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Methacryl-terminated macromers by living polymerization as precursors of IPN polymer electrolytes

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A new class of polymer electrolytes, based on the interpenetrating polymer network approach, was obtained starting from functionalised macromers, of poly-ether nature, in the presence of a lithium salt ($LiBF_4$, $LiClO_4$, $LiCF_3SO_3$) and propylene carbonate (PC) or tetraethyleneglycol dimethylether (TGME), as plasticizers.

The macromers were synthesised by living polymerisation employing a HI/I_2 system as the initiator. The macromer has a polymerisable end group, which can undergo radical polymerisation, attached to a monodisperse poly-vinylether, containing suitable ethylene oxide groups for ion coordination. Monomers and macromers were characterised by *FT*i.r., u.v.–vis, ^{1}H- and ^{13}C-n.m.r.

Self-consistent and easily handled membranes were obtained as thin films by a dry procedure using u.v. radiation to polymerise and crosslink the network precursors, directly on suitable substrates, in the presence of the plasticizer and the lithium salt. The electrolytic membranes were studied by complex impedance and their thermal properties determined by differential scanning calorimetry analysis.

Ionic conductivities (σ) were measured for PC and TGME-based membranes at various plasticizer and salt contents as a function of T (60 to -20°C). $LiClO_4$/PC/PE electrolytes, with 3.8% (w/w) salt and 63% PC, have the highest σ (1.15×10^{-3} and 3.54×10^{-4} S cm^{-1} at 20°C and -20°C, respectively). One order of magnitude lower conductivities are achieved with TGME; samples with 6% (w/w) $LiClO_4$ and 45% (w/w) TGME exhibit σ values of 2.7×10^{-4} and 2.45×10^{-5} S cm^{-1} at 20°C and -20°C. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: macromer; plasticized polymer electrolyte; ionic conductivity)

INTRODUCTION

In the last few years the research on polymer electrolytes has been focused towards the development of amorphous polymeric materials, suitable as hosts to inorganic electrolytes, mainly lithium salts, for high energy density rechargeable battery and electrochromic applications.

Polymer electrolytes suitable for batteries should exhibit an ionic conductivity of at least 10^{-3} S cm^{-1} at room temperature, which is not greatly reduced down to -20°C, high t^+, low T_g and good mechanical properties[1]. For electrochromic applications, high conductive solid polymer electrolytes (SPE) should meet the requirements of transparency, high and homogeneous surface area, together with fast and reversible response.

Many systems have been identified as potential candidates for use in electrolytic membranes. Among these amorphous comb-like polymers consisting of ethylene oxide (EO) side-chains attached to different polymer backbones, such as methacrylate[2], phosphazene[3,4], siloxane[5], itaconate[6], vinylether[7,8] exhibited conductivities up to 10^{-5} S cm^{-1} at 25°C.

Further improvements were achieved, including in the polymer network a plasticizer which provide a liquid-like environment and promote mass transport of ions[9].

Plasticisation of polymer network is a widely employed approach and can be achieved in different ways; the interpenetrating polymer network (IPN) approach[10] and the ‘gel electrolytes’ route are the more common[11]. In both cases a polymer matrix acts as host for a highly viscous liquid (plasticizer) which interpenetrates or swells the polymer. Ideally the system exhibits liquid-like ionic conductivity, while preserving the dimensional stability of a solid system. The plasticizers usually have a high dielectric constant (ϵ), to ensure strong charge dissociation. Propylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC) and γ-butyrrolactone are preferred. Low molecular weight glycols, such as diglyme, tetraglyme (TGME) and polyethyleneglycol dimethylether (PEGDME) have also been used.

Gel electrolytes in which mixtures of plasticizer (PC, EC, etc.) dissolving lithium salts are immobilised within poly-acrylonitrile (PAN), poly-vinylpyrrolidone (PVP) or poly-vinylchloride (PVC) matrices, have achieved very high σ (up to 10^{-3} S cm^{-1} at 25°C). In these systems the matrix should contribute negligibly to ionic conductivity[10].

Comparable and even higher conductivity can be obtained when plasticizers are incorporated in a poly-ether based network. In the IPN approach, membranes are usually obtained by crosslinking functionalised and conductive polymer network precursors with radiation (u.v., e.b.), in the presence of plasticizers[9,10]. A large variety of precursors, plasticizers and lithium salts are possible and homogeneous membranes with different characteristics can be obtained simply by changing the composition. This method provides a more economical and straightforward membrane preparation and avoids solvent-casting, which can introduce deleterious impurities.

This technique provides better results when the viscosity

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Table 1 Composition and molecular weight of macromers **II**

Sample	**A** (mmol)	**B** (mmol)	**A**/**B** [b] ratio	HI (mmol)	I_2 (mmol)	HI/I_2 ratio	M_w [a] (g mol^{-1})
Macro 7	1.5	7.5	5	1.5	0.75	2	1200
Macro 1	1.5	15	10	1.5	0.75	2	2100
Macro 2	1.5	15	10	1.5	0.25	6	2100
Macro 5	4.5	45	10	4.5	0.75	6	2100
Macro 6	4.5	45	10	4.5	0.75	6	2100
Macro 4	1.5	22.5	15	1.5	0.5	3	3100
Macro 3	0.6	15	25	0.6	0.3	2	5000

[a] Determined by NMR analysis
[b] **A**/**B** ratio corresponds to *n* in macromer **II** (see *Scheme 2*)

of the starting solution, containing the network precursors, the plasticizer and the lithium salt, is sufficient to avoid contraction phenomena of the solution when deposited. The viscosity can be increased by employing a macromer with reasonable molecular weight, higher than achievable with commonly employed monomers.

In this paper we report the synthesis and characterisation of a new class of polymer electrolyte, based on the IPN approach, in which the network precursor is a macromer having a polymerisable end-group attached to a monodisperse poly-vinylether, containing suitable EO groups for ion coordination.

The macromers are synthesised at controlled molecular weight by living polymerisation, employing HI/I_2 as the initiator and starting from vinylether monomers with functional pendant groups.

The poly-ether-based electrolyte can be directly prepared in the membrane producing step by free-radical photopolymerisation and supplies good performance in terms of ionic conductivity and mechanical strength. Copolymers of different types can also be envisaged by this technique.

EXPERIMENTAL

Materials

PC and TGME were purchased from Aldrich, dried on molecular sieves and distilled under vacuum. The residual water content was less than 10 ppm by Karl–Fisher titration. $LiBF_4$ (99.999% pure, AESAR) was used without further purification. $LiClO_4$ and $LiCF_3SO_3$ (Aldrich) were employed after drying at 120°C under vacuum.

Triethyleneglycol dimethacrylate comonomer (**III**) (Aldrich) was distilled under vacuum before use.

*Synthesis of monomer (***A***)* $CH_2{=}C(CH_3){-}COO(CH_2CH_2O)_2{-}{-}CH{=}CH_2$

Monomer **A** is synthesised by a two-step process, including the monovinylation of the glycol (step 1), followed by alkylation (step 2) (see *Scheme 1*).

Step 1. Diethyleneglycol (85 g, 0.8 mol), ethylvinylether (80 ml, 0.8 mol) and the catalyst, mercuric acetate $Hg(CH_3COO)_2$ (0.81 g, 0.0026 mol), are charged to a three-neck flask (250 ml), equipped with a condenser and inlets for reactants and inert gas. The system is kept under refluxing conditions, at a temperature of 70–80°C, for 10 h. The product (diethyleneglycol monovinylether) is recovered by extraction with organic solvents and separated from the corresponding divinylether by distillation.

40 g (0.3 mol) of pure product are obtained, with a yield of 40% (see *Scheme 1*).

Step 2. Diethyleneglycol monovinylether is added to a solution containing 40 ml of ethyl ether and 53 ml of pyridine. To this mixture, kept at room temperature under nitrogen, methacryloyl chloride (38.3 g, 0.37 mol) is added, dropwise, which causes the immediate precipitation of pyridinium chloride. The reaction is stopped when the disappearance of the monovinylether was observed (by g.p.c. analysis).

The product **A** is recovered via HPLC, using silica as the stationary phase and a mixture of hexane:ethylacetate (8:1) as the eluent. 42 g of 99%-pure product is obtained, which corresponds to a yield of 70%, relative to diethylene glycol monovinylether.

*Synthesis of monomer (***B***)* $CH_2{=}CH{-}O{-}(CH_2CH_2O)_3{-}CH_3$

Ethyl vinylether (130 g, 1.8 mol), triethylene glycol monomethyl ether (98.5 g, 0.6 mol) and mercuric acetate (1.82 g, 0.0057 mol) are charged to a three-neck flask (500 ml), equipped with a reflux condenser and maintained under nitrogen. The reaction mixture is heated at its refluxing temperature for approximately 10 h, then quenched by addition of potassium carbonate. Triethylenglycol-methyl-vinylether (**B**), recovered by distillation, is obtained with a purity of 99% and a yield, relatively to the starting glycol, of 80%.

Synthesis of macromer **II** (Macro 1–7)

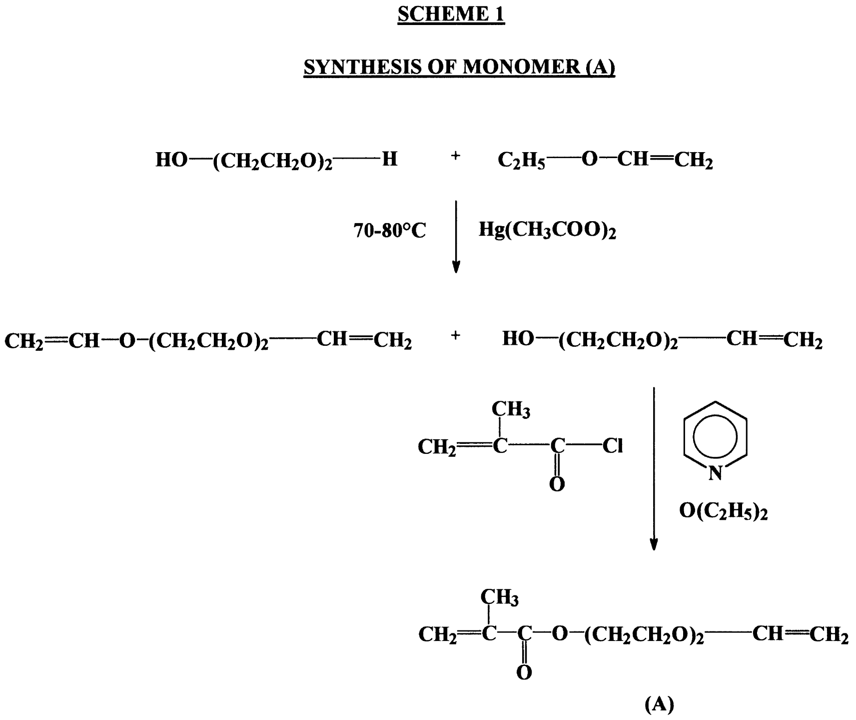
The synthesis of methacryl-terminated macromers is displayed in *Scheme 2*.

The monomer **A** (300 mg, 1.5 mmol), in 25 ml of anhydrous toluene, is charged to a 100 ml glass reactor, kept under nitrogen and cooled to − 78°C. Anhydrous hydrogen iodide, prepared according to Ref.[12], in *n*-hexane is added (3.75 ml of a 0.4 M solution, equivalent to 1.5 mmol of HI) to the solution, maintained under stirring. The reaction is allowed to proceed for approximately 1 h. Then the vinylether (**B**) (2.85 g, 15 mmol) and a solution of iodine I_2 (1.6 ml of a 0.47 M solution, equivalent to 0.75 mmol of I_2) are added, in sequence.

The temperature is then increased up to − 40°C, and the system stirred for 2 h. The reaction is terminated with prechilled ammoniacal methanol. The mixture is washed with aqueous sodium thiosulfate, in order to eliminate the excess of iodine, and then water. The macromer is recovered, after solvent extraction (methylene chloride), by evaporating until dryness.

The molecular weight of the macromer was determined via n.m.r. and confirmed by g.p.c., and resulted to be 2100 g mol^{-1}.

The same procedure was adopted to synthesize macromers having a different molar ratio of monomers **A** and **B**. In *Table 1* the molar ratios employed and the molecular weight of the corresponding macromers are reported.



Scheme 1

Electrolytical membrane preparation

A solution of the lithium salt was stirred into the plasticizer overnight for homogenisation and then added to a mixture containing the macromer **II** and the comonomer **III**, eventually with a small quantity of a promoter (benzophenone, 0.5–1 mol.%). The molar ratio **II**/**III** was kept fixed (98/2). This solution was then cast onto a Teflon mould and cured by u.v. radiation, for a time period from 10 to 150 s, as a function of the composition. The irradiation time was higher when $LiBF_4$, as the lithium salt, and TGME, as the plasticizer, were employed. The polymerisation rate can be increased by adding a radical promoter (benzophenone).

All operations were carried out in a dry box under an argon atmosphere (water and oxygen content < 10 ppm). The membranes obtained (100–200 μm thick) were generally slightly yellow coloured, homogeneous and easily handled.

Crosslinking was confirmed by the disappearance of the IR bands due to methacrylate groups (1638 cm^{-1}).

Differential scanning calorimetry

Thermal properties were determined with a Perkin Elmer d.s.c.-7, running cycles from 50 to -130°C and from -130°C to 100°C, at a scan rate of 10°C min^{-1}. T_g and T_m values did not change on repeating the cycles.

Ionic conductivity

Conductivity measurements were performed on electrolytic membranes by complex impedance analysis using a Solatron 1260 frequency response analyser coupled with a EG&G Parc mod.273. The conductivity was measured at various time intervals, in the range between 60°C and -20°C, after an equilibrium time of 2 h for each decrease in temperature, over the frequency range 1–10^5 Hz.

For impedance measurements, the membrane was lodged between two stainless steel blocking electrodes, employing a Teflon spacer to control the thickness.

RESULTS AND DISCUSSION

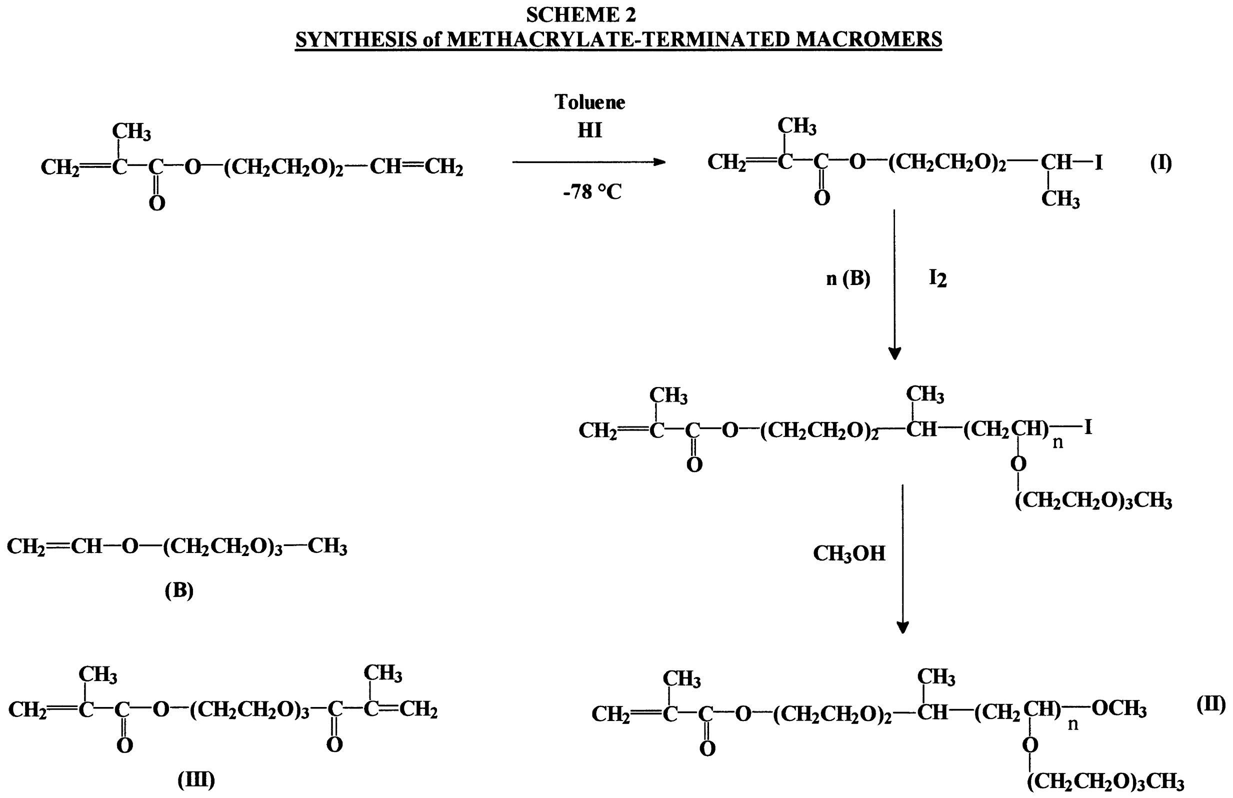
Living polymerisation discloses several advantages, in comparison to other polymerisation techniques; among these the control of molecular weight distribution and the presence of end functionalities are of paramount importance. Polymers with end and pendant functional groups, having a narrow distribution of molecular weights, can be obtained by this method. Star-shaped polymers and sequence regulated oligomers are also possible[13].

Polymers with end functionalities can be synthesised by living polymerisation following two different approaches: the functional initiator and the end-capping methods. In the functional initiator method the initiator carries a functional group that is incorporated as the head group into the polymer chain end. In the end-capping method the living polymer ends are quenched employing a reagent having a functional group, which is attached to the polymer tail via substitution reaction.

Vinylether polymers are commonly obtained by both techniques. End-functionalised vinylethers with amine, carboxyl and ester groups are, for instance, prepared by quenching the living polymer with anilines, containing the corresponding functional groups[14]. More commonly, vinylether polymers, with different functional groups, can be polymerised into living polymers by using, among others, the HI/I_2 system as the initiator. The catalyst HI/I_2 allows one to obtain monodisperse macromers, the molecular weight being controlled by the ratio between monomer and comonomer.

Mono- and di-functional poly-vinylethers with malonate and carboxyl end-groups were, for instance, obtained by this technique[15]. The HI/I_2 living process was also employed to synthesise diblock[16] and triblock copolymers[17].

In other studies, iodine is replaced by a Lewis acid such as ZnX_2 ($X = I, Cl, Br$)[18]. ZnX_2 ($X = Cl$) can also be coupled with a series of acetic acid derivatives RCOOH ($R = CF_3$, CCl_3, $CHCl_2$, CH_3) to induce living polymerisation of vinylethers[19].



Scheme 2

Living polymerisation of vinylethers has been reported to occur also with $EtAlCl_2$ in the presence of an external weak base (dioxane)[20,21].

All these systems are based on carbocation stabilisation by the growing counteranion. Higashimura and Sawamoto have proposed two different methods for living cationic polymerisation of vinylethers, based on nucleophilic stabilisation of propagating carbocations. According to them the unstable growing carbocation can be stabilised either internally, with suitable counteranions, or externally, with weak Lewis bases[13].

Macromer synthesis

The synthetic procedure for obtaining the di-functional monomer, vinyloxyethoxy-ethyl methacrylate (**A**), is reported in *Scheme 1*. The reaction proceeds by a two-step process: in particular, a first step of vinylation, followed by alkylation. *Scheme 2* shows the pathway followed for macromers synthesis. The living polymerization, initiated by HI/I_2 system, proceeds by:

- addition of HI to vinyloxyethoxy-ethyl methacrylate (**A**) to form the adduct **I**;
- addition of I_2 to activate the C–I bond;
- insertion of monomer **B** and propagation to give the living polymer.

The initial reaction is the quantitative addition of HI to **A** to yield the 1:1 adduct **I** which is employed as the initiator to induce living polymerisation of monomer **B**, in the presence of a small amount of iodine. Adduct **I** does not initiate the polymerisation itself but, in the presence of iodine, induces the polymerisation, which results in monodisperse polymers.

The molecular weight of macromers is determined by the initial HI concentration and can be easily controlled by regulating the feed ratio of monomers to initiator. On the contrary it is independent of iodine concentration (see *Table 1*). In fact, different molar ratios $[HI]/[I_2]$, in the range 2–6, do not influence the molecular weight of the final macromers, which, in turn, depend on [HI]/[**B**] and [**A**]/[**B**] ratios.

In order to have macromers with one methacryl head for each molecule, coming from monomer **A**, and a variable number of monomeric units, coming from monomer **B**, the ratio [HI]/[**A**] was kept fixed (= 1).

Depending on the [**A**]/[**B**] ratio, macromers having molecular weights in the range 1200–5000 $g\ mol^{-1}$ were synthesized (see *Table 1*).

Characterisation of monomers and macromers

The structure of monomers and macromers were confirmed by ^1H- and ^{13}C-n.m.r. and *FT*i.r. spectroscopy. The end functionality of macromers was determined by ^1H-n.m.r.

The peak assignments relative to monomer **A** by ^1H-n.m.r. are listed (in agreement with Ref. 22):

$-COO-C(\mathit{CH_3})=CH_2$	1.9 ppm
$-\mathit{CH_2}-O-$	3.62–3.8 ppm
$\mathit{CH_2}=CH-O-$	3.9 and 4.1 ppm
$-\mathit{CH_2}-COO-C(CH_3)=CH_2$	4.25 ppm
$\mathit{CH_2}=C(CH_3)-COO-$	5.5 and 6.05 ppm
$CH_2=\mathit{CH}-O-$	6.42 ppm

Characteristic bands can be individuated in *FT*i.r. spectra for the di-functional monomer **A** at 1620 and 1638 cm^{-1}, due to vinyl and methacrylate double bonds, respectively (stretching mode). An absorption band was also observed at 1718 cm^{-1} due to C=O stretching.

Adduct **I** was prepared for characterization by treatment of vinyloxyethoxyethyl methacrylate (**A**) with HI in toluene at − 78°C. Since **I** is unstable at room temperature, ^1H-n.m.r. was performed at − 25°C, from CCl_4 solution[22].

Table 2 Composition and glass transition temperature of macromer-based electrolytic membranes [a]

Sample	Composition						O/Li [b]	T_g (°C)
	Macromer		Plasticizer		Lithium salt			
	Type	% (w/w)	Type	% (w/w)	Type	% (w/w)		
PE 4/1	Macro 4	46	PC	42	$LiCF_3SO_3$	10	16	− 55
PE 4/2	Macro 4	42	PC	40	$LiCF_3SO_3$	16	8	− 61
PE 4/3	Macro 4	46	PC	43	$LiCF_3SO_3$	7	20	− 79
PE 4/4	Macro 4	31	PC	60	$LiCF_3SO_3$	7	16	− 101
PE 5/1	Macro 5	46	PC	46	$LiBF_4$	5.6	16	− 83
PE 5/2	Macro 5	47	PC	47	$LiBF_4$	3.3	24	–
PE 5/3	Macro 5	43	PC	45	$LiClO_4$	6.2	16	− 70
PE 5/4	Macro 5	46	PC	46	$LiClO_4$	4.2	24	− 90
PE 6/4	Macro 6	29.8	PC	63.1	$LiClO_4$	3.8	16	− 99
PE 6/5	Macro 6	28.2	PC	65.8	$LiBF_4$	2.2	24	− 102
PE 5/5	Macro 5	45	TGME	45	$LiClO_4$	6	16	− 82
PE 6/1	Macro 6	47.2	TGME	47.2	$LiClO_4$	2.1	52	− 95
PE 6/2	Macro 6	45.6	TGME	45.6	$LiBF_4$	5.5	16	− 87
PE 6/3	Macro 6	46.5	TGME	46.5	$LiBF_4$	3.7	24	–
PE 6/8	Macro 6	87	–	–	$LiClO_4$	9	16	− 65

[a] In membrane preparation 2 mol.% of comonomer **III**, triethylene glycol dimethacrylate, and 1.5–2% (w/w) benzophenone promoter were employed
[b] Determined considering oxygen atoms of the macromer

After treatment of **A** with HI, the absorptions of the vinyloxy group (3.9, 4.1 and 6.42 ppm) disappeared and, in turn, signals due to the α-iodo-ether adduct (**I**) were observed ($-\mathrm{CH}(CH_3)-\mathrm{I}$, doublet at 2.2 ppm, $-CH(\mathrm{CH_3})-\mathrm{I}$, quartet at 6 ppm). In contrast, methacrylate signals remain unchanged.

Peak assignments relative to macromer **II** are:

$-\mathrm{CH_2O{-}CH}(CH_3)-\mathrm{CH_2}-$	1.2 ppm
$-\mathrm{CH(CH_3)}-(CH_2\mathrm{CHO})\mathrm{n}-\mathrm{CH_2}-$	1.4 ppm
$-\mathrm{CH_2{=}C}(CH_3)\mathrm{COO}-$	1.9 ppm
$-CH_2\mathrm{O}-$	3.15–3.7 ppm
$-\mathrm{CH_2O}-CH(\mathrm{CH_3})-\mathrm{CH_2}-$	3.15–3.7 ppm
$-(\mathrm{CH_2}-CH\mathrm{O})-$	3.15–3.7 ppm
$-\mathrm{OCH_2CH_2{-}O}CH_3$	3.25 ppm
$-\mathrm{COO}-CH_2-\mathrm{CH_2O}$	4.15 ppm
$-\mathrm{CH(CH_3)}-(\mathrm{CH_2}CH\mathrm{O})-\mathrm{O}-$	4.6 ppm
$-CH_2{=}\mathrm{C(CH_3)COO}-$	5.45 and 5.95 ppm

The ^{13}C-n.m.r. spectra confirmed the proposed structure.

In *FT*i.r. spectra of the macromer **II**, the signal at 1638 cm^{-1} remains unchanged, while the 1620 cm^{-1} absorption band disappeared, confirming the n.m.r. observation.

According to ^{1}H- and ^{13}C-n.m.r. analysis, the macromers have a narrow molecular weight distribution with one methacrylate group at the chain end per each molecule. The end functionality, in term of number of methacrylate groups per macromer molecule, and then the molecular weight, was determined from the ratio of the integrated signal n.m.r. peak areas of: $(\mathrm{CH_2{=}C}(CH_3)\mathrm{COO})/(\mathrm{O}CH_3)$ (1.9 ppm)/(3.25 ppm).

N.m.r. analysis confirmed the living nature of the macromers, whose end functionalities only depend on the feed ratio of monomers to initiator (HI).

Electrolytic membranes

Electrolytic membrane were obtained starting from macromers having two different molecular weights (see *Table 1*), 2200 g mol^{-1} (Macro 5 and 6, $n = 10$) and 3100 g mol^{-1} (Macro 4, $n = 15$).

A comonomer (**III**), triethyleneglycol dimethacrylate, was added (2 mol.%) to increase the molecular weight and then the consistency of the final membrane.

A homogeneous solution of lithium salt in the plasticizer (PC or TGME) was added to a mixture containing the macromer **II** and the comonomer (**III**), eventually with a small quantity of a promoter (benzophenone, 0.5–1 mol.%). The molar ratio **II**/**III** was kept fixed (98/2). The solution was deposited on suitable Teflon moulds, at controlled thickness, and irradiated by u.v. The irradiation time ranges from 15 to 30 s, as a function of composition, when benzophenone is present, and is considerably higher ($>$ 100 s) without promoter.

Electrolytic membranes were obtained which displayed good dimensional stability and a thickness of approximately 100 μm.

The macromer tended to polymerise in the presence of $LiBF_4$ without irradiation; this is evidenced by the disappearance of the 1638 cm^{-1} methacrylic double bond in the *FT*i.r. spectra. This is further confirmed by u.v.–vis spectra (data not shown). U.v. irradiation with $LiBF_4$ was then carried out on freshly prepared solutions. In *Table 2* the composition of the different membranes tested and some characterisation data (T_g), are reported. $LiBF_4$, $LiClO_4$ and $LiCF_3SO_3$ are employed as the lithium salts, in a concentration range from 2 to 16% (w/w). PC and TGME where employed in a percentage between 40 and 66% (w/w). A few attempts were carried out employing a plasticizer content higher than 65% (w/w), but only with $LiClO_4$ and PC (see *Table 2*) were self-consistent membranes obtained in such conditions.

In most of the cases the membranes with plasticizer content higher than 60% (w/w) were brittle and had no consistency. Scarce improvements were obtained by lengthening the irradiation time, whose main effect was to strongly darken the membrane.

The glass transition temperature (T_g) of the membranes was measured by d.s.c. analysis. Electrolytic membranes were all amorphous above T_g (see *Table 2*). The glass transition temperatures of membranes were sensibly lower than that determined in completely solid systems; the solid polymer electrolyte without plasticizer has a T_g of $-$ 65°C (PE 6/8 in *Table 2*). Addition of plasticizer increases the mobility of the system, as evidenced by the decrease in the glass transition temperature: T_g values range from $-$ 55 to $-$ 102°C, depending on plasticizer and salt contents. T_g generally decreases as the plasticizer concentration increases and increases with raising salt concentration, due to greater numbers of transient crosslinks.

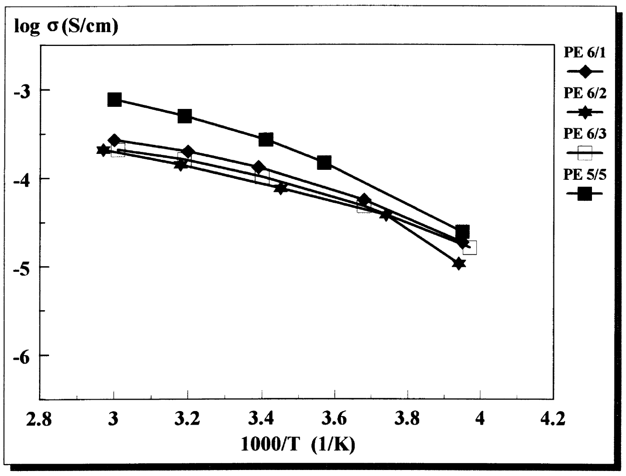


Figure 1 Temperature dependence of log σ for TGME/PE electrolytes with *ca.* 45% (w/w) TGME. Lithium salt type, concentrations (in % w/w) and O/Li ratio for samples: sample PE 6/1 ($LiClO_4$, 2.1, 52); sample PE 6/2 ($LiBF_4$, 5.5, 16); sample PE 6/3 ($LiBF_4$, 3.7, 24); sample PE 5/5 ($LiClO_4$, 6, 16)

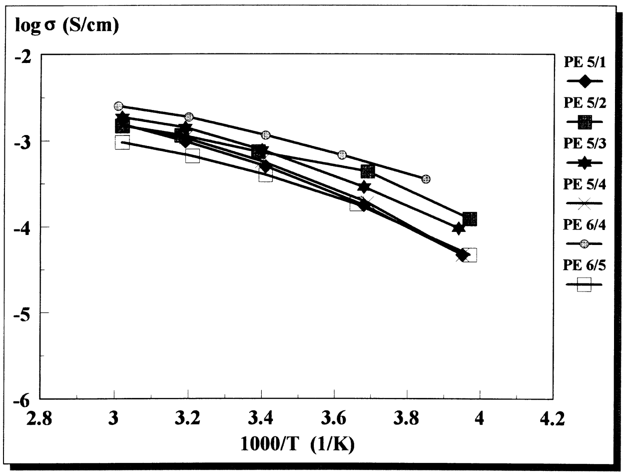


Figure 2 Temperature dependence of log σ for PC/PE electrolytes. Lithium salt type, concentrations (in % w/w), O/Li ratio and PC concentration for samples: sample PE 5/1 ($LiBF_4$, 5.6, 16, 46); sample PE 5/2 ($LiBF_4$, 3.3, 24, 47); sample PE 5/3 ($LiClO_4$, 6.2, 16, 45); sample PE 5/4 ($LiClO_4$, 4.2, 24, 46); sample PE 6/4 ($LiClO_4$, 3.8, 16, 63); sample PE 6/5 ($LiBF_4$, 2.2, 24, 66)

Ionic conductivity

The ionic conductivity was determined from impedance measurements in a range of temperatures from 60 to − 20°C (−80°C for sample PE 4/4), considering two series of electrolytic membranes, the plasticizer being PC or TGME. The plasticizer content ranged from 40 to 66% w/w and the lithium salt ($LiBF_4$, $LiClO_4$, $LiCF_3SO_3$) from 2 to 16% w/w (*Table 2*).

In *Figures 1 and 2* the ionic conductivities of membranes based on TGME and PC, respectively, and containing $LiBF_4$ or $LiClO_4$, are reported.

Higher σ values are observed for the membranes with PC (*Figure 2*) than those with TGME (*Figure 1*), mainly due to a permittivity effect (higher dielectric constant of PC), which allows greater ion dissociation. In fact, at comparable lithium salt and plasticizer contents, viscosity is not a decisive factor since d.s.c. measurements show similar T_g values (*Table 2*). Conductivity values of 1.15×10^{-3} S cm^{-1} at room temperature were obtained for systems with 63% (w/w) PC and 3.8% (w/w) $LiClO_4$ (see sample PE 6/4 in *Table 2*).

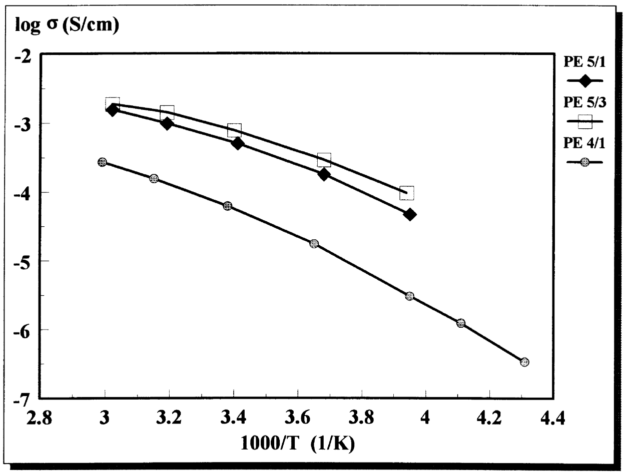


Figure 3 Temperature dependence of log σ for PC/PE electrolytes with different lithium salts and *ca.* 45% (w/w) PC. Lithium salt type, concentrations (in % w/w) and O/Li ratio for samples: sample PE 5/1 ($LiBF_4$, 5.6, 16); sample PE 5/3 ($LiClO_4$, 6.2, 16); sample PE 4/1 ($LiCF_3SO_3$, 10, 16)

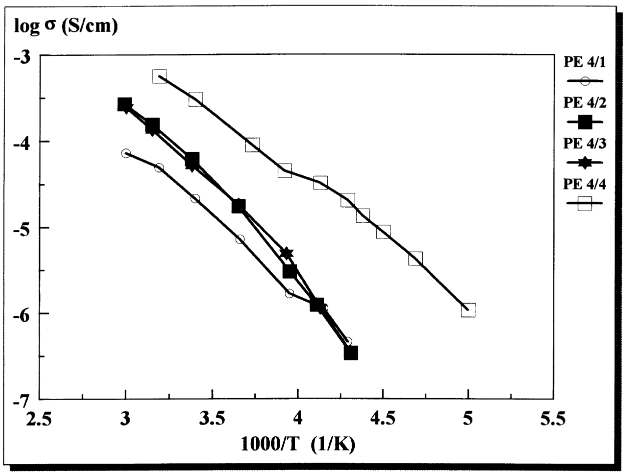


Figure 4 Temperature dependence of log σ for TGME/$LiCF_3SO_3$/PE electrolytes. Lithium salt, O/Li ratio and PC concentration (in % w/w) for samples: sample PE 4/1 (10, 16, 42); sample PE 4/2 (16, 8, 40); sample PE 4/3 (7, 20, 43); sample PE 4/4 (7, 16, 60)

The conductivity curves are similar to those observed in liquid electrolytes with negligible slopes. As a consequence, σ decreases negligibly on lowering the temperature and conductivities of 3.55×10^{-4} S cm^{-1} are obtained at − 13°C, considering the same sample. Almost comparable data were obtained at lower PC content.

Conductivity measurements for TGME-containing systems were carried out on samples containing *ca.* 45% (w/w) of plasticizer. σ reaches a maximum value of 2.7×10^{-4} S cm^{-1} at room temperature and 2.4×10^{-5} S cm^{-1} at −20°C (see sample PE 5/5 in *Table 2*). Membranes containing $LiClO_4$ and $LiBF_4$ show similar conductivity performance, for comparable composition.

Membranes containing $LiCF_3SO_3$ displayed a considerably lower conductivity, compared to analogous $LiBF_4$ and $LiClO_4$ samples (see *Figure 3*). Conductivity value around 10^{-5} S cm^{-1}, at room temperature, is observed for the $LiCF_3SO_3$ membranes containing *ca.* 40% (w/w) plasticizer, independent from lithium salt content (see *Figure 4*). The presence of a bulky organic anion ($CF_3SO_3^-$), compared to smaller and more mobile inorganic anions (BF_4^- and ClO_4^-), could contribute to raise the overall viscosity of the system and be responsible for the lower values observed. This is also confirmed by d.s.c. evidence (see *Table 2*), where higher T_g values are observed for $LiCF_3SO_3$ containing membranes, with respect to samples containing other lithium salts, at comparable O/Li ratio. Nevertheless, the ionic conductivity in $LiCF_3SO_3$ based membranes can be increased by raising the plasticizer content. More than one order of magnitude in conductivity is gained by varying the PC content from 40 to 60% (w/w). Besides the membrane, which displays a very low T_g (-101°C, see *Table 2*), is able to provide an acceptable conductivity (1.1×10^{-6} S cm^{-1}) even at a temperature as low as -70°C.

The molecular weight of macromers has apparently no influence on the ionic conductivity. Nevertheless the possibility of choosing a polymer precursor with a variable viscosity will allow one to extend the applicability of this material, and modulate the composition of the membrane in order to match the performance required.

CONCLUSIONS

The HI/I_2 system was employed as the initiating system for the living polymerisation of vinylether based monomers.

Macromers, having a radical polymerisable methacrylate end group, attached to monodisperse polyvinylether, were obtained with a narrow distribution of molecular weight ($M_w/M_n < 1.2$). Poly-vinylether contained suitable EO moieties for ion coordination, to be applied as polymer electrolytes precursors.

Macromers satisfy two important criteria: perfect end functionality and controlled molecular weight. Molecular weight of macromers is determined by the initial HI concentration, controlled by monomers to initiator feed ratio and directly proportional to the monomer conversion. On the contrary, it is independent of iodine concentration, which is, however, necessary to activate the molecule (C–I bond) for the subsequent insertion of the vinylether monomer.

Macromers are used, in addition to difunctional methacrylate comonomer to increase the consistence, as precursors of polymer electrolytes membranes. Easily handled electrolytic membranes are obtained by u.v. radiation (10–15 s) in the presence of a plasticizer (PC or TGME) and a lithium salt ($LiBF_4$, $LiClO_4$, $LiCF_3SO_3$). Ionic conductivities up to 10^{-3} S cm^{-1} are observed with PC at a concentration around 60%.

A wide applicability of this system can be envisaged, due to the possibility of producing macromers with variable viscosity, which would allow one to modulate the composition of the membrane in order to obtain the desired performances.

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