(22) Finkelmann, H.; Rehage, G. In *Advances in Polymer Science 60/61*; Springer-Verlag: Berlin, Heidelberg, FRG, 1984; pp 148–49.
(23) Shibaev, V. P.; Plate, N. A. In *Advances in Polymer Science 60/61*; Springer-Verlag: Berlin, Heidelberg, FRG, 1984; p 197.
(24) Wunderlich, B.; Grebowicz, J. In *Advances in Polymer Science 60/61*; Springer-Verlag: Berlin, Heidelberg, FRG, 1984; p 1.
(25) Denicol, I.; Doucet, J.; Craievich, A. F. *J. Chem. Phys.* **1983,** *78* (3), 1465.

Registry No. PEBP04 (homopolymer), 115181-06-1; PEBP06 (homopolymer), 115181-08-3; PEBP24 (homopolymer), 118798-37-1; PEBP26 (homopolymer), 115181-10-7; PEBP44 (homopolymer), 115181-12-9; PEBP46 (homopolymer), 115181-14-1.

Ionic Conductivity in Organic Solids Derived from Amorphous Macromolecules

D. G. H. Ballard,* P. Cheshire, T. S. Mann, and J. E. Przeworski

ICI C&P Ltd, P.O. Box 13, The Heath, Runcorn Cheshire, WA7 4QF, England.
Received April 10, 1989; Revised Manuscript Received July 18, 1989

ABSTRACT: By use of principles derived from the study of the effect of copolymerization on crystallinity and lamellae thickness in semicrystalline systems, amorphous polymers of ethylene oxide have been synthesized. It has been shown that the ionic conductivity in the presence of lithium triflate at room temperatures is significantly improved in these completely amorphous materials, provided the comonomer used has the same C:O ratio as poly(ethylene oxide). The optimum conductivity at 25 °C achieved was on the order of $2 \times 10^{-5}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ compared to $5 \times 10^{-8}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for semicrystalline PEO. The mechanical properties were, however, poor. Amorphous terpolymers were synthesized with the same composition but containing 5% of cross-linkable sites. The effect of cross-linking was to reduce the conductivity by an order of magnitude. However, mechanical properties were good. Studies of a model system dimethoxyethane with propylene carbonate showed that conductivities on the order of $10^{-2}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ were possible in organic media with lithium triflate. Extension of this concept to the amorphous cross-linked PEO systems showed that the addition of 50% propylene carbonate gave a flexible film with good mechanical properties and a conductivity of $10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$, the highest so far achieved. The use of the latter in the design of eletrochemical cells is discussed.

Introduction

The field of ionically conducting polymer electrolytes has recently attracted a great deal of interest.[1-12] This has mainly been due to their *potential* use in high energy density, solid-state batteries.[3-7] Also, more recently other possible applications have been identified. These include electrochemical displays, proton conductors, and sensors.

Polymer electrolytes are produced from polymers containing polar groups in which are dissolved a salt, usually of an alkali metal (e.g., lithium), and a "soft" anion (e.g., perchlorate). The most studied system in the literature has been poly(ethylene oxide) (PEO) in which LiX ($X^- = ClO_4^-$ or $CF_3SO_3^-$) has been dissolved. However, this material suffers from the disadvantage of forming a partially crystalline polymer–salt complex at room temperature, resulting in a multiphase system, which complicates its study. Such systems only have acceptable conductivities at temperatures in excess of 100 °C.

The view has often been stated in the literature that whatever the mechanism of ion transport in the PEO matrix, the amorphous phase only is involved.[8] However, no systematic study has been attempted to prove this observation. The reason for this is that polymer scientists do not have a clear idea of how to produce amorphous materials from monomers that normally form semicrystalline materials.

The objective of this work was to produce a stable amorphous polymer of PEO in which the ratio of carbon atoms to oxygen atoms was similiar to that in PEO. The principles involved in producing an amorphous polymer from monomers that normally polymerize to give crystallizable polymers has been the subject of a recent study in these laboratories and will be reported in detail in a separate publication.[15] However, some aspects of this work have been discussed in relation to the crystallinity of PVC[13] and polyethylene copolymers.[14] The principles involved are as follows.

(a) A comonomer unit must be chosen such that the side chain formed on copolymerizing with ethylene oxide is too large to enter the crystal lattice of poly(ethylene oxide).

(b) It follows from (a) that in a random copolymerization the distance between comonomer units will determine the average thickness of the lamellae crystals formed by chain folding.

(c) If the thickness of the lamellae is reduced below 30 Å, then, because of thermal motions of the crystallizable molecular fragments, crystallization is not possible and an amorphous structure results.

Our studies of the polyethylene, nylon, PTFE, PEO, PET, and other systems show that (a), (b), and (c) are general principles.

Experimental Section

(a) Synthesis. (i) Monomers. The glycidyl ethers were prepared by using a two-stage synthesis via the chlorohydrin.[16] They were purified by fractional vacuum distillation and their purity was checked by gas chromatography. Only material of

---

* To whom correspondence should be addressed.

0024-9297/90/2223-1256$02.50/0

Table I
Copolymerization of Ethylene Oxide with Comonomers

copolymer	epoxide comonomer	side group formed	C:O
1	epoxyoctane[a]	C_6H_{13}	8.00
2	butyl glycidyl ether[a]	$CH_2OC_4H_9$	3.5
3	methyl glycidyl ether[a]	CH_2OCH_3	2.0
4	ethoxyethyl glycidyl ether	$CH_2OCH_2CH_2OCH_2CH_3$	2.33
5	digol ethyl glycidyl ether	$CH_2O(CH_2CH_2O)_2CH_2CH_3$	2.25
6	digol methyl glycidyl ether	$CH_2O(CH_2CH_2O)_2CH_3$	2.0
7	trigol methyl glycidyl ether	$CH_2O(CH_2CH_2O)_3CH_3$	2.0
8	tetrahydrofurfuryl glycidyl ether	$CH_2OCH_2(C_4H_7O)$	3.0
9	digol methyl glycidyl ether + allyl glycidyl ether	$CH_2O(CH_2CH_2O)CH_3$ $CH_2OCH_2CH{=}CH_2$	~2.0

[a] Available from Aldrich Chemical Co. Ltd. All other comonomers were synthesized as described in the text.

greater than 99.5% purity was used in the polymerizations. A list of comonomers is given in Table I.

The ethylene oxide was an ICI, C&P Limited, product with a maximum water content of 0.05% w/w and was used without any further purification.

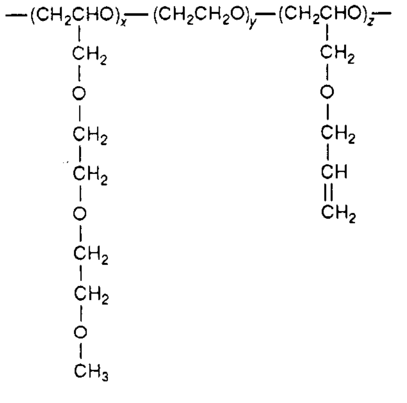
(ii) Preparation of Copolymers of Ethylene Oxide. Copolymers were prepared in toluene (BDH Analar grade, sodium dried and nitrogen purged before use) solution with Vandenberg's "chelate" catalyst[17] by a general procedure exemplified here by the copolymerization of ethylene oxide (EO) with digol methyl glycidyl ether to produce copolymer 6.

The following materials were charged into a stirred, nitrogen-purged, 400-mL stainless steel autoclave, at room temperature: toluene (200 mL), comonomer 6 (14.5 mL), 0.5 M "chelate" catalyst solution (18 mL), and ethylene oxide (18 mL). The temperature was raised to 110 °C over 20 min and after a further 2 h at 110 °C, the hot viscous polymer solution was discharged into a 1-L flask containing 5 mL of methanol to deactivate the catalyst. The autoclave was given two hot washes with a total of 500 mL of toluene and these washing were thoroughly mixed with the polymer solution. The volume of the resulting polymer solution was reduced to 300 mL by rotary evaporation. This was then cast in a PTFE tray and the solvent allowed to evaporate. The polymer was finally dried at 80 °C under vacuum. This yielded 26 g of a pale yellow rubbery product. The types of copolymers studies are summarized in Table I. In general the copolymers had the formula

$$[-CH_2CH_2O]_x-[CH_2CHRO]_y-$$

where the side group R is described in Table I and the copolymer type by the number in the first column of this table.

(iii) Preparation of Cross-Linkable Copolymers of Ethylene Oxide. These were based on copolymer 6 in which minor amounts of comonomer that produced an olefinically unsaturated side chain were present. A typical composition was as follows



$$-(CH_2\underset{CH_2OCH_2CH_2OCH_2CH_2OCH_3}{CH}O)_x-(CH_2CH_2O)_y-(CH_2\underset{CH_2OCH_2CH{=}CH_2}{CH}O)_z-$$

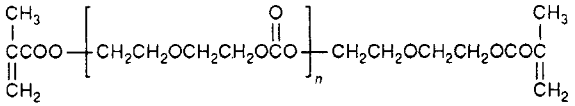
in which the mole fractions of components were $x = 0.2$, $y = 0.75$, and $z = 0.05$.

The method of synthesis was identical with that already described for polymer 6. The autoclave was charged with appropriate quantities of comonomer 6, ethylene oxide and allyl glycidyl ether. The chelating catalysts used were inactive toward the allylic double bond.

(iv) Preparation of a Methacrylate End Capped Poly(ethylene ether carbonate) with Oligomer 10. Diethylene glycol (27.7 g) and dibutyl carbonate (44.5 g) were weighed into a test tube fitted with a side arm and held under nitrogen. Sodium ethoxide solution (1 mL of 1.02 M solution) was added by syringe. The reaction mixture was stirred magnetically. The tube was immersed in an oil bath at 150 °C. The temperature was raised to 200 °C over 1 h at atmospheric pressure. The pressure in the apparatus was gradually lowered to a few millimeters of Hg over 3 h, to distill off butanol essentially completely.

After cooling, the very viscous product was dissolved in chloroform (100 mL) and washed in a separating funnel with dilute HCl (10 mL of concentrated HCl/40 mL of water) and then water (3 × 60 mL). The solution was rotary evaporated and the resin dried under vacuum at 180 °C for 2 h. Molecular weight was determined by VPO in methyl benzoate at 136 °C and found to be 1810 ± 10%.

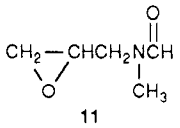
(Dimethylamino)pyridine (0.1 g) was added to this hydroxyl-terminated oligomer (5 g) followed by methacrylic anhydride (2.17 g; Aldrich, 94% pure) in a reaction flask blanketed with nitrogen. The reaction mixture was stirred magnetically at 80 °C for 3 h. The excess methacrylic anhydride was distilled out under vacuum at 80 °C. The resin was dissolved in methylene chloride and transferred to a separating funnel and washed once with dilute HCl and then three times with water. The solution was dried with $MgSO_4 \cdot H_2O$ and filtered. 4-Methoxyphenol, 200 ppm, an antioxidant, was added and the solution evaporated until most of the methylene chloride had come off. The last of the methylene chloride was removed in a dry air stream over 4 h.



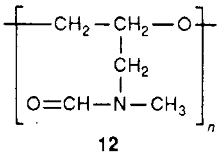
$$\underset{CH_2}{\overset{CH_3}{C}}COO-\left[CH_2CH_2OCH_2CH_2O\overset{O}{C}O\right]_n-CH_2CH_2OCH_2CH_2OCO\underset{CH_2}{\overset{CH_3}{C}}$$

10

(v) Preparation of Poly(ether amide). Monomer 11 was polymerized anionically by using KOH as a catalyst. The polymers formed had the structure 12 and were viscous liquids.



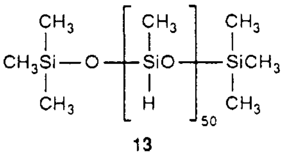
11



$$\left[-CH_2-\underset{O=CH-N-CH_3}{\underset{|}{\underset{CH_2}{\underset{|}{CH_2}}}}-O-\right]_n$$

12

(vi) Preparation of a Polysiloxane Precursor. A silicon compound with the structure



$$CH_3\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[\underset{H}{\overset{CH_3}{Si}}O\right]_{50}-\underset{CH_3}{\overset{CH_3}{Si}}CH_3$$

13

and a compound of formula $CH_2{=}CH_2O{-}(CH_2CH_2O)_n{-}CH_3$ where n = 2 or 9.5 were dissolved in dry toluene (10 mL) containing 1.0 mg of *trans*-$PtCl_2[(C_2H_5)_2S]_2$. The quantity of $CH_2{=}CHCH_2O{-}(CH_2CH_2O)_n{-}CH_3$was chosen so that 80% of the S:-H groups were reacted when the mixture was refluxed under nitrogen for 2.5 h. The toluene was removed under vacuum to give a viscous copolymer.

(b) Preparation of Electrolyte Films from Non-Cross-Linkable Polymers. (i) Copolymer (1.0 g) and lithium triflate (0.22 g, Aldrich twice recrystallized and dried at 120 °C under vacuum) were dissolved in acetonitrile (25 mL; Rathburn Chemicals HPLC Grade, dried over 3A molecular sieves) to give a clear solution. A sample (5 mL) of this solution was cast in a glass/PTFE mold and the solvent evaporated in a stream of dry nitrogen. This results in a polymer film, ~100 μm in thickness, with a polymer oxygen to lithium ratio of 16:1. The film was removed from the mold and transferred to a modified Büchi drying oven where it was dried at 65 °C under vacuum ($>10^{-3}$ mmHg) for 6 h. After it was dried, all film handling was performed in a nitrogen-purged drybox.

(ii) Preparation of Electrolyte Films from Cross-Linkable Polymers. Films of polymer **9** were cast from an acetonitrile solution to which had been added the appropriate quantities of lithium triflate and about 2.0% w/w of benzoyl peroxide. These films were then heated at 110 °C for 30 min under vacuum. This produced an insoluble rubbery material with good mechanical properties.

A casting solution was prepared from **10** (2.357 g), lithium triflate (0.3749 g), and dry benzoyl peroxide (0.046 g) in HPLC grade acetonitrile (20 mL) with stirring under nitrogen. Two milliliters of this solution was placed in a glass mold coated with a mold-release agent. The mold was placed in an oven with nitrogen blowing through it. The temperature was raised to 110 °C at 2 °C/min, held at 110 °C for 2 h, and slow cooled to room temperature overnight. The clear rubbery film could be pulled easily from the mold.

(iii) Incorporation of High Dielectric Liquids into Cross-Linked Films. Exposure of films derived from copolymer **9** to the vapors of propylene carbonate or *N*-methylpyrrolidone leads to absorption of these liquids by the film. Increases in weight of up to 50% have been observed. The process is controllable and, on a laboratory scale, is best accomplished in a vacuum desiccator in which the film is suspended above the liquid. The films were recovered from the desiccator in a drybox for subsequent conductivity measurements. The mechanical properties were such that they could be handled without difficulty. However, similar experiments with un-cross-linked films produced viscous gels.

(c) Polymer Evaluation. (i) NMR. A Jeol FX 100 or a Bruker AM 500 was used to obtain ^1H NMR spectra of epoxy monomers and copolymers in $CDCl_3$ or $CDCl_2CDCl_2$.

(ii) GPC. Molecular weights were determined at 60 °C by using 0.02% wt/vol LiBr in DMF as the solvent. Polymer Laboratories mixed gel columns were employed and calibrated by using monodispersed polystyrene standards. Molecular weights of the copolymers averaged $M_w = 1 \times 10^6$ with dispersities around 3.8.

(iii) Gas-Liquid Chromatography. A Pye Unicam GCD was used for routine comonomer analysis. The glass column was 460 mm long and had 4-mm i.d., packed with 10% OV101 on Chromasorb WHP.

(iv) Thermal Measurements. A Du Pont 912 dual-cell DSC linked to a Du Pont 9900 computer was used for these studies. The morphology of a series of copolymers, with and without dissolved lithium triflate, was examined by DSC analysis.

A standard technique was used to prepare and study all samples. Preparation involved predrying in a vacuum oven at 100 °C for 3 h and then sealing the sample in an aluminum pan. The DSC studies were performed in three stages: the temperature was raised from ambient to 100 °C; the temperature was "crash cooled" to -150 °C and then raised to +150 °C, and finally the temperature was again "crash cooled" to -100 °C, raised to -40 °C, held at -40 °C for 30 min, and then raised to +150 °C.

All heating was at a rate of 20 °C/min and the nitrogen flow rate was kept at a constant 40 mL/min. It should be noted that the annealing process in stage 3 had little effect on the DSC results when compared to that in stage 2.

(v) Conductivity Measurements. For ionic conductivity measurements on films, a portion of the dried film was placed between two blocking stainless steel electrodes of a dry conductivity cell. All manipulations were carried out in a drybox. The cell was assembled and placed in the inner compartment of the Büchi oven, which was then sealed, removed from the drybox, and evacuated. Conductivity measurements were performed with the oven under vacuum ($>10^{-3}$ mmHg). This procedure for handling the films ensured that they remained dry. A Solatron FRA 1250 linked to an IBM PC computer was used for these measurements.

For measurements with solutions of lithium triflate in mixtures of propylene carbonate and dimethoxyethane, a Dipcell manufactured by Walden Precision Instruments was used. Solvents were predried by using a molecular sieve 4A column and stored over a quantity of the sieve material. All measurements were carried out in a drybox.

(vi) IR. A Perkin-Elmer 983G spectrophotometer was used to record the IR spectra of neat epoxy monomers.

(d) Use of Ionic Conducting Films for the Construction of Thin-Film Electrochemical Cells. (i) Preparation of a Composite Cathode. A solution was prepared consisting of 43% w/w terpolymer **9** plus cross-linking agent lithium triflate, 38% w/w MnO_2, 4% w/w carbon black, and 15% w/w acetonitrile. This was cast on a glass plate and produced, on removal of a solvent and curing, a 60-μm-thick film for the cathode.

A similar solution was prepared in which the MnO_2 was replaced by polyphenylene powder. The latter was prepared with a very high surface area, using the soluble precursor obtained on polymerizing the methoxy carbonate of *cis*-dihydrocatechol.[18]

(ii) Film-Cell Assembly with Solid Electrolytes. The assembly of a cell is shown in Figure 11. The solid electrolyte film containing lithium triflate was sandwiched between a layer of cathode film and lithium foil. The compressibility of the solid electrolyte film allowed close contact between the layers, giving effective transport of lithium and triflate ions. Two PET (Melinex-ICI) films were coated on one side with nickel, which acted as a current collector, and coated on the reverse side with a polymer coating (Viclan-ICI), which acted as a barrier to air and water. The films were assembled and sealed with a hot-melt adhesive.

The resulting cell assembly was less than 1 mm thick, had an open-circuit voltage of 3.2 V, and produced a steady current density of about 120 $\mu A\ cm^{-2}$ at room temperature.

A second cell was prepared in an identical manner in which the cathodic material was based on polyphenylene powder as described above. This assembly was charged at a constant current of 50 mA to predope the polyphenylene. The resulting cell had an open voltage of about 3.7 V and a good steady working current.

Results and Discussion

Amorphous Copolymers of Ethylene Oxide. Figures 1 and 2 show the DSC results for a series of type 4 (Table I) copolymers. From the size of the endothermic peaks around +60 °C, one can see a rapid decrease in the level of crystallinity as the comonomer concentration is raised. From Figure 1 it is clear that comonomers without added salt become totally amorphous at a comonomer concentration between 37% and 54%. However, with dissolved lithium triflate, an amorphous solid is obtained with a lower comonomer content, between 10% and 22%. This suggests that copolymerization and ionic association have a synergistic effect on reducing the level of crystallinity. The glass transition temperatures measured are listed in Tables II and III. It is a feature of such amorphous polymers that after removal of crystallinity the T_g does not change significantly. More-

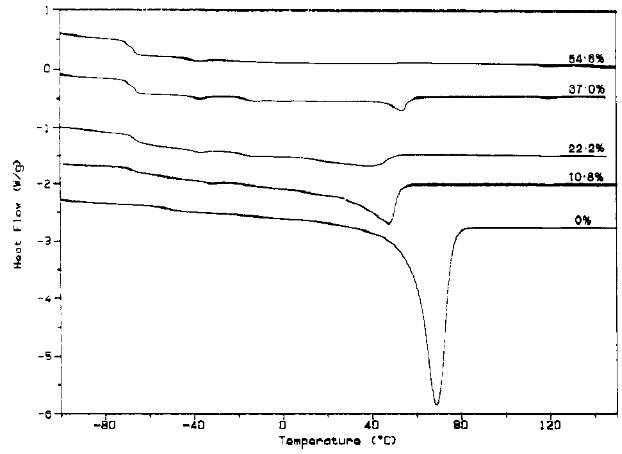


Figure 1. DSC results for ethylene oxide copolymers in which the side group has the structure **4**. The figures refer to the amount of **4** present in the copolymer.

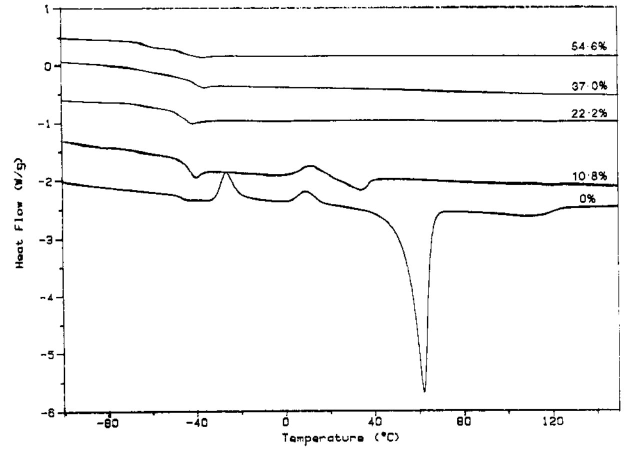


Figure 2. DSC results for the same series of copolymers described in Figure 1 with the addition of lithium triflate. The ratio of oxygen to lithium in the system was 16:1.

Table II
Variation of T_g with Composition for Copolymer 4 and the Effect Lithium Triflate at a Fixed O:Li Ratio of 16:1

proportion of comonomer, mol %	T_g, °C	T_g with Li salt present
0	-68	-50
10.8	-71	-49
22.2	-70	-53
37.0	-71	-66
54.6	-71	-67

Table III
Variation of T_g with the Composition of Copolymer 3

comonomer 3, mol%	T_g, °C
0	-68
21.3	-68.6
38.2	-64.5
52.4	-63.9
100.0	-58.7

over, increasing quantities of comonomer up to 50 mol % does not reduce T_g. The presence of the salt increases T_g.

It is evident that these copolymers are rubbers at ambient temperatures. They have very high molecular weights ($M_w = 1 \times 10^6$) and are comparable in mechanical properties to other un-cross-linked rubbers. Tests on films on the order of 1 mm thick show that they have extensions to break of 2000%.

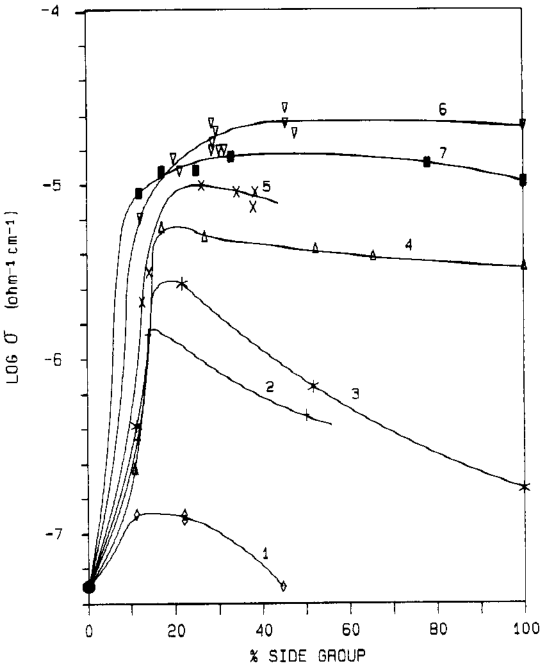


Figure 3. Variation in the ionic conductivity at 20 °C, for the series of ethylene oxide copolymers listed in Table I, in which the mole percentage of side groups is increased progressively. The numbers on the curves refer to the copolymers described in Table I. The conductivity of the homopolymer PEO is 5×10^{-8} Ω^{-1} cm^{-1} at 20 °C. Polymer oxygen to lithium ratios are 16:1.

Ionic conductivity measurements were performed on dried copolymer electrolyte films 70–150 μm in thickness, as described previously. For initial experiments the lithium triflate concentration was kept so that there was a constant polymer oxygen to lithium ratio of 16:1. This was to enable direct comparisons to be made between samples and with poly(ethylene oxide).

Figure 3 shows the variation of the logarithm of the room temperature ionic conductivity of these copolymer electrolytes as a function of the proportion of side chain present. The first point of interest is the initial rapid rise in conductivity with increasing amount of comonomer. This is observed for each of the copolymer systems and is due to a reduction in polymer crystallinity. Comparing copolymers **1**–**5**, one observes that it is preferential to have ether groups rather than alkyl groups in the side chain, as the oxygen helps promote lithium ion conduction.

In all the copolymers, conductivities tended to peak between 15% and 30% side chain content. With higher percentages of side group, a small decrease in ionic conductivity is observed but even these values are still much better than those of the poly(ethylene oxide) system, at room temperature. Equally significant is the fact that the mechanical properties of the copolymers containing high percentages of comonomer are far inferior to those containing 20% or less.

Figure 4 shows the ionic conductivity as a function of temperature for amorphous copolymers and poly(ethylene oxide). It is interesting to note that at room temperature all the copolymer electrolytes have higher ionic conductivities than the PEO system. Also because of the absence of a first-order thermal transition, there is no abrupt change in conductivity as the temperature is reduced from 75 °C to room temperatures. The poly(ethylene oxide)–lithium triflate complex has a melting point close to 60 °C (Figure 2) and the conductivity thereafter falls rapidly.

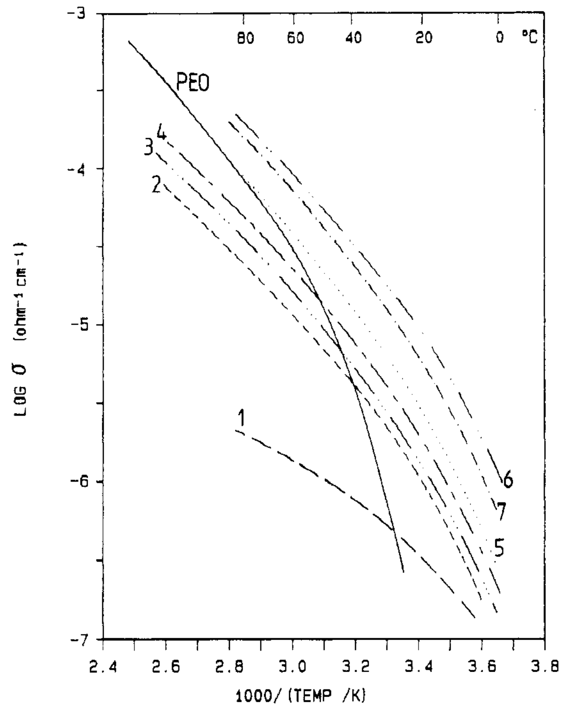


Figure 4. Ionic conductivity of copolymers described in Figure 3 as a function of temperature. The copolymer compositions chosen were those that gave the maximum conductivity at 20 °C with a minimum percentage of comonomer.

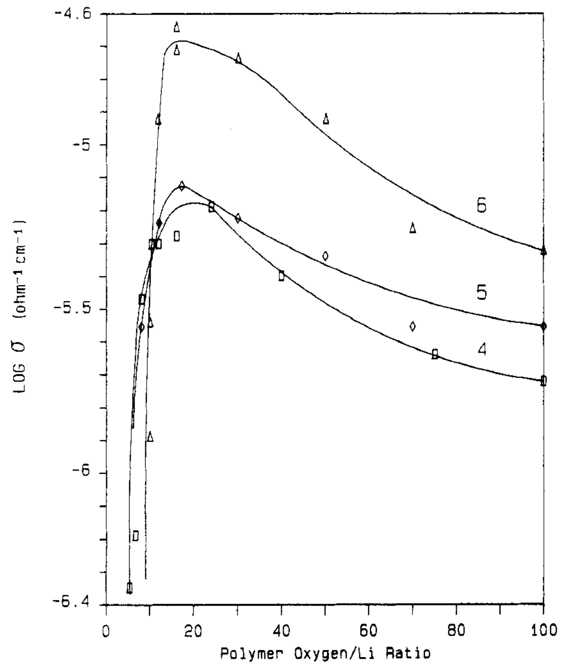


Figure 5. Variation of ionic conductivity at 20 °C with lithium triflate salt concentration for copolymer 4, 17.2% side groups; copolymer 5, 38.2% comonomer, and copolymer 6, 28.6% comonomer.

The electrolytes from copolymers 3 and 4 are much closer to the PEO system at higher temperatures and are much better (due to being less crystalline) at room temperature. Copolymer 5 is identical with PEO at higher temperatures and extends the high-temperature amorphous curve down to ice temperatures.

Studies have also been undertaken on the variation of the lithium triflate concentration in certain copolymers and these results are shown in Figure 5. It can be seen that each copolymer electrolyte system exhibits similar behavior; as the salt concentration is increased, the ionic conductivity is observed to rise slowly to a maximum near the polymer oxygen to lithium ratio of 20:1.

This rise is due to the increase in the number of charge carriers present. As the salt concentration is further increased (to polymer oxygen to lithium ratios less than 10:1), the ionic conductivity is seen to drop rapidly. This is due to both the formation of ion clusters and the increase in viscosity of the polymer electrolyte.

In addition, the possibility of adding ring structures to the side chains of the ethylene oxide backbone was investigated. Copolymers with side chains ending with tetrahydrofuran groups 8 were prepared. However, these copolymers cross-linked and became insoluble. The homopolymer (i.e., 100% comonomer) could be synthesized, but its ionic conductivity was $\sim 1.8 \times 10^{-7}\ \Omega^{-1}\ \mathrm{cm}^{-1}$, far inferior to the other results reported here.

It is clearly evident from this study of this series of ethylene oxide copolymers that ionic conductivity at 20 °C is affected by the following structural features.

The polymer must be noncrystalline. This follows from a comparison of the conductivities of PEO with its copolymers. The disappearance of crystallinity (Figure 2) coincides with the achievement of maximum conductivity (Figure 3).

The carbon to oxygen ratio must be close to 2:1. This is evident from Figure 3, since only the highest conductivities are achieved with a C:O ratio of 2.

The use of a comonomer with only a hydrocarbon side chain progressively increases the carbon to oxygen ratio to 8:1 as the comonomer content increases. The curve shows an initial increase in conductivity as the crystallinity is reduced. However, even when the copolymer becomes completely amorphous, the conductivity declines progressively with increasing amounts of comonomer 1 to the point where it is not measurable. The use of comonomer 2 shows a similar relationship between conductivity and molecular structure except the rate of decline in conductivity is less marked. It, however, confirms the relevance of this parameter in the design of the macromolecule.

Chain mobility as represented by values of T_g is also a critical parameter. The precise mechanism by which ion transport occurs within the polymer matrix is not known. It is a reasonable assumption, however, that the lithium ion coordinates oxygen atoms up to its maximum coordination number. In all probability the species formed are related structurally to lithium 12-crown-4 (1,4,7,10-tetraoxacyclododecane). In order for the lithium ions to migrate through the solid, local movements of the macromolecules are required and these must be coordinated in such a way that transport occurs. This is highlighted by comparing copolymers 3 and 6, both series of which are amorphous and have the same C:O ratio. However, as shown in Figure 3, the conductivity in the latter declines with increasing amounts of comonomer in excess of 20%. The data in Table III show that the values of T_g increase with increasing comonomer content, whereas with copolymer 6 this is not the case, as is shown in Table IV.

The influence of chain mobility has been discussed before.[9,10] This paper, however, offers firm evidence that this structural parameter is a key feature in the design of a successful solid-state ionic conductor.

Cross-Linked Copolymers of PEO

The polymers described so far represent a major advance in our understanding of the structural factors that affect ionic conductivity. However, the mechanical properties of these materials are so poor that they cannot be used to make unsupported films. They are similar in proper-

Table IV
Variation of T_g with the Composition of Copolymer 6

comonomer 6, mol %	T_g, °C
12.2	-72.0
15.4	-73.0
21.3	-76.5
28.6	-77.0
30.3	-77.0
45.0	-77.0
100.0	-76.0

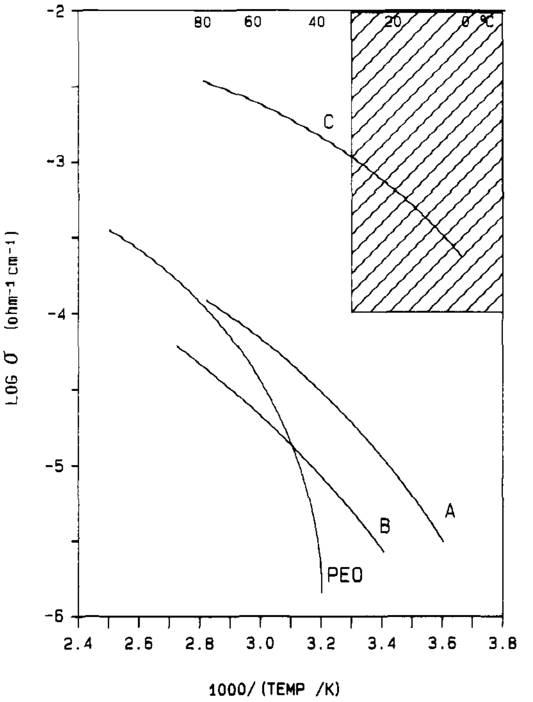


Figure 6. Variation of ionic conductivity with temperature. Curve A, terpolymer **9** (mole percentages are x = 20%, z = 5%, y = 75%), M_w = 2 × 10^6, Li:O = 16:1; curve B, terpolymer **9** cross-linked; curve C, cross-linked terpolymer **9**, which has absorbed propylene carbonate to the extent that it represents 50% of the total weight of the material.

ties to un-cross-linked rubbers and flow even when subjected to a quite modest stress. The intention of this work was to synthesize a film with properties good enough to make a thin-film plastic battery.

We therefore studied the effect of cross-linking on ionic conductivity. Terpolymers with structures similar to **9** were synthesized in order to supply unsaturated centers that could be subsequently cross-linked to give a mechanically stable material.

It was found that copolymer **6** in which 5% of allylic groups were present could be cross-linked at 80 °C, using conventional free radical generators, and in the presence of lithium triflate. The effect of this process on the ionic conductivity is shown in Figure 6B and can be compared to un-cross-linked material (Figure 6A). It shows a reduction of more than an order of magnitude. Both polymers are completely amorphous and have carbon to oxygen ratios close to 2. The loss of ability to conduct lithium ions is not due to a loss of mobility of the segments of the macromolecule between cross-links because the cross-linked material has the lower T_g. The mechanical properties of these films show that they are dimensionally stable and recover their natural shape on removal of compressive or tensional stresses. A stress–strain curve is shown in Figure 7A.

At this point the research was indicating that this system could not give a film with good mechanical properties and a high enough conductivity to be useful. In fact, we need a material with an ionic conductivity–temperature curve that traverses the hatched area of Figure 6. We therefore returned to the study of a model all-liquid system in which dimethoxyethane represented the polymer matrix.

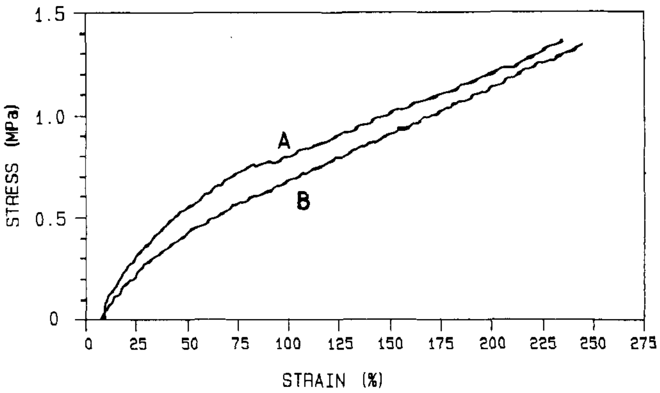


Figure 7. Stress–strain curves for copolymer **9**. Curve A, cross-linked to a density of 3%; curve B, cross-linked copolymer **9** with propylene carbonate absorbed by the film to give an increase in weight of 30%.

Table V
Maximum Ionic Conductivities of Lithium Triflate in Propylene Carbonate (PC) and Dimethoxyethane (DME) and Mixtures Thereof at 23 °C

liquid	dielectric const	viscosity, cP	conductivity × 10^3, Ω^{-1} cm^{-1}
PC	64.4	2.5	1.8
DME	7.2	0.46	1.1
PC (30%) + DME (70%)			8.9

Incorporation of Organic Liquids into the Amorphous Polymer Matrix

A study of the ionic conductivity of various salts in organic solvent leads to the identification of the following features for maximum ionic conductivity.

No single liquid can have the optimum dielectric constant, viscosity, and electron-donating properties. Mixtures of liquids can therefore produce higher ionic conductivities than the pure liquids, provided the properties of the components are complimentary. This is shown in Table V for the system propylene carbonate and dimethoxyethane.

To facilitate the ionization of the salt, a low lattice energy is required. The salt must therefore have a large anion such as triflate or perchlorate. In practice, lithium triflate is preferred since the mobilities of the cation and anion are similar. This is because the former is heavily solvated.

It is evident from Table V that the combination of propylene carbonate and dimethoxyethane with lithium triflate is unusual. It gives the highest conductivity in an organic media. In Figure 8 the effect of lithium triflate concentration on conductivity is given, showning that the maximum is achieved at about 10%, and in Figure 9 the variation in conductivity with temperature is shown. The conductivity at 25 °C is 10^{-2} Ω^{-1} cm^{-1} and represents the maximum yet achieved in organic media.

We therefore decided to study the effect of adding organic liquids to films of cross-linked terpolymer **9**.

Several liquids were studied that complemented the polyethylene oxide's good electron-donating properties by having a high dielectric constant. These included propylene carbonate, *N*-methylpyrrolidone, sulfolane, dimethylformamide, dimethyl sulfoxide, etc. It was found,

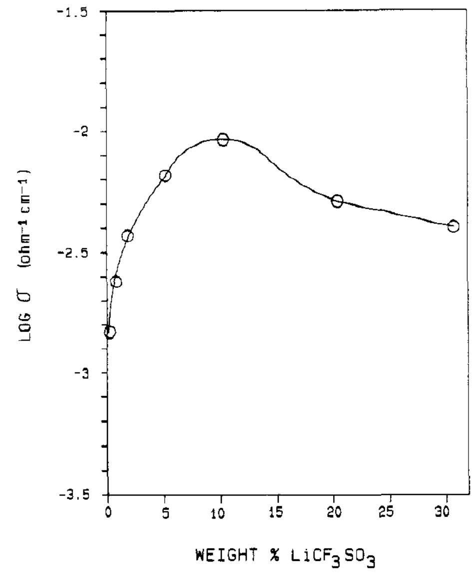


Figure 8. Ionic conductivity at 32 °C at different lithium triflate concentrations in the mixed solvent 70% w/w DME and 30% w/w PC.

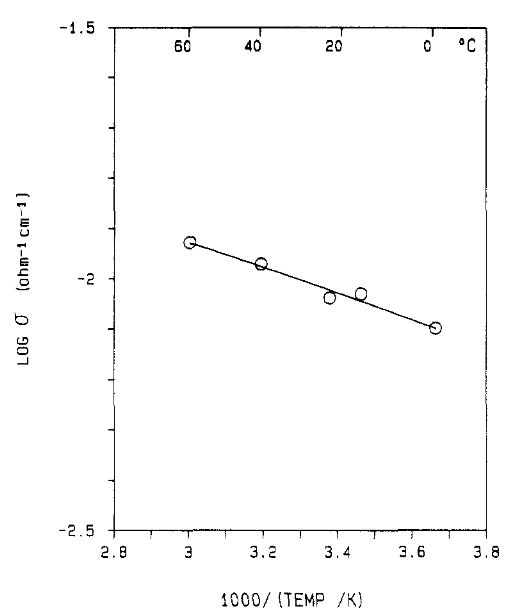


Figure 9. Ionic conductivity as a function of temperature for the system 10% w/w lithium triflate in the mixed solvent described in Figure 8.

in the case of the first two liquids, that cross-linked films of copolymer 9 absorbed vapors of these liquids to give dry flexible films with good mechanical properties that were dry to the touch.

The ionic conductivities of these films are compared in Table VI and represent the highest room temperature ionic conductivities yet achieved in the solid state. The preferred organic liquid was propylene carbonate and the effect of temperature on ionic conductivity is shown in Figure 6C. The compatability of propylene carbonate with amorphous cross-linked poly(ethylene oxide) structures is confirmed by comparison of the glass-transition temperatures of the various compositions given in Table VII.

Table VI
Ionic Conduction at 20 °C of Terpolymer 6 and Its Cross-Linked Analogue with and without Propylene Carbonate and *N*-Methylpyrrolidone

	organic liquid	amt, wt %	conductivity $\times 10^5$, Ω^{-1} cm^{-1}
terpol 6	none		2.5
X-link	none		0.14
X-link	PC	16.7	22
X-link	PC	28.5	32
X-link	PC	37.5	41
X-link	PC	50.0	75
X-link	NMP	20.0	13
X-link	NMP	33.3	25
X-link	NMP	50.0	47

Table VII
Effect of Propylene Carbonate on the Glass Transition of Completely Amorphous Cross-Linked Copolymer 4[a]

copolymer 9	T_g, °C
cross-linked	-75.4
cross-linked + $LiSO_3CF_3$	-55.3
cross-linked + $LiSO_3CF_3$ + propylene carbonate (23%)	-96.6
cross-linked + $LiSO_3CF_3$ + propylene carbonate (33%)	-105.2

[a] O:Li = 16:1.

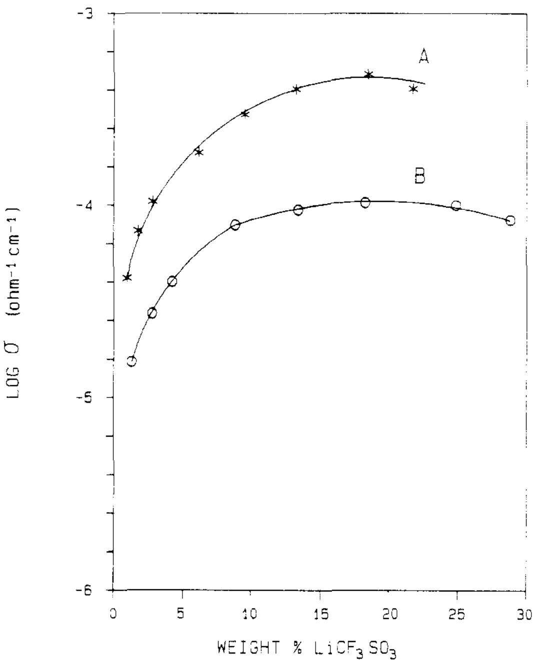


Figure 10. Variation of ionic conductivity with lithium triflate concentration at 20 °C. Curve A, copolymer 9 in which y = 3 mol %, propylene carbonate 33% w/w; curve B, copolymer 9, y = 6 mol %, propylene carbonate 23% w/w.

The relationship between ionic conductivity and concentration of lithium triflate is shown in Figure 10. Maximum conductivity is achieved with lithium triflate present to an extent that is dependent on the amount of propylene carbonate present and the degree of cross-linking. Optimization of these parameters to give the highest ionic conductivity, consistent with reasonable mechanical properties, is the main feature of the technology described in this paper. The best result at the time of writing was an ionic conductivity of 1×10^{-3} Ω^{-1} cm^{-1} at 25 °C for a material with the stress–strain curve shown in Figure 7B. The optimum lithium triflate concentration was close to 8×10^{-2} mol L^{-1}.

It is important to note that the effect of the addition of propylene carbonate on mechanical properties is trivial. This is evident from Figure 7 and Table VIII. The mechanical properties of the film are similar to those of other amorphous rubbers.

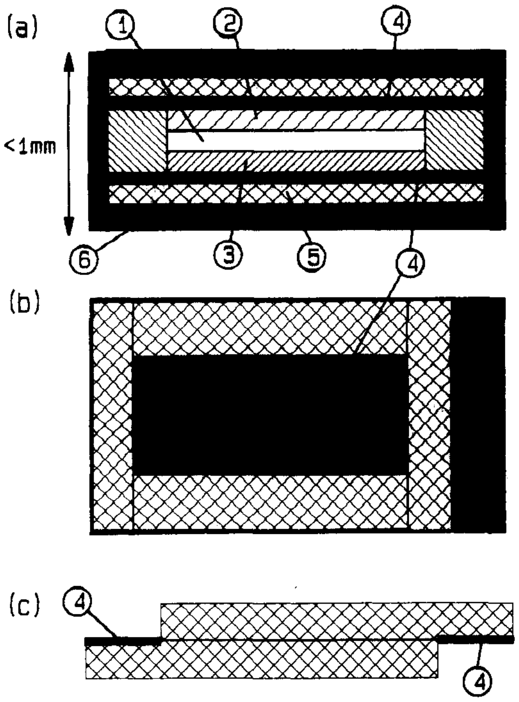


Figure 11. Thin-film solid-state electrochemical cell: (a) Side elevation of the cell in cross-section; (b) the internal layout of the latter viewed normal to the surface; (c) an external section viewed at right angles to elevation (a); (1) solid electrolyte; (2) composite cathode; (3) lithium foil, 50 nm thick; (4) current collectors, 100-μm nickel on 120-μm PET film; (5) PET film; (6) water and oxygen barrier coating.

Table VIII
Mechanical Properties of Cross-Linked Copolymer 9 Described in Figures 6 and 7[a]

copolymer 9	tensile strength, MPa	extensions to break, %
un-cross-linked	0.5	2000
cross-linked	1.41	236
cross-linked + 30% PC	1.33	241

[a] Determined at 20 °C with a strain rate of 100%/min. The un-cross-linked polymer had $M_w = 1 \times 10^6$, M_w/M_n 3.5.

Table IX
Ionic Conductions at 20 °C of Poly(ether carbonate esters) Derived from 10

polymer 10	propylene carbonate, wt %	T_g, °C	conductivity, Ω^{-1} cm^{-1}
cross-linked	none	−11.6	1.3×10^{-9}
cross-linked + propylene carbonate	33.0	−57.9	2.3×10^{-5}
cross-linked + propylene carbonate	54.0		4.8×10^{-4}

Alternative Systems

The observation that propylene carbonate and amorphous ethylene oxide copolymers were synergistic in raising the ionic conductivity suggested that superior results may be obtained by using copolymers that incorporated both these molecular characteristics. A cross-linkable poly(ether carbonate ester) **10**, which was amorphous, was therefore synthesized.

Data given in Table IX show that polymer **10** was inferior to amorphous ethylene oxide copolymers. Moreover, the films had very poor mechanical properties. Similarly incorporation of propylene carbonate into these films failed to give an advantage when compared with the previous system.

Dimethylformamide is an excellent solvent for lithium salts and very high conductivities are achieved with these solutions. Polymerization of monomer **11** gave a poly(ether amide) **12**.

Table X
Room Temperature Values of Solid-State Ionic Conductors Compared at 25 °C

system	conductance, Ω^{-1} cm^{-1}	comments
PEO homopolymer	10^{-7}	ref 20
poly(ethylenimine)	10^{-7}	ref 21
phosphazene polymers		ref 22
Li salts	1.7×10^{-5}	$t_+ = 0.32$ (50 °C)
Ag salts	1.6×10^{-4}	$t_+ = 0.03$ (50 °C)
this work		
amorphous PEO	2.0×10^{-5}	
amorphous PEO cross-linked	3.6×10^{-6}	
amorphous PEO cross-linked + 50% propylene carbonate	0.8×10^{-3}	
dimethoxyethane + propylene carbonate	1.0×10^{-2}	

The product obtained was a highly viscous liquid, which with a $T_g = -26.8$ °C and gave a maximum ionic conductivity of 10^{-8} Ω^{-1} cm^{-1}. Materials obtained by cross-linking had very poor mechanical properties.

Finally, poly(ethylene oxide) side chains grafted onto a polysiloxane backbone **13** were studied. The resulting products were oils with conductivities of 3.25×10^{-5} Ω^{-1} cm^{-1}, but films were obtained on cross-linking. The latter had $T_g = -75.7$ °C and conduction to 3.0×10^{-5} Ω^{-1} cm^{-1}. However, again mechanical properties were not good and attempts to improve conductivities by incorporating propylene carbonate were of limited success because of poor compatability.

Use of Ionic Conducting Films in Construction of Electrochemical Cells

An organic film with an ionic conductivity of 10^{-3} Ω^{-1} cm^{-1} at 25 °C can be used to construct a battery in which the materials used are predominantly organic films. Such an assembly is described in the Experimental Section. So far only primary cells have been made. The overall characteristics are listed in Table X.

Polyphenylene can be used in two modes:

Anode Reaction

$$m\text{Li} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} m\text{Li}^+ + me^-$$

Cathode n Doping

$$(\text{C}_6\text{H}_4)_n + me^- + m\text{Li}^+ \overset{\text{discharge}}{\rightleftharpoons} (\text{C}_6\text{H}_4)_n^{m-}\cdot m\text{Li}^+$$

The cell voltage predicted was 1.4 V. If polyphenylene is initially p-doped, then

$$(\text{C}_6\text{H}_4)_n + m\text{X}^- - me^- \rightarrow (\text{C}_6\text{H}_4)_n^{m+}\cdot m\text{X}^-$$

and the discharge reactions are

$$(\text{C}_6\text{H}_4)_n^{m+}\cdot m\text{X}^- + me^- + m\text{Li}^+ \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} (\text{C}_6\text{H}_4)_n + m\text{LiX}$$

The cell voltage predicted was 4.4 V. The actual voltage found was 3.7 V.

The energy storage ability of thin-film plastic batteries is on the order of 160 (W h)/kg compared to 30 (W h)/kg for the lead acid battery.

Conclusion

Table X compares the results presented in this paper with those obtained by other authors in publications known to us at the end of 1988.

It is evident from the study of the conductivity of the model system consisting of a mixture of organic liquids, dimethoxyethane and propylene carbonate, that this defines the upper limit of a totally organic system as 10^{-2} Ω^{-1} cm^{-1} at 25 °C. Replacement of dimethoxyethane by an amorphous cross-linked PEO matrix, with only the loss of 1 order of magntidue, is remarkable. In all probability a further increase in conductivity may be possible and a value of 5×10^{-3} Ω^{-1} cm^{-1} is foreseen.

The work described in this paper is featured in a European patent[19] and copending applications in the USA and elsewhere.

References and Notes

(1) Wright, P. V. *Br. Polym. J.* **1975**, *7*, 319.
(2) Kelly, I.; Owen, J. R.; Steele, B. C. H. *J. Electroanal. Chem.* **1984**, *168*, 467.
(3) Hooper, A.; North, J. M. *Solid State Ionics* **1983**, *9/10*, 1161. Elsevier Science Publishers.
(4) Armand, M. B. *Solid State Ionics* **1983**, *9/10*, 745.
(5) Gauthier, M.; Fauteux, D.; Vassort, G.; Bélanger, A.; Duval, M.; Ricoux, P.; Chabagno, J.-M.; Rigaud, P.; Armand, M. B.; Deroo, D. *J. Electrochem. Soc.* **1985**, *140*, 1333.
(6) Sequeira, C. A. C., Hooper, A., Eds. Solid State Batteries. NATO ASI Series E No. 101; Martinus Nijhoff Publishers, 1985.
(7) MacCallum, J. R., Vincent, C. A., Eds. *Polymer Electrolyte Reviews-1*; Elsevier Applied Science Publishers: Barking, UK, 1987.
(8) Weston, J. E.; Steele, B. C. H. *Solid State Ionics* **1981**, *2*, 347. Elsevier Science Publishers.
(9) Druger, S.; Ratner, M. A.; Nitzan, A. *Solid State Ionics* **1983**, *9/10*, 1115.
(10) Angell, C. A. *Solid State Ionics* **1986**, *18/19*, 72.
(11) *Solid State Ionics* **1983**, *9/10*, 1101-1061 and references therein.
(12) *Solid State Ionics* **1986**, *18/19*, 252-343 and references therein.
(13) Ballard, D. G. H.; Burgess, A. N.; Dekoninck, J. M.; Roberts, E. A. *Polymer* **1987**, *28*, 329.
(14) Ballard, D. G. H. The Discovery of Polyethylene and its effect on the evolution of Polymer Science. In *History of Polyolefines*; Seymour, R. B., Cheng, T., Eds.; D. Reidel Publishing Company: PO Box 17, 3300 AA Dordrecht, Holland, 1986; p 23.
(15) Ballard, D. G. H.; Dekonick, J. M., unpublished results.
(16) Van Zyl, G.; Zuidema, G. D.; Zack, J. F., Jr., Droman, P. B. *J. Am. Chem. Soc.* **1953**, *75*, 5002.
(17) Vandenbert, E. J. *J. Polym. Sci., Part A1* **1969**, *7*, 525.
(18) Ballard, D. G. H.; Courtis, A.; Shirley, I. M.; Taylor, S. C. *Macromolecules* **1988**, *21*, 294.
(19) Ballard, D. G. H.; Cheshire, P.; Mann, T. S.; Przeworski, J. E. European Patent No. 0260 847.
(20) Rietman, E. A.; Kaplan, M. L.; Cava, R. J. *Solid State Ionics* **1985**, *17*, 67. Elsevier Science Publishers.
(21) Harris, C. S.; Shriver, D. F.; Ratner, M. A. *Macromolecules* **1986**, *19*, 987.
(22) Blonsky, P. M.; Schriver, D. F.; Austin, P.; Allcock, H. R. *J. Am. Chem. Soc.* **1984**, *106*, 6854.

Registry No. 1, 124604-86-0; 2, 88752-55-0; 3, 64786-16-9; 4, 124604-87-1; 5, 124618-70-8; 6, 115401-75-7; 7, 124604-88-2; 8, 124604-89-3; 9, 115383-11-4; 11 (homopolymer), 124618-72-0; PC, 108-32-7; DME, 110-71-4; NMP, 872-50-4; $LiSO_3CF_3$, 33454-82-9; (dibutyl carbonate)(diethyl glycol) (copolymer), 124604-90-6; methacrylic anhydride, 760-93-0.

Group-Transfer Polymerization on a Polymeric Support

W. R. Hertler,* D. Y. Sogah, and F. P. Boettcher

Central Research and Development Department,[†] *E. I. du Pont de Nemours & Co., Inc., Experimental Station, Wilmington, Delaware 19880-0328.*

Received April 19, 1989; Revised Manuscript Received July 28, 1989

ABSTRACT: Three silyl ketene acetals (4, 7, and 9) bonded to cross-linked polystyrene beads were synthesized from chloromethylated polystyrene. Suspensions of these supported silyl ketene acetals in tetrahydrofuran (THF) containing methyl methacrylate (MMA) and anion catalysts for group-transfer polymerization (GTP) gave rapid formation of graft polymers, almost without formation of ungrafted, soluble PMMA. Initiation of the GTP of MMA with 7 in acetonitrile gave insignificant chain transfer to solvent. Initiation of the GTP of acrylonitrile with 9 at −50 °C gave quantitative conversion to graft copolymer, while initiation at room temperature gave soluble poly(acrylonitrile) as well. In contact with gaseous MMA or acrylonitrile, catalyst-doped 4 was converted to graft copolymer. The GTP of MMA in THF solution in the presence of cyanomethyl-substituted cross-linked polystyrene beads (1) gave a graft copolymer as a result of chain transfer.

Introduction

The success of the Merrifield peptide synthesis on polymeric supports[1] and the growing importance of surface modification by graft polymerization led us to investigate the potential of group-transfer polymerization (GTP)[2] on polymeric supports. In principle, techniques analogous to those for the synthesis of peptides could be used for the construction of highly designed addition polymers, taking advantage of the living nature of GTP. In this paper we report the synthesis of several kinds of silyl ketene acetals on cross-linked polystyrene and their use in initiation of GTP of acrylic monomers. Objectives were to gain insight into chain-transfer processes in GTP through the use of supported initiators and chain-transfer agents and to obtain mechanistic information on the GTP of acrylonitrile, a monomer that is difficult to study because of its high propagation rate. DNA-binding studies using graft copolymers prepared by these techniques will be reported elsewhere. Otsu and co-workers have described the successful grafting of polystyrene and poly(methyl methacrylate) onto cross-linked polystyrene containing dithiocarbamate groups by use of a free radical photoiniferter technique.[3]

[†] Contribution No. 5002.

0024-9297/90/2223-1264$02.50/0