*Supplementary files*

# Use of a mixture of polyols based on metasilicic acid and recycled PLA for synthesis of rigid polyurethane foams susceptible to biodegradation

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## 1. Analysis of GPC and MALDI ToF of MSA-polyol

MALDI ToF spectra (Matrix-Assiated Laser Desorption Ionization Time of Flight) of oligoetherols were obtained on Voyager-Elite Perceptive Biosystems (US) mass spectrometer working at linear mode with delayed ion extraction, equipped with nitrogen laser working at 352 nm. The method of laser desorption from matrix gold was used. Therefore the observed peaks corresponded to the molecular ions plus Au and $K^+$ (from catalyst) ions. The samples with diluted with water to 0.5 mg/cm$^3$.

Molecular mass (number-averaged and weight-averaged) and polydispersity of oligoetherol was determined by gel permeation chromatography using the following parameters: 25 ± 0.1°C temperature, 1 cm$^3$ / min volume flow of eluent, 20 μdm$^3$, volume of inlet chamber, 4 - 5 mg / cm$^3$ polymer concentration, 30 minutes analysis time, eluent: N,N-dimethylformamide, calibration reference: polystyrene.

In order to identify side products (glycols and polyglycols) formed in the reaction of semi-product MSA : GL = 1 : 4 with EC and the compounds formed in consecutive reactions with EC, the oligoetherols were separated chromatographically using cyklohexanone (analytical grade S.A. POCH, Gliwice, Poland) as internal standard. The gas chromatograph HP 4890A was used, equipped with HP-FFAP column of 30 m length, 0,53 mm diameter, 1,5 μm film thickness and 220 °C port temperature and temperature profile: 50 – 220 ºC, with 20 deg/min heating rate, the helium flow 18,3 cm$^3$/min, and 0,2 μdm$^3$ sample volume. Series of reference substances were used: ethylene glycol (MEG), diethylene glycol (DEG), triethylene glycol (TEG) tetraethylene glycol (TeEG), (pure Aldrich, UK). The percentage of diols in products was determined based on calibration curves with the same internal standard using equation (S1):

$$\frac{S_{cd}}{S_t} = a \times \left( \frac{m_{cd}}{m_t} \right) + b \qquad \text{(S1)}$$

where: $m_{cd}$, $m_t$ – diol mass or consecutive product of its reaction with alkylene carbonate and mass of standard, respectively,
$S_{cd}$, $S_t$ – integrated peak area of diol or consecutive product and standard, respectively,
a, b – experimental coefficients of calibration curves.

The calibration coefficients and retention times of diols are collected in Table S1. Mass of products obtained from EC and water and mass of products of consecutive reactions bet-ween diols and alkylene carbonates were calculated from formula (1) ($m_{cd}$). The percentage of side products were calculated considering total sample mass ($m_p$) according to the equation S2:

$$p_{cd} = \left( \frac{m_{cd}}{m_p} \right) \times 100\% \qquad \text{(S2)}$$

**Table S1.** Side products of EC reaction used for calibration of gas chromatography.

| Substance | Retention time [min] | Coefficients from equation (1) | | Correlation coefficient |
|---|---|---|---|---|
| | | a | b | |
| cyclohexanone | 8.53 | - | - | |
| MEG | 13.64 | 2.7939 | 0.1006 | 0.9982 |
| DEG | 17.47 | 2.4917 | 0.1694 | 0.9988 |
| TEG | 20.83 | 2.6634 | 0.2392 | 0.9987 |
| TeEG | 25.95 | 4.4556 | 0.2740 | 0.9993 |

The composition of oligoetherols can be determined by MALDI-ToF spectrometry method (Table S2). The spectra showed trace amounts of substrates identified by the appropriate low M/z, and also corresponding to oligomeric forms of MSA of the general formula $(H_2SiO_3)_n$, where n = 2, 3 or 4 From detailed analysis of MALDI-ToF spectra it can be concluded that even at the appropriate molar ratio of reagents the mixtures are obtained, in which MSA is hydroxyalkylated with GL at various level and the product of reaction between the semiproduct and EC at various level of hydroxyalkylation. Thus, the satellite peaks with masses increased by M/z = 74 or by masses of attached ions from matrix, and also the peaks of masses diminished by M/z =18 due to elimination of water in self-condensation of MSA are present The series of peaks differing by M/z = 44 derived from consecutive addition of EC are also present.

**Table S2.** Interpretation of MALDI-ToF spectrum of oligoetherol obtained from MSA

| Entry | Signal position m/z | Relative inten-sity of signal [%] | The molecular ion structure | Calc. molecular weight [g/mol] |
|---|---|---|---|---|
| 1. | 75.145 | 12.5 | GL + $H^+$ | 75.087 |
| 2. | 87.134 | 5.6 | EC | 88.062 |
| 3. | 89.145 | 2.5 | EC + $H^+$ | 89.070 |
| 4. | 97.034 | 3.8 | MSA + $H_2O$ + $H^+$ | 97.122 |
| 5. | 101.143 | 9.6 | MSA + $Na^+$ | 101.089 |
| 6. | 124.981 | 26.1 | EC+ 2 $H_2O$ | 124.092 |
| 7. | 129.142 | 50.0 | 2GL - $H_2O$ | 130.143 |
| 8. | 133.001 | 2.4 | MSA + GL - $H_2O$ | 134.163 |
| 9. | 140.954 | 42.9 | GL + OE + $Na^+$ | 141.122 |
| 10. | 145.117 | 63.4 | GL + 2OE – $H_2O$ | 144.170 |
| 11. | 159.146 | 44.4 | GL + OE + $K^+$ | 157.230 |
| 12. | 173.147 | 55.4 | MSA + GL - $H_2O$ + $K^+$ | 173.261 |
| 13. | 189.130 | 80.4 | 2GL + $K^+$ | 187.257 |
| 14. | 203.144 | 68.0 | 3GL - $H_2O$ | 204.222 |
| 15. | 219.129 | 65.3 | MSA + GL + OE + $Na^+$ | 219.221 |
| 16. | 233.146 | 83.3 | 2 MSA – 2$H_2O$ + GL + $K^+$ | 233.345 |
| 17. | 249.144 | 50.6 | 2 MSA + GL + $H_2O$ + $H^+$ | 249.300 |
| 18. | 263.149 | 56.3 | MSA + 2GL + $K^+$ | 265.355 |
| 19. | 277.167 | 66.0 | MSA + 2GL – $H_2O$ + OE + $Na^+$ | 275.285 |
| 20. | 279.127 | 21.5 | 4GL - $H_2O$ + $H^+$ | 279.309 |
| 21. | 289.168 | 58.7 | 2 MSA – $H_2O$ + 2GL - $H_2O$ + $Na^+$ | 291.316 |
| 22. | 307.172 | 100.0 | MSA + 2GL + OE + $K^+$ | 309.408 |
| 23. | 323.154 | 57.5 | 2 MSA – $H_2O$ + 2GL + $K^+$ | 325.439 |
| 24. | 333.187 | 17.1 | 4 MSA - 3$H_2O$ + GL + $H^+$ | 333.438 |
| 25. | 337.177 | 49.2 | 2 MSA - $H_2O$ + Au + $H^+$ | 335.960 |
| 26. | 351.191 | 71.0 | 5GL - $H_2O$ | 352.380 |

| | | | | |
|---|---|---|---|---|
| | | | MSA + GL + Au + $H^+$ | 350.153 |
| 27. | 363.193 | 51.4 | 2 MSA + GL + 3OE + $H^+$ | 363.444 |
| 28. | 381.200 | 88.1 | MSA + 2GL + 3OE + $Na^+$ | 381.406 |
| 29. | 393.934 | 31.5 | MSA + GL + OE + Au | 393.198 |
| 30. | 397.187 | 43.5 | 3 MSA - 2$H_2O$ + Au + $H^+$ | 396.242 |
| 31. | 407.214 | 17.6 | MSA + 2GL - $H_2O$ + Au + $H^+$ | 406.217 |
| 32. | 411.205 | 41.8 | 2 MSA + 2GL + 2OE + $H_2O$ + $H^+$ | 411.485 |
| 33. | 425.220 | 66.3 | 2 MSA + 3GL + OE + $H^+$ | 423.496 |
| 34. | 437.222 | 38.3 | MSA + GL + 2OE + Au | 437.251 |
| 35. | 453.200 | 27.4 | 2 MSA - $H_2O$ + GL + OE + Au | 453.282 |
| 36. | 455.229 | 69.4 | 4 MSA - 3$H_2O$ + Au | 455.318 |
| 37. | 467.228 | 22.5 | MSA + 2GL + OE + Au | 467.277 |
| 38. | 469.229 | 17.3 | 3 MSA - 2$H_2O$ + GL + Au | 469.313 |
| 39. | 485.230 | 33.5 | 2 MSA - $H_2O$ + 2GL + Au + $H^+$ | 484.316 |
| 40. | 499.251 | 52.9 | 7GL - $H_2O$<br>2 MSA - $H_2O$ + GL + 2OE + Au +$H^+$ | 500.538<br>498.343 |
| 41. | 511.249 | 27.1 | MSA + 2GL + 2OE + Au | 511.330 |
| 42. | 527.525 | 18.5 | 2 MSA - $H_2O$ + 2GL + OE + Au | 527.361 |
| 43. | 529.256 | 51.0 | 4 MSA - 3$H_2O$ + GL + Au | 529.397 |
| 44. | 541.257 | 15.4 | 2 MSA - $H_2O$ + GL + 3OE + Au | 541.388 |
| 45. | 543.270 | 18.2 | MSA + 3GL + OE + Au + $H^+$ | 542.364 |
| 46. | 559.259 | 23.2 | 2 MSA - $H_2O$ + 3GL + Au + $H^+$ | 558.395 |
| 47. | 573.277 | 40.4 | 4 MSA - 3$H_2O$ + GL + OE + Au | 573.450 |
| 48. | 585.279 | 18.5 | MSA + 3GL + 2OE + Au<br>2 MSA - $H_2O$ + GL + 4OE + Au | 585.409<br>585.441 |
| 49. | 590.900 | 39.5 | 2 MSA + 2GL + 2OE +Au | 589.429 |
| 50. | 603.287 | 34.9 | 4 MSA - 3$H_2O$ + 2GL + Au | 603.476 |
| 51. | 619.267 | 13.1 | 3 MSA - 2$H_2O$ + 3GL + Au + $H^+$<br>4 MSA - 3$H_2O$ + GL + 2OE + Au + $H^+$ | 618.479<br>618.551 |
| 52. | 633.287 | 15.4 | 3 MSA - 2$H_2O$ + 2GL + 2OE + Au +$H^+$ | 632.506 |
| 53. | 647.309 | 28.7 | 4 MSA - 3$H_2O$ + 2GL + OE + Au | 647.529 |
| 54. | 659.290 | 12.1 | MSA + 4GL + 2OE + Au | 659.488 |
| 55. | 663.288 | 11.0 | 3 MSA - 2$H_2O$ + 3GL + OE + Au + $H^+$ | 662.532 |
| 56. | 677.318 | 20.5 | 4KK - 3$H_2O$ + 3GL + Au | 677.555 |
| 57. | 693.297 | 6.8 | 3 MSA - 2$H_2O$ + 4GL + Au + $H^+$<br>4 MSA - 3$H_2O$ + 2GL + 2OE + Au + $H^+$ | 692.558<br>692.590 |
| 58. | 707.315 | 9.6 | 3 MSA - 2$H_2O$ + 3GL + 2OE + Au +$H^+$<br>2 MSA - $H_2O$ + 5GL + Au + $H^+$ | 706.585<br>706.553 |
| 59. | 721.340 | 19.8 | MSA + 6GL + Au + $H^+$ | 720.548 |
| 60. | 737.315 | 7.5 | 4 MSA - 3$H_2O$ + 2GL + 3OE + Au + $H^+$<br>3 MSA - 2$H_2O$ + 4GL + OE + Au + $H^+$ | 736.643<br>736.611 |
| 61. | 751.350 | 12.1 | 4 MSA - 3$H_2O$ + 4GL + Au | 751.634 |
| 62. | 781.341 | 5.3 | 2 MSA - $H_2O$ + 6GL + Au + $H^+$ | 780.632 |
| 63. | 795.368 | 11.4 | 4 MSA - 3$H_2O$ + 4GL + OE + Au | 795.687 |
| 64. | 825.357 | 7.1 | 4 MSA - 3$H_2O$ + 5GL + Au | 825.713 |
| 65. | 839.406 | 4.8 | 4 MSA - 3$H_2O$ + 4GL + 2OE + Au | 839.740 |
| 66. | 869.414 | 6.9 | MSA + 8GL + Au + $H^+$ | 868.706 |

MSA*, GL and EO – the structural fragments formed upon reaction of MSA with GL and EC, respectively.*

The obtained oligoetherols were analyzed by gas chromatography in order to determine the amount of side products formed in reaction of EC with water released from products of MSA hydroxyalkylation or with diols. In separate control experiments the products of EC with reference diols

like glycol and polyglycols were analyzed chromatographically (Table S1). It has been found that the percentage of glycols and their consecutive products has not exceeded 20 mass % in the products (Table S3). The presence of low molecular products in oligoetherol corroborate well with hydroxyl number (Table S2) which is 807 mg KOH/g, The number-averaged molecular mass was determined by GPC chromatography as 314 g/mol, due to the presence of low molecular weight admixtures. Weight-averaged molecular mass was 899 g/mol with polydispersity degree 2.86. The result on $M_n$ and $M_w$ are in good accordance with the masses calculated from assumed oligoetherol and side products (Table S3), which were Mn = 333 g/mol and Mw = 917 g/mol, respectively.

**Table S3.** Amount of side products [wt. %] in obtained oligoetherol from MSA

| ED | DEG | TEG | TeEG | ∑ |
|---|---|---|---|---|
| 7.9 | 9.0 | 2.4 | 0.6 | 19.9 |

## 2. GPC analysis of PLA-polyol

The GPC chromatogram of eco-polyol based on waste PLA is shown in Figure S1. The interpretation of the obtained chromatogram is presented in Table S4.

**Figure S1.** GPC chromatogram of eco-polyol based on PLA waste

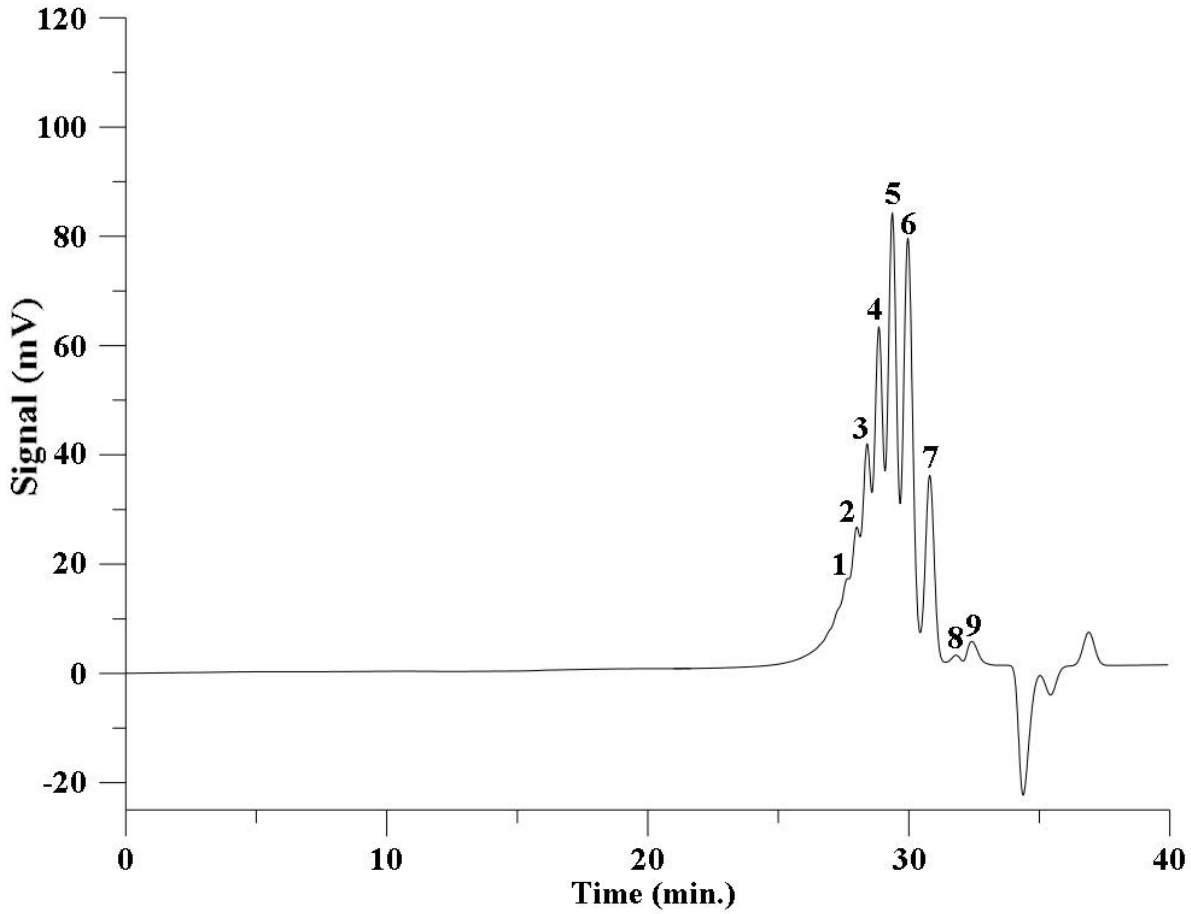

**Table S4.** Results of GPC chromatography analysis

| Number of peak | $M_n$ (g/mol) | $M_w$ (g/mol) | D (-) |
|---|---|---|---|
| **1.** | 647 | 671 | 1.04 |
| **2** | 494 | 494 | 1.00 |
| **3** | 431 | 431 | 1.00 |
| **4** | 372 | 373 | 1.0. |
| **5** | 315 | 315 | 1.00 |
| **6** | 259 | 259 | 1.00 |
| **7** | 198 | 199 | 1.01 |
| **8** | 146 | 146 | 1.00 |
| **9** | 116 | 117 | 1.01 |
| **Average weight** | **309** | **351** | **1.14** |