# Gel electrolytes on the basis of oligo(ethylene glycol)$_n$ dimethacrylates—thermal, mechanical and electrochemical properties in relationship to the network structure

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## Abstract

Gel electrolytes were prepared by photoinitiated polymerization of oligo(ethylene glycol)$_n$ dimethacrylates ((EG)$_n$DMA) with $n = 3$, 9 and 23 in the presence of a plasticizer, e.g. various oligo(ethylene glycol)$_n$ derivatives, and LiCF$_3$SO$_3$. The thermal, mechanical and electrochemical properties of the gel electrolytes were studied in dependence on their network structure and the type of the plasticizer. The molecular weights $M_c$ of the chains between the network junction points were determined for the pure networks from their dynamic storage modulus at $T \approx T_g + 60$ K above the glass transition temperature. Gel electrolytes on the basis of poly((EG)$_n$DMA) with $n \geq 9$ are single phase systems at room temperature. On the contrary, gels prepared by photopolymerization of ((EG)$_3$DMA) in a solution of LiCF$_3$SO$_3$ in oligo(ethylene glycol)$_{11}$ dimethylether ((EG)$_{11}$DME) show two glass transition temperatures, one of the plasticizer salt solution and one of the polymer above 100°C. These heterogeneous materials are able to embed up to 75 wt% of (EG)$_{11}$DME, preserving high mechanical stability, showing ionic conductivities around $10^{-4}$ S/cm at 25°C and cationic transference numbers $t^+ \approx 0.55$. The increase in the polarity of the electrolytes by copolymerization with the polar comonomer cyanomethyl methacrylate (CyMA) or by the addition of polar plasticizers reduces the ionic association, but does not result in a remarkable increase in the ionic conductivity. Investigations of the gel electrolytes by cyclic voltammetry indicate that their electrochemical stability will be higher if the polar groups are fixed at the polymer and not at the plasticizer. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer gel electrolyte; Oligo(ethylene glycol)$_n$ dimethacrylate; Network structure

## 1. Introduction

Polymer gel electrolytes provide growing interest for the potential application as electrolyte and separator in rechargeable lithium batteries. Commonly, these electrolytes were prepared as films by casting or extrusion techniques [1–3]. In situ film forming techniques are relatively seldom described in the literature, e.g. the radical polymerization of various oligo(ethylene glycol)$_n$ methacrylates in the presence of a plasticizer and a salt [4–9].

The potential application as an electrolyte in lithium batteries requires film properties like high mechanical and thermal stability and an uncomplicated film forming technique with technical suitability. From this point of view, in situ film forming techniques like the former [8] should be very appropriate. Preparation of thin films should be possible directly on the surface of the active materials of a battery.

Changes in the polymerization conditions like the variation of the type and the concentration of the monomer and the plasticizer used were found to have remarkable influence on the course of polymerization and the electrochemical properties of the resulting polymer electrolyte gels [6–11].

A study of the photopolymerization of (EG)$_{23}$DMA in solutions of LiCF$_3$SO$_3$ in (EG)$_n$DME with $n = 3$ and 11 by means of differential scanning calorimetry (DSC), FT-Raman spectroscopy and sol gel analysis indicated a higher polymerization rate in (EG)$_{11}$DME [7]. Linking of parts of (EG)$_{11}$DME to the polymer network caused by chain transfer reactions was observed for the polymerization of (EG)$_{23}$DMA in $\leq 50$ wt% of (EG)$_{11}$DME but was neglectable using (EG)$_3$DME as a plasticizer [7]. The effect was found to be more pronounced for gel electrolytes on the basis of copolymers of (EG)$_{23}$DMA with polar comonomers like cyanomethyl methacrylate (CyMA), acrylonitrile (AN) and cyclocarbonatopropyl methacrylate (CPMA),

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respectively [6,8]. These copolymers with enhanced polarity were used as a polymer matrix for gel electrolytes with the intention to influence the charge carrier separation and with that the ionic conductivity.

Concerning the mechanism of the charge carrier transport in gel electrolytes, previous studies indicate [10,11], that the ionic conductivity is dominated by the mobility of the plasticizer. However, the contribution of the cations to the ionic conductivity depends on the ability of the plasticizer to coordinate cations in competition to the polymer, i.e. it can be enhanced by reducing the EG spacer length of the polymer [10,11] and by enlarging the cation coordinating ability of the plasticizer, i.e. by use of a good electron donor [9,12]. An increase in the polarity of the electrolyte system by use of polar plasticizers or the insertion of polar comonomers in the poly((EG)$_{23}$DMA) network resulted in a distinct decrease in the ionic association, but not in remarkably higher ionic conductivities [10,11,13]. This behavior was explained by a reduced mobility due to the partial incorporation of the plasticizer in the polymer [6,8] as mentioned above, and a reduced mobility due to strong dipol–dipol interactions of the polar plasticizers with itself and the polymer [10,11].

Until now, the influence of the polymerization conditions on the polymer network structure and with that on the mobility of the ions and the plasticizer in the gel as well as the electrochemical properties of the gel electrolyte have not been described. Therefore, this paper focuses on the relationship between the polymer structure and the electrochemical properties of gel electrolytes on the basis of poly((EG)$_n$DMA) with $n = 3$, 9 and 23 and its copolymers with CyMA containing various oligo(ethylene glycol) derivatives as plasticizer. To characterize the network structure, the molar mass $M_c$ of the network chains was determined by means of dynamic mechanical analysis (DMA). The thermal and mechanical properties of the gel electrolyte films were investigated by DSC and DMA. The charge carrier transport was characterized in terms of ionic association, ionic conductivity, self-diffusivity of plasticizer and charge carriers and the cationic transference number. The electrochemical stability was studied by CV in dependence on the type of the polymer and the plasticizer.

## 2. Experimental

### 2.1. Materials

(EG)$_{11}$DME, ethylene carbonate (EC), diethyl carbonate (DEC), γ-butyrolactone and LiCF$_3$SO$_3$ were purchased from FLUKA, (EG)$_{23}$DMA and (EG)$_3$DMA from Merck and (EG)$_9$DMA and the photoinitiator Lucirin (2,4,6-trimethyl-benzoyldiphenylphosphineoxide) from the BASF AG. THF (FLUKA) was dried over Na and distilled. LiCF$_3$SO$_3$ was dried in vacuum at 120°C for 24 h. The (EG)$_n$DMA with $n = 3$ and 9 and (EG)$_{11}$DME were dried over molecular

sieves 4A. (EG)$_{23}$DMA was freeze dried before use. Details are given in Ref. [14]. CyMA was prepared according to the method described by Ueda et al. [15] by the reaction of chloracetonitrile and methacrylic acid in the presence of triethyl amine [6]. The oligo(ethylene glycol)$_n$ dicyanoethyl ethers ((EG)$_n$(CN)$_2$) with $n = 1$ and 2 and cyanoethylated butanol (But-CN) were prepared by reaction of the corresponding glycols or alcohol with acrylonitrile [16].

### 2.2. Film preparation

Films of 100–300 μm thickness were prepared by in situ photopolymerization. The mixture of monomer, plasticizer and salt was polymerized initiated by Lucirin (2 mol% per C=C double bond) by irradiation with ultra violet light ($\lambda = 254$ nm) (Fa. Konrad Benda Typ NVV8) on a Teflon® disc in a distance of 10 cm at room temperature for 5 min in an argon filled glove box. To obtain mechanically stable electrolyte films (EG)$_n$DMA with $n = 9$ and 23 were polymerized in the presence of ≤50 wt% plasticizer and (EG)$_3$DMA and its copolymers with (EG)$_9$DMA or CYMA in the presence of 70–75 wt% of plasticizer.

The films were annealed at 80°C for 12 h to complete the conversion of the monomers [6,12]. The double bound conversion was checked by FT-Raman spectroscopy [7]. No analyzable $\nu$(C=C) modes were detected in the spectra of the annealed gel electrolyte films.

### 2.3. Sol–gel analysis

For the determination of the sol and gel content, ca. 0.5 g of the samples were extracted four times with 20 ml THF and dried in vacuum at 40°C. The analysis of the unified sol solutions with regard to their content of plasticizer and residual monomers was carried out by means of a gel permeation chromatograph (GPC) of Knauer equipped with a PSS LiChrogel column and a differential refractometer as a detector. THF was used as an eluent. The extracted gel was characterized by elemental analysis after drying in vacuum at 40°C until constant weight.

### 2.4. Raman spectroscopy

Raman spectra were performed by means of a Bruker Fourier transform infra-red spectrometer IFS 66 equipped with the Raman module FRA 106 (Nd-YAG diode laser, 300 mW). The C=C stretching band (1639 cm$^{-1}$) of the monomer was analyzed to determine the conversion of C=C double bonds in the gel electrolyte films. The content of free anions was calculated via the intensity ratio of the single components of the SO$_3$ stretching mode of the anion of LiCF$_3$SO$_3$ (1030–1075 cm$^{-1}$). To describe the ability of the system to form symmetrical ether oxygen complexes with the Li cation, the ratio of the intensities of the LiO$_6$ breathing mode (866 cm$^{-1}$) and the CF$_3$ symmetrical bending mode (753 cm$^{-1}$) $I_{LiO6}/I_{CF3}$ was determined. For manipulation and evaluation of the spectra, Bruker OPUS
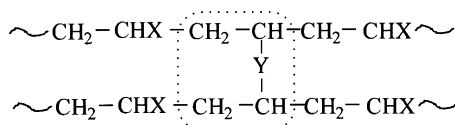
Scheme 1.

software was used. The details are given in Refs. [7,13,14,17].

### 2.5. Thermal studies

For the study of the thermal properties a differential scanning calorimeter, DSC 220 C (SEIKO Instruments Inc.) was used with a heating rate of 10 K/min.

### 2.6. DMA measurements

Dynamic mechanical measurements were performed by a DMA 242/1/F from NETZSCH between −100 and 200°C. Specimens with a diameter of 10 mm and a height of 1–2 mm were prepared by UV-irradiation for 2 h and annealing at 80°C for 12 h. Generally, the compression modus was used, with the following parameters: limit dynamic force 6 N, frequency 1 Hz, amplitude 60 $\mu$m, heating rate 3 K/min.

To determine the average of the molecular weights $M_c$ of the chains between the network junction points, the samples were fully extracted with THF and dried. $M_c$ was calculated from the dynamic storage modulus $E'$ measured at a temperature $T = T_g + 60$ K by DMA in the compression mode. The following equation was used under the assumption of the non-affine phantom model [18]

$$G = \frac{(f-2)}{f}\left(\frac{\rho RT}{M_c}\right) \tag{1}$$

with $G'$ as the shear modulus, $f$ the functionality of the network junction point and $\rho$ the density of the crosslinked polymer. $G'$ was calculated from the dynamic storage modulus $E'$ with $G = E'/3$ [18].

### 2.7. PFG–NMR measurements

$^1$H-, $^{19}$F-, and $^7$Li-PFG–NMR experiments were carried out with a home-built spectrometer FEGRIS 400 (400 MHz) to measure the self diffusion coefficients $D$ of the plasticizer,
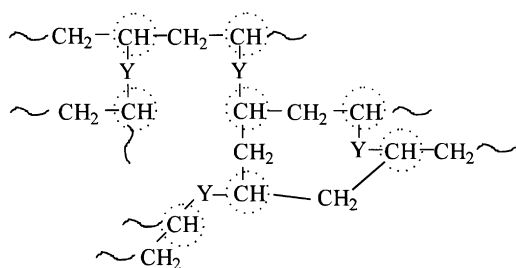
the cations and the anions in the gel. The self-diffusivity $D$ was calculated from the spin-echo attenuation $S_{inc}(q,t)$ due to the applied field gradients. Generally, only one self-diffusion coefficient was observed. The experimental error of the self-diffusion coefficients does not exceed ±10%. The details are given in Refs. [19,20].

### 2.8. AC and DC measurements

AC and DC data were obtained using a combination of a Potentiostat/Galvanostat (model 263 A) and a frequency response analyzer (model 1025) from EG&G. The complex impedance plots of the samples were recorded in the frequency range from 1 to $10^5$ Hz. The cationic transference numbers $t^+$ were determined by the steady state current technique proposed by Bruce and Vincent [21]. The details are given in Ref. [10]. Ni was used as a working electrode ($A = 0.5$ cm$^2$) and Li as counter and reference electrode for cyclic voltammetry with a scanning rate of 1 mV/s.

## 3. Results and discussion

### 3.1. The network structure

Usually, crosslinking copolymerizations of a monovinyl monomer are carried out with a low fraction of a divinyl monomer. In this case, the $M_c$ values of the network can be calculated from the molar ratio of the two monomers assuming an ideal network structure, where:

* every divinyl monomer unit forms a network junction point of the functionality $f = 4$;
* the mass of the network junction point can be neglected compared with that of the network chains;
* cyclization reactions do not occur (Scheme 1).

However, for homopolymerizations of divinyl monomers or their copolymerization with a monovinyl monomer where the fractions of both monomers are similar, the molar mass of the divinyl monomer unit is the only or an essential factor for the calculation of $M_c$ (Scheme 2). It is apparent from Scheme 2 that the functionality $f = 3$ has to be used for the calculation of $M_c$ according to Eq. (1).

Table 1 gives a summary of the molecular weights $M_c$ between the network junction points for fully extracted samples prepared by photopolymerization of (EG)$_n$DMA with $n = 3$, 9 and 23 in the presence of a solution of LiCF$_3$SO$_3$ in (EG)$_{11}$DME and for samples prepared by photopolymerization in bulk. Generally, a high network density was observed.

A relatively good correspondence was found between the experimental determined $M_{c\,exp}$ with $f = 3$ and $M_{c\,calc}$ calculated from the molar mass of the monomer under the assumption of the formation of an ideal network for poly((EG)$_9$DMA) obtained by bulk polymerization. Compared with this, (EG)$_{23}$DMA as a crosslinker leads to a network with a lower $M_{c\,exp}$ than expected, which is explicable



Scheme 2.

Table 1
Molar weights between the network junction points $M_c$, $T_g$ of the polymer and the dynamic storage modulus $E'$ at 25°C of poly((EG)$_n$DMA) $n = 3, 9, 23$ determined for samples polymerized in mass and for various gel electrolytes on the basis of poly((EG)$_3$DMA) and its copolymers with CyMA after extraction of (EG)$_{11}$DME and 0.6 mol/kg LiCF$_3$SO$_3$

| Poly((EG)$_n$DMA) $n$ | (EG)DME $n$ | Plasticizer (wt%) | $M_{c\ calc.}$ (g/mol) | $M_{c\ exp.}$ (g/mol) | $T_g$ (°C) and (tan $\delta_{max}$) of the extracted gel | $T_g$ (°C) and (tan $\delta_{max}$) of the polymer of the gel electrolyte | $E'_{25°C}$ of the gel electrolyte (MPa) |
|---|---|---|---|---|---|---|---|
| 23 | – | – | 570 | 350 | −31 (0.46)[a] | | 7 |
| | 11 | 50 | 570 | 820 | −36 (0.69) | −41 (0.50) | 9 |
| | 4 | 50 | 570 | 630 | −30 (0.70) | −66 (0.70) | 3 |
| 9 | – | – | 255 | 260 | 24 (0.43)[a] | | 32 |
| | 11 | 40 | 255 | 300 | 26 (0.41) | 22 (0.44) | 13 |
| | 4 | 40 | 255 | 495 | 24 (0.55) | −12 (0.55) | 4 |
| 3 | – | – | 127 | 355 | 150 (0.16)[a] | | 30 |
| | 11 | 60 | 127 | 365 | 177 (0.20) | 126 (0.28) | 27 |
| | 11 | 75 | 127 | – | – | 122 (0.44) | 32 |
| | 4 | 60 | 127 | 470 | 146 (0.22) | – | – |
| | | 70 | 127 | – | – | 87 (0.35) | 10 |
| Content of CYMA (mol%) in poly((EG)$_n$DMA-*co*-CyMA) | | | | | | | |
| 5 | 11 | 75 | 129 | 480 | 128 (0.33) | 92 (0.32) | 26 |
| 20 | 11 | 75 | 134 | 500 | 126 (0.39) | 81 (0.37) | 27 |
| 50 | 11 | 75 | 158 | 2130 | 109 (0.73) | 48 (0.39) | 26 |
| 75 | 11 | 75 | 221 | 3960 | 111 (1.20) | 12 (0.49) | 3 |
| 90 | 11 | 75 | 407 | 4850 | 86 (1.24) | 7 (0.64) | 4 |

[a] Bulk polymerization.

by chain transfer reactions to the EG spacer. On the contrary, poly((EG)$_3$DMA) based networks show higher $M_{c\ exp}$ values than calculated. This is assumed to be a result of cyclization reactions. Cyclization reactions also explain the differences between the calculated and the measured $M_c$ for gel electrolyte networks determined after extraction of the plasticizer-salt solution. These intramolecular reactions should be more pronounced, if the fraction of the plasticizer in the gel electrolyte is increased. This effect is observable in the case of networks from (EG)$_{23}$DMA only when the gels were prepared with (EG)$_{11}$DME, however, not with (EG)$_4$DME.

The insertion of a comonomer, e.g. CyMA into the network by copolymerization with (EG)$_3$DMA leads to a much stronger enlarging of $M_{cexp}$ than the calculated (Table 1) explicable again by the occurrence of cyclization reactions. Additionally, the incorporation of (EG)$_{11}$DME into the network has to be also considered [7] resulting in an increase of $M_c$. The incorporation of (EG)$_{11}$DME was found to be 9% in the case of gel electrolytes containing (EG)$_3$DMA with 20 mol% of CyMA and 15% for copolymers of (EG)$_{23}$DMA with the same CyMA content.

### 3.2. Thermal properties

The thermal properties of the electrolyte films change dramatically by variation of the spacer length $n$ of (EG)$_n$DMA (Table 1).

The glass transition temperatures of poly((EG)$_n$DMA) prepared by bulk polymerization rise from −47 to 170°C if the spacer length $n$ is reduced from 23 to 3. No further thermal transitions were observed in the DSC and DMA plots as shown in Fig. 1.

The DSC plots of the gel electrolytes indicate the glass transition and the melting of the plasticizer salt solution (Fig. 1b, on the top). Although the crystallization of (EG)$_{11}$DME is reduced in the presence of the polymer network and the salt, it could not be fully restricted (Table 2) [19]. However, a further depression of the crystallization of (EG)$_n$DME with $n = 4$ and 11 in the gel electrolyte films was observed if cyanoethylated ethylene glycols were added to (EG)$_{11}$DME (Table 2).

The glass transition of the polymer in the gel electrolytes was clearly detected by DMA (maximum of tan $\delta$) (Fig. 1b, on the bottom). DMA plots of gel electrolytes on the basis of poly((EG)$_n$DMA) with $n = 9$ and 23 and their copolymers with CyMA show only one signal. Therefore, these gel electrolytes can be regarded as single-phase systems. On the contrary, the DMA plots of gel electrolytes on the basis of poly((EG)$_3$DMA) and its copolymers with (EG)$_9$DMA and with ≤50 mol% of CyMA, respectively, show additional signals besides the glass transition of the polymer which can be related to the glass transition and the melting of (EG)$_{11}$DME considering the DSC results (Figs. 1b and 2). Consequently, these gel electrolytes are heterogeneous materials.

Of course, the glass transition temperatures of the polymers by copolymerization of (EG)$_3$DMA with CyMA are lower than that of poly((EG)$_3$DMA) corresponding to the enlargement of the $M_c$ values (Table 1). Gels with ≥75 mol% CyMA are homogeneous (Fig. 2).
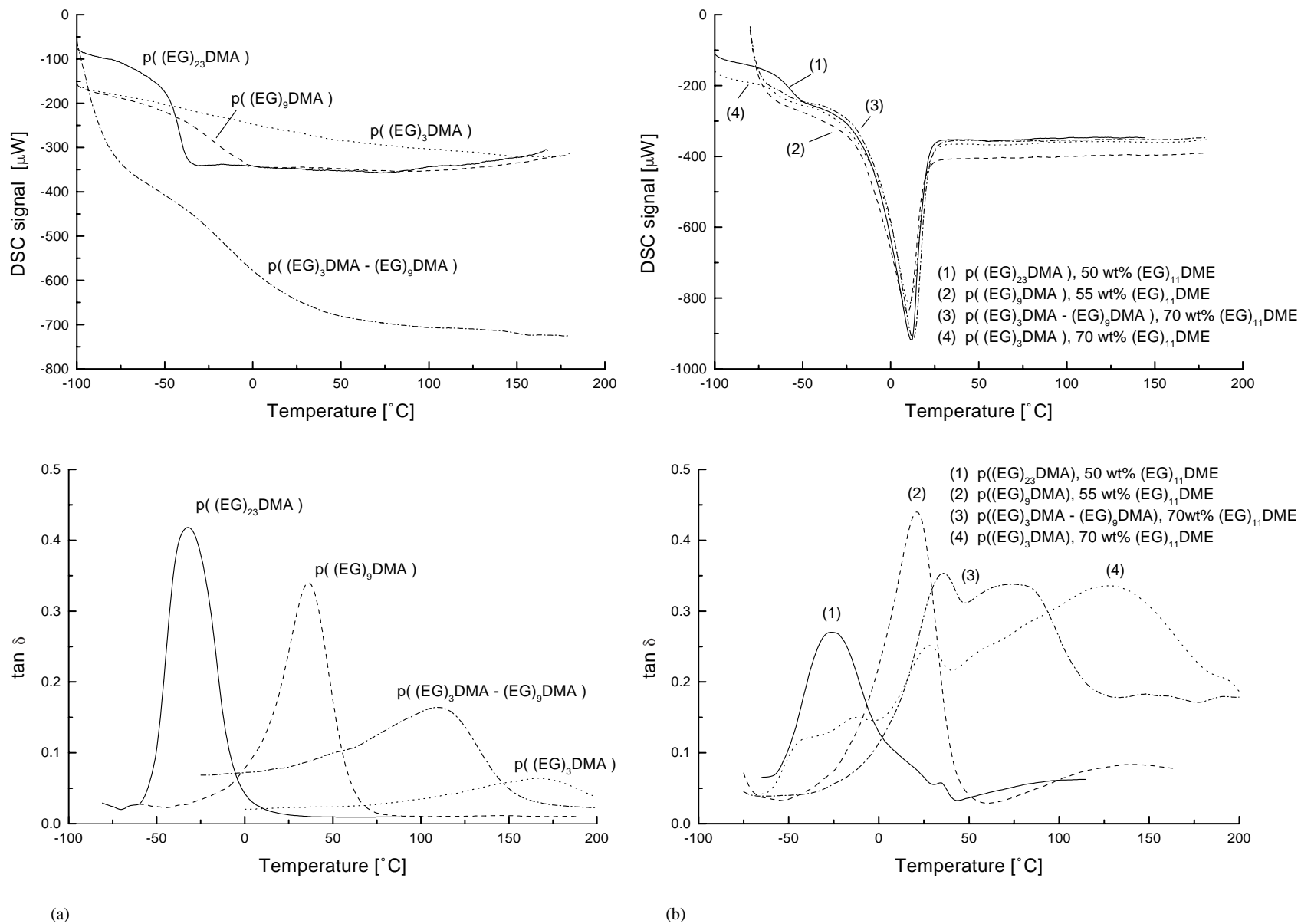
Fig. 1. DSC-thermograms and DMA plots of networks of $(EG)_nDMA$ with $n = 3$, 9 and 23: (a) polymerized in mass; and (b) polymerized in the presence of $(EG)_{11}DME$ and 0.6 mol/kg $LiCF_3SO_3$.

Table 2
Thermal properties of various gel electrolytes on the basis of poly((EG)$_3$DMA) compared with the corresponding plasticizers

|  | Plasticizer (wt%) | $c_{LiCF_3SO_3}$ (mol/kg) | $T_g$ (°C) | $T_m$ (°C)[a] | $\Delta H_m$ (mJ/mg) |
|---|---|---|---|---|---|
| (EG)$_4$DME | 100 | 0.70 | −78 | −34 | 95 |
| (EG)$_{11}$DME | 100 | 0.72 | −68 | 10 | 76 |
| But-CN | 100 | 0.30 | – | – | – |
| EG$_2$CN$_2$ | 100 | 0.30 | −74 | – | – |
| (EG)$_{11}$DME | 70 | 0.62 | −66 | −11 | 62 |
|  | 65 | 0.61 | −70 | −17 | 47 |
|  | 50 | 0.71 | −63 | −10 | 20 |
| But − CN/(EG)$_4$DME = 1 g/1 g | 65 | 0.59 | – | – | – |
| But − CN/(EG)$_{11}$DME = 1 g/1 g | 65 | 0.55 | −69 | 5 | 5 |
| EG$_2$CN$_2$/(EG)$_{11}$DME = 1 g/1 g | 65 | 0.55 | −68 | – | – |

[a] Onset of the signal.

A direct dependence of $T_g$ of extracted gel networks on the network density was only observed for the polymers of (EG)$_n$DMA with $n = 3$ and 9 as well as their copolymers all prepared in the presence of (EG)$_{11}$DME and for the co-polymers with CyMA (Table 1). The opposite relationship has to be established for gels from (EG)$_{23}$DMA with increasing content of the plasticizer (EG)$_{11}$DME. Obviously, the decreasing incorporation of (EG)$_{11}$DME into the network at increasing contents of the former results in higher $T_g$ of the polymer network despite its decreasing network density.

### 3.3. Mechanical properties

The mechanical strength of the gel electrolyte films depends on the type and the content of the plasticizer used.

The dynamic storage modulus $E'$ at 25°C determined by DMA in the compression mode was used to compare the
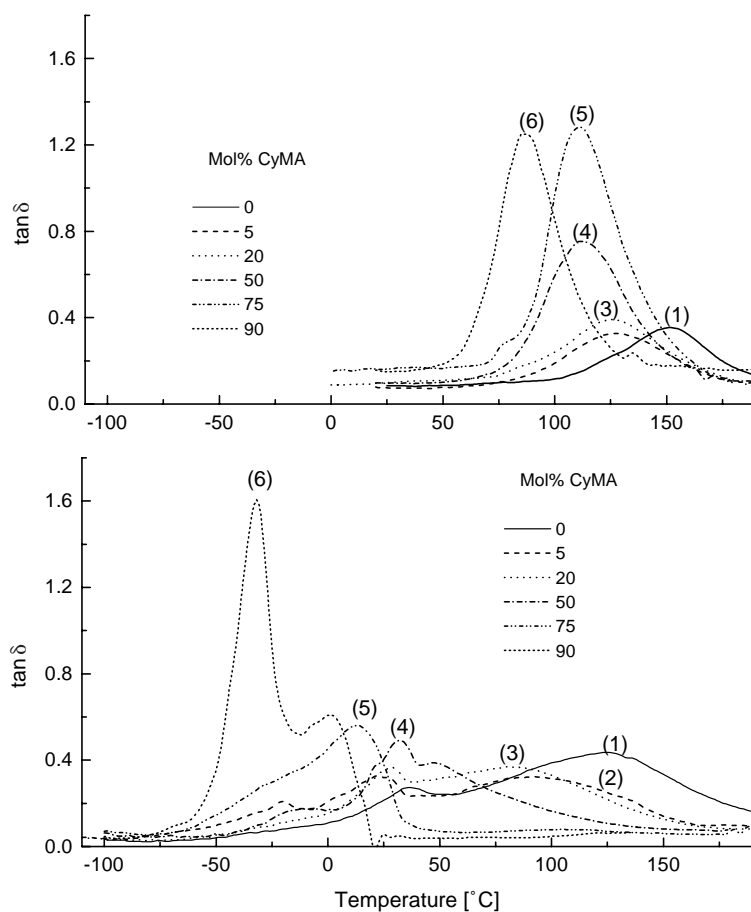


Fig. 2. DMA plots for gel electrolytes on the basis of copolymers of (EG)$_3$DMA with CyMA polymerized in 75 wt% (EG)$_{11}$DME with 0.6 mol/kg LiCF$_3$SO$_3$: (a) extracted gel; and (b) gel electrolyte film.

Table 3
The deviation from the Nernst–Einstein equation (2) expressed by $H_R$ and the cationic transference numbers $t^+$ for various gel electrolytes

| Polymer | Plasticizer | wt% | $c_{LiCF_3SO_3}$ (mol/kg) | $H_R$ | $t^+$ (PFG-NMR) | $t^+$ (DC technique) |
|---|---|---|---|---|---|---|
| – | $(EG)_{11}DME$ | 100 | 0.74 | 2.6 | 0.36 | |
| Poly $((EG)_3DMA)$ | $(EG)_{11}DME$ | 50 | 0.57 | 26 | 0.43 | |
| | | 75 | 0.64 | 2.1 | 0.45 | 0.55 |
| Poly $((EG)_9DMA))$ | $(EG)_{11}DME$ | 50 | 0.6 | 4.7 | 0.41 | 0.49 |
| Poly $((EG)_{23}DMA))$ | $(EG)_{11}DME$ | 50 | 0.72 | 1.9 | 0.35 | 0.40 |
| Poly$((EG)_{23}DMA$-co-CyMA (22 mol %)) | $(EG)_{11}DME$ | 50 | 0.72 | 1.9 | 0.37 | 0.36 |
| | | 65 | 0.72 | 2.9 | 0.40 | 0.43 |
| Poly $((EG)_3DMA$-co-CyMA (22 mol %)) | $(EG)_{11}DME$ | 50 | 0.54 | 20 | 0.41 | |
| | | 80 | 0.65 | 2.6 | 0.42 | 0.48 |
| | $(EG)_{11}DME/(EG)_4DME = 1 \, g/1 \, g$ | 75 | 0.60 | 7.5 | 0.5 | 0.47 |
| | $(EG)_{11}DME/But-CN = 1 \, g/1 \, g$ | 75 | 0.6 | 1.3 | 0.42 | [a] |
| | $(EG)_{11}DME(EC-DEC) = 1 \, g/1 \, g$ | 75 | 0.6 | 1 | 0.35 | 0.2[a] |
| | $(EG)_{11}DME/\gamma$-butyrolactone $= 1 \, g/1 \, g$ | 75 | 0.6 | 1 | 0.46 | 0.13[a] |

[a] High charge transfer resistances.

mechanical stability of the gel electrolyte films (Table 1). The highest mechanical stabilities, ca. 30 MPa, were achieved for gel electrolytes on the basis of poly($(EG)_3DMA$) and its copolymers with $(EG)_9DMA$ or CyMA ($\leq$20 mol%) containing $(EG)_{11}DME$ as the plasticizer. This behavior can be explained with the glassy state of the polymer at room temperature.

The need to reach high conductivities requires the use of mobile plasticizers with low viscosity and high polarity, e.g. the cyanoethylated oligo(ethylene glycol)s or linear and cyclic alkylcarbonates. However, their application reduces the mechanical stability dramatically (Fig. 3). It was shown for the polymerization of $(EG)_{23}DMA$ that the polymerization rate decreased if the low viscous $(EG)_3DME$ was used as a plasticizer instead of $(EG)_{11}DME$ [7], because the diffusion controlled chain terminating reaction occurs faster

in low viscous solvents. The polymer network formed under these conditions should contain a relatively high fraction of dangling chain ends. The latter do not influence the values of $M_c$ as determined by DMA. However, they should decrease the modulus $E'$ of the gels. An acceptable mechanical stability can be guaranteed by use of solvents with low viscosity in combination with $(EG)_{11}DME$ (Fig. 3).

### 3.4. Ionic association

The technique to study the ionic association by analysis of the $SO_3$ symmetric stretching mode of the salt, e.g. $LiCF_3SO_3$, in the Raman spectra was originally developed and is commonly used for liquid electrolytes [22]. However, it is also possible to identify the components of the $SO_3$ symmetric stretching mode and the $Li-O_6$ breathing mode
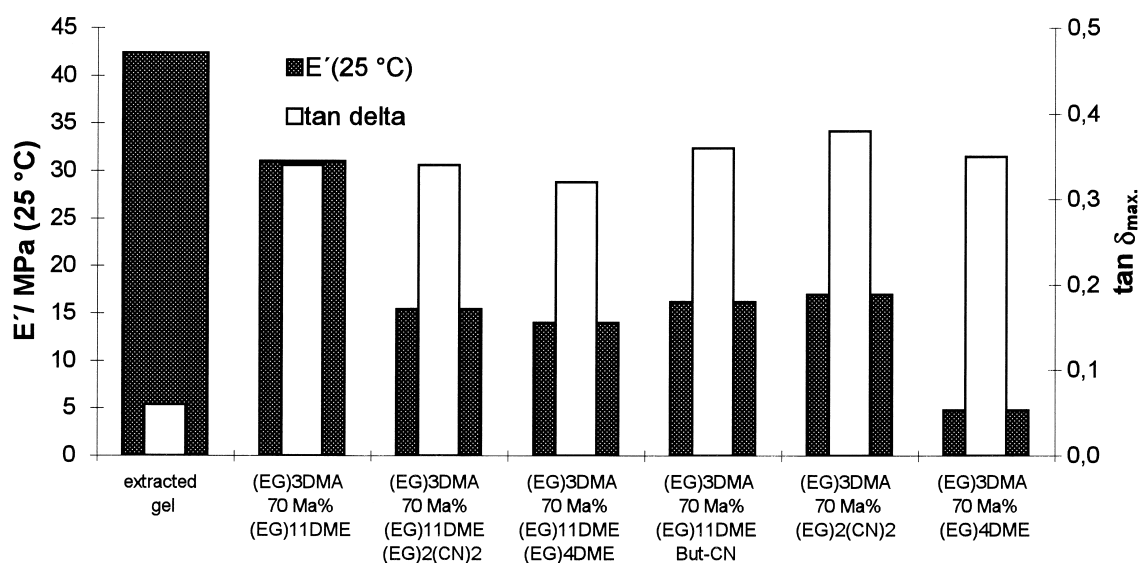


Fig. 3. $E'_{25°C}$ and tan $\delta_{max}$ determined by DMA in the compression mode for gel electrolytes on the basis of poly($(EG)_3DMA$) and 70 wt% of different plasticizers.
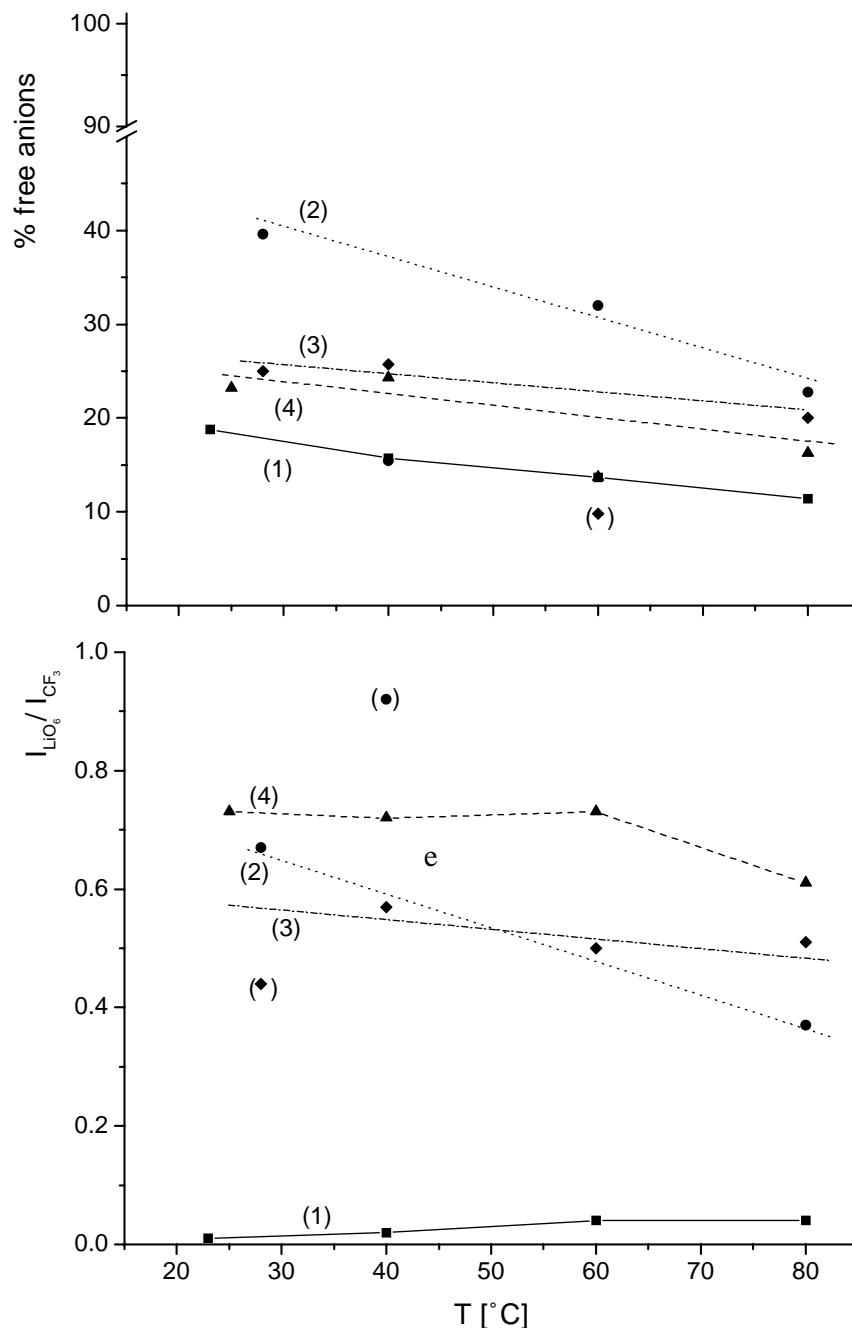
Fig. 4. Content of free anions and relative intensity of the $LiO_6$ bond as a function of the temperature determined for gel electrolytes on the basis of poly$((EG)_n DMA)$ with different $(EG)_{11} DME$ content, 0.6 mol/kg $LiCF_3SO_3$, 25°C, (1) 50 wt%$(EG)_{11} DME$ in poly$((EG)_{23} DMA)$, (2) 45 wt%$(EG)_{11} DME$ in poly$((EG)_9 DMA)$, (3) 60 wt%$(EG)_{11} DME$ in poly$((EG)_9 DMA$-*co*-$(EG)_3 DMA)$, (4) 65 wt%$(EG)_{11} DME$ in poly$((EG)_3 DMA)$.

in Raman spectra of gel electrolytes [6,13]. As indicated by Fig. 4, gel electrolyte films on the basis of $(EG)_n DMA$ with $n = 3$, 9 and 23, $(EG)_{11} DME$ and 0.6 mol/kg $LiCF_3SO_3$ show a content of free anions between 15 and 40% in dependence on the temperature and the type of the monomer. Only the content of free anions is plotted in Fig. 4, because an equilibrium between free anions and ion pairs and no signs of the presence of higher ionic aggregates were detected. Both the content of free anions and the relative intensity of the $LiO_6$ breathing mode decrease with increasing

temperature corresponding to the decrease in the dielectric permittivity of polyether based electrolyte systems with temperature [19] caused by conformational changes [23]. A relatively low content of free anions and a very low relative intensity of the $LiO_6$ mode were observed for homogeneous gel electrolytes on the basis of poly$((EG)_{23} DMA)$ (Fig. 4) compared to the other gel electrolytes studied and also compared to the corresponding liquid electrolyte which showed a content of ca. 40% of free anions and an $I_{LiO6}/I_{CF3}$ intensity ratio of 0.6 at room temperature [17]. In these
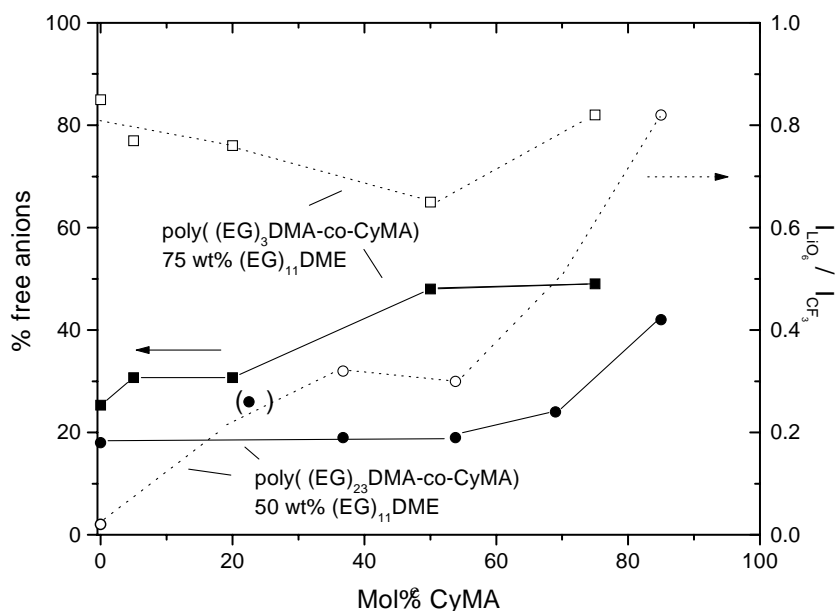
Fig. 5. Content of free anions and relative intensity of the $LiO_6$ bond as a function of the content of CyMA in the polymer determined for gel electrolytes on the basis of poly($(EG)_n$DMA-*co*-CYMA), $n = 3, 23$, with $(EG)_{11}$DME, [EG]/[LiCF$_3$SO$_3$] = 25, 25°C.

homogeneous gel electrolytes both the plasticizer and the polymer solvate the salt. The similar interaction of the cations with the EG groups of the immobile polymer and the plasticizer seems to hinder the formation of stable symmetrical $LiO_6$ complexes which explains also the reduced content of free anions in these electrolyte systems. With decreasing EG spacer length $n$ of the polymer, i.e. increasing heterogeneity of the system (Fig. 1), a slight increase of the content of free anions and a distinct enlargement of the relative intensity of the $LiO_6$ mode was detected (Fig. 4). A similar behavior is also observed for the gels containing copolymers of $(EG)_3$DMA with CyMA (Fig. 5) and for recently described heterogeneous gel electrolyte systems on the basis of alternating copolymers [24]. The similarity of the degree of ionic association and the relative intensity of the $LiO_6$ mode obtained for the heterogeneous gel electrolyte systems and their corresponding liquid electrolytes indicates, that the salt is mainly solvated in the liquid phase of the gels.

The higher polarity of gel electrolytes on the basis of copolymers of $(EG)_n$DMA ($n = 3$ and 23) with CyMA results in a lower degree of ionic association [6,13], especially for higher contents of CyMA (Fig. 5). The $I_{LiO6}/I_{CF3}$ intensity ratio for poly($(EG)_{23}$DMA-*co*-CyMA) gel electrolytes increases with enlarged content of CyMA. An enhanced content of symmetrical $LiO_6$ complexes compared to poly($(EG)_{23}$DMA) based gels was also detected for copolymers of $(EG)_{23}$DMA with AN and CPMA, respectively, [13]. The decreasing content of $(EG)_{23}$DMA in the copolymer obviously intensifies the interaction of the charge carriers with the plasticizer.

The ionic association was also reduced by use of mixtures of $(EG)_{11}$DME with polar plasticizers as shown for gel electrolytes on the basis of poly($(EG)_3$DMA-*co*-CyMA) (Fig. 6). The plasticizer mixtures were used with respect to the mechanical properties (Fig. 3).

### 3.5. Conductivity and self-diffusivity

Fig. 7 shows the temperature dependence of the conductivity of gel electrolytes on the basis of poly($(EG)_n$DMA) ($n = 3, 9, 23$) with $(EG)_{11}$DME as a plasticizer. The plasticizer content chosen corresponds to an optimum between the different ability of the polymers to embed $(EG)_{11}$DME and the maximum conductivity which can be reached.
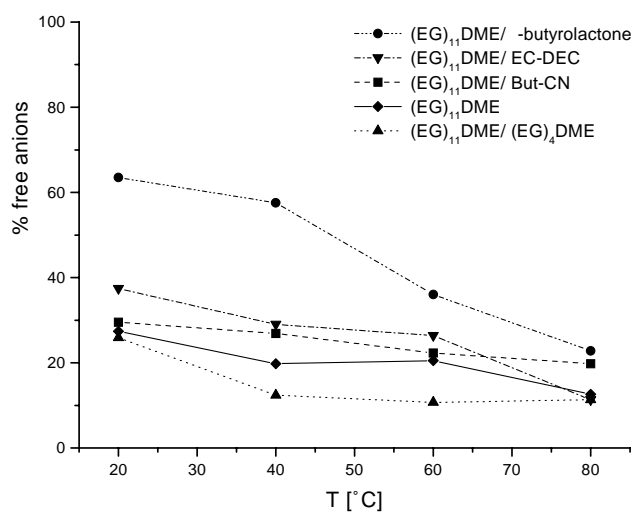


Fig. 6. Content of free anions as a function of the temperature determined for gel electrolytes on the basis of poly($(EG)_n$DMA-*co*-CYMA), with 75 wt% of mixtures of $(EG)_{11}$DME with various polar plasticizers (1 g/1 g), 0.6 mol/kg LiCF$_3$SO$_3$, 25°C.
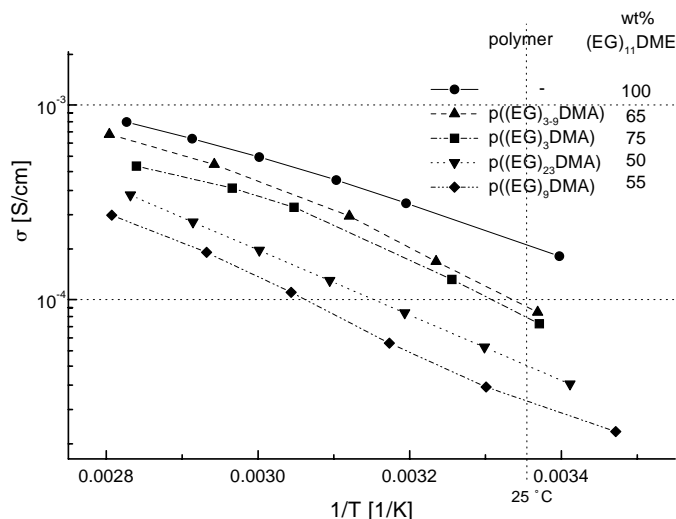
Fig. 7. Arrhenius plot of the conductivity of gel electrolytes on the basis of poly((EG)$_n$DMA) with $n = 3$, 9 and 23 with (EG)$_{11}$DME and 0.6 mol/kg LiCF$_3$SO$_3$ compared with the corresponding liquid electrolyte.

Therefore, a relationship between the conductivity and the EG spacer length cannot be expected. However, it can be shown by Fig. 7, that the conductivity is higher for heterogeneous gel electrolytes on the basis of poly((EG)$_3$DMA) with a large plasticizer content than for homogeneous poly((EG)$_n$DMA) based systems with $n = 9$ or 23.

The highest conductivities for gel electrolytes with (EG)$_{11}$DME as a plasticizer were achieved with copolymers of (EG)$_3$DMA with (EG)$_9$DMA and CyMA, respectively (Figs. 7 and 9). This could be explained in the latter case by the increased dissociation of the salt due to the insertion of the polar comonomer (Fig. 5). Further, it should be considered for explanation that the network density and $T_g$ (ca. 80°C) of the polymer are reduced as a result of the insertion of these two comonomers (Table 1).

The conductivity of the heterogeneous gel electrolytes is strongly dependent on the plasticizer content. If the latter is too low, discontinuities will be observed in the Arrhenius plots of the conductivity (Fig. 8). The discontinuities are not directly related to thermal transitions (Section 3.2), but it can be assumed that they are a result of the homogenization of the materials due to the successively softening of the polymer network with increasing temperature.

Hence, the reason for the higher conductivity of the heterogeneous gel electrolyte systems is caused by their ability to insert large amounts of plasticizer compared with the homogeneous gels on the basis of poly((EG)$_n$DMA) with $n \geq 9$.

A maximum of conductivity was observed both for poly ((EG)$_3$DMA-*co*-CyMA) and poly((EG)$_{23}$DMA-*co*-CyMA) based gel electrolytes with 20 mol% CyMA. A higher comonomer content reduces the conductivity again (Fig.
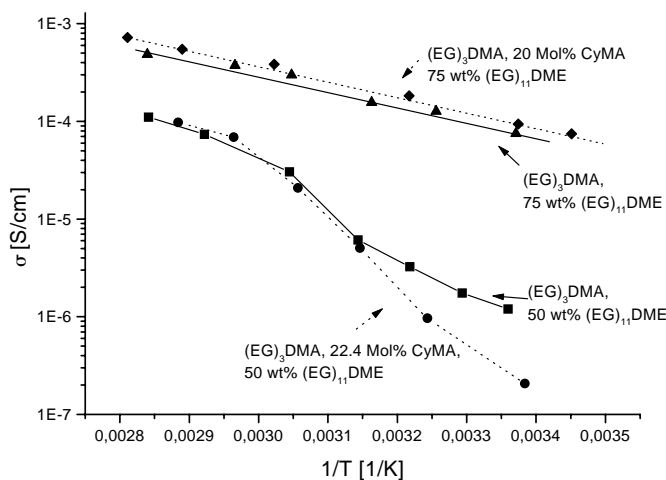


Fig. 8. Arrhenius plot of the conductivity of gel electrolytes on the basis of poly((EG)$_3$DMA) and of poly((EG)$_3$DMA-*co*-CyMA) in dependence on the (EG)$_{11}$DME content, 0.6 mol/kg LiCF$_3$SO$_3$.
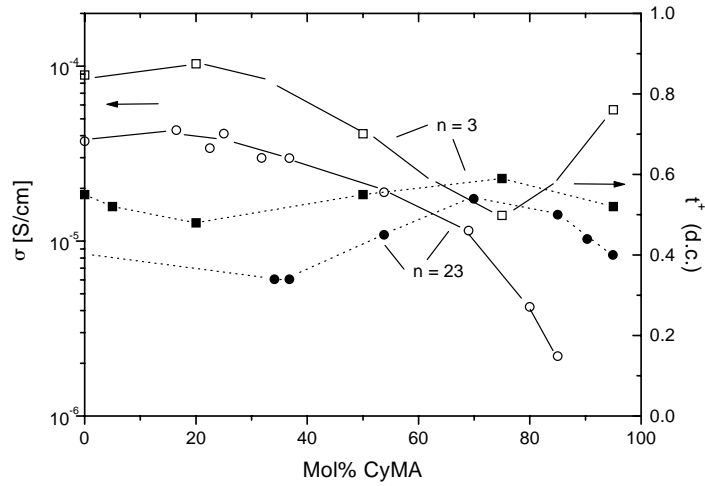
Fig. 9. Conductivity $\sigma$ and cationic transference numbers $t^+$ (DC technique) of gel electrolytes on the basis of poly((EG)$_n$DMA-$co$-CyMA) with $n = 3, 23$ and a different CyMA content, with 75 and 50 wt% (EG)$_{11}$DME, respectively, at 25°C.
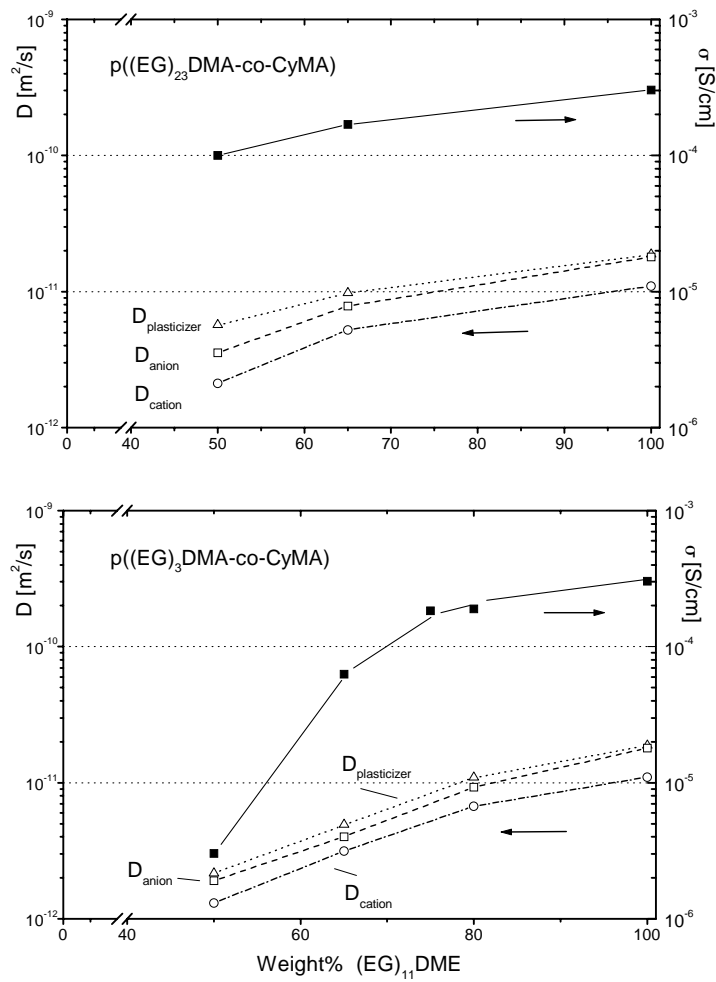


Fig. 10. Conductivity $\sigma$ and self-diffusion coefficients $D$ of the plasticizer and the charge carriers of gel electrolytes on the basis of poly((EG)$_n$DMA-$co$-CyMA) with $n = 3, 23$ and 22 mol% CyMA in dependence on the (EG)$_{11}$DME content, 0.6 mol/kg LiCF$_3$SO$_3$, 40°C.

Table 4
The activation energy $E_A$ for conductivity and self-diffusivity of charge carriers and plasticizer of various gel electrolytes

| Polymer | Plasticizer | Plasticizer (wt%) | LiCF$_3$SO$_3$ (mol/kg) | $E_A$ (eV) | | | |
|---|---|---|---|---|---|---|---|
| | | | | $D_{plasticizer}$ | $D_{anion}$ | $D_{cation}$ | $\sigma$ |
| | (EG)$_{11}$DME | 100 | 0.74 | 0.27 | 0.29 | 0.35 | 0.25 |
| Poly((EG)$_{23}$DMA) | (EG)$_{11}$DME | 50 | 0.72 | 0.34 | 0.36 | 0.39 | 0.33 |
| Poly((EG)$_9$DMA) | (EG)$_{11}$DME | 50 | 0.6 | 0.33 | (0.23) | (0.26) | 0.34 |
| Poly((EG)$_3$DMA) | (EG)$_{11}$DME | 50 | 0.57 | 0.36 | 0.37 | 0.42 | Non-linear behavior |
| | (EG)$_{11}$DME | 75 | 0.64 | 0.36 | 0.38 | 0.37 | 0.3 |
| Poly((EG)$_{23}$DMA-*co*-CyMA (22 mol %)) | (EG)$_{11}$DME | 50 | 0.72 | 0.35 | 0.39 | 0.38 | Non-linear behavior |
| | (EG)$_{11}$DME | 65 | 0.72 | 0.31 | 0.36 | 0.37 | 0.31 |
| Poly ((EG)$_3$DMA-*co*-CyMA (22 mol %)) | (EG)$_{11}$DME | 50 | 0.54 | 0.47 | 0.38 | 0.39 | Non-linear behavior |
| | (EG)$_{11}$DME | 65 | 0.59 | 0.4 | 0.4 | 0.36 | 0.48 |
| | (EG)$_{11}$DME/(EG)$_4$DME = 1 g/1 g | 75 | 0.60 | 0.24 | 0.27 | 0.35 | 0.24 |
| | (EG)$_{11}$DME/But − CN = 1 g/1 g | 75 | 0.6 | 0.35 | 0.33 | 0.34 | Non-linear behavior |
| | (EG)$_{11}$DME/$\gamma$ − butyrolactone = 1 g/1 g | 75 | 0.6 | 0.35 | 0.4 | 0.37 | Non-linear behavior |
| | (EG)$_{11}$DME/EC − DEC = 1 g/1 g | 75 | 0.6 | 0.35 | 0.38 | 0.42 | 0.39 |

9), probably due to the above mentioned linking of (EG)$_{11}$DME to the polymer network, which has to be taken into account for gel electrolytes on the basis of copolymers of (EG)$_n$DMA with the polar comonomers AN, CPMA and CyMA, respectively, especially in the case of higher comonomer contents [8].

Charge carrier self-diffusivity and ionic conductivity are related according to the Nernst–Einstein relationship. Small deviations from it were usually observed in the field of polymer electrolytes. Referring to the theory of lattice gases, these deviations were commonly explained as a result of correlated motions contributing to the self-diffusivity but not to the conductivity [25–28]. To describe these small deviations, a correction factor $H_R$ can be introduced in the Nernst–Einstein equation [25]:

$$\sigma = (1/H_R)(e^2 N_A/kT)c_0(D_{exp}(Li) + D_{exp}(F)) \qquad (2)$$

$\sigma$ denotes the measured conductivity, $c_0$ the molar concentration of LiCF$_3$SO$_3$, $N_A$ the Avogadro constant and k$T$ has its usual meaning. $D_{exp}(Li)$ and $D_{exp}(F)$ are the measured self-diffusivities of the Li- and F-containing species in the system.

For the explanation of the deviations from the Nernst–Einstein equation in the field of polymer electrolytes, it should be taken into account that the self-diffusivities $D_{exp}(Li)$ and $D_{exp}(F)$ as measured by PFG-NMR are averaged diffusivities of all Li- and F-containing species, also of those species which do not contribute to the conductivity. The Li- and F-containing species exchange fast between the two states (contributing to the conductivity and non-contributing to the conductivity) since always one averaged self-diffusion coefficient is observed by PFG-NMR [19,20].

For the studied electrolyte systems values of $H_R$ between 2 and 3 were mainly calculated (Fig. 11, Table 3). This is in accord with the usually reported values in the literature for polymer electrolytes [20,26–28]. The dependence of the conductivity and the self-diffusivity of the charge carriers and the plasticizer on the content of the plasticizer is represented in Fig. 10 for gel electrolytes on the basis of poly((EG)$_n$DMA-*co*-CyMA) with $n = 3$ and 23. In agreement with the literature [9,19], the self diffusivities of charge carriers and plasticizer agree in their magnitude and follow the sequence $D_{plasticizer} \geq D_{exp}(F) > D_{exp}(Li)$. No correlation between conductivity and self-diffusivity according to the Nernst–Einstein equation was found for the gel electrolytes on the basis of poly((EG)$_3$DMA) and its copolymer with 22 mol% CyMA, containing $\leq$65 wt% (EG)$_{11}$DME (Fig. 10). A similar behavior was also observed for gel electrolytes on the basis of alternating copolymers [24]. For these electrolytes the self-diffusion coefficients of charge carriers and plasticizer were generally measured in the range of the corresponding liquid electrolyte, despite comparably low conductivities [24]. The high deviations from the Nernst–Einstein equation in this case were explained with the heterogeneity of the polymer gels. The conductivity is a macroscopic quantity. Contrary, PFG–NMR which was used to study the self-diffusivity records, the micrometer scale and with that the liquid phase of the heterogeneous systems [24].

The activation energies $E_A$ of the conductivity and the self-diffusion coefficients of the charge carriers and plasticizers were determined in the case of Arrhenius behavior (Table 4). As expected, $E_A$ for the gel systems containing (EG)$_{11}$DME as plasticizer is generally higher than for the corresponding liquid electrolyte reflecting the interactions between the polymer and the charge carriers. This is also discussed by other authors, [26,29]. Mainly values between 0.3 and 0.4 eV were calculated in the sequence $E_A(D_{plasticizer}) \approx E_A(\text{conductivity}) < E_A(D_{anion}) < E_A(D_{cation})$ reflecting once more the dependence of the conductivity on the mobility of the plasticizer and the interactions of the cations with the polymer.

To achieve higher conductivities, plasticizer with lower viscosities and higher polarity than that of (EG)$_{11}$DME were

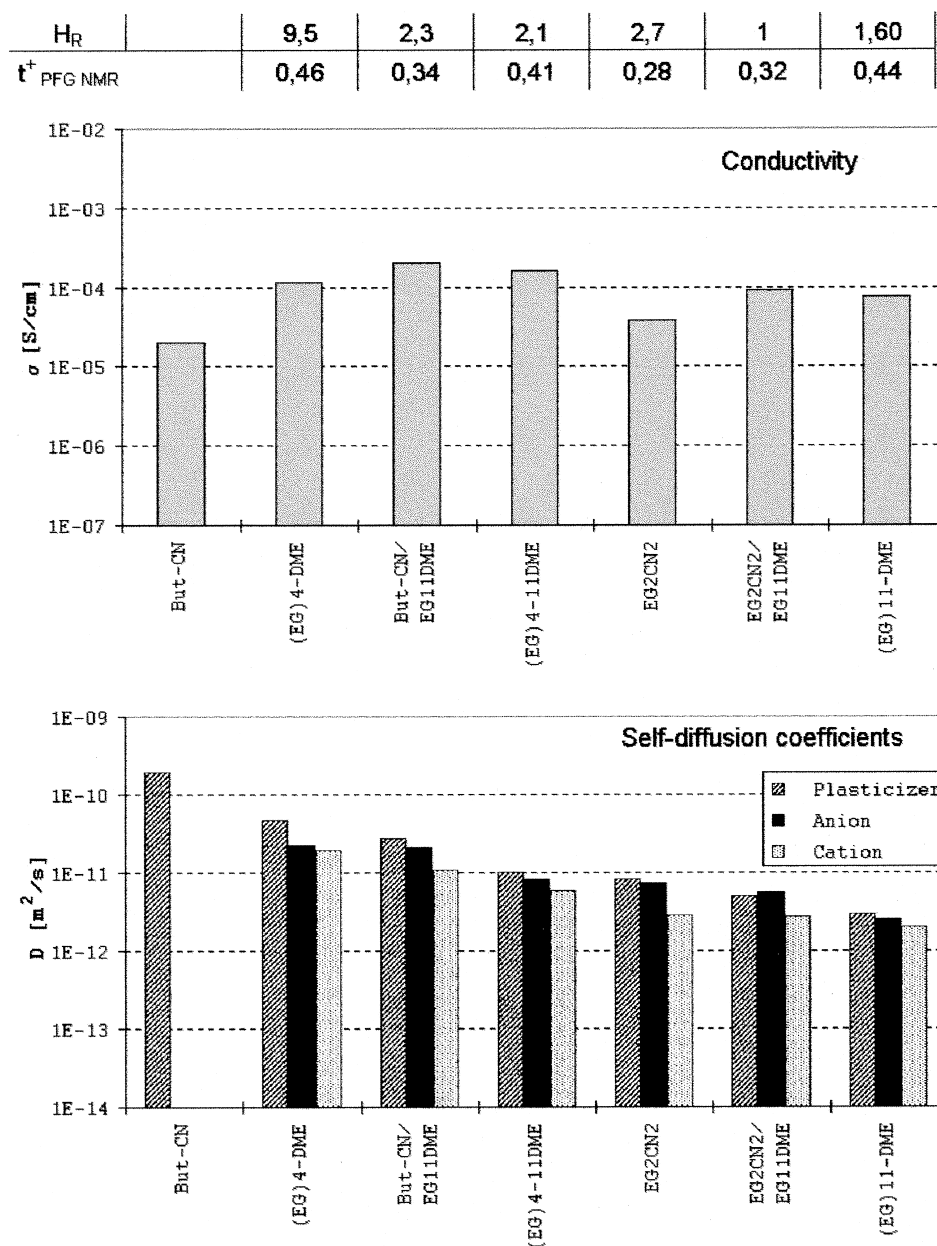| $H_R$ | | 9,5 | 2,3 | 2,1 | 2,7 | 1 | 1,60 |
|---|---|---|---|---|---|---|---|
| $t^+_{PFG\ NMR}$ | | 0,46 | 0,34 | 0,41 | 0,28 | 0,32 | 0,44 |



Fig. 11. Conductivity $\sigma$ and self-diffusion coefficients $D$ of different plasticizers and the charge carriers of gel electrolytes on the basis of poly((EG)$_3$DMA) with 75 wt% of plasticizers, 0.6 mol/kg LiCF$_3$SO$_3$, 20°C. The deviation from the Nernst–Einstein equation expressed as $H_R$ and the cationic transference number $t^+$ as calculated from the self-diffusion coefficients of the charge carriers are summarized above.

used as mixtures with (EG)$_{11}$DME. As shown in Fig. 6, the ionic association can be depressed by use of these plasticizers. However, as indicated by Figs. 11 and 12, the conductivity was not remarkably increased. For gel electrolytes with plasticizer mixtures of (EG)$_{11}$DME with EC/DEC, γ-butyrolactone or But-CN (Fig. 12) a good correlation between conductivity and self diffusivity according to the Nernst–Einstein equation was found with $H_R \approx 1$ (Table 3). However, both the conductivity and the self-diffusivity are unexpectedly low. The low deviation from the Nernst–Einstein equation can also indicate an increasing contribution of slightly mobile species to the overall

diffusivity [20]. In agreement with this, gel electrolytes on the basis of poly((EG)$_3$DMA) commonly show a larger deviation from the Nernst–Einstein equation, with $H_R \geq 2$, see Fig. 11. (EG)$_4$DME with a lower viscosity than (EG)$_{11}$DME is not appropriate as a cosolvent, because it has a low ability to solvate the salt indicated by enhanced ionic association (Fig. 6) and high values of $H_R$ (Fig. 11 and Table 3) as a result of the high concentration of ion pairs, which do not contribute to the ionic conductivity. This is also discussed in Refs. [26,28].

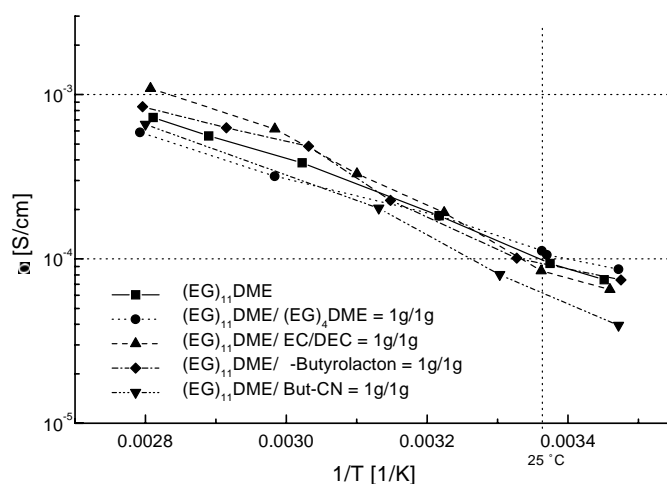The cationic contribution to the ionic conductivity is generally higher for gel electrolyte systems on the basis of

Fig. 12. Arrhenius plot of the conductivity $\sigma$ of gel electrolytes on the basis of poly((EG)$_3$DMA-*co*-CyMA (20 mol%)) with 75 wt% of various plasticizer mixtures (1 g/1 g), 0.6 mol/kg LiCF$_3$SO$_3$.

poly((EG)$_3$DMA) and their copolymers than for gel electrolytes on the basis of poly((EG)$_{23}$DMA) due to the lower ability of the former polymer to interact with the cation (Table 3, Fig. 11). Commonly, cationic transference numbers $t^+$ of the gel electrolytes based on poly((EG)$_3$DMA) were calculated between the value of the corresponding liquid electrolyte and 0.5. The discrepancies between $t^+$ measured by PFG-NMR and $t^+$ determined by the DC technique for the gels on the basis of poly((EG)$_3$DMA-*co*-CyMA (20 mol%)) (Table 3) can be probably explained by the formation of high charge transfer resistances during the measurement which adulterate the results.

### 3.6. Electrochemical stability

The Li plating stripping efficiency of gel electrolytes on the basis of poly((EG)$_n$DMA) with $n = 3$, 9 and 23 and (EG)$_{11}$DME as plasticizer (Fig. 13) was generally low. A Li cycling efficiency of only ca. 30% was reached. This is in agreement with investigations of Aurbach [30] who found, that the reactivity of polyethers versus lithium is relatively low. Hence, the Li surface chemistry is dominated by the reduction of the salt anion and the contaminants. The passivation properties of these surface layers are poor [30].

The electrolytes studied in this work were stable up to 3.8 V versus Li (Ni as WE) (Fig. 13a). A slight decrease of both the Li cycling efficiency and the anodic stability was observed with the increasing EG spacer length $n$ of the polymer and increasing (EG)$_{11}$DME content.

Compared with this, a remarkable increase in the Li-cycling ability up to values of approximately 50% was registered for gel electrolytes on the basis of copolymers of (EG)$_3$DMA with CyMA (Fig. 13b) which have higher conductivities as shown in Section 3.5. However, the anodic stability decreases with increasing content of CyMA in the copolymers. The increasing anodic stability of gel electrolytes

on the basis of poly((EG)$_{23}$DMA-*co*-CyMA) with increasing CyMA content described in Refs. [6,31] contrary to the above is probably an effect of the decreasing salt content. The [EG]/[LiCF$_3$SO$_3$] ratio was the same in these gel electrolytes, hence the salt concentration decreases with increasing CyMA content in the polymer. An improved Li cycling efficiency was also observed for gel electrolytes on the basis of copolymers of poly((EG)$_{23}$DMA-*co*-acrylonitrile (80 mol%)) with 50 wt% EG$_{11}$DME and [EG]/[LiCF$_3$SO$_3$] = 25 [31].

By use of plasticizers with reduced viscosity for the gel electrolytes, the conductivity was not remarkably increased (Fig. 12) and, as indicated by Fig. 13c, the Li plating stripping efficiency was usually low. Only for gel electrolytes on the basis of poly((EG)$_3$DMA) with a mixture of (EG)$_{11}$DME, EC and DEC an enhanced Li cycling ability was observed. This electrolyte also showed the highest anodic stability. (EG)$_4$DME as plasticizer component in poly((EG)$_3$DMA) based gel electrolytes and its copolymers with 20 mol% CYMA reduces the Li cycling efficiency remarkably, values of ca. 10%.

Gel electrolytes with plasticizers on the basis of cyanoethylated oligo(ethylene glycol)s or alcohols were generally not stable against lithium (Fig. 13c; Table 4), although gel electrolytes on the basis of copolymers with (EG)$_n$DMA with CyMA or AN showed relatively good electrochemical properties compared with the other materials studied.

## 4. Conclusions

Gel electrolytes on the basis of poly((EG)$_n$DMA) with $n = 3$, 9 and 23 and different types of plasticizers, e.g. (EG)$_{11}$DME and cyanoethylated oligo(ethylene glycol)s were studied. In contrast to (EG)$_n$DMA with $n = 9$ and
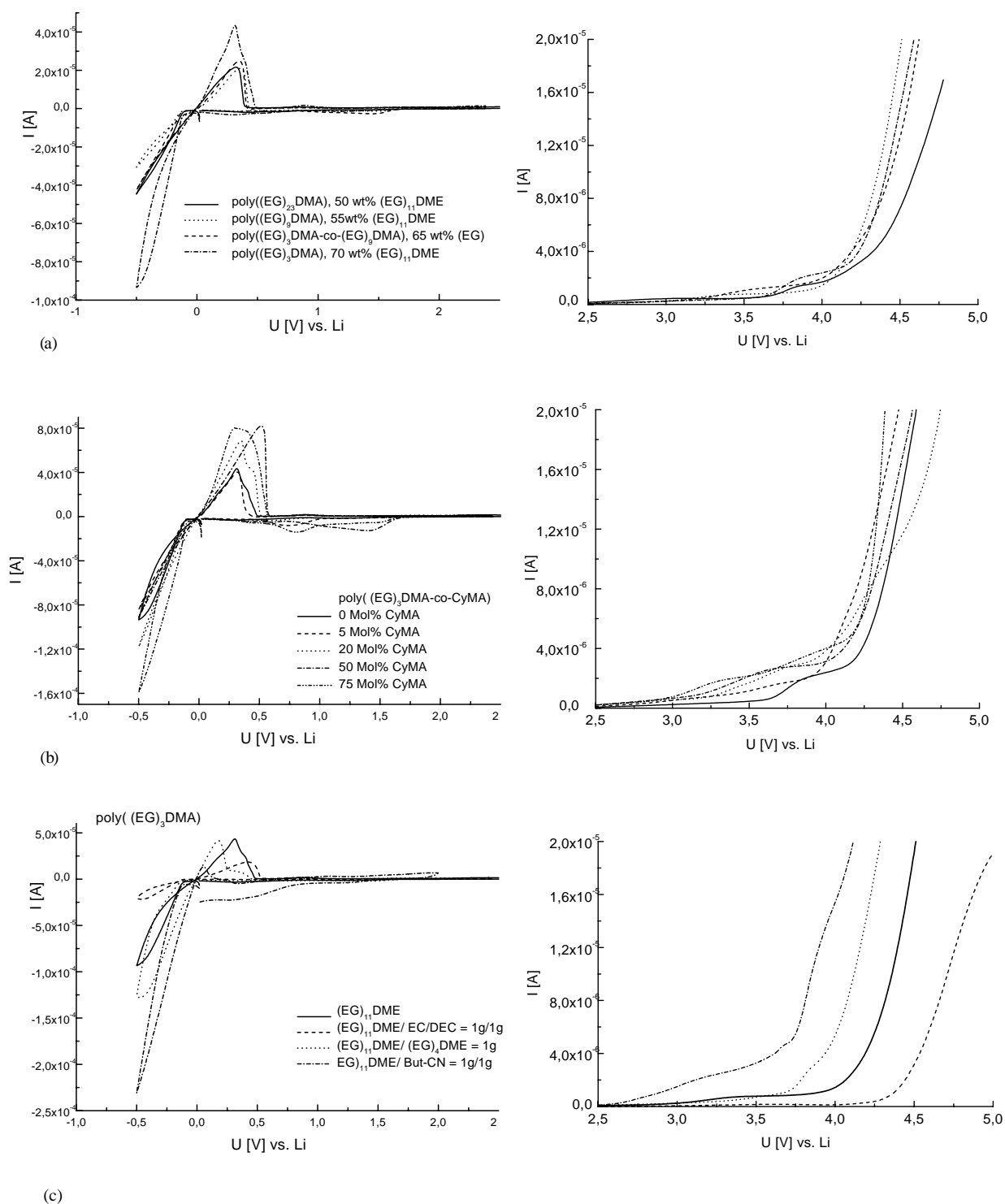
(a)

(b)

(c)

Fig. 13. Cyclic voltammogram of (a) gel electrolytes on the basis of poly$((EG)_n DMA)$ with $n = 3, 9, 23$ with $(EG)_{11}DME$ and 0.6 mol/kg LiCF$_3$SO$_3$, 25°C, 1 mV/s, Ni as WE, Li as CE and RE (b) gel electrolytes on the basis of poly$((EG)_3 DMA$-$co$-$CyMA)$ in dependence on the CyMA content in the copolymer, 75 wt% $(EG)_{11}DME$, $c_{LiCF3SO3} = 0.6$ mol/kg, 25°C, 1 mV/s, Ni as WE, Li as CE and RE (c) gel electrolytes on the basis of poly$((EG)_3 DMA)$ with 75 wt% of mixtures of $(EG)_{11}DME$ with various plasticizers, $c_{LiCF3SO3} = 0.6$ mol/kg, 25°C, 1 mV/s, Ni as WE, Li as CE and RE.

23, the use of $(EG)_3 DMA$ as a crosslinker leads to the formation of heterogeneous gel electrolyte films. The glassy state of the resulting polymer at room temperature and its high network density provide a maximum in mechanical stability.

It can be shown that the ionic association and the ionic conductivity are clearly dependent on the structure of the polymers. Contrary to the first expectation conductivities of $1 \times 10^4$ S/cm at room temperature with a cationic transference

number around 0.5 can be only reached with poly $((EG)_n DMA)$ with a short EG spacer length, e.g. heterogeneous gel electrolyte films on the basis of poly $((EG)_3 DMA)$ and its copolymers with $(EG)_9 DMA$ or CYMA. The films are able to embed high plasticizer contents up to 75 wt% $(EG)_{11} DME$.

Various plasticizers with a reduced viscosity were used to reach higher conductivites. However, the conductivity could only be enhanced slightly. The use of low molecular plasticizers with high polarity is considered as essential to achieve high conductivities, but from the point of the electrochemical stability it seems to be better to insert polar groups in the polymer than to modify the plasticizer.

## Acknowledgements

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