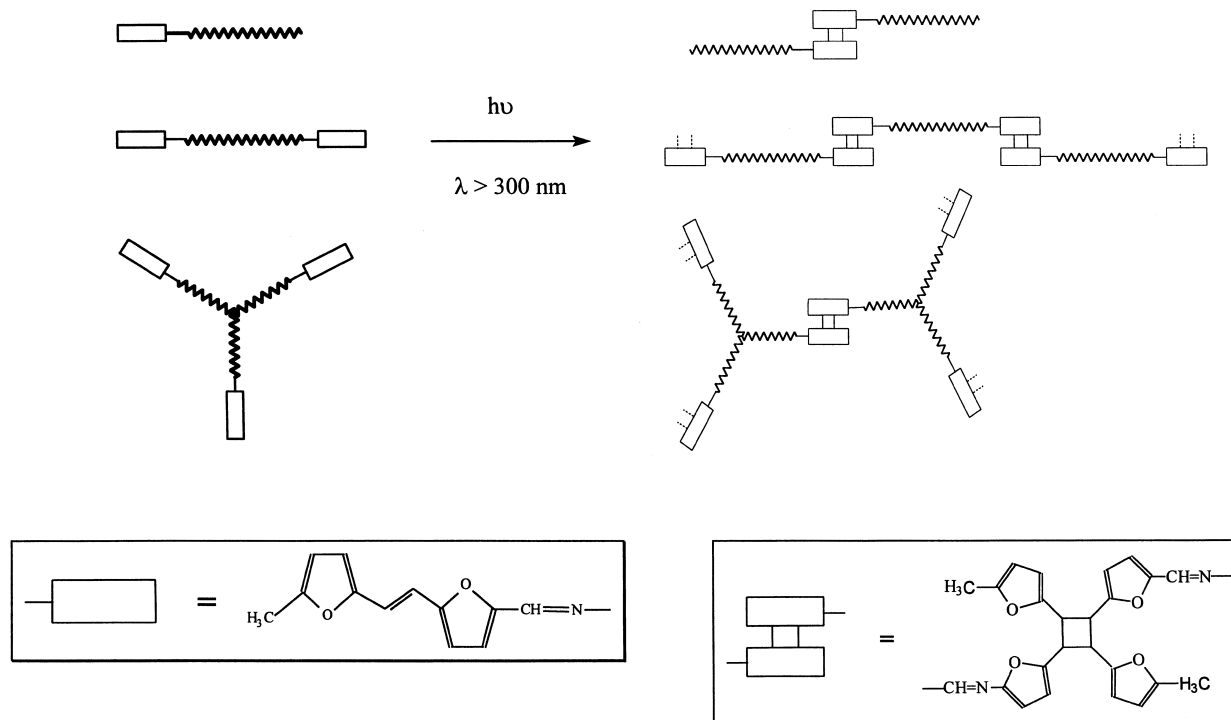


Figure 1 FTIR spectra taken before (a) and after (b) the irradiation of a thin liquid film of the Schiff base derived from MFVF + 1 between two NaCl plates. $\lambda_{\text{irr}} > 300 \text{ nm}$, $T = 25^\circ\text{C}$

which the cyclodimerization between two alkenyl moieties was the dominant mechanism, as indicated by the evolution of their FTIR spectra. In fact: (i) the bands corresponding to the alkenyl moieties at 3060, 1625 and 980 cm^{-1} decreased progressively; (ii) the carbonyl absorption moved correspondingly from 1640 cm^{-1} to higher frequencies as the C=C band at 1625 cm^{-1} decreased; and (iii) a band attributed to the cyclobutane ring appeared and grew at 1530 cm^{-1} . Figure 1 illustrates these changes in a typical photodimerization reaction.

No other significant change was recorded, suggesting that the photochemistry was predominantly molecular in character with no contribution from free radical reactions.

This point was confirmed by carrying out several experiments in the presence of a free radical trap, which displayed the same features as those described above. Further evidence corroborating the $[\pi 2 + \pi 2]$ cyclodimerization mechanism included the $^1\text{H-NMR}$ spectra of the soluble products which again showed the disappearance of alkenyl protons around 6 ppm and their replacement by resonances typical of cyclobutane protons around 4 ppm, as in a previous structural study⁴. The u.v.-visible spectra brought additional support in favour of intermolecular coupling between alkenyl moieties through a strong decrease in λ_{max} , which went from 365 nm for the various Schiff bases prepared from MFVF to 280 nm after their irradiation,



Scheme 2

because of the drastic loss of conjugation associated with the disappearance of the unsaturation between the two furan heterocycles.

Thus, coupling between terminal chromophores occurred as shown in *Scheme 2* for the three types of photoactive structures. In that scheme the oligoether chains (**PEO** or **PPO**, M_n from 250 to 2000) are symbolized by a wavy line.

In the specific instance of polymer electrolytes, the irradiation of trifunctional oligomers based on **PEO** gave crosslinked products (see *Scheme 2*) with glass transition temperatures below -50°C , good mechanical properties and remarkable film-forming aptitudes when thin layers of the viscous precursors were used. The introduction of high concentrations of lithium perchlorate in the various thermoplastic oligoether precursors did not change their photochemical behaviour and allowed the preparation of **PEO**-based crosslinked polymer electrolytes through a very simple *in fine* operation. The ionic conductivity of these systems was close to $10^{-5} \text{ S cm}^{-1}$ at room temperature, i.e. a good performance for **PEO**-based networks containing lithium salts of strong acids¹⁻³. The value of the conductivity for a given system did not change appreciably

upon irradiation suggesting that crosslinking did not alter the ionic mobility in a significant way.

Conclusion

The general procedure reported here opens a simple but original way to crosslink oligoethers containing lithium salts as the *last* operation in the synthesis and processing of polymer electrolytes as thin films. Work is in progress to gain a deeper insight into the preparation and properties of these novel materials.

References

1. Gandini, A., Le Nest, J. F. and Schoenenberger, C., *Trends Polym. Sci.*, 1994, **2**, 432.
2. Gandini, A. and Le Nest, J. F., in *Polymeric Materials Encyclopedia*, Vol. 8, ed. J. C. Salamone. CRC Press, New York, 1996, p. 7809.
3. Schoenenberger, C., Le Nest, J. F. and Gandini, A., *Electrochim. Acta*, 1995, **40**, 2281.
4. Baret, V., Gandini, A. and Rousset, E., *J. Photochem. Photobiol.*, 1997, **A103**, 169.
5. Hui, Z., Mélares, C. and Gandini, A., *Polymer*, 1996, **37**, 2237.