

# Synthesis and characterization of UV-cured poly(siloxane-urethane) elastomers containing polyethylene oxide segments – as potential membrane materials

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**Abstract:** Conductive polymeric membranes based on poly(siloxane-urethane)s (PSUR) and designed for potential application as separators in Li-ion batteries were obtained through consecutive heat and UV curing of compositions containing NCO-terminated PSUR prepolymers with both polysiloxane (SIL) and poly(ethylene oxide) (PEO) segments in the polymer chain and unsaturated diols as chain extenders. Lithium salts in the form of solutions in ethylene carbonate/dimethyl carbonate (EC/DMC) mixture were incorporated into PSUR after curing (“post-cure” method) or (in some experiments only) also before curing (*in situ* method). The effect of polymer structural parameters (PEO segments content, NCO/OH ratio) as well as curing conditions and method of lithium salt incorporation on mechanical and thermal properties, swelling ability and specific conductivity of the corresponding membranes were investigated. Supramolecular structure of membranes was studied using scanning electron microscopy with X-ray analysis (SEM/EDS) technique. The selected membranes were tested as potential separators in lithium batteries.

**Keywords:** silicone-urethanes, poly(siloxane-urethane)s, UV-curing, lithium batteries.

## Synteza i charakterystyka elastomerów poli(siloksano-uretanowych) zawierających segmenty poli(tlenku etylenu) – jako potencjalnych materiałów membranowych

**Streszczenie:** W wyniku utwardzania na gorąco i następnie utwardzania promieniowaniem UV kompozycji prepolimerów poli(siloksano-uretanowych) (PSUR), o łańcuchach zakończonych ugrupowaniem NCO, i nienasyconych dioli, pełniących rolę przedłużaczy łańcucha, otrzymano membrany przewodzące przeznaczone do wykorzystania jako separatory w bateriach litowo-jonowych. Prepolimery PSUR zawierały segmenty polisiloksanowe (SIL) oraz segmenty pochodzące z poli(tlenku etylenu) (PEO). Sole litu w postaci roztworów w mieszaninie węglanu etylenu (EC) z węglanem dimetylu (DMC) wprowadzono do PSUR po utwardzeniu kompozycji (metoda „post-cure”) lub (w niektórych doświadczeniach) przed utwardzeniem kompozycji (metoda *in situ*). Zbadano wpływ parametrów strukturalnych (zawartość segmentów PEO, stosunek NCO/OH), a także warunków utwardzania i metody wprowadzania soli litu na właściwości mechaniczne, stopień spęcznienia i przewodnictwo właściwe membran. Strukturę nadcząsteczkową membran określono metodą skaningowej mikroskopii elektronowej ze spektroskopią dyspersji energii promieniowania rentgenowskiego (SEM/EDS). Wybrane membrany testowano jako separatory baterii litowo-jonowych.

**Słowa kluczowe:** silikono-uretany, poli(siloksano-uretany), utwardzanie UV, baterie litowo-jonowe.

Silicone-urethanes<sup>a)</sup> containing poly(ethylene oxide) (PEO) segments and modified with lithium salts were tested as potential membranes in lithium batteries [1–3] and it was anticipated that ion conductivity observed in such systems could be facilitated by Li<sup>+</sup> ion complexation

not only by oxyethylene segments, but also by urethane moieties, similarly as suggested for polyurethanes with PEO segments [4]. The results of studies on swelling ability, mechanical properties and supramolecular structure of films made from moisture-cured silicone-urethanes,

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<sup>a)</sup> The term “silicone-urethanes” is commonly used for poly(siloxane-urethane)s, poly(siloxane-urethane-urea)s and poly(siloxane-urea)s.

*i.e.*, poly(siloxane-urethane-urea)s (PSURUR) synthesized with the objective to evaluate them as potential membrane materials in lithium batteries were described in our earlier paper [5] and specific conductivity of  $10^{-3}$  S/cm was achieved for such films swelled with lithium salt solutions in ethylene carbonate(EC)/dimethyl carbonate(DMC) solvent mixture.

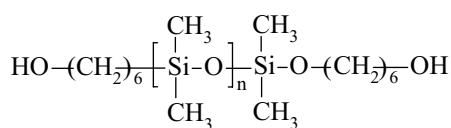
UV-curable polymer systems containing lithium salts were widely investigated as gel polymer electrolytes or solid-state polymer electrolytes for lithium batteries [6–21] and, *inter alia*, it was found that UV-curing "...caused a decrease in the degree of crystalline structure which contributed to increase in ionic conductivity" [19]. In some of those polymer systems polyurethanes [18–20] or polysiloxanes [14, 21] were successfully applied and specific conductivities of the resulting membranes in the range of  $10^{-4}$ – $10^{-5}$  S/cm were reported. Taking into account extremely high speed of UV-curing reaction [22] and also the advantage of UV-curable systems if applied in fabrication of membranes for lithium batteries which is the possibility of incorporating the lithium salts in the system prior to curing [10], so troublesome process of soaking the membrane in lithium salt solution can be avoided, we decided to test whether silicone-urethanes can be used in such systems.

In this paper, the results of studies on the effect of polymer chain composition and method of preparation on the mechanical and thermal properties, supramolecular structure and electrical conductivity of poly(siloxane-urethane) (PSUR) elastomers obtained by UV-curing of corresponding NCO-terminated PSUR prepolymers containing PEO segments and double bonds and modified with lithium salts will be presented. Modification of PSUR elastomers with lithium salts was conducted either "post-cure" by soaking the cured films in lithium salt solution in EC/DMC solvent mixture or *in situ* by dissolving PSUR prepolymers in lithium salt solution in the same solvent mixture and curing the films which already contained lithium salt.

## EXPERIMENTAL PART

### Materials

Isophorone diisocyanate (IPDI) was obtained from Evonik, PEO with 1000 molecular weight was obtained from Merck, polysiloxane diol (SIL) with structure shown in Formula (I) (Tegomer 2311) was obtained from Tego Chemie. Dimethyl carbonate (DMC) and ethylene carbon-



$n = 30$

(I)

ate (EC) solvents, unsaturated diol – *cis*-2-butene-1,4-diol, and lithium salt  $\text{Li}(\text{CF}_3\text{SO}_3)$  were obtained from Aldrich. Dibutyltin dilaurate catalyst (DBTL) was obtained from POCH (Poland). UV-curing initiator Irgacure 2022 was obtained from CIBA.

### Synthesis of NCO-terminated PSUR prepolymers containing PEO segments

SIL and PEO were dehydrated by heating for 2 h at 120 °C under vacuum. The polyaddition reaction of SIL and PEO with IPDI was carried out at 80 °C in 0.75 dm<sup>3</sup> glass reactor equipped with anchor type agitator and inert gas inlet in the presence of DBTL catalyst until the band corresponding to OH groups (3500–3200 cm<sup>-1</sup>) was not detected by FTIR. Free NCO content of the resulting prepolymers was determined by titration.

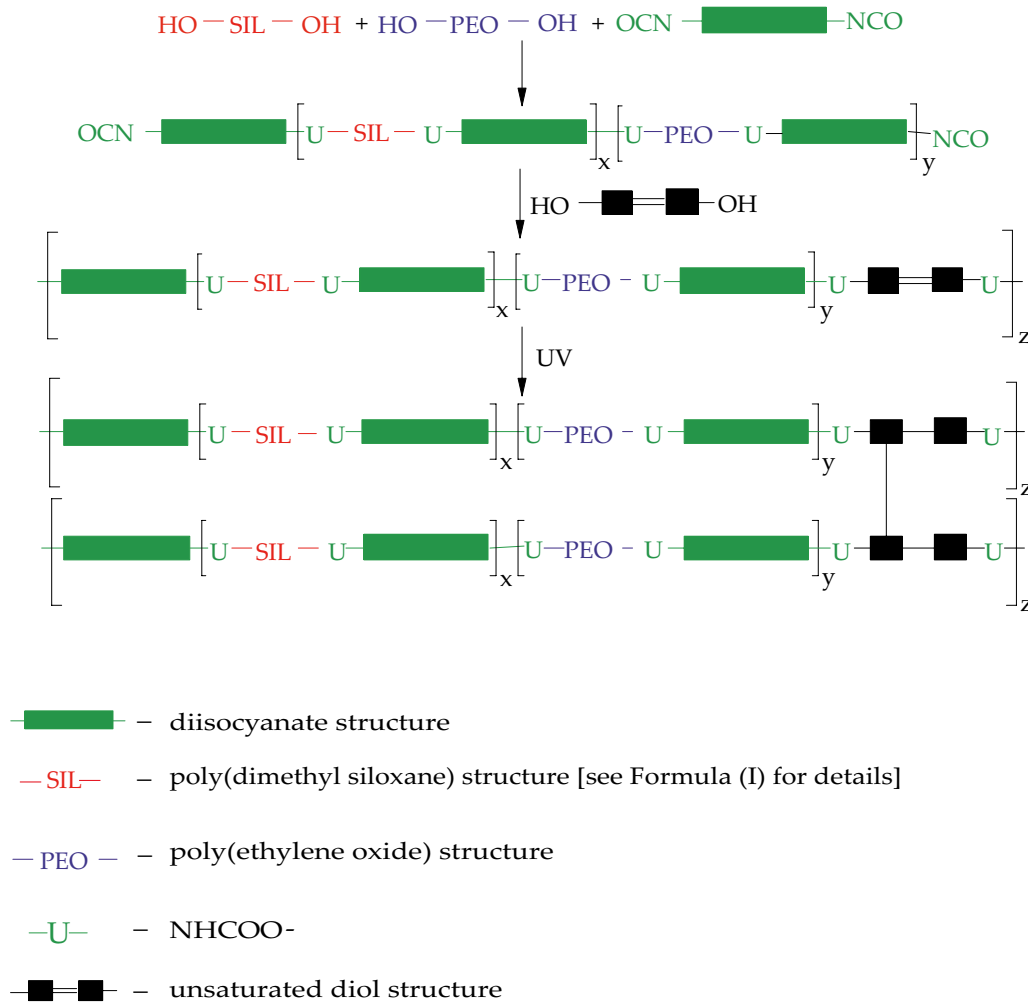
### Curing of PSUR prepolymers to obtain PSUR elastomers

Liquid PSUR prepolymers were mixed with unsaturated diol and photoinitiator and the resulting compositions were cast on polytetrafluoroethylene (PTFE)-coated steel plates in the MBraun dry chamber using the applicator with appropriate gap size and heated at fixed temperature over fixed time period. Next, the plates with half-cured film were placed under 450 W UV lamp (at a distance of 10 cm from the lamp) and subjected to UV radiation for 30, 60 or 120 s. After that time 60 µm to 500 µm thick moisture-cured elastomer films were removed from the plates and used for the experiments. The process of synthesis of PSUR elastomers applied in this study is presented in Scheme A.

In some experiments prior to curing the prepolymers were dissolved in EC/DMC = 1/2 mixture and/or mixed with 0.25 M or 1 M lithium salt solution in that solvent mixture (*in situ* method of lithium salt incorporation). In those investigations the content of lithium salt in PSUR film was supposed to be the same as the content of lithium salt in the swelled film (see further text). For instance, if 1 M lithium salt was incorporated *in situ*, the proportion of prepolymer to lithium salt solution was set at a level corresponding to 12.5 % of lithium salt in a dried film, *i.e.*, to the same lithium salt content in a dried film as that resulting from soaking of cured film in 1 M lithium salt solution over 0.5 hour.

### Preparation of samples

Dumbbell-shaped specimens (62 × 10 mm) for testing the mechanical properties (Instron testing machine, 50 mm/min pulling rate) and round-shaped specimens (10 mm diameter) for film swelling experiments and conductivity determinations were cut from the films obtained earlier.



Scheme A

## Methods of testing

### Film swelling experiments

Prepared samples were weighed ( $m_0$ ) and immersed in EC/DMC (1/2) solvent (or in 1 M lithium salt solution in that solvent) for the prescribed time intervals, thoroughly dried with filter paper and weighed again ( $m_1$ ). Swell ( $S$ , %) was calculated from the Equation (1):

$$S = (m_1 - m_0)/m_0 \cdot 100 \% \quad (1)$$

where:  $m_1$ ,  $m_0$  – masses of the film after and before immersion.

When lithium salt solution was used all operations were conducted in the appropriately sealed glove box (MBraun).

### Conductivity determinations and preliminary testing of the membranes as separators in a lithium battery

Prepared specimens (in the form of round-shaped membranes) were put between two stainless steel ele-

ments of the measurement Swagelok type steel cells and, after wetting with a drop of  $30 \cdot 10^{-3} \text{ cm}^3$  of EC/DMC = 1/2 solvent mixture, were tested using impedance analyzer (Solartron Analytical, model SI 1260). The impedances ( $R$ ) expressed in ohms obtained from Nyquist diagram (Fig. 1) were recalculated to specific conductivities ( $\sigma$ ) expressed in S/cm for a given specimen thickness ( $l$ ) and surface area ( $A$ ) of the specimens from the Equation (2):

$$\sigma = l/(R \cdot A) \quad (2)$$

The mean value obtained from impedance values obtained for 5 specimens was taken as the result.

The selected membranes prepared as described earlier were also tested as separators in lithium batteries. For that purpose the membranes were first wetted with a drop of  $30 \cdot 10^{-3} \text{ cm}^3$  of EC/DMC = 1/2 solvent mixture and then placed between electrodes of a lithium cell (lithium mini-battery). Anode was liquid Li and cathode was  $\text{LiMn}_2\text{O}_4$ . 0.05 C current was applied in charging the battery with experimental membranes and up to 20 charging-discharging cycles were conducted during tests. As a reference, standard Celgard® 2400 separator

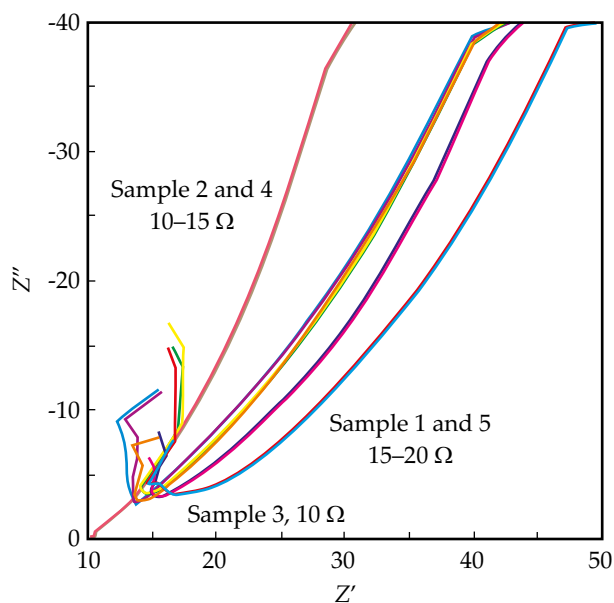


Fig. 1. Example of Nyquist diagram from which the impedances of PSUR samples were taken (sample 1769 E)

soaked in lithium salt solution in EC/DMC = 1/2 solvent mixture was used.

#### DSC studies

DSC studies were conducted using Perkin Elmer DCS 7 apparatus at 20 °C/min heating rate.

#### Structural studies

Scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS) investigations were conducted using SEM microscope Jeol JSM – 6490LV.

## RESULTS AND DISCUSSION

### Effect of PEO/SIL and NCO/OH molar ratio in the heat-curing process and final UV curing time on mechanical properties and swelling ability of PSUR films

In Table 1 the mechanical properties of PSUR elastomer films obtained by consecutive heat-curing and final UV-curing of PSUR prepolymers obtained at different PEO/SIL molar ratios, different NCO/OH (prepolymer/extending unsaturated diol) molar ratios and different UV-curing times are shown. In the preliminary investigations different diols were used as chain extenders in the heat-curing process and eventually *cis*-2-butene-1,4-diol was selected and applied in this study. When other unsaturated diols (*e.g.*, trimethylolpropane monoallyl ether) were applied the mechanical properties of the films obtained by final UV-curing of heat-treated diol-extended prepolymers were quite poor.

Data presented in Table 1 clearly show that the content of PEO segments in PSUR elastomer films did not

affect significantly the mechanical properties of the films. Then, it can be concluded that PSUR obtained through PSUR prepolymer chain extension with unsaturated diol and subsequent UV-curing behaved similarly to poly(siloxane-urethane-urea)s (PSURUR) obtained through moisture curing of PSUR prepolymers [5]. It can also be noted from data presented in Table 1 that increasing NCO/OH (prepolymer/unsaturated diol) molar ratio resulted in moderate increase in mechanical properties while increasing UV-curing time led to diminishing the elongation at break which may be explained by polymer crosslinking during the UV-curing process.

Selected PSUR elastomer film samples listed in Table 1 were swelled in EC/DMC solvent mixture in order to test the effect of PEO segments content, NCO/OH ratio and UV curing time on their swelling ability. The results of that experiment are shown in Table 2.

The following observations can be made based on the results showed in Table 2:

- Swell ( $S$ , %) of the films increases with swelling time and after some time an equilibrium is reached.
- Swelling ability of the films increases with increase in POE segments content in the PSUR chain ( $1764 < 1768 < 1769 < 1771$ ). Similar phenomenon was observed for PSURUR with similar structure obtained through moisture-curing process [5].

NCO/OH molar ratio seems to influence significantly swelling ability of the films – generally lower NCO/OH molar ratio results in higher  $S$  value. This phenomenon can be explained by lower molecular weight of extended PSUR prepolymer which was obtained in the case when lower NCO/OH ratio was applied.

### Effect of NCO/OH molar ratio in the heat-curing process on specific conductivity of PSUR films swelled in lithium salt solution

The effect of NCO/OH molar ratio in the heat-curing process on specific conductivity of PSUR films swelled in  $\text{Li}(\text{CF}_3\text{SO}_3)$  solution in EC/DMC = 1/2 solvent mixture is shown in Fig. 2.

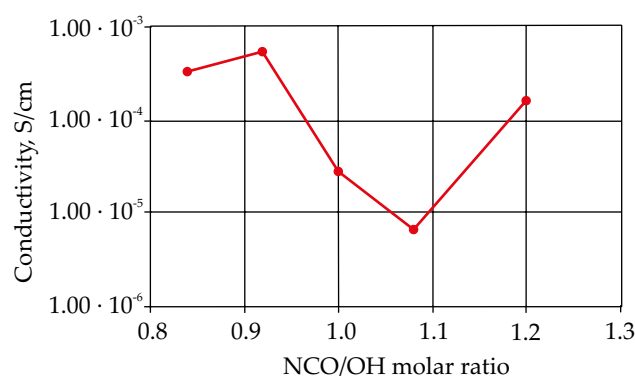


Fig. 2. Effect of NCO/OH molar ratio in the heat-curing process on specific conductivity of PSUR films swelled in lithium salt solution in EC/DMC = 1/2 mixture

**Table 1. Mechanical properties of PSUR elastomer films**

Sample designation	Sample composition			Mechanical properties	
	PEO/SIL molar ratio	NCO/OH molar ratio	PEO segments content in the film wt %	Stress at break $\delta$ , MPa	Strain at break $\epsilon_r$ , %
1761 A-30	3/1	0.84/1	36.37	0.9	282
1761 A-60	3/1	0.84/1	36.37	1.2	225
1761 B-60	3/1	0.92/1	37.58	0.8	326
1764 A-30	1/3	0.84/1	8.73	0.8	436
1764 A-60	1/3	0.84/1	8.73	0.7	243
1764 A-120	1/3	0.84/1	8.73	1.4	226
1764 B-30	1/3	0.92/1	8.79	1.7	461
1764 B-60	1/3	0.92/1	8.79	1.4	272
1764 B-120	1/3	0.92/1	8.79	1.9	204
1768 A-30	1/1	0.84/1	27.21	Not tested	Not tested
1768 A-60	1/1	0.84/1	27.21	0.4	632
1768 A-120	1/1	0.84/1	27.21	1.8	379
1769 A-30	3/1	0.84/1	36.37	1.2	238
1769 A-60	3/1	0.84/1	36.37	Not tested	Not tested
1769 A-120	3/1	0.84/1	36.37	1.2	160
1769 B-30	3/1	0.92/1	37.58	0.8	146
1769 B-60	3/1	0.92/1	37.58	Not tested	Not tested
1769 B-120	3/1	0.92/1	37.58	1.1	124
1771 A-30	4/1	0.84/1	40.91	4.3	346
1771 A-60	4/1	0.84/1	40.91	2.6	196
1771 A-120	4/1	0.84/1	40.91	3.0	222
1771 B-30	4/1	0.92/1	41.18	2.6	238
1771 B-60	4/1	0.92/1	41.18	2.6	205
1771 B-120	4/1	0.92/1	41.18	3.2	116
1772 A-30	0/1	0.84/1	0	1.9	345
1772 A-60	0/1	0.84/1	0	1.0	260
1772 A-120	0/1	0.84/1	0	1.4	231
1772 B-30	0/1	0.92/1	0	2.1	334
1772 B-60	0/1	0.92/1	0	1.3	253
1772 B-120	0/1	0.92/1	0	3.0	247

SIL = Si(CH<sub>3</sub>)<sub>2</sub>O; PEO = CH<sub>2</sub>-CH<sub>2</sub>O. A-30/60/120 = sample that was heat-cured at 100 °C over 1 h using 0.84 NCO/OH molar ratio and UV-cured over 30/60/120 s; B-30/60/120 = sample that was heat-cured at 0.92 NCO/OH molar ratio and UV-cured over 30/60/120 s.

**Table 2. Swelling ability of obtained PSUR elastomer films**

Sample designation	S, % after					
	0.5 h	1 h	1.5 h	2 h	16 h	24 h
1764 A-60	33	55	69	86	167	180
1764 B-60	31	48	67	69	82	103
1768 A-60	141	222	233	253	298	279
1768 B-60	207	237	253	253	295	304
1769 A-60	152	265	298	350	394	405
1769 B-60	114	144	139	146	157	156
1771 A-60	158	210	187	200	200	224
1771 B-60	88.5	95	128	136	110	164
1772 A-60	Sample was dissolved after 30 min					
1772 B-60	Sample was dissolved after 30 min					

Sample designation – the same as in Table 1.

Based on the results presented in Fig. 2 it can be concluded that increasing NCO/OH molar ratio in the heat-curing process up to *ca.* 1/1 led to significant decrease in specific conductivity of the PSUR films swelled in lithium salt solution while after further increase in NCO/OH molar ratio over 1/1 specific conductivity started to increase. This phenomenon can be explained by changes of the molecular weight of PSUR with changes in NCO/OH ratio. For relatively high molecular weight PSUR obtained at NCO/OH close to 1/1 the mobility of Li<sup>+</sup> ions in the swelled film was too low to ensure good conductivity.

### Effect of the method of Li<sup>+</sup> salt incorporation on specific conductivity of PSUR films

The effect of the method of lithium salt incorporation on specific conductivity of PSUR films is shown in Table 3. For these investigations PSUR films characterized by structural parameters corresponding to sample 1769 B (see Table 1), *i.e.*, PEO/SIL = 3/1 and NCO/OH = 0.92/1 were used. Samples were thermally cured at 100 °C for 60 min and UV-cured for 120 s.

Based on the results shown in Table 3 it can be noted that:

- Using *in situ* method of lithium salt incorporation into PSUR films it was possible to obtain samples with quite reasonable specific conductivity which was comparable with conductivity of corresponding samples with lithium salt incorporated *via* “post cure” method. This is very important from the practical point of view because troublesome swelling of films can be avoided.
- For lithium salt containing films obtained using *in situ* method a drastic (4-fold) diminishing the lithium salt content in PSUR had only slight negative effect on film conductivity and in the case of films swelled in lithium salt solution conductivity slightly increased with decreasing Li salt content. It means that optimization of lithium salt content in PSUR will be needed in order to achieve optimal film conductivities.

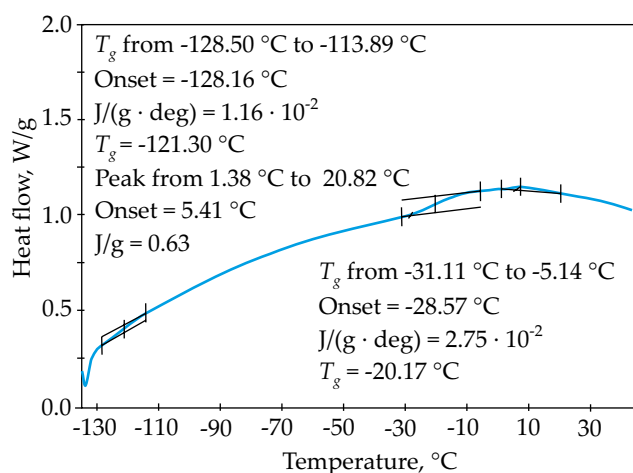


Fig. 3. DSC diagram of film obtained in the process shown in Scheme A (sample 1769 B)

### Effect of PEO/SIL molar ratio on specific conductivity of PSUR films containing Li salt incorporated *via in situ* method

The effect of PEO/SIL molar ratio on specific conductivity of PSUR films containing Li salt incorporated *via in situ* method is shown in Table 4. In those investigations 1 M lithium salt was used. All samples were prepared at 0.92/1 NCO/OH molar ratio and were thermally cured at 100 °C for 60 min and UV-cured for 120 s.

Data shown in Table 4 clearly prove that PEO segments content in PSUR has crucial role in determining the conductivity of samples containing Li salt. When PEO/SIL molar ratio was low (samples 1764 D and 1768) specific conductivity was 10 times lower than when PEO/SIL molar ratio was high (samples 1769 E and 1771). This observation is consistent with the results from our earlier investigations of specific conductivity of moisture-cured PSURUR samples with different PEO/SIL molar ratios swelled in Li salt solution [5].

### Thermal properties of PSUR films

Thermal properties of UV-cured PSUR films containing PEO segments were investigated using DSC in order to learn whether in such elastomers crystallization of PEO segments had been diminished, similarly as it was proved for PSURUR obtained *via* moisture-curing of PSUR prepolymers [5], so there could be a good chance that after modification with lithium salts those new materials might be examined as membranes in lithium batteries. Typical DSC diagram of PSUR film obtained in the process shown in Scheme A is presented in Fig. 3.

It is clear from Fig. 3 that similarly to PSURUR containing PEO segments cured with moisture [5] also typical PSUR containing PEO segments cured with temperature and UV (sample designated as 1769 B in Table 1) showed two  $T_g$  values – one (around -120 °C below zero) that corresponded to glass transition of polysiloxane segments and another (around -30 °C below zero) that could be attribut-

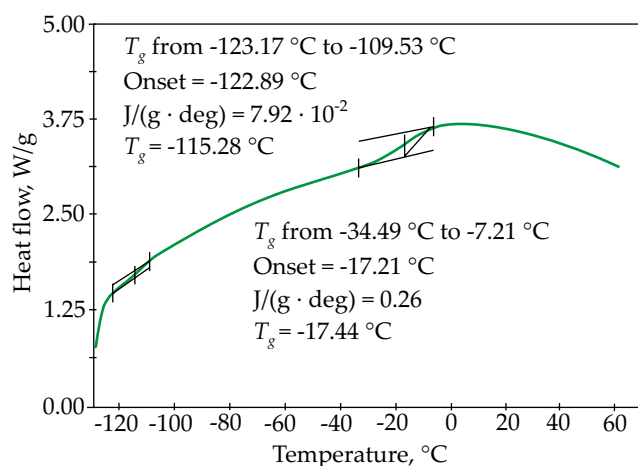


Fig. 4. Standard DSC diagram of film obtained in the process shown in Scheme A (sample 1769 C)

**Table 3.** Effect of the method of Li salt incorporation on specific conductivity of PSUR films

Sample designation	Method of Li salt incorporation	Film thickness, cm	Specific conductivity, S/cm
1769 E	1 M Li(CF <sub>3</sub> SO <sub>3</sub> ) in EC/DMC = 1/2 incorporated <i>in situ</i> before thermal curing	1 – 0.0118 2 – 0.0104 3 – 0.0064 4 – 0.0098 5 – 0.0124	1 – 4.45 · 10 <sup>-4</sup> 2 – 5.89 · 10 <sup>-4</sup> 3 – 3.62 · 10 <sup>-4</sup> 4 – 5.55 · 10 <sup>-4</sup> 5 – 4.83 · 10 <sup>-4</sup> <b>Mean = 4.87 · 10<sup>-4</sup></b>
1769 F	Fully cured sample swelled for 0.5 h in 1 M Li(CF <sub>3</sub> SO <sub>3</sub> ) in EC/DMC = 1/2 ("post-cure" method)	1 – 0.0352 2 – 0.0314 3 – not tested 4 – 0.0328 5 – 0.0374	1 – 3.62 · 10 <sup>-4</sup> 2 – 2.54 · 10 <sup>-4</sup> 3 – 2.32 · 10 <sup>-4</sup> 4 – 4.23 · 10 <sup>-4</sup> 5 – 4.23 · 10 <sup>-4</sup> <b>Mean = 3.18 · 10<sup>-4</sup></b>
1769 G	Fully cured sample swelled for 0.5 h in 0.25 M Li(CF <sub>3</sub> SO <sub>3</sub> ) w EC/DMC = 1/2 ("post-cure" method)	1 – 0.0526 2 – 0.0406 3 – 0.0396 4 – 0.0360 5 – 0.0464	1 – 5.95 · 10 <sup>-4</sup> 2 – 6.21 · 10 <sup>-4</sup> 3 – 6.40 · 10 <sup>-4</sup> 4 – 7.28 · 10 <sup>-4</sup> 5 – 6.56 · 10 <sup>-4</sup> <b>Mean = 6.48 · 10<sup>-4</sup></b>
1769 H	0.25 M Li(CF <sub>3</sub> SO <sub>3</sub> ) in EC/DMC = 1/2 incorporated <i>in situ</i> before thermal curing	1 – 0.0172 2 – 0.0176 3 – 0.0152 4 – 0.0156 5 – 0.0176	1 – 1.03 · 10 <sup>-4</sup> 2 – 1.05 · 10 <sup>-4</sup> 3 – 2.33 · 10 <sup>-4</sup> 4 – 2.05 · 10 <sup>-4</sup> 5 – 1.72 · 10 <sup>-4</sup> <b>Mean = 1.63 · 10<sup>-4</sup></b>

**Table 4.** Effect of PEO/SIL molar ratio on specific conductivity of PSUR films containing Li salt incorporated *via in situ* method

Sample designation	PEO/SIL molar ratio	PEO wt % in PSUR	Film thickness cm	Specific conductivity S/cm
1764 D	1/3	8.79	1 – 0.0100 2 – 0.0118 3 – 0.0062 4 – 0.0118 5 – 0.0084	1 – 1.72 · 10 <sup>-5</sup> 2 – 3.04 · 10 <sup>-5</sup> 3 – 26.99 · 10 <sup>-5</sup> 4 – 2.12 · 10 <sup>-5</sup> 5 – 0.95 · 10 <sup>-5</sup> <b>Mean = 6.96 · 10<sup>-5</sup></b>
1768	1/1	27.21	1 – 0.0052 2 – 0.0072 3 – 0.0138 4 – 0.0138 5 – 0.0118	1 – 1.01 · 10 <sup>-5</sup> 2 – 1.83 · 10 <sup>-5</sup> 3 – 2.38 · 10 <sup>-5</sup> 4 – 1.62 · 10 <sup>-5</sup> 5 – 1.18 · 10 <sup>-5</sup> <b>Mean = 1.60 · 10<sup>-5</sup></b>
1769 E	3/1	37.58	1 – 0.0118 2 – 0.0104 3 – 0.0064 4 – 0.0098 5 – 0.0124	1 – 4.45 · 10 <sup>-4</sup> 2 – 5.89 · 10 <sup>-4</sup> 3 – 3.62 · 10 <sup>-4</sup> 4 – 5.55 · 10 <sup>-4</sup> 5 – 4.83 · 10 <sup>-4</sup> <b>Mean = 4.87 · 10<sup>-4</sup></b>
1771	4/1	41.18	1 – 0.0192 2 – 0.0130 3 – 0.0134 4 – 0.0144 5 – 0.0311	1 – 8.36 · 10 <sup>-4</sup> 2 – 2.94 · 10 <sup>-4</sup> 3 – 5.83 · 10 <sup>-4</sup> 4 – 6.27 · 10 <sup>-4</sup> 5 – 1.30 · 10 <sup>-4</sup> <b>Mean = 4.94 · 10<sup>-4</sup></b>

ed to glass transition of PEO segments which did not form crystallites. Similarly as for moisture-cured PSURUR, no  $T_g$  over zero which corresponded to hard segments (IPDI + UR + urea) was detected and since no sharp peak corresponding to melting of PEO crystallites was observed it indicated that no significant crystallization of PEO segments occurred and thus PEO segments were mobile enough to facilitate Li<sup>+</sup> ions movement in the film.

In order to check the effect of solvent presence during curing on the final properties of cured PSUR a DSC diagram was obtained for the sample designated as 1769 C which had the same composition and was cured using identical conditions as sample 1769 B, but the starting composition containing PSUR prepolymer was dissolved in EC/DMC = 1/2 solvent mixture before heat curing started. As it can be seen in Fig. 4, for the sample which was



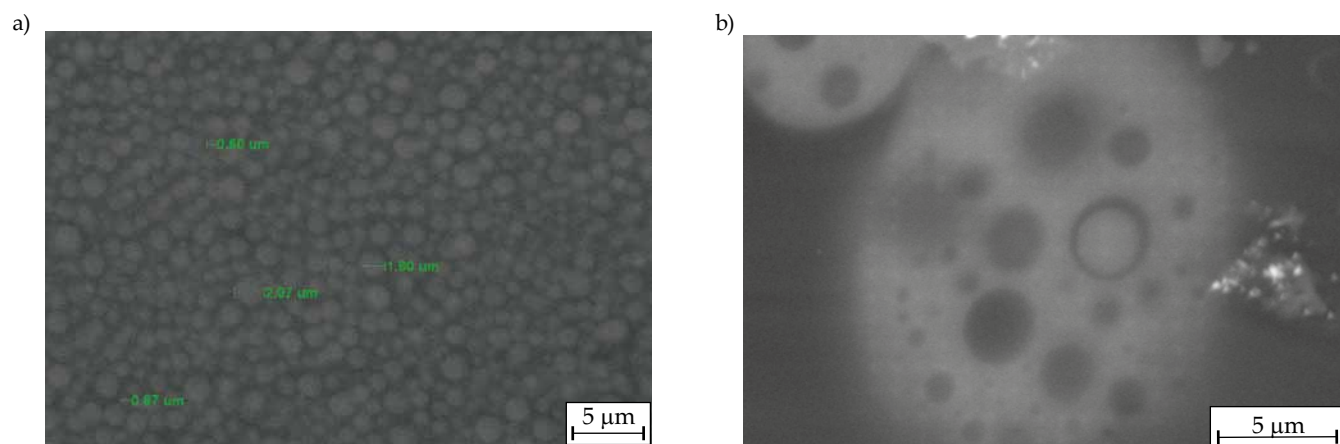


Fig. 5. Effect of solvent presence during curing on supramolecular structure of PSUR film: a) sample 1769 B, b) sample 1769 C

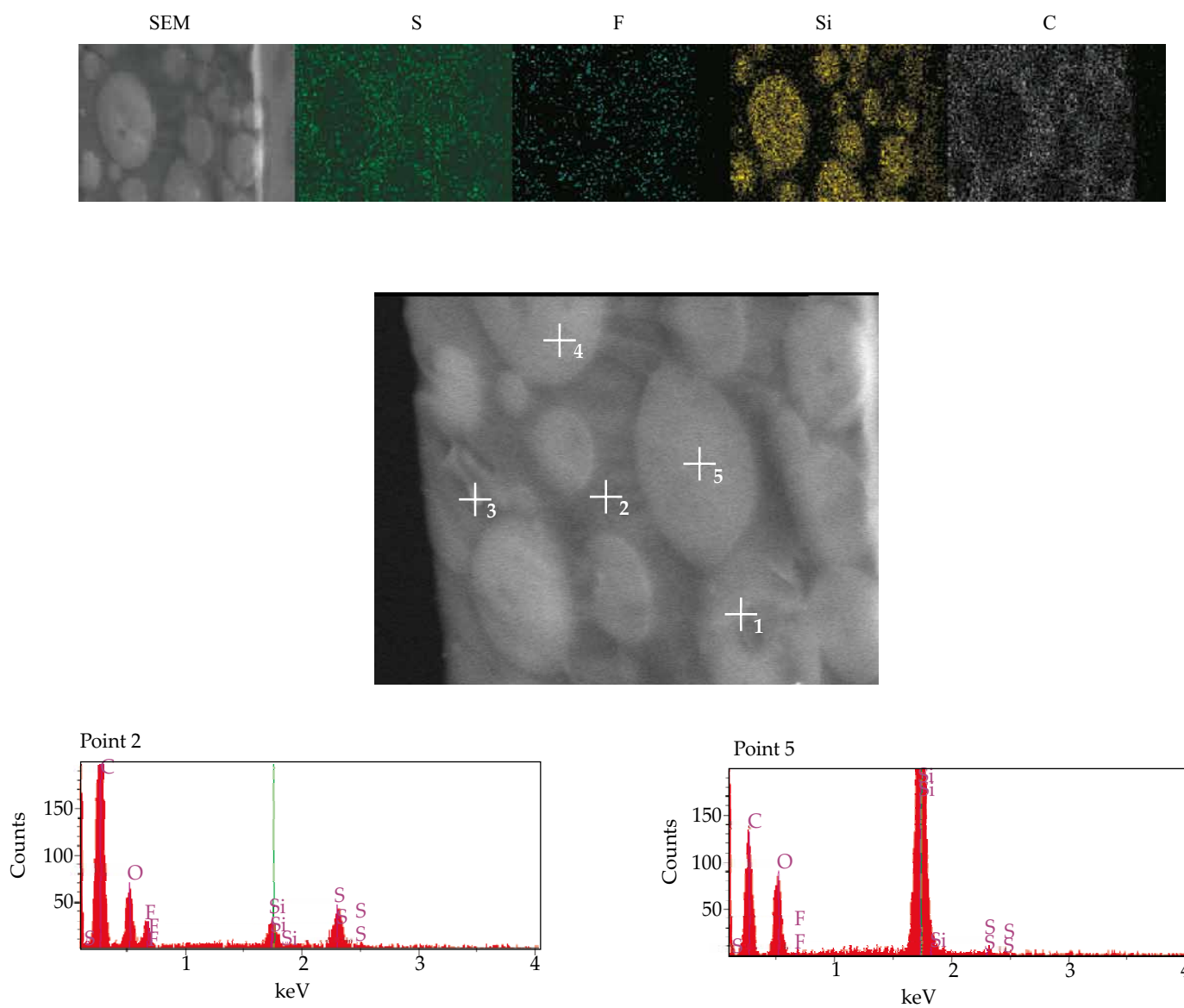


Fig. 6. Supramolecular structure of cured PSUR film containing lithium salt incorporated *via in situ* method (SEM); distribution of different elements in the film as detected by EDS is also shown, compare concentration of F and S (originating from  $-\text{CF}_3\text{SO}_3$ ) on the surface of and inside of polysiloxane domains (points 2 and 5, respectively)



cured in the presence of solvents also two  $T_g$  values were observed, though both  $T_g$  values were higher than the corresponding ones observed for sample that was cured without solvents present. This phenomenon could be explained by formation of different PSUR film supramolecular structure of both films at the curing process. As it has been proved both by lack of a peak corresponding to solvent evaporation on DSC diagram and also by SEM studies (see further) such explanation appeared to be correct.

#### Effect of the method of Li salt incorporation on supramolecular structure and specific conductivity of PSUR membranes

As it was indicated earlier, while most of the experiments carried out in the study described in this paper

were conducted using PSUR films swelled in lithium salt solution in EC/DMC = 1/2 ("post-cure" method) we also tested the possibility of introducing the lithium salt to PSUR prepolymer before heat/UV curing (*in situ* method). Since in the *in situ* method lithium salt had to be incorporated into PSUR prepolymer in the form of solution in EC/DMC we first checked the effect of that solvent presence during the process of formation of PSUR on supramolecular structure of the resulting PSUR film before we attempted to apply *in situ* method. It was found that the supramolecular structure of PSUR film obtained without EC/DMC solvent and in the presence of that solvent differed very much (see Fig. 5).

While polysiloxane segments formed small (1–2  $\mu\text{m}$ ) domains in PSUR film obtained from PSUR prepolymer composition without solvent present (sample 1769 B),

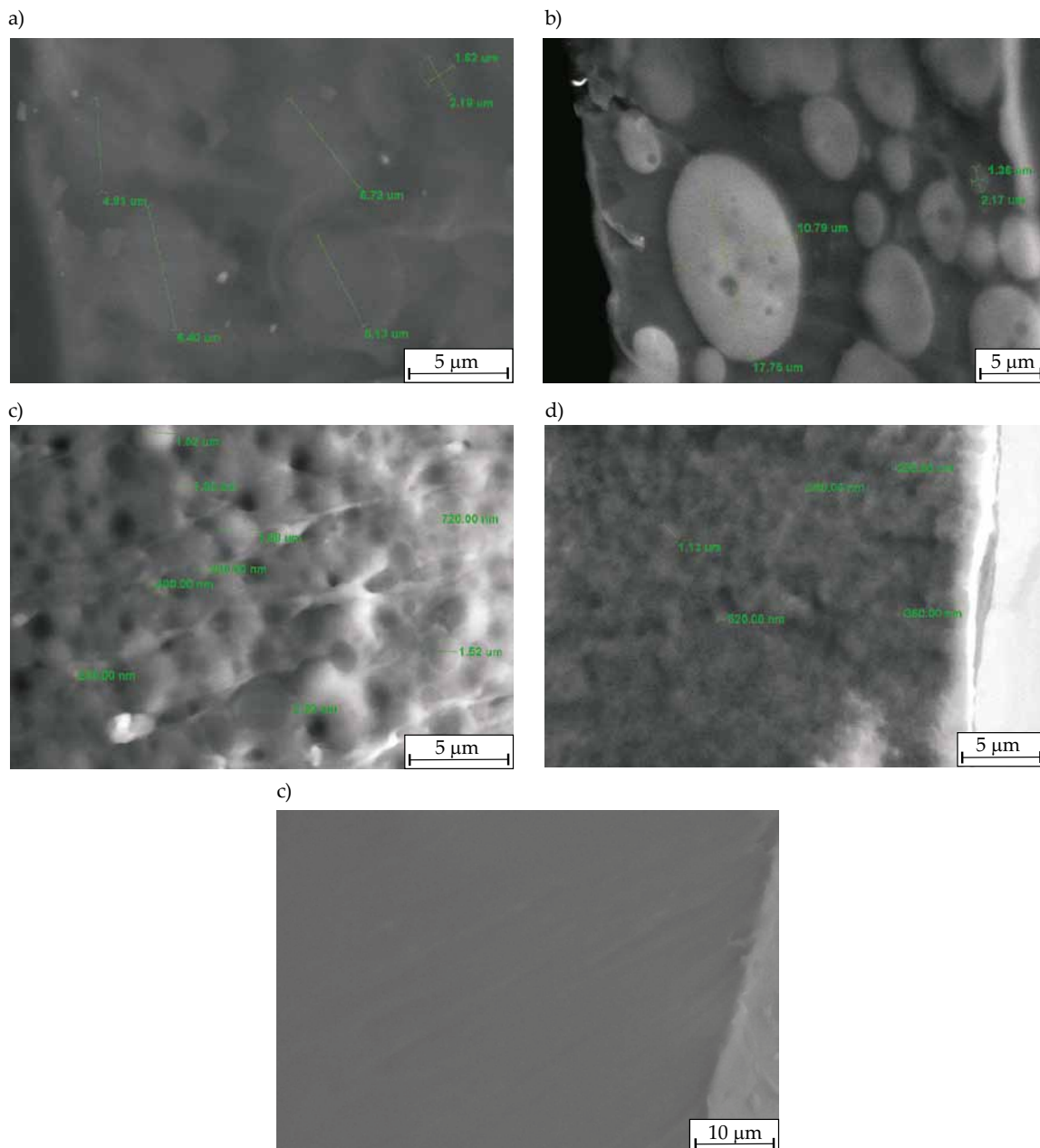


Fig. 7. Effect of POE segments content in lithium salt containing UV-cured PSUR on its supramolecular structure, Li salt was incorporated using *in situ* method: a) 41.18 wt % POE, b) 37.58 wt % POE, c) 27.21 wt % POE, d) 8.79 wt % POE, e) 0 wt % POE

large (10–20  $\mu\text{m}$ ) polysiloxane domains containing smaller (1–3  $\mu\text{m}$ ) PEO domains were observed in PSUR film obtained from PSUR prepolymer composition containing EC/DMC solvent. Formation of similar large polysiloxane domains in the cured PSUR film was also observed when 1 M lithium salt solution in EC/DMC was used instead of EC/DMC solvent to prepare starting composition containing PSUR prepolymer (Fig. 6). As it was proved by EDS, lithium salt (see F and S distribution) was present only in the continuous phase composed mostly from POE segments, and their highest concentration was close to the surfaces of polysiloxane domains, *i.e.*, where the urethane moieties which bridged the polysiloxane and POE parts of the polymer were expected to be. That observation can be considered as quite significant since it strongly supported the theoretical assumptions presented in the earlier paper [4] that coordination bonds can occur between urethane moieties and  $\text{Li}^+$  ions.

#### Effect of PEO content on supramolecular structure of PSUR film

In Fig. 7 the effect of PEO segments content in UV-cured PSUR samples containing lithium salt incorporated using *in situ* method (1 M Li salt solution in EC/DMC = 1/2 was applied) on supramolecular structure of the samples is presented. It is clear that domain structure disappears with decrease of PEO segments content in PSUR. Furthermore, some kind of interlinkages between domains can be observed for sample with highest content of POE segments. Perhaps because of the presence of those interlinkages, which are constructed mostly from silicone part of the polymer, the specific conductivity of sample 1771 containing 41.18 wt % PEO is only slightly better than the conductivity of sample 1769 E containing 37.58 wt % PEO (see Table 4). It is interesting that the transformation of supramolecular structure can be observed with diminishing of POE segments content in PSUR. In sample 1768 (27.21 wt % POE) phase inversion occurs, *i.e.*, silicone part of the polymer becomes continuous phase and that is reflected in drastic diminishing of specific conductivity (see Table 4). In sample without POE segments only one, continuous phase can be observed.

#### Testing lithium cells (experimental lithium mini-batteries) with Li salt – containing PSUR films used as separators

UV-cured PSUR films containing Li salt incorporated *via* “post-cure” and *in situ* methods were tested as separators in lithium cells (experimental lithium mini-batteries) as compared to standard separator (Celgard® 2400) soaked in lithium salt solution in EC/DMC = 1/2 solvent. It was found that discharging proceeded much faster in the batteries with PSUR separators than in batteries with standard separator and that there was no significant difference in that regard between batteries with PSUR

containing Li salt incorporated “post cure” and *in situ*. The reason for faster discharging in the case of batteries with PSUR separators could be some interaction between PSUR and electrode material. After 20 charging-discharging cycles *ca.* 40 % of the initial specific capacity of the cells was left.

### CONCLUSIONS

It was found that it was possible to obtain PSUR containing PEO segments capable for UV-curing through chain extension of PEO segments containing PSUR prepolymer with unsaturated diol. Through thermal curing of the resulting double bonds-containing polymer followed by UV-curing PSUR films could be obtained. Mechanical properties of the films were not much affected by PEO segments content in the PSUR chain. Increasing NCO/OH (prepolymer/unsaturated diol) molar ratio resulted in moderate increase in mechanical properties while increasing UV curing time led to diminishing the elongation at break which may be explained by polymer crosslinking during the UV curing process. Swelling ability of the films in EC/DMC = 1/2 solution that is commonly used in lithium batteries increased with increase in PEO segments content in the PSUR chain what corresponded to the results of our earlier studies on moisture-cured PSUR containing PEO segments [5]. Swelling ability also increased with decrease in NCO/OH molar ratio and this phenomenon can be explained by lower molecular weight of extended PSUR prepolymer which was obtained in the case when lower NCO/OH ratio was applied. NCO/OH ratio also quite distinctly influenced conductivity of PSUR films swelled in 1 M lithium salt [ $\text{Li}(\text{CF}_3\text{SO}_3)$ ] solution in EC/DMC = 1/2 solvent mixture. Studies on the effect of the method of Li salt incorporation and PEO/SIL molar ratio on specific conductivity of PSUR films revealed that Li salt can be introduced in PSUR *in situ* (*i.e.*, before curing process) without significant decrease in specific conductivity of the film as compared to films swelled in Li salt solution “post cure”. It was also confirmed that high PEO segments content in PSUR was crucial for achieving good specific conductivity of the film while the amount of Li salt in PSUR practically did not matter much in that respect. When DSC determinations of the UV-cured PSUR films were conducted it was confirmed that no crystallization of PEO occurred in PSUR and that EC/DMC = 1/2 solvent presence in the polymer composition before thermal and UV-curing had some effect on film  $T_g$ . That phenomenon was explained by different supramolecular structure of the films which were cured with and without solvent. Investigation of the effect of PEO content in PSUR modified with Li salt *in situ* on supramolecular structure of the films showed that when PEO content in PSUR decreased the phase inversion occurred and silicone part of the polymer became continuous phase.

Selected PSUR swelled in Li salt and modified with Li salt *in situ* were tested as separators in lithium cells

(experimental lithium mini-batteries) and it was found that their charging-discharging characteristics were similar to observed for standard Li ion batteries though discharging proceeded faster for batteries where PSUR separators were used.

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