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POLYMER GEL ELECTROLYTES BASED ON GLYCIDYL METHACRYLATE HOMOPOLYMER AND COPOLYMERS

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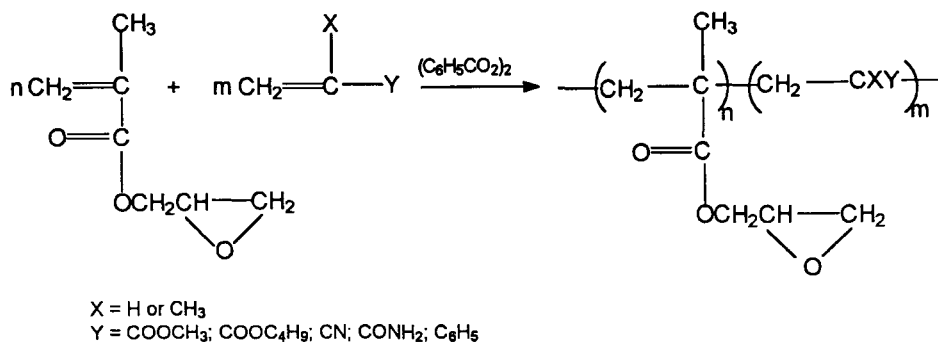
ABSTRACT

Gel electrolytes have been prepared by two-step polymerization or copolymerization of glycidyl methacrylate (2,3-methoxypropyl methacrylate) in the presence of LiClO_4 and propylene carbonate or other organic solvents. In the first step a free-radical initiator was used and then the linear polymers were crosslinked by means of SO_2 or BF_3 . The conductivity of the electrolytes obtained was studied by means of impedance spectroscopy. It was found that several of the electrolytes exhibit ambient temperature conductivities exceeding 10^{-3} S/cm and retain conductivities as high as 10^{-5} S/cm up to -50°C . The temperature dependence of conductivity for several samples above room temperature can be analyzed according to the classical Arrhenius plot, whereas at subambient temperature they exhibit Vogel–Tammann–Fulcher-type behavior. The conductivity and activation energy values obtained indicate that charge transfer occurs mainly in the liquid phase. The conducting properties of the electrolytes studied strongly depend on the polymer and salt concentration and the kind of solvent used, but are scarcely affected by changes in the structure of the polymer network.

INTRODUCTION

Ternary gels comprising polymers, organic solvents, and alkali metal salts have been recently intensively studied in respect to their potential application as electrolytes in lithium batteries and other electrochemical devices. One of the ap-

proaches has involved the application of linear macromolecules capable of forming three-dimensional networks around the solvent due to the interactions between crystalline regions. Among them, systems containing polyacrylonitrile as a matrix for conducting solutions have attracted the greatest attention [1-3]. However, chemically crosslinked polymers are used for this purpose much more often. This last strategy involves radiation crosslinking of linear polymers [mainly poly(ethylene oxide)] or free-radical polymerization of bi- and trifunctional acrylic type monomers in the presence of appropriate solvents and salts [4-6]. Several systems containing 70-80 wt% of the solvent still exhibit good mechanical properties, and their ambient conductivity is in the 10^{-4} to 10^{-3} S/cm range, i.e., a few orders of magnitude higher than those reported for solid polymeric electrolytes. In this paper we described the conducting properties of a new family of gel electrolytes obtained in two-step polymerizations according to different mechanisms. In the first step a solution of the homopolymer or copolymers of glycidyl methacrylate (GMA) and lithium salts were obtained in the presence of a free-radical initiator.



In the second step the oxirane rings were polymerized by means of cationic initiators, SO_2 or $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$.

EXPERIMENTAL

Materials

Monomers, ethylene carbonate, propylene carbonate, and benzoyl peroxide (reagent grade) were purified by distillation or crystallization. LiClO_4 and LiCF_3SO_3 (Aldrich) were dried under vacuum for 24 hours at 150 and 125°C, respectively. BF_3 etherate (Aldrich) was dissolved in propylene carbonate to form a 20-wt% solution. Sulfur dioxide (Aldrich) was kept over P_2O_5 and distilled before use. Cyclic sulfites were obtained from SO_2 and ethylene oxide, propylene oxide, or epichlorohydrin according to procedures described elsewhere [7, 8].

Gel Preparation

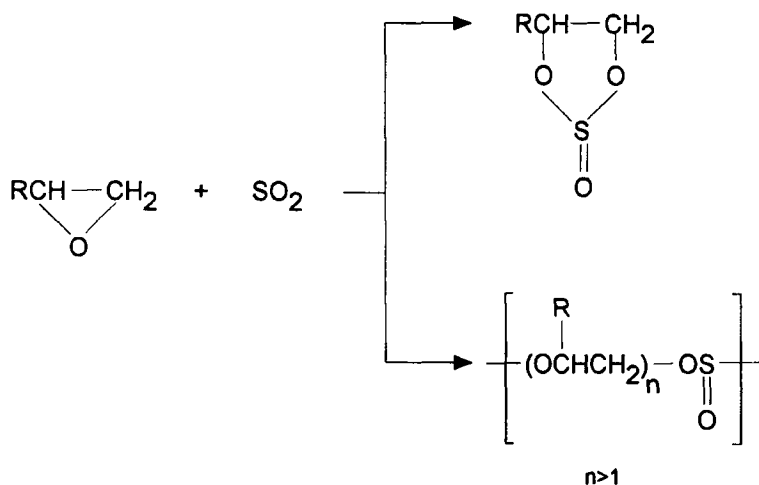
Monomers (0.3-0.5 g), salt solution in the solvent studied, and benzoyl peroxide were placed in a glass pressure ampule and heated for 3 hours at 70°C. The ampule was then cooled to -78°C, and SO_2 and BF_3 etherate were added. The SO_2/GMA weight ratio equals ~ 1 , and that of of BF_3 etherate/GMA ~ 0.005 . The

crosslinking in the presence of SO_2 was carried out at 50°C and in that of BF_3 at ambient temperature. In some experiments with BF_3 an additional 10 cm^3 acrylonitrile was added and after about 30 seconds the reaction mixture was poured onto Teflon plates, which enabled films to be obtained. In other cases the gels obtained were pressed into films between electrodes. The conductivities of the samples were measured by impedance spectroscopy. Experiments were performed in the frequency range from 5 Hz to 500 kHz by applying stainless steel blocking electrodes. The sample holder was placed in an evacuated glass vessel and vacuum pumped for 2 hours prior to measurements. The electrode area was equal to 1.5 cm^2 , and the sample thickness was $\sim 1\text{ mm}$. The samples were kept for 0.5 hour at each experimental temperature.

RESULTS AND DISCUSSION

The polymerization of GMA in propylene carbonate at 70°C at 50–80 wt% of the solvent in the presence of 0.5 wt% benzoyl peroxide is complete after about 90 minutes. The viscous solutions obtained are completely homogeneous. When the reactions are carried out in the presence of LiClO_4 (8 wt%) in systems containing 50 and 60 wt% propylene carbonate, spontaneous crosslinking proceeds, leading to the formation of homogeneous gels. The mechanism of this reaction has not been established, but it is known that at elevated temperature LiClO_4 may initiate the crosslinking of oligomers with a high epoxide groups concentration [9]. However, if the solvent constitutes 70 wt% or more of the reaction mixture, crosslinking does not proceed, even upon heating the sample at 70°C for 100 hours. In the presence of SO_2 (~ 1.2 molar excess in relation to the epoxide group), the crosslinking can be carried out at 50°C . Homogeneous and transparent gels are formed after 12–24 hours, depending on the monomer concentration. A rise in the reaction temperature above 60°C usually resulted in a slight coloring of the reaction mixture. Elemental analysis of the polymer washed off the solvent and LiClO_4 indicates a 43 mol% content of SO_2 monomeric units.

From studies on the reaction of oxiranes with SO_2 it is known that they lead to the formation of cyclic sulfites and linear poly(ether sulfite)s [7, 8, 10]:



In the IR spectrum of the polymer obtained, bands characteristic for cyclic sulfites mainly occur ($\nu\text{S}=\text{O} \approx 1200$; $\nu\text{C}-\text{O} \approx 1005, 910$; $\nu\text{S}-\text{O} \approx 740$).

Studies on the model reactions using glycidyl acetate instead of poly(glycidyl methacrylate) indicated that under analogous conditions the conversion of oxirane rings is almost complete and about 90% of it takes place in the cyclization. The SO_2 content in the linear products did not exceed 10 mol% ($n \geq 10$). Thus, one can also expect that under the gelling conditions most of the oxirane rings are consumed for the formation of cyclic products and no more than 20% are involved in cross-linking.

In systems containing more than 80 wt% propylene carbonate, phase separation is clearly observed. Gels containing up to 80 wt% of the solvent are homogeneous and they can be easily pressed to thin films, simultaneously maintaining dimensional stability under the conductivity measurements conditions.

In Table 1 are presented the conductivities of this type of electrolytes at 25°C. As can be seen, at a constant concentration of the salt the conductivity clearly increases with an increase in the solvent content. For gels containing 80 wt% propylene carbonate, the conductivity reaches values of $\sim 2 \times 10^{-3}$ S/cm at salt concentrations of 5–8 wt%. As can be seen from Fig. 1, the maximum of specific conductance for gels is about 2 times lower than those reported for pristine solutions of LiClO_4 in propylene carbonate [11]. It is well known that in electrolyte solutions

TABLE 1. Conductivity and Activation Energies for Gels Based on Poly-(Glycidyl Methacrylate) [Poly(GMA)] Polymers Crosslinked with Sulfur Dioxide^a

Sample	Polymer	PC, wt%	LiClO_4 , wt%	σ_{25} , S/cm	E_a , kJ/mol
1	Poly(GMA)	60	8	1.8×10^{-4}	VTF ^f
2		70	8	2.6×10^{-4}	26.1
3		80	8	2.2×10^{-3}	20.7
4		80	6	2.1×10^{-3}	17.6
5		80	5	1.7×10^{-3}	
6		80	4	1.1×10^{-3}	25.6
7		80	3	6.9×10^{-4}	21.4
8		80	8 ^b	3.1×10^{-4}	17.7
9		80 ^c	8	2.2×10^{-3}	10.2
10		70 ^d	8	6.3×10^{-5}	32.2
11	Poly(GMA-co-methyl acrylate)	80	8	1.8×10^{-3}	22.1
12	Poly(GMA-co-acrylonitrile) ^e	80	8	2.0×10^{-3}	VTF
13	Poly(GMA-co-acrylamide) ^e	80	8	3.3×10^{-3}	VTF
14	Poly(GMA-co-styrene) ^e	80	8	No gel was formed	

^aSolvent: propylene carbonate (PC); salt: LiClO_4 .

^b $\text{CF}_3\text{SO}_3\text{Li}$ was used as the salt.

^cSolvent: propylene sulfite.

^dSolvent: 3-chloropropylene sulfite.

^eComonomer mole ratio = 1:1.

^fVTF: Vogel-Tammann-Fulcher.

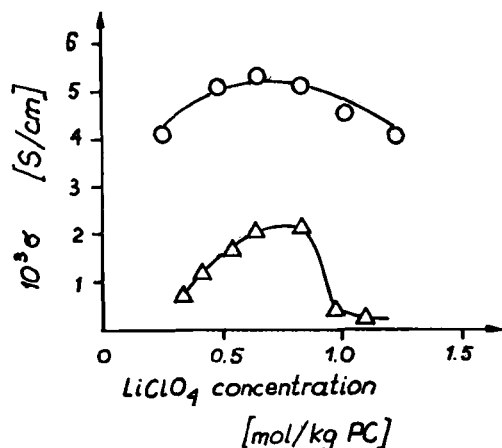


FIG. 1. Comparison of specific conductivity of LiClO_4 in propylene carbonate (PC) solution (○) (from Ref. 11), and in polymer gel electrolyte (△) containing poly(glycidyl methacrylate) and PC (Samples 1-7, Table 1).

the maximum specific conductance is observed at a certain salt concentration. This follows from the competition of two factors: a conductance-increasing term caused by an increase in the density of free ions and a conductance-decreasing term resulting from the lowering of ionic mobility as the electrolytes concentration increases. In gel electrolytes the mobility of ions is additionally affected by the presence of polymer chains. In the range of the gel compositions studied, conductivity decreases monotonically with increasing polymer concentration (Fig. 2).

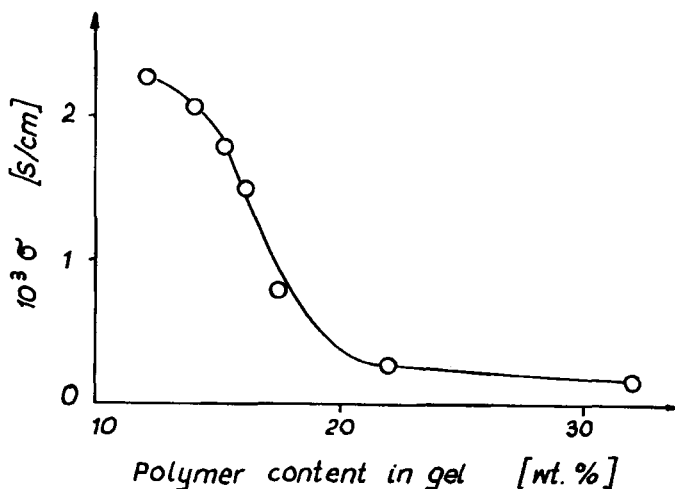


FIG. 2. Dependence of specific conductivity on polymer content in gel electrolytes comprising poly(glycidyl methacrylate), propylene carbonate, and LiClO_4 (Samples 1-7, Table 1).

Gels of high ambient conductivity and good dimensional stability can also be prepared in a similar manner from equimolar copolymers of glycidyl methacrylate with some acrylic-type monomers like methyl acrylate, acrylonitrile, and acrylamide (Table 1). However, due to the lower concentration of oxirane groups, the gelation by means of SO_2 occurs slower than in an analogous reaction with poly(glycidyl methacrylate), and at 50°C the reaction time was about 24 hours. The crosslinking ability also depends on the kind of comonomer used; for example, no network was obtained in systems with equimolar poly(glycidyl methacrylate-*co*-styrene).

The crosslinking of glycidyl methacrylate copolymers occurs very fast in the presence of BF_3 etherate. In order to obtain homogeneous gels it was necessary to work with solutions of the initiator (~ 20 wt% propylene carbonate). By means of IR spectroscopy it was found that at room temperature in the presence of 0.1 wt% BF_3 all the oxirane rings are practically consumed after about 5 minutes.

As can be seen from Table 2, the various copolymers crosslinked by BF_3 form gels of ambient temperature conductivity exceeding 10^{-3} S/cm at 80 wt% propylene carbonate content and 10^{-4} S/cm at that of 70 wt%. Due to the high activity of the initiator in this system, the crosslinking also proceeds in the case of copolymers with styrene, which did not undergo crosslinking by means of SO_2 .

From a comparison of the data for equimolar copolymers with methyl acrylate, acrylonitrile and acrylamide presented in Tables 1 and 2, it appears that the mode of crosslinking has hardly any effect on the conductivity of the gels obtained.

One can also observe that the kind of comonomer used has a negligible effect on the conductivity of gels, except the systems containing acrylamide monomeric units that seem to improve the conducting properties of the gel electrolytes. A change in the dielectric constant due to the presence of strongly polar $[\text{O}=\text{C}-\text{NH}_2 \leftrightarrow ^-\text{O}-\text{C}=\text{NH}_2^+]$ amide groups in the polymer matrix may be the reason for this. However, in general, the effect of polar substituents is much smaller than that observed in solid polymeric electrolytes based on poly(ethylene oxide) blends [12-

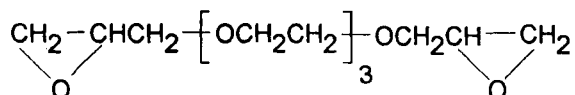
TABLE 2. Conductivity of Gels Based on Glycidyl Methacrylate (GMA) Copolymers with Monomers A of Various Polarities^a

Sample	Comonomer A	GMA contribution in copolymer, mol%	Conductivity at 298 K, S/cm	E_a , kJ/mol
15	Methyl acrylate	50	2.0×10^{-3}	22.1
16	Butyl acrylate	50	2.2×10^{-3}	18.4
17	Methyl methacrylate	30	2.1×10^{-3}	17.1
18	Acrylamide	50	3.5×10^{-3}	
19	Acrylonitrile	50	2.2×10^{-3}	
20	Styrene	60	1.8×10^{-3}	17.6
21	Poly(ethylene glycol) diglycidyl ether	55	1.9×10^{-3}	

^a LiClO_4 : 8 wt%; propylene carbonate (PC): 80 wt%; crosslinking agent: BF_3 etherate (0.1 wt%) (20% solution in PC).

14] or in networks plasticized with a small amount of low molecular weight polyethers [15].

It is interesting that the glycidyl methacrylate homopolymer does not form gels with propylene carbonate and LiClO_4 after crosslinking with BF_3 . The formation of a brittle powder and separation of the solvent occurred in this reaction. This is probably connected with the too high crosslinking density, which results in network segments too short to successfully bond the solution of the salt and assure elasticity of the system. As was mentioned, during crosslinking by means of SO_2 only a small part of the oxirane rings were used for network formation, which assured an appropriate length of the linear segments between the network nodes. In systems with BF_3 an appropriate distance between the network nodes which permits stable elastic gels to be obtained has to be maintained by the presence of comonomers. We found that it is sufficient to use 15 mol% glycidyl methacrylate monomeric units in copolymers with other acrylic monomers to obtain stable gels after crosslinking with BF_3 . The crosslinking density can also be reduced by copolymerization of the glycidyl methacrylate homopolymer with diglycidyl compounds, in which the epoxide groups are separated from each other by an elastic segment of the following structure:



The copolymerization proceeds in the crosslinking step. As can be seen from Table 2, this type of gels can also exhibit conductivity over 10^{-3} S/cm at 25°C . When using $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$, gels can be obtained directly in the form of films. In

TABLE 3. Conductivity and TGA Results of Gels Based on Glycidyl Methacrylate Copolymers with Butyl Acrylate^a

Sample	Solvent	Plasticizer contribution, wt%	Conductivity at 298 K, S/cm	Mass loss, wt%, at			E_a , kJ/mol
				60°C	100°C	150°C	
22	Propylene carbonate	72	1.8×10^{-4}	1.1	6.9	23.0	31.8
23	Propylene carbonate/ propylene sulfite (1:1)	72	5.3×10^{-4}	1.2	7.2	25.3	27.5
24	Propylene carbonate/ ethylene carbonate (1:1)	70	4.8×10^{-4}	1.2	7.2	27.7	19.1
25	Propylene carbonate/ ethylene carbonate (1:1)	70 ^b	3.6×10^{-4}	0.8	5.3	20.3	16.3

^aThe gels were doped with 8 wt% LiClO_4 ; $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ was used as the crosslinking agent.

^b $\text{CF}_3\text{SO}_3\text{Li}$ was used as the salt.

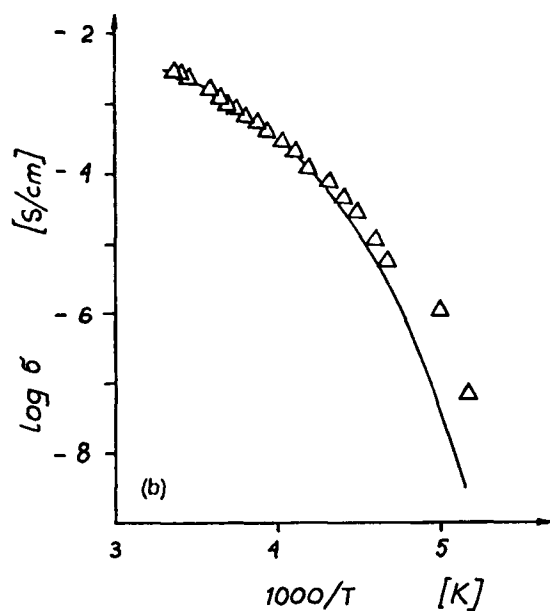
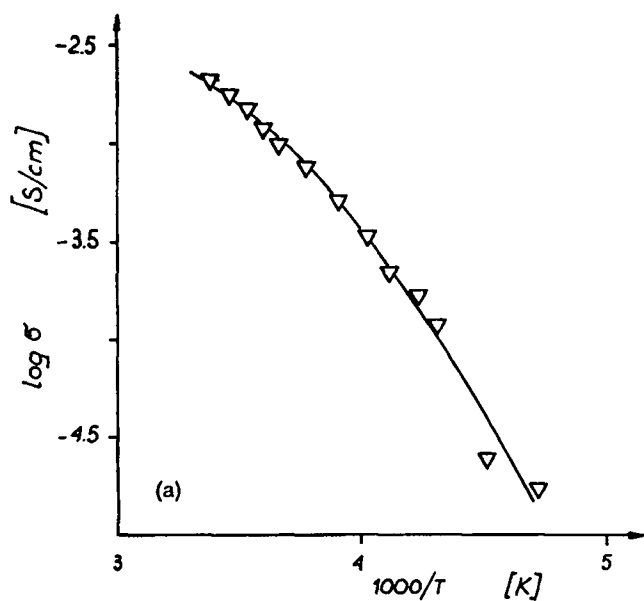


FIG. 3. Log conductivity–reciprocal temperature plots for (a) Sample 3, Table 4; (b) Sample 5, Table 4; (c) Sample 12, Table 4. Full lines denote theoretical curves for the VTF equation with parameters given in Table 4.

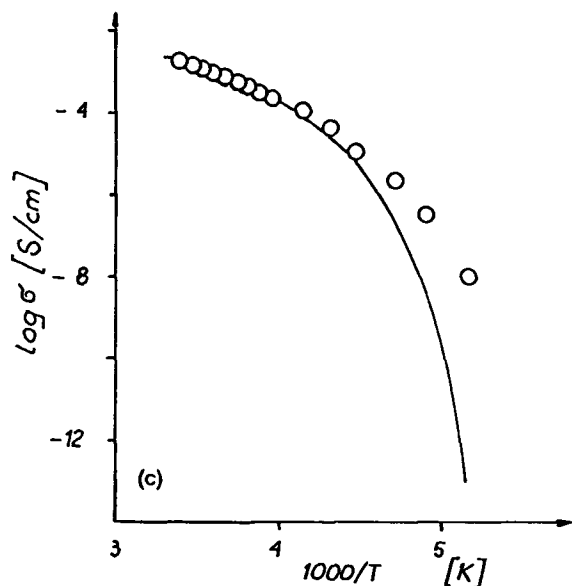


FIG. 3 (continued).

Table 3 are presented a number of such films obtained and the mass losses of these films at several chosen temperatures. The thermal stability of these samples up to about 60°C can be assumed to be good. At elevated temperature the mass loss is slightly larger than that reported for commonly used materials based on bi- and trifunctional methacrylates in a one-step procedure (2–3 wt% at 100°C) [5].

The temperature dependence of conductivity in the 20–80°C range for several samples based on homo- and copolymers of glycidyl methacrylate can be analyzed according to the Arrhenius plot where:

$$\sigma = A \exp(-E_a/kT)$$

The activation energy values calculated from this equation are presented in Tables 1–3. It can be noticed that for most samples of high propylene carbonate content, E_a reaches values in the 17–22 kJ/mol range. These values are very close to those reported for solutions of LiClO_4 in propylene carbonate [11] (for example ~16 kJ/mol for the optimum salt concentration at 15°C). For comparison, in solid polymeric electrolytes the E_a values are usually in the 60–100 kJ/mol range. Thus, the activation energies obtained indicate that charge transfer occurs mainly in gel electrolytes in the solvent phase, which is in agreement with the commonly accepted opinion. The exact nature of the polymer–solvent–salt is complicated and not easily understood. One possibility is that the polymer net serves only as a frame that provides the system with dimensional stability and can be treated as a dispersed phase that increases the viscosity of the system (for example, according to Einstein's suggestion [16] the viscosity of a colloidal suspension should increase linearly with an increase in the volume fraction of the dispersed particles). On the other hand, the gels can be treated as plasticized networks, and recent calculations presented by Farrington [17] showed that in such a case the polymer chain may somewhat contribute to ionic transportation. Assuming this model, it can be expected that conduc-

tivity-temperature plots will be described by free volume or configurational entropy-dependent parameters. We found that the conductivity data for subambient temperature tend to be non-Arrhenius (Fig. 3) and are best analyzed using the Vogel-Tammann-Fulcher (VTF) equation:

$$\sigma = \sigma_0 \exp(-B/T - T_0)$$

where the preexponential factor σ_0 is proportional to the reciprocal value of the square root of the temperature, B is proportional to the activation energy, and T_0 denotes the thermodynamic glass transition temperature.

A deviation from the theoretical curve is observed at temperatures close to the glass transition temperature. The VTF fit data for several samples are presented in Table 4. It can be observed that the T_0 value calculated from this equation is very close to the T_g value determined by means of DSC (Table 4). Thus, the systems studied do not conform to the Adams-Gibbs [18] configurational entropy model developed for solid systems in which T_0 is predicted theoretically to be 50 K lower than T_g . This suggests that in gel systems of high solvent content the chain movements may affect the ion transportation, but there is no direct relation between ionic mobility and the motion of the polymer network as predicted by the free volume and configurational entropy theories. A plausible explanation is that ion transportation may occur in the systems studied both according to the thermally activated hopping of charge carriers and the mechanism governed by polymer chain movements. This possibility was also postulated by Vincent et al. [19, 20] for some solid electrolytes based on ethylene oxide copolymers. They showed that the temperature dependence for cation diffusion satisfies the Arrhenius equation, whereas the anion diffusion coefficient displayed a temperature dependence according to the VTF equation.

It seems that in systems of high solvent content the participation of the transport mechanism related to the polymer chain motion is smaller than that in solid electrolytes and its importance increases with a lowering of the measurement temperature. However, in some systems, e.g., in electrolytes containing acrylamide or acrylonitrile copolymers, VTF-type plots were observed in the whole temperature range studied (Fig. 4).

The values of the pseudoactivation energy calculated for the gel electrolytes studied are two to three times lower than those reported for solid polymeric electrolytes or salt solutions in liquid oligomeric systems [e.g., 21, 22]. It should be stressed

TABLE 4. VTF Fit Data and T_g Values for Different Gel Electrolytes

Sample	Temperature range, K	σ_0 , $S \cdot K^{0.5} \cdot cm^{-1}$	B , K^{-1}	T_0 , K	T_g , K
3	194-297	3.73	581	162	177
5	201-296	2.79	662	143	176
12	194-295	1.33	432	178	181
18	291-369	1.22	439	174	181
19	291-365	1.92	392	186	188

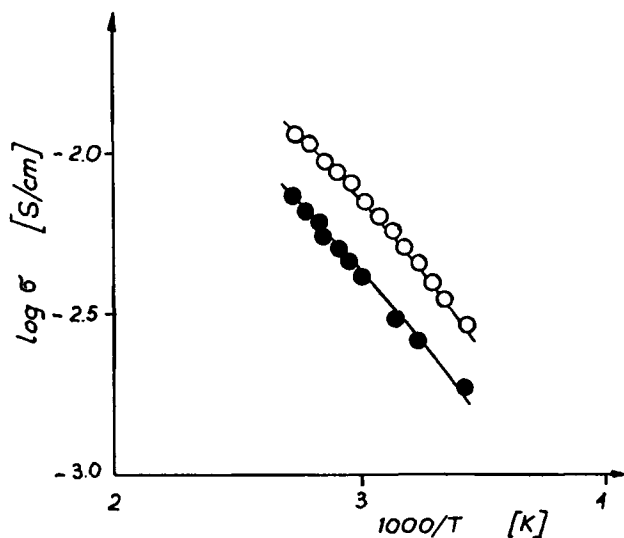


FIG. 4. Log conductivity–reciprocal temperature plots for (●) Sample 18, Table 4; (○) Sample 19, Table 4. Full lines denote theoretical curves for the VTF equation with parameters given in Table 4.

that the conductivity of several gel electrolytes containing 80 wt% propylene carbonate and 4–8 wt% LiClO_4 is still close to 10^{-3} S/cm at 0°C and is higher than 10^{-5} S/cm at -50°C . This permits us to consider them as suitable candidates for practical application in electrochemical devices working at ambient and subambient temperatures.

Attempts have also been made to obtain gels in which cyclic sulfites were used as solvents: ethylene sulfite (1,3,2-dioxathiolane-2-oxide), propylene sulfite (4-methyl-1,3,2-dioxathiolane-2-oxide), and 3-chloropropylene sulfite (4-chloromethyl-1,3,2-dioxathiolane-2-oxide). Studies of LiClO_4 solutions in these solutions indicated that at 20°C the conductivity increases with an increase in the salt concentration up to saturation (Fig. 5). In the case of ethylene sulfite the maximal salt concentration was found to be ~ 1.3 mol/kg and $\sigma_{\max} = 3.0 \times 10^{-2}$ S/cm, for propylene sulfite 1.55 mol/kg and 2.2×10^{-2} S/cm, and for 3-chloropropylene sulfite 1.2 mol/kg and 3.6×10^{-3} S/cm, respectively. The activation energies determined for samples of those concentrations in the 20 – 60°C temperature range are equal to 4.8, 9.9, and 19.1 kJ/mol, respectively. The conductivity of LiClO_4 solutions in ethylene and propylene sulfites are significantly higher and the activation energies significantly lower than those reported for LiClO_4 solutions in propylene carbonate [11]. However, the ambient temperature conductivity of gels obtained from poly(glycidyl methacrylate), LiClO_4 , and propylene sulfite is almost the same as for analogous systems with propylene carbonate (Table 1), but the activation energy of conductivity is significantly lower (10.2 kJ/mol). Gels with 3-chloropropylene sulfite exhibited conductivities one order of magnitude lower. Attempts to obtain stable gels with ethylene sulfite were unsuccessful since slow evaporation of this solvent from the samples occurred even at room temperature. In several

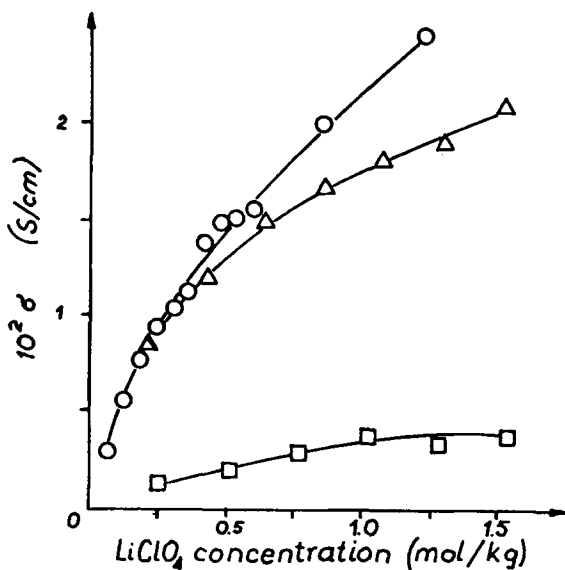


FIG. 5. Specific conductivity for LiClO_4 solutions in (○) ethylene sulfite, (△) propylene sulfite, (□) 3-chloropropylene sulfite.

this solvent from the samples occurred even at room temperature. In several experiments LiCF_3SO_3 was used as the salt, but the gels obtained with this compound exhibited lower conductivity than for analogous systems with LiClO_4 (Tables 1 and 3). In view of the recent work of Prud'homme et al. [23], it seems that ion pairing takes place to a lesser extent in LiClO_4 electrolytes. This results from the higher polarization of the "soft" CF_3SO_3^- anion in comparison to the "hard" ClO_4^- anion.

Preliminary observations showed that other oxiranes having unsaturated $\text{C}=\text{C}$ bonds may also be applied to the formation of gels of high conductivity. For example, by means of SO_2 we obtained gels in a one-step copolymerization with allyl glycidyl ether. The conductivity has been studied of electrolytes comprising 22 wt% copolymer, 8 wt% LiClO_4 and 70 wt% propylene carbonate, or propylene sulfite, or 3-chloropropylene sulfite. The following conductivity values were determined at 20°C : 1.5×10^{-3} , 1.6×10^{-3} , and 2.0×10^{-4} S/cm, respectively.

CONCLUSIONS

- Glycidyl methacrylate homopolymers and copolymers are convenient precursors for the synthesis of polymer gel electrolytes.
- The solutions of these polymers and inorganic salts in appropriate solvents can be easily converted into gels as a result of crosslinking via oxirane groups in the presence of cationic initiators.
- In order to obtain stable elastic gels of high solvent content (up to 80 wt%), the oxirane side group taking part in crosslinking should be separated by other monomeric units (1-6) which assure an appropriate distance between the network nodes.

- The high conductivity values (exceeding 10^{-3} S/cm at ambient temperature and 10^{-5} S/cm at -50°C) and low activation energies (10–30 kJ/mol) in many of the systems studied indicate that charge transportation occurs mainly in the solvent phase. However, in some systems the temperature dependence of conductivity of the VTF-type relationship is observed, which suggests that ion movements are also affected by segmental polymer chain motions.

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