



New type of gel polymer electrolytes based on selected methacrylates and their characteristics. Part II. Fluorinated Co-polymers



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ABSTRACT

An extensive study on gel electrolyte systems based on 2-ethoxyethyl methacrylate (EOEMA) with various cross-link monomers is conducted with experimental techniques such as thermal analysis, stress-strain measurements and conductivity characterisation by impedance spectroscopy in order to clarify the influence of varying composition of the samples on their resulting properties. Furthermore, the addition of fluorinated side chains, used here predominantly with the aim of decreasing flammability of the ether-oxygen rich systems while boosting its ionic conductivity values, is investigated in terms of resulting mechanical, thermal and electrochemical properties.

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1. Introduction

Lithium batteries are used in many significant areas including transportation, electronics and home appliances as well as biomedical applications. One crucial component for the performance, safety, reliability, cost and efficiency of the whole battery system is its electrolyte. Using materials based on polymers originates from the need for a self-standing, leak-free battery system. These so called polymer electrolytes (PEs) have the potential to fulfil requirements of a solid system such as mechanical stability and no leakage, yet at the same time they exhibit high, liquid-like, ionic conductivity [1–5].

Acrylates are a group of easily UV-polymerizable monomers with an unending possibility of polymer chain compositions which can thus be optimised to meet the desired material properties. Different types and amounts of selected monomer units, the length and composition of the main polymer chain as well as chemistry of the side-chains can be varied and the polymer structure can be further altered by cross-links [6–8]. By introducing lithium salt dissolved in a solvent into a monomer mixture subsequent cross-linked by polymerisation, an amorphous polymer network or gel polymer is obtained. A polymer network formed by cross-linking of

monomeric units in the presence of solvent obtains a structure greatly influenced by the solvent volume factor and the interactions of the solvent-network units. Thus, the performance of the final gel polymer system will depend on the conditions of its formation as well as on its composition [9].

Operational safety of batteries is of paramount importance including high requirements on a stable charge – discharge process with no danger of overheating, prevention of electrolyte leakage and fire safety. Both the often used oxygenated polymer chains and carboxyl-based solvents are highly flammable which is why decreased flammability of electrolyte materials has been frequently approached by choice of fire-retarding additives and components such as fluorinated, phosphazene- or sulphone-based co-monomers, fillers or ionic-liquids [10–18]. In an attempt to decrease flammability the previously investigated studied system contained up to 40 wt% of 3-(trimethoxysilyl) propyl methacrylate (SPMA). However, although flammability was indeed decreased while stability of the gels were successfully enhanced, usability of these materials as electrolytes was hampered by a sharp decrease in conductivity [19].

In this work, a fluorine-containing co-monomer, 2-(perfluorooctyl) ethyl methacrylate (F17EMA), was introduced to the gel material, again based on EOEMA and the same glycol-based dimethacrylates, in an alternative effort to decrease flammability and simultaneously boost sufficient ionic mobility of the investigated system.

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2. Experimental

2.1. Materials and samples

2-ethoxyethyl methacrylate (EOEMA) and 2-(perfluorooctyl) ethyl methacrylate (F17EMA) in various ratios were used in this study as polymer back-bone material, and were cross-linked with one type of either ethylene glycol- (EDMA), diethylene glycol- (DEGDMA), triethylene glycol- (TEGDMA), or tetra ethylene glycol- (TTEGDMA) dimethacrylate monomers. All methacrylates were purchased as commercial monomers with high purity (99%) from Aldrich, together with UV polymerization initiator benzoin ethyl ether (BEE – 0.75 wt% used in all samples), LiClO₄ salt and propylene carbonate (PC). All mentioned chemicals were dried, liquids by molecular sieve (3 Å), and used without any further treatment. The exclusion of water was checked analytically (hr-NMR). An overview of all used components is given in Table 1.

2.2. Sample preparation

Initial sample mixtures were prepared and kept in dry conditions and contained monomers, one cross-linking agent (0.5 mol% in monomer) and the initiator of radical polymerization benzoin ethyl ether (0.75 wt%). Subsequently, pre-calculated amounts of lithium salt dissolved in PC solvent were added. Chosen amounts of the components as given in Table 1 were predetermined during a pilot study, not presented here, and optimised regarding their mechanical coherence. Gels were prepared using UV-initiated radical polymerization at room temperature. The procedure was carried out in moulds from PTFE

plate, packing distance silicon rubber frame and glass plates. Moulds were tightened using screw clamps. Obtained samples with area 8 cm × 8 cm and thickness corresponding to the type of used silicon rubber seal (1.0 ± 0.1 mm) were more or less elastic and transparent depending on composition. Ready samples were stored and investigated in dry conditions.

2.3. Used techniques

2.3.1. Conductivity measurements

Conductivity measurements were performed using impedance spectroscopy, whereby the influence of temperature was studied in the temperature range 25–85 °C. A slice of each film (18 mm diam.) was sandwiched between two parallel stainless-steel electrodes in a conductivity cell EL CELL[®] placed in a glove-box and a single potential impedance spectrum was measured in the frequency range 1000 kHz–500 mHz. Obtained spectra were analysed by EC-Lab software. The resulting ohmic resistance values were converted to specific resistivity and conductivity values respectively.

2.3.2. Mechanical properties

Mechanical properties – Young's modulus of elasticity, elongation (strain at break) and strength (stress at break) were measured using Instron Tester 6025 with computer evaluation.

2.3.3. Thermal analysis

Thermogravimetric analysis (TGA) was conducted on Perkin Elmer Thermogravimetric Analyzer Pyris 1 in the temperature

Table 1
Components used, their amounts and abbreviations.

2-ethoxyethyl methacrylate EOEMA 100–90 mol% MONOMERS	2-(perfluorooctyl)ethyl methacrylate F17EMA 0–10 mol%
ethylene glycol dimethacrylate EDMA	diethylene glycol dimethacrylate DEGDMA
ethylene glycol trimethacrylate TEGDMA CROSS-LINKERS 0.5 mol% 1 M LiClO ₄ salt in propylene carbonate (PC) SOLVENT 30–50 wt%	tetraethylene glycol dimethacrylate TTEGDMA

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