Effect of Crosslinking on Polymer Electrolytes Based on Cellulose

Marcin Chelmecki, Wolfgang H. Meyer, Gerhard Wegner

Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

ABSTRACT: Polymer electrolytes based on biogenic and commercially available substrates have been crosslinked thermally to improve their mechanical properties with only negligible effects on their conductivity. The new materials consist of oligo(ethylene oxide) side chains grafted via ether linkages to a cellulose backbone [poly(ethylene oxide)–2-hydroxypropylcellulose (PEO–HPC)]. PEO–HPC with a degree of side-chain substitution up to 3.0, as determined by NMR, has been blended with lithium bis(trifluoromethylsulfone)imide in molar ratios of $0.02 \leq [Li]/[O] \leq 0.2$. The effect of the salt concentration on the thermal behavior and ionic conductivity has been investigated by impedance spectroscopy, differential scanning calorimetry, and thermogravimetric analysis. The uncrosslinked materials are viscous liquids. The PEO–HPC/lithium salt blends have been thermally crosslinked with the application of urethane chemistry. The crosslinking reactions have been monitored by dynamic mechanical analysis. Crosslinking renders the liquid materials into mechanically stable films with a storage modulus of 10^5 Pa at 100°C. Surprisingly, their conductivities remain rather unaffected and reach at best 2.5×10^{-4} S/cm. The applicability of the PEO–HPC/lithium salt blends as separators in lithium-ion batteries has been demonstrated by the construction of a storage cell that is rechargeable. A freshly constructed cell reveals a voltage of about 3.2 V and can be recharged with a constant direct-current voltage up to the open circuit voltage of 3.65. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 25–29, 2007

Key words: electrochemistry; mechanical properties; thermal properties

INTRODUCTION

A separator membrane is crucially important for the function of batteries and fuel cells. In lithium-ion batteries, this membrane as well as the matrix material of the electrodes may consist of polymer electrolytes, which are liquid-free lithium-ion conductors. The use of a polymer rather than a liquid electrolyte offers advantages with respect to the electrochemical, mechanical, and thermal stability and the safety of the battery system.[1]

Over the past years, a wide variety of solid polymer electrolytes based on poly(ethylene oxide) (PEO) and its derivatives and networks have been investigated.[2] However, a promising alternative to liquid systems for industrial applications as yet has not been found, especially when we consider the complexity and cost of the synthesis of the materials. Previous reports have described reasonable improvements in materials with PEO grafted to polymers with a low glass-transition temperature (T_g).[3] One of the most convenient approaches is the use of cellulose derivatives as cheap starting materials to which polyether is grafted with mono- or diisocyanates[4] or the synthesis of cellulose esters with PEO as ester side chains.[5] Cellulose esters principally may suffer from hydrolysis and exhibit rather low conductivity when not plasticized or when not swollen with low-molecular-weight solvents.

Our new approach for solid-state polymer electrolytes offers the following advantages:

- Biogenic and commercially available substrates, that is, hydroxypropylcellulose and PEO derivatives as starting materials.
- Convenient and easily upscaleable synthesis, giving rise to a high degree of cellulose substitution.
- Combination of appropriate membrane properties with good conductivity based on a crosslinking reaction, which affects the cellulose backbone rather than the PEO side chains.

EXPERIMENTAL

Synthesis of Poly(ethylene oxide)–2-Hydroxypropylcellulose (PEO–HPC)

The convenient grafting of PEO side chains onto cellulose followed the recipes worked out by Nishaburi[6] and Xiao and Ritcey.[7] It started from α-tosyl-ω-ethoxy-

TABLE I
File Names, Compositions, and T_g Values of All Samples Used in This Study

File name	DS	PU/OH	Li/O	T_g (°C)
30PU00	3.0	0	0	−65
28PU21	2.8	2 : 1	0	
28PU11	2.8	1 : 1	0	−53
28PU23	2.8	2 : 3	0	−52
28PU12	2.8	1 : 2	0	−54
30PU00Li009	3.0	0	0.09	−25
28PU00Li010	2.8	0	0.10	−17
28PU21Li009	2.8	2 : 1	0.09	−15
28PU11Li009	2.8	1 : 1	0.09	−11
28PU23Li010	2.8	2 : 3	0.10	−7
28PU12Li010	2.8	1 : 2	0.10	−8

DS = degree of substitution of cellulose with respect to substitution with TEO; PU/OH = ratio of the diisocyanate reagent to the free OH groups in cellulose; Li/O = molar ratio of $LiN(SO_2CF_3)_2$ to oxygen atoms in cellulose and side chains.

tris(oxyethylene) (TEO) and commercially available 2-hydroxypropylcellulose [HPC; Aldrich; weight-average molecular weight = 80,000, degree of substitution (DS) = 3]. To obtain the maximum DS of 3, the TEO reagent was added with a 110% molar excess (with respect to the OH groups in HPC) to tetrahydrofuran (THF) at room temperature, and this was followed by the addition of the same molar amount of potassium t-butylate at 0°C and stirring of the mixture at 0°C for 3 days. The details of the synthesis, purification, and analysis are reported in ref. 8.

Preparation of the PEO–HPC blends with lithium salt

The dried polymer material and the appropriate amount of lithium salt were blended in a drybox. Under a constant argon flow, the polymer and salt were dissolved in dry THF and stirred for a few hours. Finally, the solvent was carefully evaporated *in vacuo*, and the remainder was dried in a high vacuum at 80°C for at least 48 h. The compositions of the blends are provided in terms of Li/O, where Li is the molar amount of the lithium salt and O is the molar amount of all the oxygen atoms in the polymer and side chains (see Table I). In this study, only lithium bis(trifluoromethylsulfone) imide [$LiN(SO_2CF_3)_2$] was used as a salt.

Crosslinking of PEO–HPC

For crosslinking, a PEO–HPC with DS = 2.8 was synthesized to provide residual HO groups at the cellulose backbone, which could be used for the crosslinking reaction.

A diisocyanate-terminated oligoether synthesized from tri(ethylene glycol) and toluene diisocyanate was used for thermal crosslinking. The idealized structure

of the crosslinker can be derived from Figure 1; its synthesis is described in ref. 8. In ref. 8, details of crosslinking PEO–HPC with UV light are also reported.
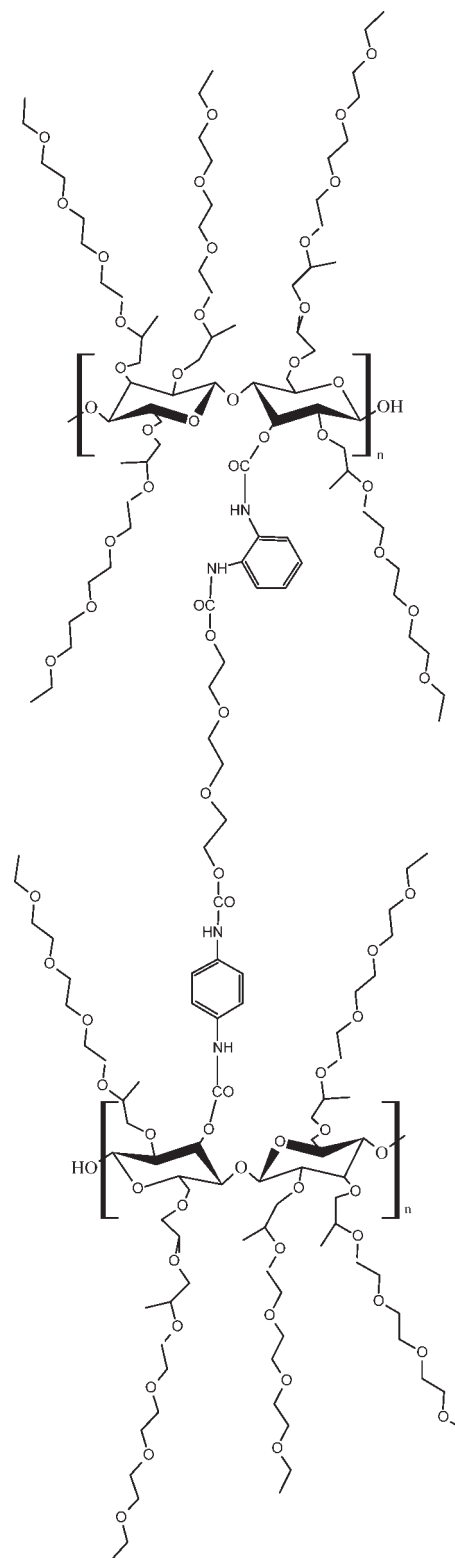

Figure 1 Idealized chemical structure of cellulose grafted with oligo(ethylene oxide) side chains and thermally crosslinked with a diisocyanate derivative.
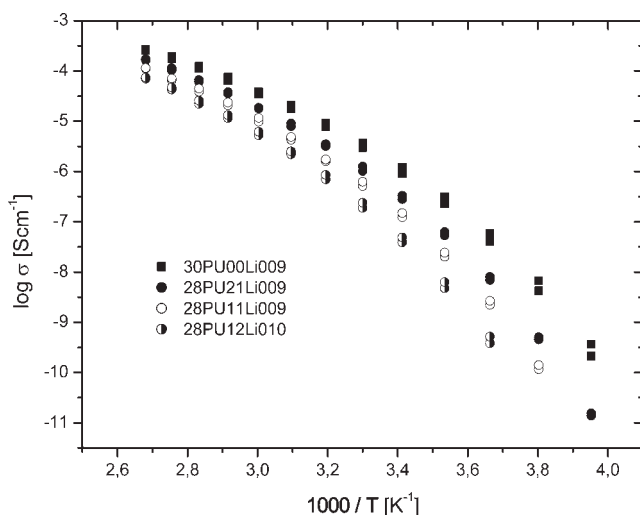
Figure 2 Temperature-dependent conductivity (σ) of cellulose derivatives with lithium salt and with and without crosslinking. Data from both heating and cooling cycles are displayed for comparison (for the composition details, see Table I).

Carefully dried portions of PEO–HPC with DS = 2.8 (or the appropriate blends with lithium salt) were dissolved in dry THF under an argon atmosphere, the appropriate amount of the freshly prepared diisocyanate crosslinking agent was added, and the mixture was stirred for 1 h. Films were cast from the solution, and the solvent evaporated. The samples were cured *in vacuo* for 12 h at 120°C to complete the crosslinking reaction. The compositions and file names of all the samples are listed in Table I (only the ratios of the crosslinker to the free OH groups before the crosslinking reaction are displayed because the actual number of urethane linkages in the films has not been determined). In cases with a higher ratio of the diisocyanate reagent to the free OH groups, unreacted isocyanate groups probably were hydrolyzed during the curing procedure and finally ended up as NH_2 groups.

Conductivity measurements

The direct-current conductivities were obtained from the low-frequency plateau of the real part of the alternating-current conductivities (and from the extrapolation of complex impedance Z^* to the real axis in the Z''/Z' plot with Z'' as the imaginary part and Z' the real part of the impedance). The alternating-current conductivities were determined with temperature- and pressure-dependent impedance spectroscopy with a Schlumberger (Hampshire, England) SI 1260 impedance/gain phase analyzer with a homemade dielectric interface (10^{-1}–10^6 Hz). The samples were prepared on platinum electrodes and measured under nitrogen and temperature control (Novocontrol, Hundsangen, Germany).

Thermoanalysis

The T_g values were determined with differential scanning calorimetry at a heating rate of 10 K/min under N_2 (DSC-30, Mettler, Giessen, Germany).

Dynamic mechanical analysis

The dynamic mechanical analysis measurements were performed with an RMS-800 parallel-plate rheometer (Rheometrics Inc., Piscataway, NJ) with a cooling rate of 10 K/min and at a constant frequency of 10 rad/s. The samples were hot-pressed into cylindrical tablets with a diameter of 6 mm and a thickness of 2 mm.

RESULTS AND DISCUSSION

Conductivity

Temperature dependence

The temperature dependence of the direct-current conductivity of uncrosslinked and crosslinked samples is displayed in an Arrhenius plot in Figure 2. All samples exhibit Vogel-Tamman-Fulcher (VTF) behavior that is typical for ion-conducting polymers in which the ionic transport is supported by the segmental motions of the polymer.[9] The uncrosslinked PEO–HPC (30PU00Li009) exhibits the best conductivity and reaches 3.2×10^{-4} S/cm at 100°C, whereas the PEO–HPC with the highest crosslinker ratio (28PU12Li010) reaches only 0.75×10^{-4} S/cm at 100°C. In the sample with the lowest crosslinker ratio (28PU21Li009), the conductivity is only negligibly reduced to 2.5×10^{-4} S/cm at 100°C. Thus, at high temperatures, the conductivity is reduced by means of crosslinking by a factor between 1.3 and 4 only, depending on the crosslinker ratio. However, this effect
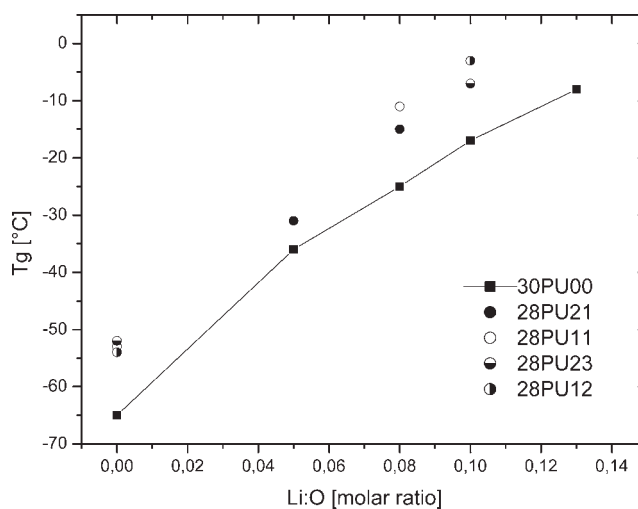

Figure 3 T_g values of cellulose derivatives with and without crosslinking as a function of the lithium salt content. The line for sample 30PU00 is only a guideline (for the composition details, see Table I).
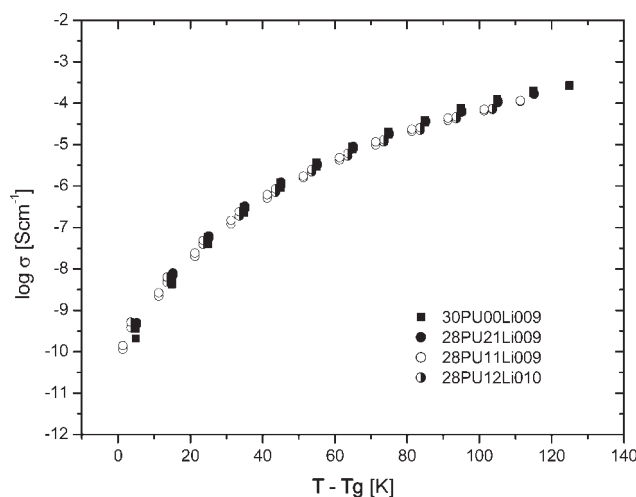
Figure 4 Conductivity (σ) of cellulose derivatives with lithium salt and with and without crosslinking (for the composition details, see Table I) as a function of the reduced temperature ($T - T_g$).

becomes stronger with decreasing temperature. The crosslinking effect on the conductivity is surprisingly small because the conductivities of crosslinked polymer electrolytes typically are some orders of magnitude lower than those of equivalent uncrosslinked systems.[2]

Influence of T_g on the conductivity

T_g of the uncrosslinked PEO–HPC increases almost linearly with the salt content. The observed glass transitions are in the temperature range that is typical for the softening of PEO side chains.[10] Crosslinking increases the glass transition further in PEO–HPC with and without lithium salts (Fig. 3). At first glance, this seems unexpected because the crosslinking takes place between the cellulose backbones rather than between the side chains (Fig. 1). If the side chains were crosslinked, a much stronger increase in the T_g values would be expected. The rather moderate increase in T_g that we observe as the result of crosslinking may just be the effect of exchanging two PEO side chains with loose ends (in 30PU00) against one PEO chain that is pinned on both ends via the urethane bonds to the cellulose backbone (in 28PU21, etc.) with some constraints on neighboring PEO side chains.

Taking the different T_g values of the different samples into account, we find that all the temperature-dependent conductivity data coincide with the same VTF-type curve (Fig. 4). This proves that the change in T_g is the only reason for the moderate conductivity decrease as a result of crosslinking.

Mechanical stability

As an indicator for the mechanical stability, the shear modulus of the PEO–HPC samples has been deter-

mined to be temperature-dependent (Fig. 5). The pure PEO–HPC with DS = 3.0 (30PU00) loses its mechanical strength already below $-50°C$ when the sample undergoes its glass transition and becomes a highly viscous liquid with a shear modulus around 10^3 Pa at room temperature.

The PEO–HPC blend with DS = 2.8 and a lithium salt content of Li/O = 0.10 (28PU00Li010) experiences the same severe stability loss, but at higher temperatures according to the shift in T_g.

In contrast to the uncrosslinked samples, the shear modulus of the crosslinked sample (28PU23Li010) starts decreasing at just the same temperature as that of the appropriate uncrosslinked sample (28PU00Li010), but the decrease is much less pronounced, so the shear modulus levels off around 10^5 Pa. This means that even at temperatures above the glass transition, the mechanical strength of the crosslinked PEO–HPC remains on a level that is comparable to that of a hard rubber.

Electrochemical performance

To demonstrate the applicability of the membrane material and to test its performance and stability, a simple lithium-ion cell was prepared. For the construction of the cell, two easily available electrodes were used, which did not necessarily provide the best overall performance. The battery involved exclusively all-solid, solvent-free parts:

Metallic lithium was used as a reversible anode, the source of lithium ions during discharge. The corresponding lithium-ion sink (cathode) was prepared separately as a mixture of 60% (by weight) $LiCoO_2$, 20% carbon black, and 20% PEO–HPC/$LiN(SO_2CF_3)_2$ ([Li]/[O] = 0.10, DS = 2.8). The cathode material was
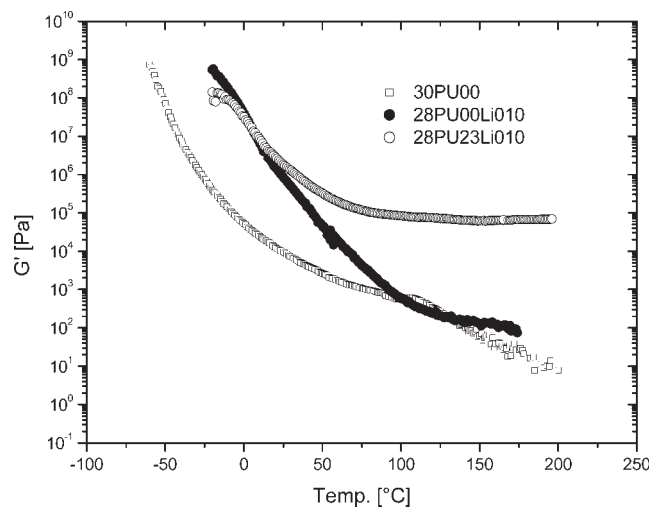

Figure 5 Temperature dependence of the shear modulus (G') of cellulose derivatives with and without lithium salt and with and without crosslinking (for the composition details, see Table I).
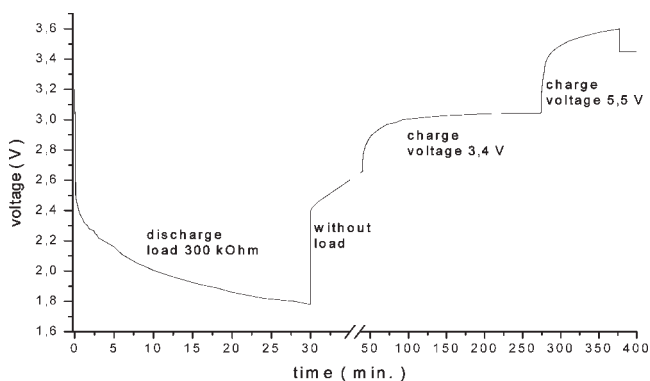
Figure 6 Charge and discharge curves of a lithium-ion cell assembled with 28PU23Li010 (see Table I) as a separator.

cast onto copper foil as a current collector and was carefully dried.

The anode and cathode were separated by a thin film of 28PU23Li010 (see Table I). The battery was assembled in an argon-operated drybox and also kept under argon during the cycling experiments.

The parameters of the constructed cell were a current collector thickness of 0.025 mm, a cathode thickness of 0044 mm, a cathode area of 45 mm × 45 mm, a separator thickness of 0.07 mm, an anode thickness of 0.75 mm, and an anode area of 45 mm × 45 mm.

The freshly assembled cell revealed a voltage of about 3.2 V (Fig. 6). After charging at a constant direct-current voltage, the cell showed an open-circuit voltage of 3.65 V. After discharging to 1.75 V, the cell could be recharged up to 3.65 V again. The charging and discharging were carried out in a controlled way with a voltage/time recorder. The discharge of the cell was realized with a constant load of 300 kΩ. The charging process was carried out at a constant direct-current voltage, which initially was set to 4.5 V and after 4 h increased to 5.6 V.

The investigated cell shows the typical properties of a secondary battery; that is, the cell is reversibly rechargeable. The maximum cell voltage of 3.65 V is similar to the voltage of a commercial lithium-ion battery. The very low discharge current of 10 μA is probably caused by large internal battery resistance. The overall performance certainly could be improved when internal contacts and other resistances are minimized. However, the cycling experiment shows that the separator material operates well and is electrochemically stable under the experimental conditions used.

CONCLUSIONS

New materials consisting of oligo(ethylene oxide) side chains grafted via ether linkages to a cellulose backbone have been synthesized with a degree of side-chain substitution up to 3.0 and have been blended with lithium salts in molar ratios of $0.02 \leq [\text{Li}]/[\text{O}] \leq 0.2$.

The PEO–HPC/lithium salt blends have been thermally crosslinked. Crosslinking renders the liquid materials into mechanically stable films with a storage modulus of 10^5 Pa at 100°C, whereas their conductivities are only moderately influenced by crosslinking and remain at best 2.5×10^{-4} S/cm.

The concept of improving the mechanical properties by means of crosslinking or microphase separation in one component of the material while keeping the liquid-like matrix for the ionic conductivity in the other component appears promising and may be realized also with materials with other superstructures, such as dendrimers.

The applicability of the PEO–HPC/lithium salt blends as separators in lithium-ion batteries has been proved with the construction of a single cell that is rechargeable. A freshly constructed cell reveals a voltage of about 3.2 V and can be recharged with a constant direct-current voltage up to the open circuit voltage of 3.65 V.

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