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Copies to: Richard A. Marsh

INTRODUCTION

Polymeric electrolytes are usually obtained by dissolution of alkali metal salts in ion - coordinating macromolecules (solid electrolytes) or in gels containing three - dimensional polymeric networks and a low molecular weight solvent of high permittivity (gel electrolytes). In such systems cations and anions are both mobile, although usually only cations take part in the electrode reactions. Anions accumulate at the anode and become depleted at the cathode since they can neither be formed nor discharged at the electrodes. For ideal systems in which the salt dissociates fully into cations and anions the steady-state current I_s^+ and the voltage ΔV applied are related to the cation concentration at the anode c_a and cathode c_c by the expressions:

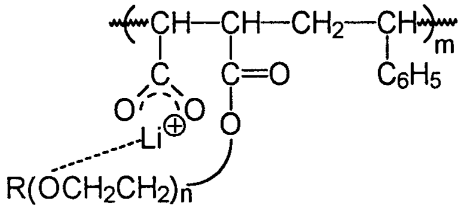
$$- I_s^+ = 2F_t (c_a - c_s) D_+$$

$$\Delta V = \frac{2RT}{F} \ln(c_a/c_s)$$

where D_+ is the cationic diffusion coefficient

Polymer electrolytes are not ideal systems, since the interactions between the ions and the salt are always likely to be significant. Several expressions for I_s^+ and ΔV, taking into account the thermodynamic enhancement, coupling between ionic fluxes and migration of associated group of ions such as ion pairs or ion triplets have been developed [1-3]. In most of the solid electrolytes the anionic contribution in total charge transportation outweighs that from the cations, which strongly limits the performance of electrochemical cells. Although the reliability of transference numbers determination in this system is not high, one can roughly estimate that for classical systems based on PEO and lithium salt. the t_+ values are in the 0.06 - 0.30 range [1,4-7]. Significantly higher t_+ values (0.4 - 0.6) were recently reported by Scrosati et al. for some gel electrolytes [8]. Surprisingly, these values are even higher than those usually obtained for the parent pure liquid solutions, which might suggest that the polymer component influences the short range lithium ion mobility and thus their transference number.

In order to increase the t_+ value, a number of methods leading to the preparation of polymeric electrolytes having immobilized anions were developed [9-16]. Most often those are mixtures of polyelectrolytes with PEO or salts of polyanions containing ethylene oxide monomeric units sequences in their molecules. However, usually the preparation of an electrolyte exhibiting $t_+ \sim 1$ was followed by a drastic decrease in its ionic conductivity with respect to the system in which cations and anions are both mobile. Our preliminary studies [17] showed that some lithium electrolytes based on comb-like half-esters of poly(ethylene glycol)s and maleic anhydride - styrene copolymer **I** may exhibit ambient temperature conductivity in the 10^{-5} - 10^{-6} S/cm range. This is one - two orders of magnitude higher than those reported for PEO/salt systems.



I R = H

II R = CH_3

III R = $CH_2CH{=}CH_2$

In our opinion the specific properties of this system result from the very effective complexation of Li^+ ions by oxyethylene sequences resulting from the small distance between the carboxylic group and polyether chain.

Taking into account that this type of electrolytes may be obtained from cheap and easily available starting materials, within this project detailed studies have been carried out on the conductivity of these types of systems and especially on the possibility of using them as monoconducting polymeric matrices in gel electrolytes. For this purpose we developed a method for the synthesis of copolymers containing polyoxyethylene groups terminated with allyl groups (**III**), enabling the formation of networks as a result of the free radical polymerization.

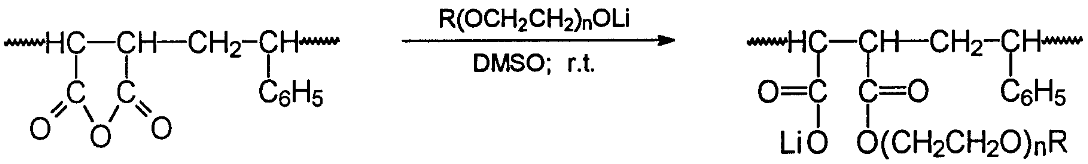
EXPERIMENTAL PART

Materials

Maleic anhydride, styrene, DMSO, propylene carbonate and ethyl alcohol were purified by double distillation over drying agents. The commercially available poly(ethylene oxide) glycols and monomethyl ethers of poly(ethylene oxide) glycols (Aldrich, Loba Chemie) were dried over molecular sieves in a nitrogen atmosphere. The poly(ethylene oxide) glycols terminated by an allyl group were obtained by anionic polymerization of ethylene oxide in allyl alcohol according to the general method described elsewhere [18]. The average degree of polymerization was determined from the end group analysis by means of ^{1}H-NMR spectroscopy (spectra were recorded in $CDCl_3$ on a Bruker 300 spectrometer). Benzoyl peroxide was purified by crystallization. *n*-Butyllithium in hexane (15 wt %, Merck) and the photoinitiator Irgacure 184 (CIBA) were used as received.

Electrolyte preparation

An alternating maleic anhydride and styrene copolymer of $M_n \approx 3.2\times10^5$ was used as the initial polymeric product for the synthesis of electrolytes. The copolymer was obtained by free radical copolymerization carried out at 60 °C in toluene. A solution of the copolymer (0.5 g) in 15 cm^3 of DMSO was added dropwise to an equimolar amount of poly(ethylene glycol) alcoholate obtained from corresponding glycols and *n*-butyllithium (~ 25 mmol in 15 cm^3 of DMSO).



The reaction course was controlled by measuring the intensity of bands of the C=O bonds stretching vibrations at 1770 cm^{-1} (in the anhydride groups) and at 1720 cm^{-1} (in ester groups) according to the procedure presented earlier [19].

When using poly(ethylene glycol)s of M_n up to 750 g/mol, after about 12 hours of reaction at room temperature complete conversion of the anhydride groups was achieved. When using glycols of M_n 1000 and 2000 the degree of conversion reached ~ 85 % and both the prolongation of the reaction time and rise of the temperature did not cause a further increase in the yield.

The thus obtained lithium salt solutions were processed by two methods., A and B.

In method A (in the case of type **I** electrolytes) DMSO was removed under reduced pressure from thin solution layers, so that the sulfur content in the end product was below 0.3 wt. %. In the case of the type **II** electrolytes, 1 wt. % of benzoyl peroxide (with respect to the salt) was added to the solution, and in some experiments also propylene carbonate. The thin solution layer formed was heated for ~ 1 hour at 70 °C in order to obtain a gel. The solvent content was determined by means of elemental analysis.

In method B the electrolyte solution in DMSO was poured onto acidified water. The polymer precipitated was filtered off and purified by dissolution in methanol and precipitation in water. Finally, the acidic form of the electrolyte (0.2 g) was dissolved in 3 cm^3 of absolute methanol and converted into a salt by dropping in solutions of lithium, sodium or potassium methanolates. An appropriate amount of plasticizers and free radical initiator or photoinitiator were added to the solution. A thin layer was poured out and methanol was removed. Gels were obtained by thermal crosslinking at 70 °C for ~ 1 hour or by UV irradiation for ~ 10 minutes.

Measurements

AC impedance analysis was used to determine the bulk conductivity of electrolytes using a SOLARTRON 1255 frequency analyzer (10^{-2} - 10^{5} Hz frequency range). Fig. 1 shows a schematic diagram of the conductivity cell of controlled geometry constructed for these measurements. Test studies show that due to using a PID type control system, the temperature can be controlled with a 0.01 deg accuracy in the -50 - +120 °C temperature range. At temperature changes of 10 °C the temperature stabilizes within several minutes. The range of measurable resistance lies within 50 Ω - 500 kΩ limits. The most exact results are obtained in the 200 - 1000 Ω range. We estimated that the experimental error should not exceed 10 % of the reported conductivity data.

Calorimetric investigations were performed on a UNIPAN 605 and DuPont TA 2910 scanning calorimeter between -110 and 150 °C. The heating rate was 10 °C/min.

The diffractograms were registered for the Bragg angles 2θ between 20 and 70 deg using a DRON 2.0 powder diffractometer.

RESULTS AND DISCUSSION

Solid electrolytes

DSC and X-ray diffraction studies proved that the polymers obtained with polyoxyethylene side chains of $M_n \leq 750$ are amorphous both in the acidic form and the lithium salt form. In the case when M_n of the poly(ethylene glycol) used was 1000 or 2000 the occurrence of a crystalline poly(ethylene oxide) phase was observed. The melting points of the crystalline phase in lithium salts were in the 318 - 320 K temperature range and the degree of crystallinity of the poly(ethylene glycol) chains was ~ 85 %. No signals indicating the possibility of forming crystalline complexes between lithium carboxylates and polyglycol chains were observed. However, the existence of interactions between lithium ions and side chains is indicated by an increase in the T_g value to ~ -37 - -51 °C (Table 1) with respect to that for poly(ethylene oxide), which is ~ 65 °C.

Changes of ionic conductivity for lithium polyelectrolytes with various side chain length versus reciprocal temperature are shown in Fig. 2.

An electrolyte containing two oxyethylene units and an OH end group exhibits ambient temperature conductivity below 10^{-8} S/cm, which increases by about one order of magnitude at 100 °C.

Therefore, it can be assumed that the formation of hydrogen bonds between the OH groups and carboxylic anion does not cause an increase in the mobility of lithium ions. The positive induction effect of the methyl group may be a factor enabling the complexation of these cations by ethereal groups in the side chain. An increase in the average molecular weight of the side chain to 200, which corresponds to the average ethylene oxide monomeric units sequence length $n \approx 4.5$, leads to a rapid increase in the conductivity of the system, which at room temperature is ~ 10^{-5} S/cm. At this oxyethylene sequence length the lithium cations can probably be fully coordinated by single side chains, which considerably increases the probability of the macrosalts dissociation. The ambient temperature conductivity values observed for these systems are only about half an order of magnitude lower than those of amorphous electrolytes containing mobile anions and cations.

A further increase in the side chain length leads to a decrease in conductivity. This decrease is significant when the average number of ethylene oxide monomeric units sequences is higher than 13. Thus, it can be assumed that the transfer along the side chain does not play an essential role in the conductivity mechanism, but a key role is played by cation hoppings between carboxylic groups. The charge carrier concentration decreases with an increase in chain length. At an average number of ethylene oxide monomeric units in the ester group $n \approx 4.5$ it is equal to 2.4 mol/kg and at $n \approx 14$ about 1.2 mol/kg. For comparison, in classic polymeric electrolytes based on lithium salts and poly(ethylene oxide) the optimum lithium ions concentration lies within the 1.8 - 2.2 mol/kg range.

In Figs 3 and 4 are presented the changes of conductivity versus temperature for similar systems but containing Na^+ and K^+ cations. It can be noticed that in these systems, at $n \approx 4.5$, low conductivity values are obtained (~ 10^{-8} S/cm) and they change only slightly in a wide temperature range. This results from the larger size of Na^+ and K^+ cations than that of the Li^+ cation, and thus a greater number of ethylene oxide monomeric units is necessary to complex the cation. For Na^+ ions the highest conductivity values were obtained for n = 7 and 16, and for K^+ ions for n = 13 and 22 (in the 10^{-6} - 10^{-7} S/cm range at ambient temperature).

The temperature and frequency dependence of conductivity of some of the samples studied was analyzed by the Almond - West formalism [20] developed recently by us for the studies of polymeric electrolytes [21]. This method permits to determine, independently of each other, the activation energy of charge carriers creation (E_c) and migration (E_m). The results obtained are presented in Table 2.

It can be noticed that the E_c value is close to zero, which means that with a rise of temperature no essential change in the charge carriers occurs in these systems and only the hopping frequency (ω_p) increases. This parameter can be estimated from the equation:

$$\omega_p = (\sigma_{dc}/A)^{1/n}$$

where σ_{dc} is the direct current conductivity, A and n are temperature dependent material parameters.

The A and n parameters were determined by the non-linear least squares fitting procedure using the Jonscher's universal power law [22]:

$$\sigma_\omega = \sigma_{dc} + A\omega^n$$

where ω is frequency and σ_ω conductivity at a given frequency.

In Fig. 5 is presented the log ω_p versus 1/T dependence for a number of samples. It can be noticed that in the case of sodium and potassium electrolytes the ω_p values considerably increase for electrolytes of longer oxyethylene units sequences (n = 13 - 22) in comparison with those of short side chains (n = 2 - 4.5). Thus, it can be assumed that cations complexed by a polyglycol chain become more mobile. In the case of a lithium long chain (n = 22) electrolyte the average ambient temperature cation mobility is low, which is connected with the high content of the crystalline phase. After crossing the melting point of this phase a remarkable increase in the cation mobility is observed. In the case of electrolytes of long oxyethylene ions sequences, at above 70 °C no essential changes in the Li^+, Na^+ and K^+ cations mobility is observed.

Such studies can be carried out only for systems in which a clearly Arrhenius type relationship occurs. However, in many systems, like e.g. in the one presented in Fig. 6, one cannot univocally assign neither the hopping ion transport described by the Arrhenius equation, nor the mechanism controlled by segmental motions of polymer chains described by the Vogel-Tamman-Fulcher (VTF) equation.

A copolymer with a side chain of $n \approx 4.5$ was used also with poly(ethylene oxide) (20 : 80). It was found that a decrease in the lithium ions concentration causes a decrease in conductivity by two orders of magnitude ($\sim 1.5\times10^{-8}$ S/cm at 25 °C and 2.1×10^{-7} S/cm at 50 °C), despite that the system is characterized by high elasticity (T_g = -62 °C). Thus, the effect of external salt dissolution acts similarly as the side chain elongation. An addition of 5 mol % of $LiClO_4$ to this system assures conductivity of $\sim 1\times10^{-5}$ S/cm at 25 °C and 6.1×10^{-5} S/cm at 50 °C. The system obtained contains over 95 % of an amorphous phase of high elasticity (T_g = -45 °C).

Polymer Gel Electrolytes

Effect of side chain length

In Table 3 are presented the conductivities at 25 and 50 °C for lithium gel electrolytes of various oxyethylene chain length in the presence of dimethylsulfoxide (DMSO) and propylene carbonate (PC). The highest ambient temperature conductivities of above 10^{-4} S/cm are obtained for electrolytes containing three oxyethylene units. The clearly higher conductivity values of these systems than those of $n = 0$ indicate that the presence of OCH_2CH_2 units in the side chain has an essential effect on the conducting properties of the gel. Probably even in the presence of the solvent the possibility of the internal coordination of lithium ions has a significant effect on the charge carriers mobility and salt dissociation constant. The conductivity decreases with elongation of the oxyethylene chain as a result of a decrease in the charge carrier concentration. The side chain length has also an essential effect on the mechanical properties of the system. Films characterized by good mechanical properties are obtained for $n \leq 4$ at the total solvent content up to about 70 - 75 wt. %. At longer side chains the films containing over 30 wt. % of solvent are not dimensionally stable and are practically not suitable as electrolytes.

In the Table are presented also two results of measurements for sodium electrolytes for a system of n = 4. It can be noticed that at a small amount of solvent (20 wt %, DMSO) the sodium electrolytes conductivity is significantly lower than that for an analogous system with Li^+. However, at a high solvent content the sodium electrolytes conductivity is somewhat higher than that of the lithium electrolytes. This observation is in agreement with the results obtained for solid electrolytes. It appears from them that the complexation of sodium ions requires a larger number of solvating ligands than in the case of complexing lithium ions.

The data presented in Table 3 indicate that the activation energy for conducting processes is small. For a majority of systems it can be approximately calculated from the Arrhenius equation and the results obtained lie within 22 - 45 kJ/mol. However, in the case of some electrolytes the VTF type relationship [$\sigma = \sigma_o exp(-B/T - To)$] seems to be more correct. In this case the preexponential factor σ_o is proportional to the square root of T, B is proportional to the activation energy and T_o denotes the thermodynamic glass transition temperature. Figs 7-10 show examples of such a fitting, calculated values of VTF parameters and real T_g values for these systems. One can observe that for systems of low solvent content the T_o values are very similar to the T_g values determined by the DSC method,. This is quite typical for different types of amorphous electrolytes, both solid [1, 23] as well as some gel ones [24].

The differences between T_g and T_o increase at a higher solvent content. As can be seen from the diagrams presented, clear deviation from the VTF type relationship is usually observed at low temperature in the 1.15 - 1.30 T_g range. We observed a similar phenomenon also in other polymeric electrolytes [25]. Some polymer segments and ionic motions are probably “frozen in” below this temperature for the appropriate time scale and therefore they have no essential effect on the conductivity of the system.

The pseudoactivation energy B calculated for this system is ~ 600 K^{-1}, which is approximately 1.5 times higher than those reported by us for some gel electrolytes in which both cations and anions are mobile [24, 26].

The solvent effect

From the data presented in Table 3 for electrolytes of n = 3 it appears that gels of high conductivity are obtained at a solvent content of 20 to 80 wt. %. Phase separation of the solvent occurred at higher solvent contents. Higher conductivity values were assured when using a solvent mixture than in the case of using systems with one solvent. Systems containing 20 wt. % of DMSO and 20 - 25 % of propylene carbonate seem to be most favorable from the point of view of conductivity and mechanical properties. A further increase in the propylene carbonate content to about 40 wt. % causes only a slight increase in the conductivity of the systems. The use of an excess of DMSO causes a worsening of both the mechanical properties and conductivity of the system. We found that continuos, slow evaporation of DMSO occurs from systems of high content of that solvent, which results from its too low boiling point (189 °C). Thermogravimetric studies showed that electrolytes containing ~ 20 wt. % of DMSO loose during heating at a 10 ° / min rate at 50 °C about 3 % of their weight and at 150 °C about 18 %. About 3 - 4 % of DMSO is bound permanently with the electrolytes, and it cannot be removed even upon applying high vacuum. These are probably molecules of the solvent in a solvation surrounding of Li^+ ions. A somewhat higher stability is shown by a mixture of DMSO and PC. For example, at 20 wt. % content of each of the solvents the weight loss at 150 °C is ~ 5 % during heating with a constant rate. Nevertheless, even from such systems evaporation of DMSO to a 4 -5 wt. % content occurs after a long time.

Therefore, for an expected long working time, mixtures of low DMSO content, or even not containing it, should be considered. As can be seen on the example of electrolytes of n = 4, systems of high conductivity can be obtained at low DMSO content and high PC content. The choice of the solvent is very important also from the point of view of the stability of the electrolyte - electrode interface. This factor actually seems to be much more important than the conductivity alone.

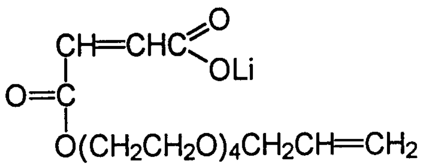
Therefore, in the next step of investigations studies were carried out on whether DMSO / PC systems can be replaced without significant loses in conductivity. These studies were carried out for the electrolyte of n = 4. The conductivity values at several chosen temperatures are presented in Table 4. The following solvents were used: diethylsulfoxide (DESO), 2-cyanoethyl sulfide (CES), 2-cyanoethylsulfoxide (CESO), propylene sulfide (PS), ethylene carbonate (EC), diethyl carbonate (DEC), butyrolactone (BL), adipic acid dinitrile (AAN), benzonitrile (BN), methyl cyanoacetate (MCA) and poly(ethylene glycol) dimethyl ether of M_n 420 (PEG). Some of them were used in combination with propylene carbonate. DESO forms stable gels of good mechanical properties, the conductivity of which is 20 - 30 % lower than that in systems with DMSO, both when using one solvent or in combination with PC. The larger share of the non-polar aliphatic substituent is probably the reason for this. CESO is a solid and does not form elastic films with a crosslinked matrix. However, it can form gel electrolytes in combination with other solvents, e.g. with PEG or PC. The conductivity values of electrolytes with these systems are lower or similar as those in systems with DESO / PC. An increase in the polarity of the aliphatic group did not lead to an improvement of the conducting properties of the system. Perhaps this results from the fact that the nitrile group abstracts electrons from S→O bonds and therefore weakens the complex formation properties. Initial studies with the use of a sulfoxide containing electron donor OCH_3 groups indicate that it has better complex formation properties than DMSO. A full set of experiments with this compound has not been, however, completed yet.

Other organic sulfur derivatives (PS and CES) exhibit weaker lithium cation complexing properties than sulfoxides, and gels containing these solvents have relatively low conductivity, in the 10^{-6} - 10^{-5} S/cm range. Moreover, they are characterized by weak mechanical properties. Considerably lower conductivity values in the 10^{-8} - 6×10^{-7} S/cm range were obtained also in systems, in which nitriles of high boiling point (AAN, BN, MCA) were used as solvents, despite that the analog - acetonitrile is commonly used as an agent well solvating cations. This seems to result mainly from the low elasticity of matrices containing these solvents (the T_g values are from -11 to -31 °C, and some of the electrolytes show a tendency towards crystallization at -4 - -15 °C). In the case of using MCA, upon evaporation of the solvent a spontaneous reaction proceeds in the system leading to a decrease in the elasticity of the foils and change of their coloring to dark red. A condensation reaction probably proceeds here, resulting from the generation of a cyanoacetatomethine carbanion. Such a high reactivity of the solvent in the presence of a nucleophilic agent (such as carboxylic ions) excludes its use in electrochemical devices. Moreover, from the hitherto studies on the stability of different solvents towards a lithium electrode it results that nitriles are not recommended for such applications [8].

From studies on classic gel electrolytes and also on non-aqueous liquid electrolytes it is known that the best conductivity values and slowest increase in resistance on the electrolyte / electrode interface is achieved for solvents comprising a mixture of linear and cyclic carbonates and γ-butyrolactone [27]. From our studies it appears that this type of solvents, in the case of a monoconducting electrolyte of n = 4, assures conductivities in the 2.5 - 3.0×10^{-5} S/cm range, i.e. two to three times smaller than that of systems containing sulfoxides. Thus, it seems that a monoconducting system considered for use in lithium batteries should contain a small addition of sulfoxides, and therefore the determination of the influence of these compounds on the lithium passivation rate should be the key problem. The high conductivity of sulfoxide mixtures with PEG is very promising, since the stability of ethers in reactions with lithium is much larger than that of carbonates and carboxylic acid esters.

Effect of the addition of lithium salts and type of matrix

The possibility of increasing the lithium cations concentration in the monoconducting electrolytes was studied by introducing to the system a maleic acid half-ester salt (MAS) containing an unsaturated bond in the side group.



$LiOC(=O)CH{=}CH-C(=O)-O(CH_2CH_2O)_4CH_2CH{=}CH_2$

MAS

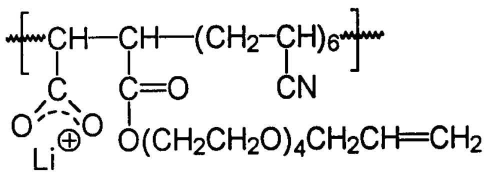
We found that this salt is incorporated to the polymeric systems during crosslinking. As can be seen from Table 5, the non plasticized matrix containing MAS and an electrolyte of n = 4 exhibits ambient temperature conductivity slightly above 10^{-8} S/cm, that is one to two orders of magnitude lower than those found for solid (non-crosslinked) electrolytes of similar side chain length (Fig. 2). The plasticized samples containing ~ 50 wt. % of solvents exhibit similar conductivities to those found for non-modified systems. Thus, one can conclude that the lithium cations concentration in electrolytes of relatively short side chains ($n \leq 4$) is not a factor limiting the conductivity.

We studied also how the gel conductivity is affected by the addition of $LiClO_4$, i.e. of a salt in which both the cations and anions are mobile (Table 5). In the case of a strongly conducting gel based on polyelectrolytes of $n = 4$ containing 28 wt. % of DMSO and 37 wt. % of propylene carbonate, the addition of up to 8 wt. % of the salt does not cause essential changes in conductivity within the 20 - 90 °C temperature range. The ambient temperature conductivity values are of the order of 6.8×10^{-4} S/cm and at 90 °C of 5×10^{-3} S/cm. These observations indicate that in highly polar solvents the concentration of charge carriers is sufficiently high enough and that the presence of mobile anions has no effect on the total bulk conductivity. This seems to confirm the hypothesis of Scrosati et al. [8] of high cation transfer numbers in gel electrolytes.

The situation is quite different in the case of gels containing solvents of a lower than DMSO polarity. For example, in gels containing PEG, the addition of 4 % of $LiClO_4$ causes an increase in conductivity by two orders of magnitude, and in systems with DESO by one order of magnitude. Therefore, it can be assumed that in the case of systems characterized by small polarity, the salt dissociation ability becomes the factor decisive of the conductivity.

The addition of $LiClO_4$ has a very advantageous influence on the improvement of the mechanical properties of the system. The mechanical properties of the gel can be also improved by the addition of non-conducting inorganic fillers. For example, the addition of only 3 wt. % of glass wool enables the obtaining of the electrolytes in the form of a stiff plate, which does not creep under pressure up to about 130 °C. However, this is accompanied by a decrease in conductivity by about one order of magnitude.

The possibility of improving the conducting properties of gels by using maleic anhydride copolymers with other than styrene comonomers was also investigated. Copolymers with very polar comonomers, like acrylonitrile, acrylamide and diethylene glycol allyl methyl ether, were obtained. These copolymers were then transformed into half-esters analogous to **III**, containing on an average four oxyethylene units.



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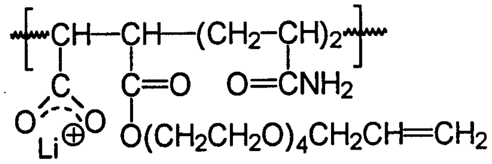

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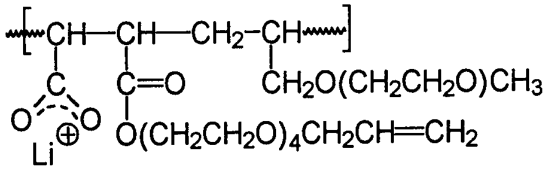

VI

Polyelectrolyte **V,** containing acrylamide monomeric units, upon crosslinking in an organic solventsmedium, does not form a film but isolates in the form of brittle precipitates. The polyelectrolyte **IV**, upon crosslinking in a DMSO medium, forms films characterized by relatively weak mechanical properties, since probably due to the too large distance between the allyl groups, the crosslinking density is too small. (The introduction to the system of a larger number of maleic anhydride monomeric units is very difficult due to the unfavorable reactivity ratio values of these monomers). At a DMSO content of ~ 7 wt. % the ambient temperature conductivity of these electrolytes is ~ 2×10^{-6} S/cm and at that of ~ 30 wt. % about 3×10^{-5} S/cm. These values are close to those obtained for the type **III** electrolytes of n = 9, which are characterized by a similar Li^+ ions concentration as that in the systems studied.

Electrolyte **VI**, upon crosslinking, forms films of good mechanical properties, At a DMSO content of ~ 10 % they achieve a conductivity of ~ 10^{-4} S/cm and at a 20 wt. % of DMSO and 20 wt. % of PC content, of 7×10^{-4} S/cm. These are nearly identical values as those for the best systems containing a type **III** electrolyte.

Thus, it can be assumed that the type of comonomer used for the copolymerization with maleic anhydride has only a small effect on the conductivity of the electrolytes studied, similarly as in classic gel electrolytes.

CONCLUSIONS

1. Monoconducting solid electrolytes based on maleic anhydride copolymers exhibit various conductivity values, depending on the oxyethylene units chain length in the ester group and kind of cations. The highest conductivity values of ~ 10^{-5} S/cm at ambient temperature and ~ 10^{-4} S/cm at 85 °C were obtained for lithium electrolytes containing at an average 4.5 ethereal units in the side chain. They can be considered as materials working at 50 - 120 °C.
2. Monoconducting gel electrolytes containing crosslinked lithium salts of maleic anhydride copolymers and various organic solvents exhibit conductivities in the range of 10^{-6} - 8×10^{-4} S/cm at 25 °C and 10^{-7} - 10^{-5} S/cm at -40 °C. The highest conductivity values are usually exhibited by systems containing mixed solvent systems, most favorably sufoxides and propylene carbonate. The most favorable side chain length is 3 - 4 oxyethylene units. The kind of the comonomer used in the reaction with maleic anhydride has no essential effect on the conductivity values.
3. In the case of electrolytes containing polar solvents, such as DMSO or PC, an increase in the lithium salt concentration by incorporation of a larger number of ionogenic groups to the matrix, as well as the addition of $LiClO_4$, do not lead to an increase in the conductivity values. This means that the concentration of mobile charge carriers in these systems is high, despite that the anions are immobilized. In the case of solvents of lower polarity, like DESO or PEG, the effect of the addition of $LiClO_4$ on conductivity is very clear and it can be assumed that in this case this is a system very close to that of classic gels, in which the polyelectrolyte plays the role of an inert matrix.
4. The ionic conductivity values of gels is not a factor determining their usefulness as electrolytes, since it is known that a number of solvents react with electrode materials and the resistivity and other properties of the passivation layer on the electrode - electrolyte interface becomes a decisive factor in terms of the performance of electrochemical devices. Thus, further optimization of the gel conducting properties does not seem to be necessary. The main effort in further work will be stressed on stability studies of the lithium electrolyte and lithiated carbon Li_xC_6 - electrolyte interfaces.

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Table 1. Glass transition temperatures of various salts of a maleic anhydride - styrene copolymer esterified with protected glycols

Molecular weight of glycol	T_g (°C)		
	Li	Na	K
120	-51		-
350	-58	-59	-
750	-44	-44	-50

Table 2. Activation Energies Calculated on the Basis of the Almond - West Formalism for Charge Carriers Creation (E_c) and migration (E_m)

Cation	n	E_c kJ/mol	E_m kJ/mol
Li^+	22	3	64
Na^+	2	2	23
Na^+	16	2	46
K^+	4.5	5	14
K^+	13	2	30
K^+	22	0	39

Table 3. Conductivity of Gel Electrolytes Based on Polymer **III** of Different Numbers of OCH_2CH_2 monomeric units (n).

n	Method of synthesis	Solvent		Li content in polymer	Ionic conductivity	
		DMSO	PC		25 °C	50 °C
		wt. %	wt. %	wt. %	S/cm	S/cm
0	B	0	80		9.0×10^{-6}	2.2×10^{-5}
	B	30	50		2.2×10^{-5}	4.9×10^{-5}
	B	40	40		1.8×10^{-5}	7.2×10^{-5}
3	A	10	-	1.76	1.0×10^{-4}	2.9×10^{-4}
	A	17	-	1.76	2.4×10^{-4}	1.0×10^{-3}
	A	20	20	1.76	7.7×10^{-4}	1.9×10^{-3}
	A	21	42	1.76	8.1×10^{-4}	2.1×10^{-3}
	B	0	80	1.76	1.6×10^{-5}	2.7×10^{-5}
	B	20	25	1.76	7.8×10^{-4}	1.9×10^{-3}
	B	20	40	1.76	8.0×10^{-4}	2.1×10^{-3}
	B	50	20	1.76	2.1×10^{-4}	1.6×10^{-5}
4	B	15	0	1.58	1.1×10^{-5}	7.0×10^{-5}
	B	8	70	1.58	9.0×10^{-5}	1.8×10^{-4}
	B[a]	20	0	1.58	5.0×10^{-6}	2.6×10^{-5}
	B[a]	5	70	1.58	1.7×10^{-4}	2.6×10^{-4}
6	A	20	-	1.32	2.2×10^{-5}	8.1×10^{-5}
	A	24	-	1.32	4.8×10^{-5}	7.8×10^{-5}
	A	28	-	1.32	6.1×10^{-5}	1.3×10^{-4}
7	A	50	-	1.27	8.6×10^{-5}	2.7×10^{-4}
	A	22	53	1.27	1.1×10^{-4}	2.2×10^{-4}
9	A	20	-	1.06	7.3×10^{-6}	3.9×10^{-5}
	A	27	-	1.06	2.7×10^{-5}	1.1×10^{-4}

[a] sodium electrolyte

Table 4. Conductivity of Gel Electrolytes Based on Polymer **III** of $n \approx 4$ containing various types of solvents

Solvent (wt. %)	Ionic Conductivity at -40 °C	25 °C	50 °C	90 °C
DMSO (15)	2.1×10^{-8}	1.1×10^{-5}	6.7×10^{-5}	1.7×10^{-4}
DMSO (8); PC (70)	4.9×10^{-6}	9.2×10^{-5}	1.8×10^{-4}	2.9×10^{-4}
DMSO (30); PC (50)		6.6×10^{-4}	1.6×10^{-3}	4.1×10^{-3}
DESO (60)	8.2×10^{-8}	1.5×10^{-5}	5.4×10^{-5}	1.9×10^{-4}
DESO (30); PC (30)		6.1×10^{-5}	2.2×10^{-4}	5.6×10^{-4}
CESO (20); PC(30)		1.9×10^{-6}	1.8×10^{-5}	2.7×10^{-5}
CESO (20); PEG (45)	8.2×10^{-8}	6.1×10^{-5}	1.8×10^{-4}	2.9×10^{-4}
CESO (10); PEG (35); PC(35)	1.5×10^{-7}	5.5×10^{-5}	1.4×10^{-4}	2.9×10^{-4}
CES (65)		1.0×10^{-5}	3.4×10^{-5}	1.2×10^{-4}
CES (26); PC (30)	3.5×10^{-7}	6.4×10^{-5}	2.5×10^{-4}	6.5×10^{-4}
CES (30); PEG (30)		1.7×10^{-5}	4.2×10^{-5}	9.3×10^{-5}
PS (50)		6.5×10^{-7}	1.9×10^{-6}	4.0×10^{-6}
PEG (50)		2.3×10^{-7}	1.6×10^{-6}	6.9×10^{-6}
PEG (25); PC (25)		7.3×10^{-6}	1.3×10^{-6}	1.7×10^{-5}
EC (35); DEC (35)		3.3×10^{-5}	8.1×10^{-5}	1.5×10^{-4}
BL (60)		3.1×10^{-5}	9.0×10^{-5}	2.3×10^{-4}
AAN (60)		6.8×10^{-7}	2.5×10^{-6}	5.2×10^{-6}
BN (60)		2.7×10^{-7}	8.9×10^{-7}	1.1×10^{-6}
MCA (60)		1.8×10^{-8}	3.5×10^{-7}	7.2×10^{-7}

[a] list of abbreviations is shown on pages 10 an 11.

Table 5. Conductivity of gel electrolytes based on polymer **III** of n = 4 containing various additives

Solvent	Additive	Ionic Conductivity		
(wt. %)	(wt. %)	25 °C	50 °C	90 °C
PC (30); DMSO (20)	glass wool	1.2×10^{-5}	2.7×10^{-5}	5.3×10^{-5}
-------	MAS[a] (50)	4.1×10^{-8}	8.8×10^{-8}	1.3×10^{-7}
PC (25)	MAS[a] (25)	1.3×10^{-8}	8.2×10^{-8}	1.5×10^{-7}
PC (30); DMSO (10)	MAS[a] (25)	6.2×10^{-6}	1.5×10^{-5}	1.5×10^{-4}
PC (30); PEG (20)	MAS[a] (25)	2.1×10^{-5}	5.6×10^{-5}	1.8×10^{-4}
PC (40); DMSO (30)	$LiClO_4$ (8)	9.2×10^{-4}	2.4×10^{-3}	5.5×10^{-3}
DESO (60)	$LiClO_4$ (10)	9.8×10^{-4}	3.4×10^{-3}	5.6×10^{-3}
PEG (78)	$LiClO_4$ (5)	2.9×10^{-4}	5.8×10^{-4}	1.0×10^{-3}

[a] formula on page 12

Figure 1

Simplified schema of the cell for impedance measurements

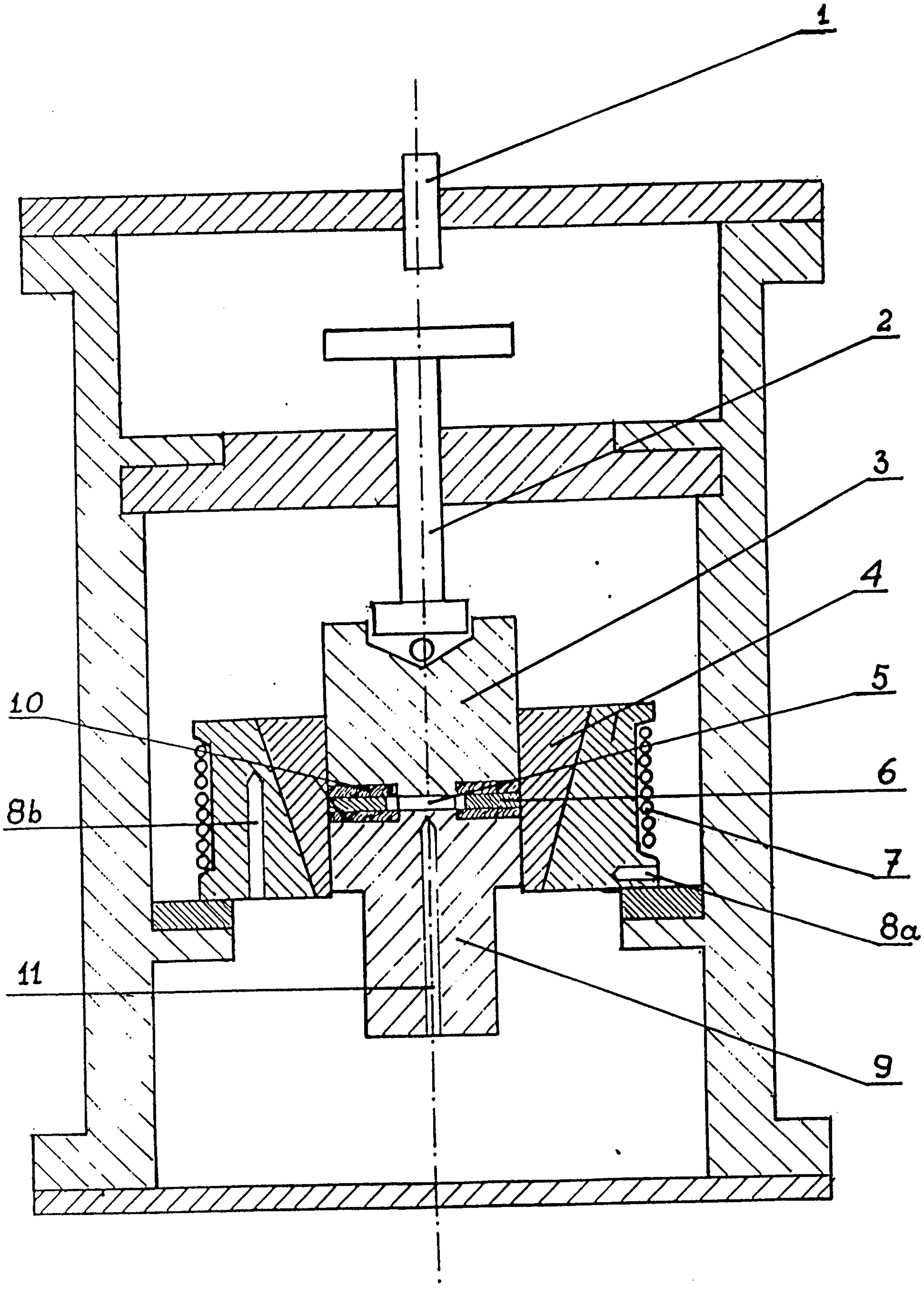

Figure 1

Simplified schema of the cell (vessel) for impedance measurements

1. To vacuum pump / inert gas line. The cell is gas-tight and on demand the inner space (in contact with the sample) can be either evacuated or filled with an inert gas.
2. Load screw.
3. Upper electrode block. Upper and lower electrodes with 0.5 cm^2 discs exposed for measurement, isolated from spacers and chassis.
4. Copper heating block.
5. Sample - polymer foil or complete cell.
6. Spacer. Movable rings controlling the thickness of the sample in the 100 μm - several mm range.
7. Heater.
8. a) and b): Pt 100 resistance thermometers - coupled with a PID type temperature controller.
9. Lower electrode block.
10. Isolating rings.
11. Pt 100 resistance thermometer - direct measurement under the sample.

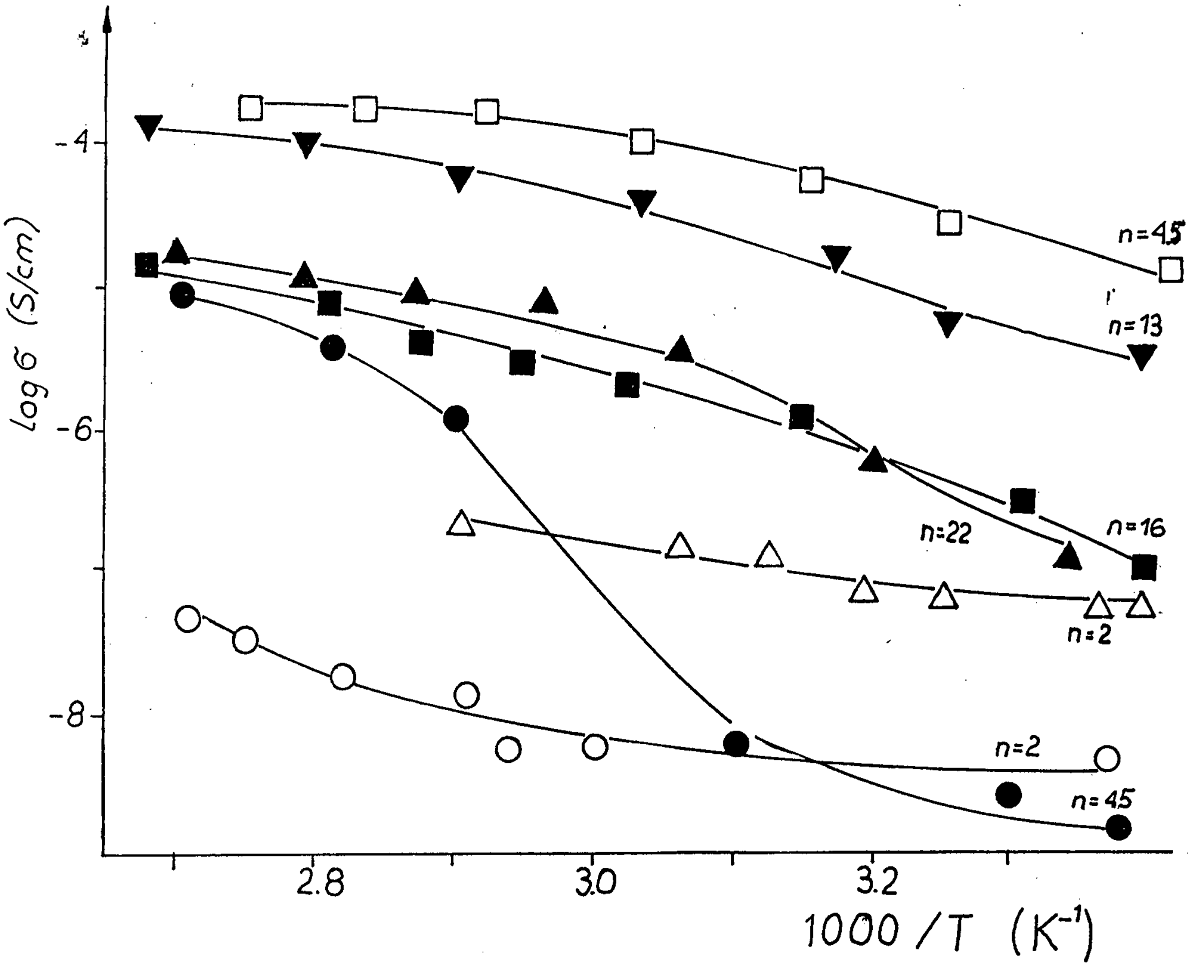

Fig. 2. Ionic conductivity versus reciprocal temperature for comb-like lithium polyelectrolytes (samples of different molecular weight, M_n, of PEG in the side chain). (o) - M_n = 106 g/mol, n = 2, terminated with OH; (Δ) - M_n = 120 g/mol, n = 2, terminated with CH_3; (□) - M_n = 200 g/mol, n = 4.5, terminated with OH; (▾) - M_n = 600 g/mol, n = 13, terminated with OH; (▴) - M_n = 1000 g/mol, n = 22, terminated with OH; (■) - M_n = 750 g/mol, n = 16, terminated with CH_3; (•) - M_n = 2000 g/mol, n = 45, terminated with OH.

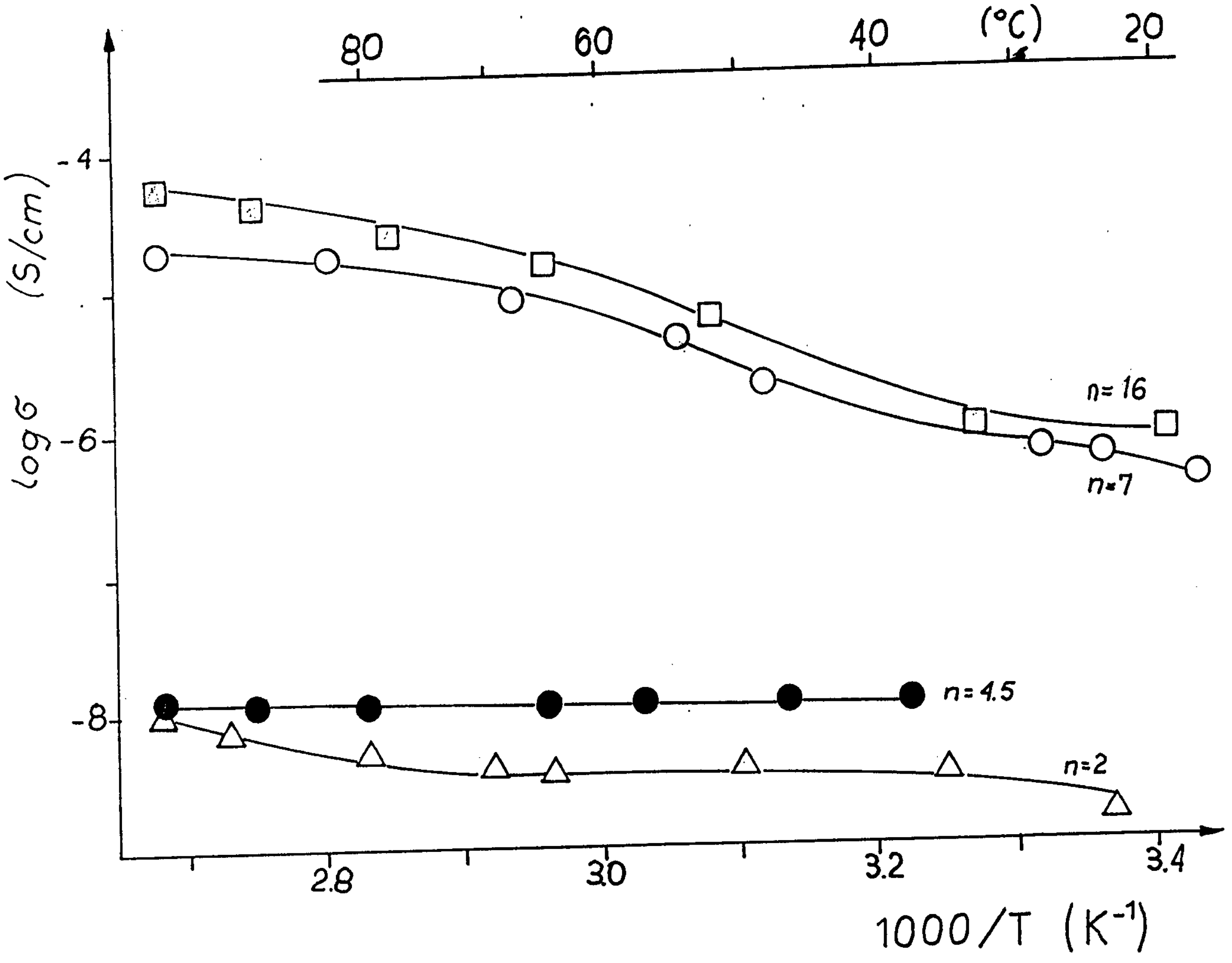

Fig. 3. Ionic conductivity versus reciprocal temperature for comb-like sodium polyelectrolytes (samples of different molecular weight, M_n, of PEG in the side chain). (Δ) - M_n = 120 g/mol, n = 2, terminated with CH_3; (•) - M_n = 200 g/mol, n = 4.5, terminated with OH; (o) - M_n = 350 g/mol, n = 7, terminated with CH_3; (∇) - M_n = 750 g/mol, n = 16, terminated with OH.

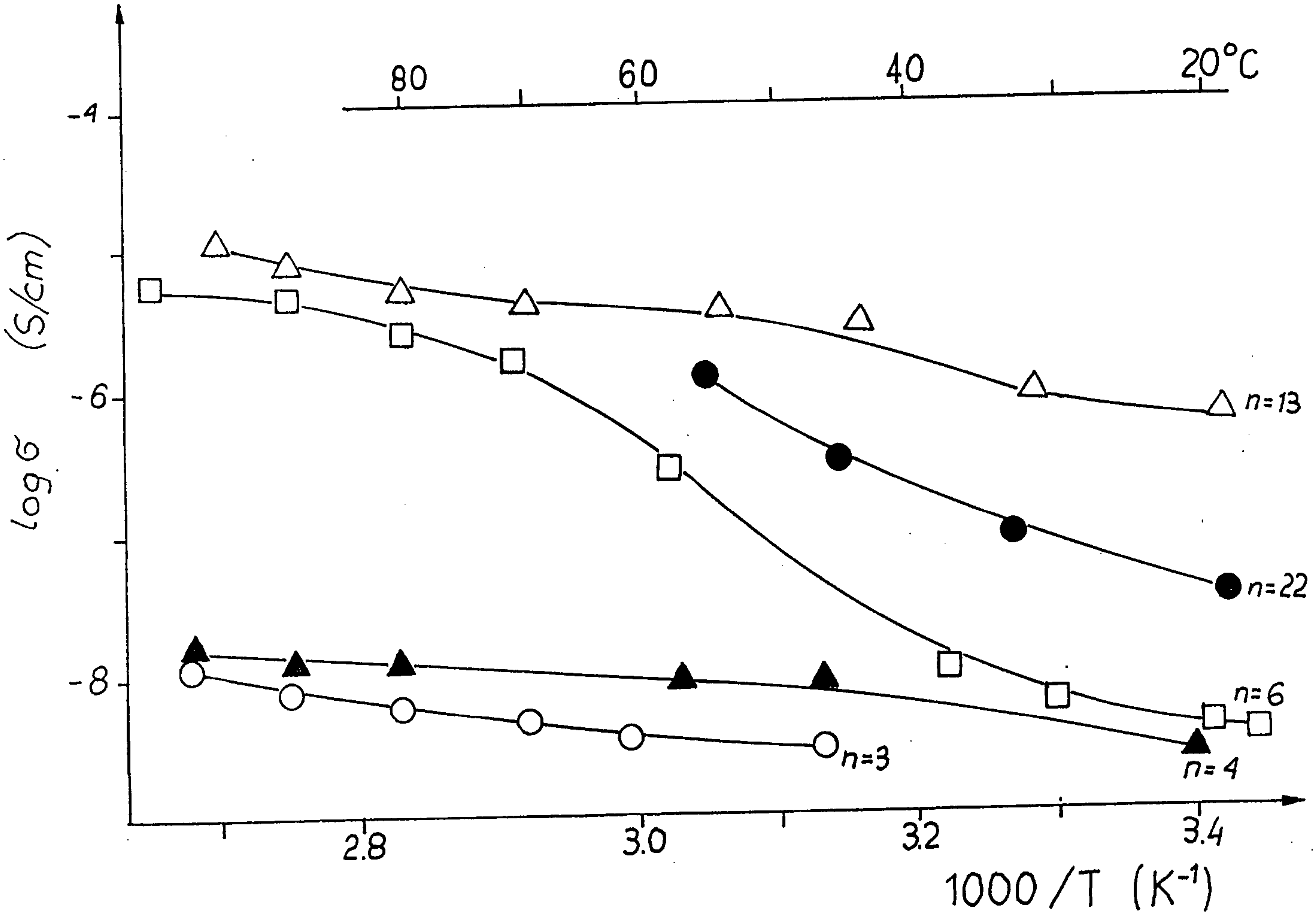

Fig. 4. Ionic conductivity versus reciprocal temperature for comb-like potassium polyelectrolytes (samples of different molecular weight, M_n, of PEG in the side chain). (o) - M_n = 150 g/mol, n = 3, terminated with OH; (▲) - M_n = 200 g/mol, n = 4.5, terminated with OH; (□) - M_n = 300 g/mol, n = 6, terminated with OH; (Δ) - M_n = 600 g/mol, n = 13, terminated with OH; (●) - M_n = 1000 g/mol, n = 22, terminated with OH.

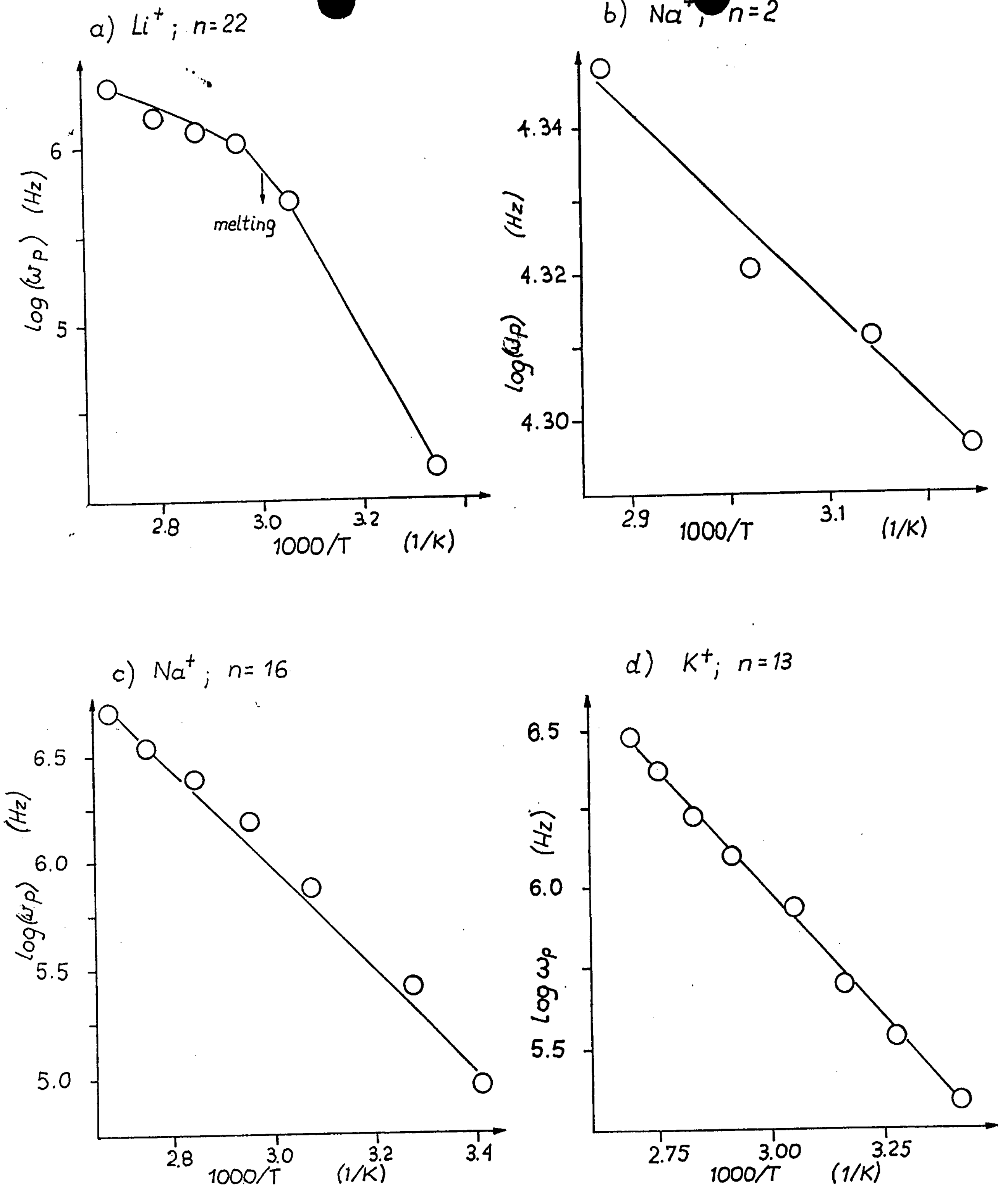

Fig. 5. Dependence of log hopping frequency (ω_p) on reciprocal temperature for some solid electrolytes based on polymer **I**: a) K^+, n = 22, b) Na^+, n=2; c) Na^+, n = 16; K^+, n = 13.

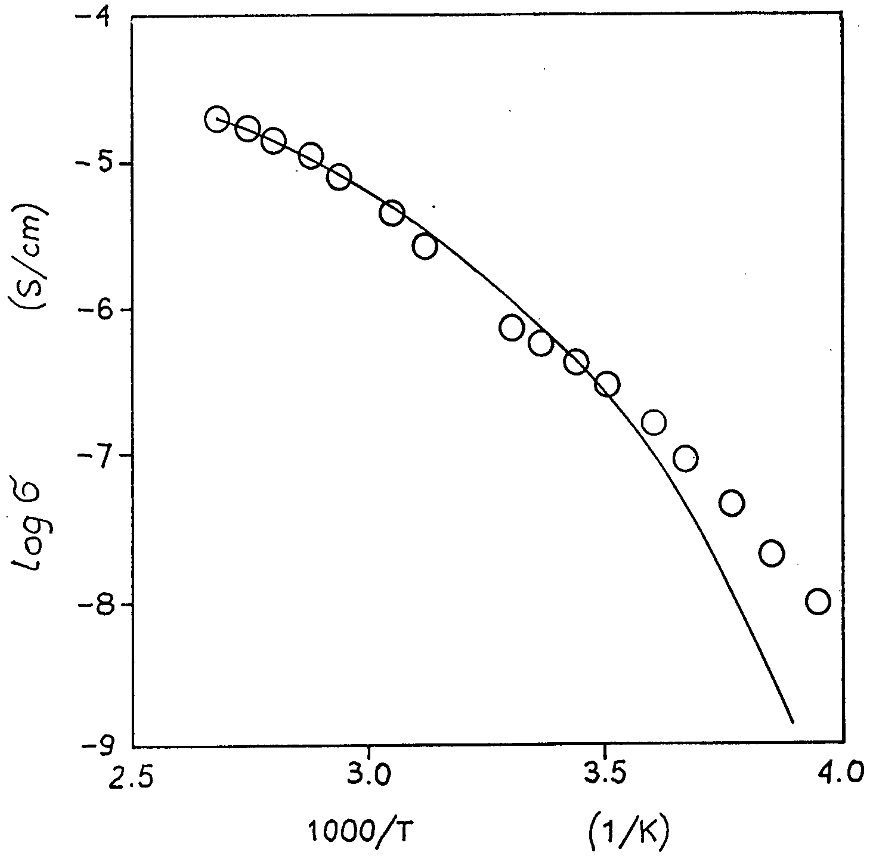

Fig. 6. Ionic conductivity versus reciprocal temperature for solid Na^+ electrolyte of n = 7. Solid line - theoretical VTF curve for $\sigma_o = 2.01\times10^{-2}$ $S\times K^{0.5}\times cm^{-1}$, B = 641 K^{-1} and T_o = 210 K.

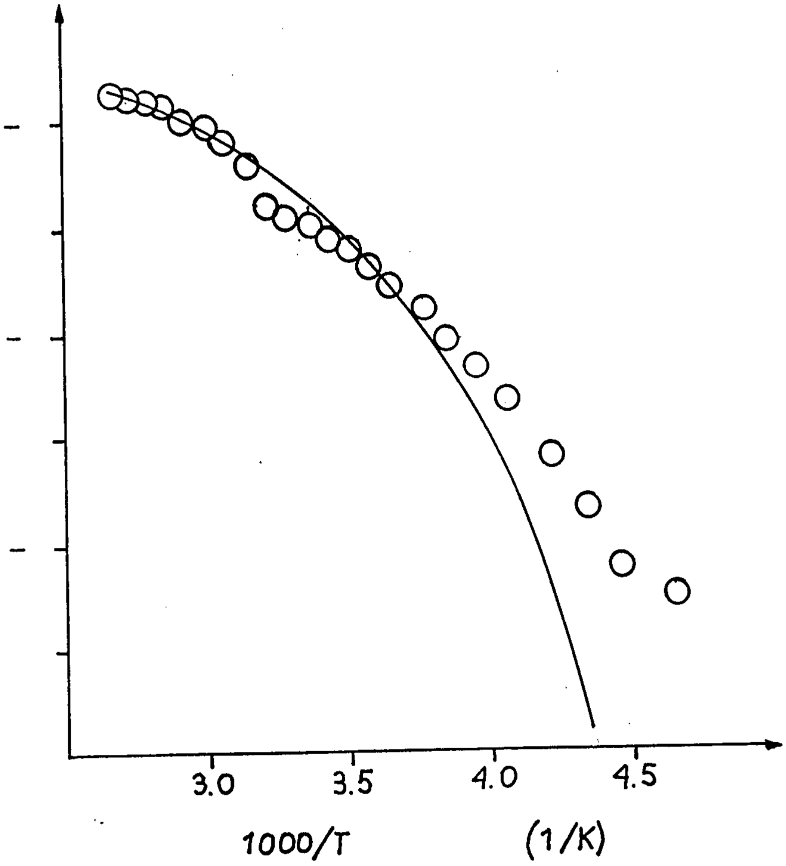

Fig. 7. Temperature dependence of conductivity for a lithium gel electrolyte based on polymer **III** of n = 4 containing 15 wt. % of DMSO. Full line denotes the theoretical VTF curve with the following parameters σ_o = 12×10^{-2} $SxK^{0.5}xcm^{-1}$, B = 613 K^{-1}, T_o = 195 K, T_g from DSC = 198 K.

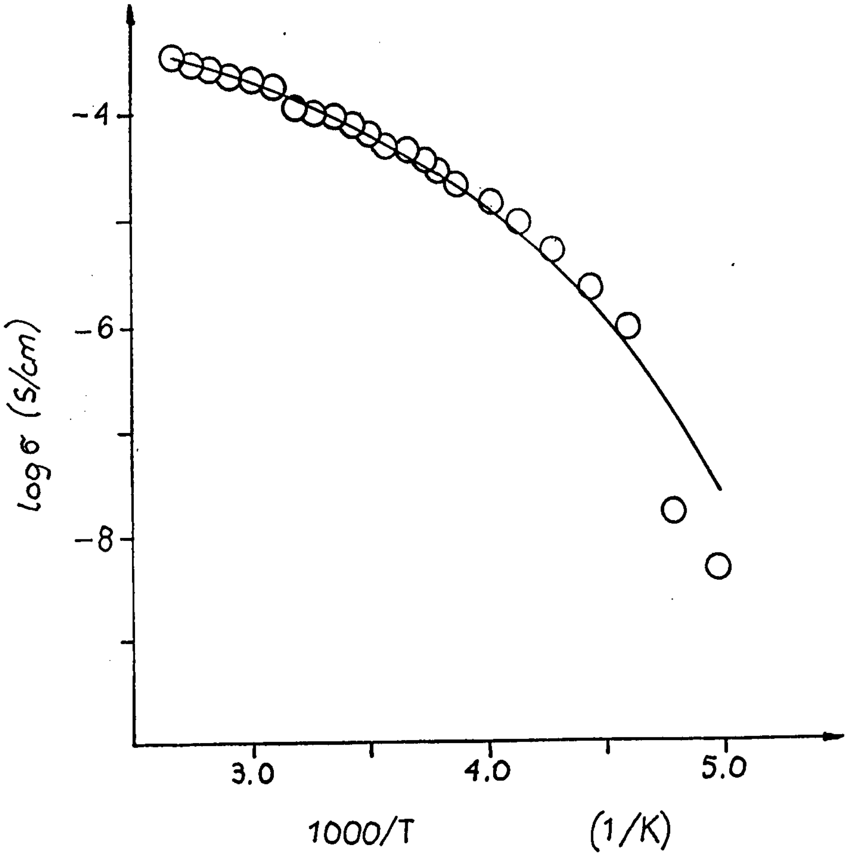

Fig. 8. Temperature dependence of conductivity for a lithium gel electrolyte based on polymer **III** of n = 4 containing 8 wt. % of DMSO and 70 wt. % of propylene carbonate. Full line denotes the theoretical VTF curve with the following parameters σ_o = 19.7×10^{-2} S×$K^{0.5}$×cm^{-1}, B = 597 K^{-1}, T_o = 152 K, T_g from DSC = 166 K.

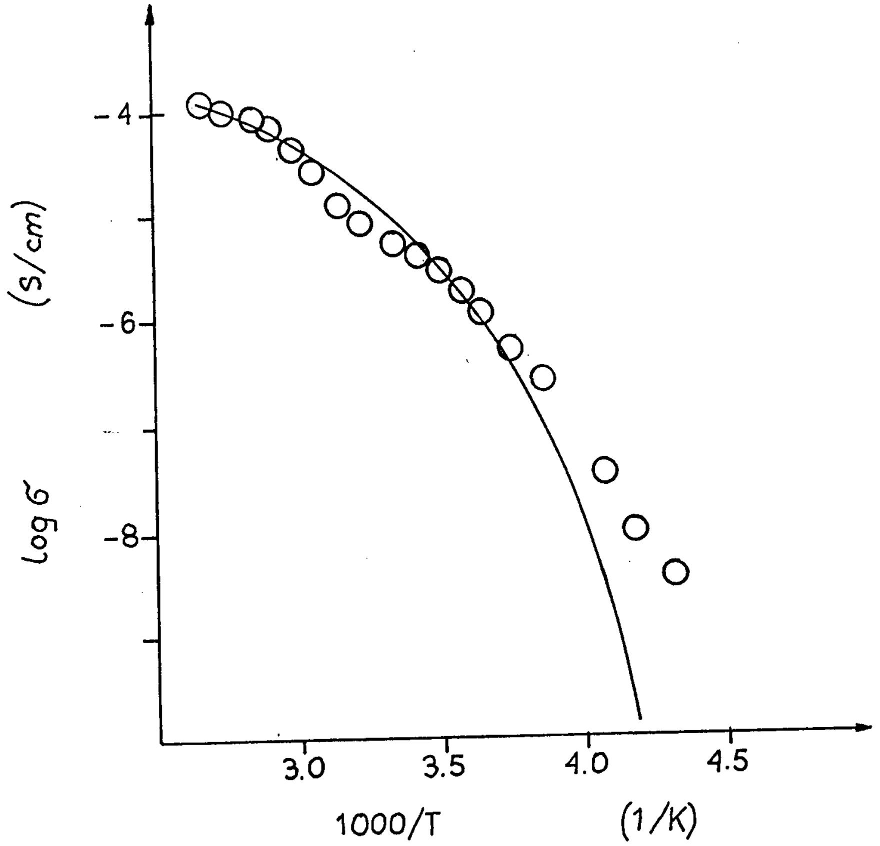

Fig. 9. Temperature dependence of conductivity for a sodium gel electrolyte based on polymer **III** of n = 4 containing 20 wt. % of DMSO. Full line denotes the theoretical VTF curve with the following parameters σ_o = 10x10^{-2} Sx$K^{0.5}$xcm^{-1}, B = 649 K^{-1}, T_o = 200 K, T_g from DSC = 203 K.

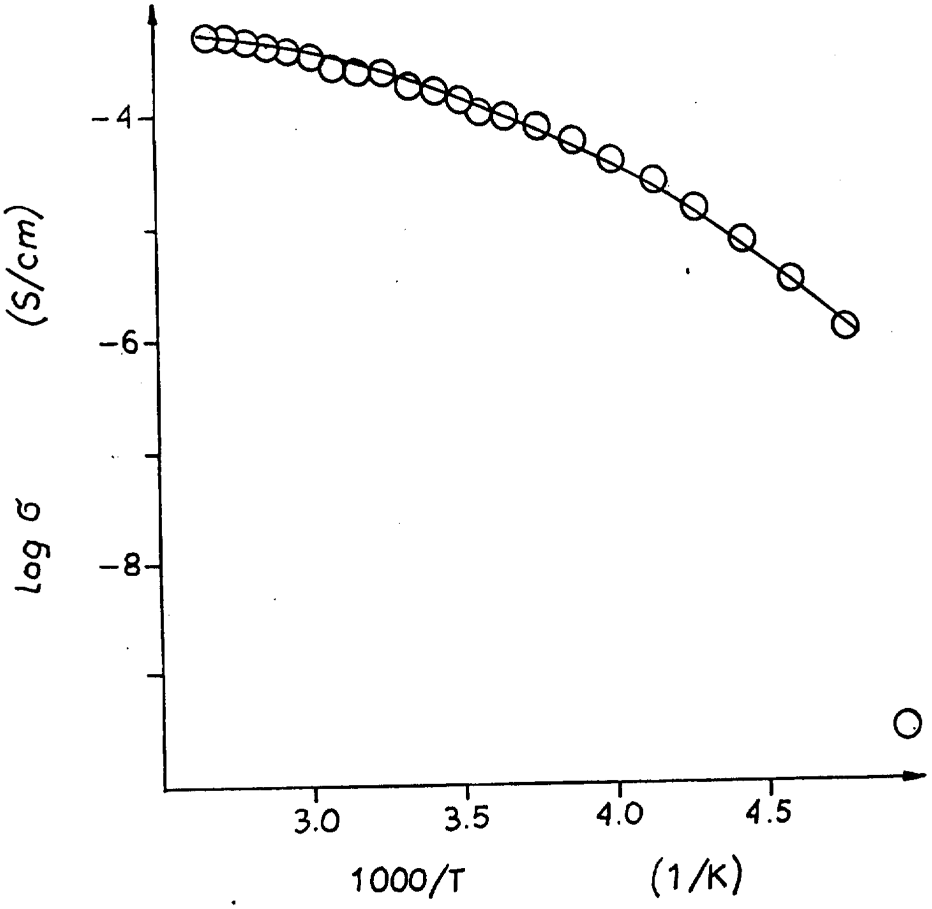

Fig. 10. Temperature dependence of conductivity for a sodium gel electrolyte based on polymer **III** of n = 4 containing 4 wt. % of DMSO and 70 wt. % of propylene carbonate. Full line denotes the theoretical VTF curve with the following parameters σ_o = 13×10^{-2} $SxK^{0.5}xcm^{-1}$, B = 588 K^{-1}, T_o = 143 K, T_g from DSC = 194 K.