

# Polymer gel electrolytes synthesized by photopolymerization in the presence of star-shaped oligo(ethylene glycol) ethers (OEGE)

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## Abstract

The photoinitiated cross-linking polymerization of tri(ethylene glycol) dimethacrylate and its copolymerization with cyanomethyl methacrylate in the presence of  $\text{LiCF}_3\text{SO}_3$  and of various oligo(ethylene glycol) methyl ethers as plasticizer was studied for potential use of the resulting polymer gel electrolytes in lithium batteries. Comparing linear and star-shaped (three and four arm molecules) oligo(ethylene glycol) methyl ethers, the influence of the architecture of the plasticizers on the polymerization course was investigated by means of differential scanning calorimetry. Linear and star-shaped plasticizers with molar masses  $< 1000$  g/mol differ from each other concerning the dependence of their viscosity on their molar mass but not concerning the influence of the viscosity on the polymerization rate. Compared with linear plasticizers, the star-shaped ones have as an essential advantage a distinctly lower tendency to crystallize which is even completely suppressed in some cases. The gels were characterized with regard to the network density of their polymer matrix, to their thermal transitions, thermo-mechanical properties and ionic conductivity. The conductivity of solutions and gels with star-shaped plasticizers was slightly lower than that with linear ones at temperatures above room temperature.

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## 1. Introduction

The photoinitiated free-radical polymerization of various monomers in the presence of a lithium salt and a solvent or plasticizer proved as an appropriate method to prepare directly applicable films of polymer gel electrolytes for the potential use in lithium batteries [1–8]. The films may be produced by this method with a significantly less expenditure of time compared with films commonly obtained by solvent casting. In the latter case, only soluble polymers are applicable to form the gel electrolyte films. Their thermal stability and with that their shape resistance may be low. In contrast to this, cross-linking monomers can be photopolymerized yielding gel electrolyte films of highly thermal and mechanical stability because of the cross-linked structure of the polymer matrix.

Poly(ethylene glycol) is the unique solvating polymer for an extremely wide range of metal salts. Therefore, both cross-linking monomers and plasticizers including segments of oligo(ethylene glycol) ( $\text{EG}_n$ ) have been studied as components for gel electrolyte films [4–10].

Earlier, we reported the preparation of gel electrolyte films by photoinitiated polymerization of oligo(ethylene glycol) dimethacrylates ( $\text{EG}_n\text{DMA}$ ) with  $n=3, 9$  and  $23$  in the presence of oligo(ethylene glycol) dimethylethers ( $\text{EG}_n\text{DME}$ ) with  $n=4$  and  $11$  and of  $\text{LiCF}_3\text{SO}_3$  as the ion conducting salt [6]. Only the highly cross-linked networks from  $\text{EG}_3\text{DMA}$  yielded gel electrolyte films of appropriate mechanical stability, also at high contents of plasticizer, e.g. 75 wt%. The films had a heterogeneous structure exhibiting separate glass transitions of the polymer and of the solution of the salt in the plasticizer.  $\text{EG}_{11}\text{DME}$  rendered, especially advantageously as a plasticizer relating to the polymerization rate (strong gel effect owing to its high viscosity) and the mechanical as well as electrochemical stability of the gel electrolytes compared to gels containing  $\text{EG}_4\text{DME}$ . On the

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other hand, the low viscosity of the latter brings about a higher mobility of the ions and with that a higher ionic conductivity.

The content of free ions of the system can be increased by introduction of polar groups both into the polymer [4–7] and the plasticizer [9]. It has been shown, that the cationic transference numbers and the electrochemical stability of the gel electrolytes will be higher if the polymer include the polar groups and the plasticizer a sufficient number of EG units for the optimum solvation and transport of  $\text{Li}^+$  cations. However, the mobility of the latter and of  $\text{EG}_{11}\text{DME}$  is restricted already at room temperature due to the high tendency to crystallization of this plasticizer [6].

Therefore, we prepared three arm (OEGE-3) and four arm (OEGE-4) oligo(ethylene glycol) methyl ethers of various molecular weights (Scheme 1) as a new type of plasticizer with the expectation that their viscosity and their tendency to crystallization may be reduced compared with those of linear  $\text{EG}_n\text{DME}$  of similar molecular weight. The use of star-shaped OEGE with three and four arms as a plasticizer for gel electrolytes has already been proposed in [11].

Since the viscosity of the plasticizer influences the course of the free-radical polymerization and with that the properties of the resulting gel electrolyte, we investigated the photoinitiated homopolymerization of  $\text{EG}_3\text{DMA}$  and its

copolymerization with cyanomethyl methacrylate (CyMA) (Scheme 1) as a polar comonomer in the presence of linear and star-shaped plasticizers and of the ion conducting salt  $\text{LiCF}_3\text{SO}_3$ . The polymerization rate was monitored by means of differential scanning calorimetry (DSC). The viscosity and thermal properties of solutions of the salt in these plasticizers as well as the thermo-mechanical properties and the ionic conductivity of the corresponding gel electrolytes are reported.

## 2. Experimental part

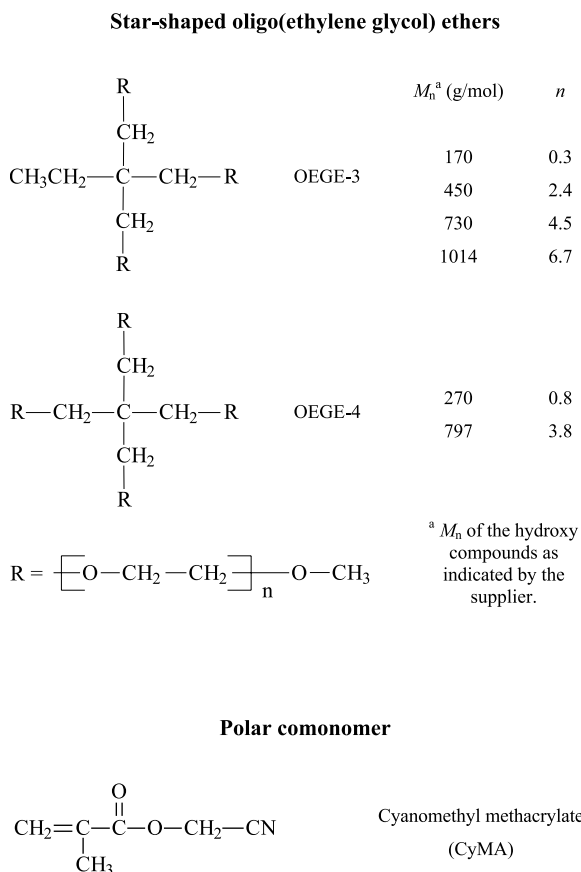
### 2.1. Materials

The linear oligo(ethylene glycol) dimethyl ethers  $\text{EG}_3\text{DME}$ ,  $\text{EG}_4\text{DME}$ ,  $\text{EG}_{5-6}\text{DME}$  and  $\text{EG}_{11}\text{DME}$  were purchased from Merck and  $\text{EG}_3\text{DMA}$  from Aldrich, and they were dried over molsieves  $4 \text{ \AA}$ . The photoinitiator Lucirin TPO (2,4,6-trimethylbenzoyldiphenylphosphineoxide) was purchased from the BASF AG.  $\text{LiCF}_3\text{SO}_3$  (Fluka) was dried in vacuum at  $120 \text{ }^\circ\text{C}$  for 24 h. Dioxane, toluene, hexane and acetone were distilled.

Cyanomethyl methacrylate (CyMA) was prepared according to a procedure described by Ueda et al. [12] by the reaction of chloroacetonitrile and methacrylic acid in the presence of triethyl amine.

### 2.2. Synthesis of star-shaped OEGE

Three arm OEGE were synthesized from trimethylolpropane ethoxylates (TMPE) (Aldrich) ( $M_n = 170, 450, 730$  and  $1014 \text{ g/mol}$ , respectively) and four arm OEGE from pentaerythrit ethoxylates (PEE) (Aldrich) ( $M_n = 270$  and  $797 \text{ g/mol}$ ) by methylation of the hydroxyl end groups. An example is given as follows:  $50 \text{ g}$  trimethylolpropane ethoxylate with  $M_n = 730 \text{ g/mol}$  (TMPE 730) ( $68.5 \text{ mmol}$ ),  $17.3 \text{ g}$  potassium hydroxide powder ( $0.308 \text{ mol}$ ) (Merck),  $12.5 \text{ mg}$  2,6-di-*tert*-butyl-4-methylphenol ( $5.67 \times 10^{-2} \text{ mmol}$ ) and  $100 \text{ ml}$  dioxane were charged into a three necked round-bottom flask, then stirred and refluxed for 1 h under an argon atmosphere. Then  $43.8 \text{ g}$  methyl iodide ( $0.308 \text{ mol}$ ) (Merck) were added slowly, and the mixture was refluxed with continuous stirring for 5 h. After cooling to room temperature the solution containing the product was filtered from the precipitated potassium iodide. Then dioxane and the excess of methyl iodide were removed in vacuum, and the product was decanted from the precipitate formed again. In this way, only conversions of 80–90% of the OH groups were reached as found by IR and  $^1\text{H}$  NMR spectroscopy. Therefore, the isolated product was reacted again with  $2.3 \text{ g}$  potassium hydroxide ( $41.1 \text{ mmol}$ ) and  $5.8 \text{ g}$  methyl iodide ( $41.1 \text{ mmol}$ ) in  $100 \text{ ml}$  dioxane in the same procedure described above to convert the residual OH groups. After filtering the solution, dioxane and the excess of methyl iodide were removed in vacuum. The product was



Scheme 1.

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