Electronic Supplementary Information (ESI)

The application of spatially restricted geometries as a unique route to produce well-defined poly(vinyl pyrrolidones)

Magdalena Tarnacka[a,b*], Paulina Maksym[a,c], Andrzej Zięba[d], Anna Mielańczyk[e], Monika Geppert-Rybczyńska[f], Laia Leon-Boigues[b], Carmen Mijangos[b*], Kamil Kamiński[a,c*], Marian Paluch[a,c]

[a] *Institute of Physics, University of Silesia, ul. Uniwersytecka 4, 40-007 Katowice, Poland*
[b] *Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain*
[c] *Silesian Center of Education and Interdisciplinary Research, University of Silesia, ul. 75 Pulku Piechoty 1A, 41-500 Chorzow, Poland*
[d] *Department of Organic Chemistry, School of Pharmacy with the Division of Laboratory Medicine in Sosnowiec, Medical University of Silesia in Katowice, ul. Jagiellońska 4, 41-200 Sosnowiec, Poland*
[e] *Department of Physical Chemistry and Technology of Polymers, Faculty of Chemistry, Silesian University of Technology, ul. M. Strzody 9, 44-100 Gliwice, Poland*
[f] *Institute of Chemistry, University of Silesia, ul. Szkolna 9, 40-007 Katowice, Poland*

Corresponding Authors: (MT) e-mail: magdalena.tarnacka@smcebi.edu.pl; (CM) e-mail: cmijangos@ictp.csic.es; (KK): kamil.kaminski@us.edu.pl

EXPERIMENTAL SECTION

1. Materials

1-Vinyl-2-pyrrolidinone (VP, 97%), 2,2′-Azobis(2-methylpropionitrile) (AIBN) and 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%) were purchased from Sigma-Aldrich. Anodised aluminium oxide membranes (AAO) of defined pore diameter, *d,* used as nanoreactors were prepared *via* a two-step electrochemical anodization process. AAO membranes, composed of highly dense uniaxial channels (open from both sides) are extremely stable (independently of the applied reaction conditions) and might be reused after the proper purification. AAO membranes of various pores diameters (140, 60 and 40 nm) have been prepared from aluminium sheets of high purity (99,999%) of around 12 cm² under different anodization conditions in oxalic acid at a controlled temperature of T = 2- 3° C, as described elsewhere[1,2,3].

2. Methods
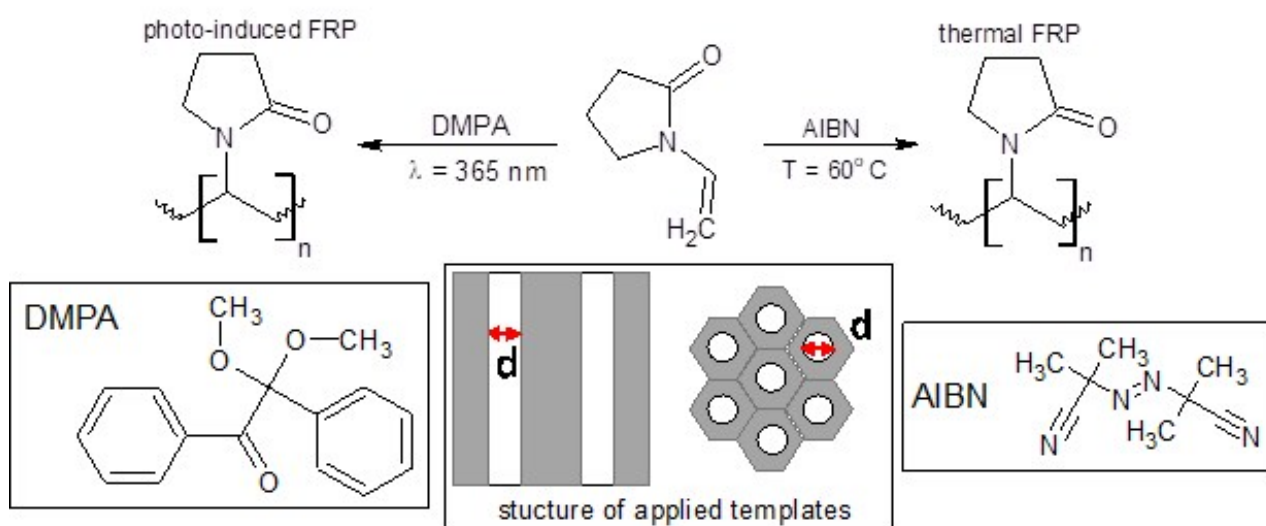
Fig. S1. Chemical structures of investigated systems together with the scheme of the reactions and structure of applied AAO templates acting as nanoreactors.

Thermal FR polymerisation of VP at the macroscale. VP (1 g, 9 mmol) and AIBN (0.005g, 0.03 mmol, 0.5 % wt in respect to VP) were placed in a flask with a magnetic stirring bar. After the vial was purged with nitrogen for 20 min, the flask was heated to T = 60° C, for different

times. The polymerisation was quenched after a predetermined time by cooling and exposing the reaction mixture to air. The polymer was isolated and purified by ultrafiltration in methanol using a membrane (Millipore, Regenerated Cellulose, YM10, NMWL: 1000), and then dried under reduced pressure. NMR measurements determined the conversion of the monomer. All the other polymerisations were performed under identical experimental conditions.

Photo-induced FR polymerisation of VP at the macroscale. VP (1 g, 9mmol) and DMPA (0.0015g, 0.006mmol, 0.15 % wt in respect to VP) were placed in a flask with a magnetic stirring bar. After the vial was purged with nitrogen for 20 min, the mixture was irradiated by a lamp emitting light nominally at 365 nm at room temperature. After a given time (from 5 to 40 minutes), the resulted polymer was isolated by ultrafiltration in methanol using a membrane (Millipore, Regenerated Cellulose, YM10, NMWL: 1000), and then dried under reduced pressure. Conversion of the monomer was determined by NMR measurements.

The polymerisation of VP at the nanoscale. We have prepared two mixtures (1) VP+AIBN (0.5 % wt. in respect to VP) for thermal polymerisation and (2) VP+DMPA (0.15 % wt. in respect to VP the same conditions as in the case of polymerisation at the macroscale, see the description above). In each case, the mixture was transferred into the flask together with the AAO membrane. Before the filling, AAO membranes were dried in an oven at $T = 100\,^{\circ}C$ under vacuum to remove any volatile impurities from the nanochannels. Then, the whole system was maintained at $T = 25\,^{\circ}C$ in a vacuum (10^{-2} bar) for 0.5 h to let the mixture flow into the nanocavities. After completing the infiltration process, the top and bottom surface of the AAO membrane was dried and the excess sample on the surface removed by use of a paper towel. Then the infiltrated membranes were either heated to $T = 60^{\circ}\,C$ (FRP) or irradiated by a lamp emitting light nominally at 365 nm at room temperature. In the experiment, we used membranes of pores diameters: 140, 60 and 40 nm. The total amount of reaction mixture incorporated into the AAO membrane was found to be ~5-6 mg, leading to approximately ~5 mg of produced

linear PVP. After the polymerisation, the polymer was extracted from the membranes by submerging in chloroform-d, and the sample from the reaction mixture has been analysed by NMR to get the information of monomer conversion. Then the solvent was evaporated, and the resulted polymer was washed with a large excess of diethyl ether and then dried under vacuum to a constant mass. Finally, the SEC analysis of recovered polymer has been performed.

Nuclear Magnetic Resonance Spectroscopy (NMR). Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded using a Bruker Ascend 600 spectrometer operating at 600 MHz in CDCl$_3$ as a solvent. Standard experimental conditions and standard Bruker program were used. A typical ^{1}H NMR spectrum of a typical PVP thermal polymerisation mixture performed in AAO templates is shown in **Fig. S2.** The monomer conversion was calculated based on the scheme described in the literature,[4,5] by comparing the integrals of residual vinyl protons of VP (b, 1H, δ=7.11 ppm) with the integrals of the methylene protons adjacent to the lactam ring of PVP (c', 2H, δ=2.75-3.40 ppm). Note that the an alternative calculation methods including comparison of the vinyl protons in the remaining monomer (b, 1H, δ=7.11 ppm) to the protons connected to the lactam ring of PVP (b', 1H, δ=3.60-4.00 ppm) or the vinyl protons of VP (b, 1H, δ=7.11 ppm) to the overlapping resonance between VP (e, 2H, δ=3.45 ppm) and PVP (b', c', 3H, δ=2.75-4.00 ppm) gave practically the same results (please see **Fig. S2**).

^{1}H NMR of PVP (600 MHz, CDCl$_3$) δppm: 1.42-1.68 (2H, -CH$_2$-CH$_2$-C=O); 1.98 (2H, -CH$_2$-CH-N-); 2.24-2.40 (2H, -CH$_2$-CH$_2$-C=O); 3.24 (2H,-N-CH$_2$-CH$_2$); 3.60 (1H, -CH$_2$-CH-N-).
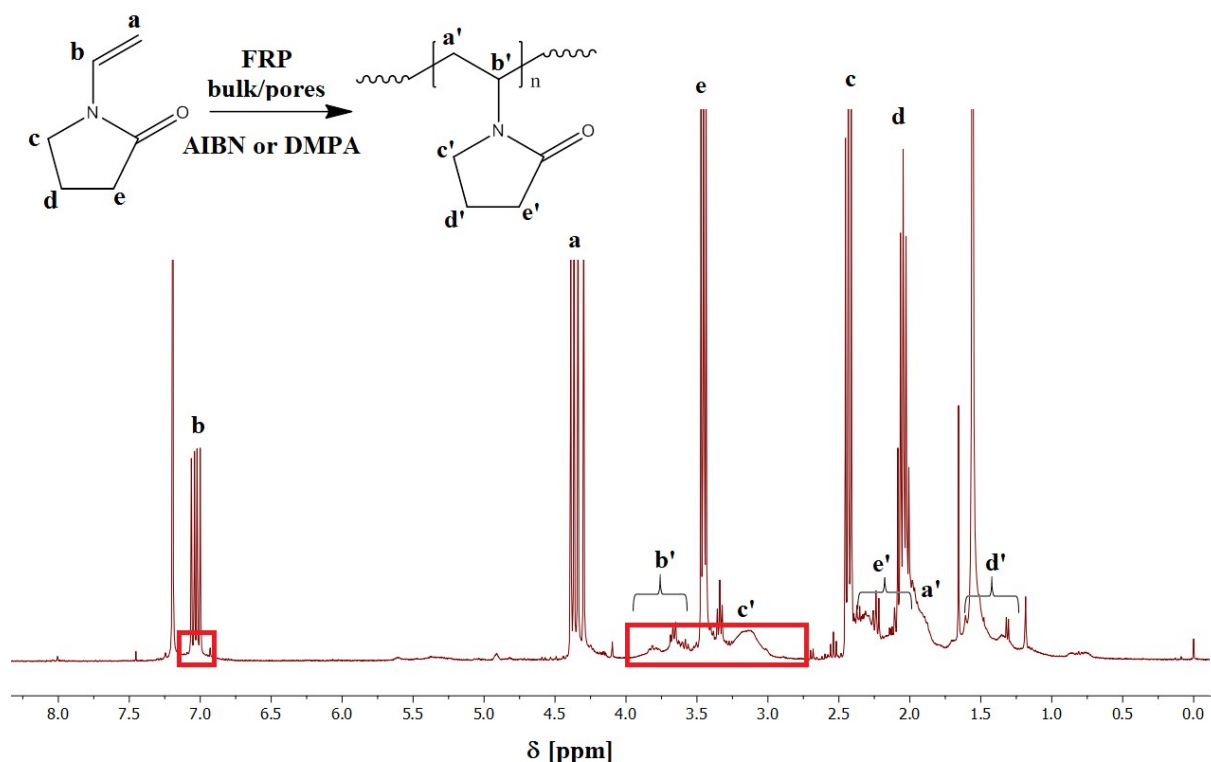
Fig. S2. ^{1}H NMR spectrum of a typical PVP thermal polymerisation mixture performed in AAO templates.

Size exclusion chromatography. Molecular weights and dispersity indices (Đ) were determined by size-exclusion chromatography (SEC, Agilent Technologies, Santa Clara, CA, USA) equipped with an 1100 Agilent 1260 Infinity isocratic pump, autosampler, degasser, thermostatic box for columns, and differential refractometer MDS RI Detector. Addon Rev. B.01.02 data analysis software (Agilent Technologies, Santa Clara, CA, USA) was used for data collecting and processing. The SEC calculated molecular weights were based on calibration applying linear polystyrene standards (M_p = 580–1 390 000 g/mol). Pre-column guard 5 μm (50 × 7.5 mm) and two columns: PLGel 5 μm MIXED-C (300 × 7.5 mm) and Malvern Visocotek T6000M (300 x 8 mm) were used for separation. The measurements were carried out in DMF (HPLC grade) as the eluent containing 10 mM LiBr, at T = 40° C with a flow rate of 0.8 mL/min.

Surface Tension and Contact Angle Measurements. The solid surface energy of aluminium oxide, γ_S, was calculated using the surface tension and contact angles for test liquids (water and ethylene glycol) according to Fowkes method.[6,7] This procedure regards the surface tension, γ_L, as a sum of dispersive, d, and non-dispersive components, nd: ($\gamma_L = \gamma_L^d + \gamma_L^{nd}$). The non-dispersive contribution is the sum of all parts of γ_L resulting from non-dispersion intermolecular interactions present in a liquid (the same is for solid) such as hydrogen bonds and base-acid interactions. Since the contact angle, θ, is related to surface energy, γ_S, interfacial energy, γ_{SL}, and to the surface tension, γ_L, accordingly to the Young equation is:

$$\gamma_{SL} = \gamma_S - \gamma_L \cos\theta, \qquad (S1)$$

The work of adhesion is equal:

$$W_a = \gamma_L + \gamma_S - \gamma_{SL}, \qquad (S2)$$

and assuming that:

$$W_a = 2\left(\sqrt{\left(\gamma_S^d \cdot \gamma_L^d\right)} + \sqrt{\left(\gamma_S^{nd} \cdot \gamma_L^{nd}\right)}\right), \qquad (S3)$$

the solid surface energy can be calculated with dispersive and non-dispersive components accordingly to the following relation:[8]

$$\frac{\gamma_L \cdot (1 + \cos\theta)}{2 \cdot \sqrt{\gamma_L^d}} = \sqrt{\gamma_S^{nd}} \sqrt{\frac{\gamma_L^{nd}}{\gamma_L^d}} + \sqrt{\gamma_S^d}, \qquad (S4)$$

The Fawkes approach gives a reliable estimation of the surface energy, what was reported earlier.[9,10,11] Previously estimated solid surface energy of aluminium oxide was equal to $\gamma_S = 58.97 \cdot 10^{-3}$ N·m⁻¹, with the non-dispersive part $\gamma_S^{nd} = 55.6 \cdot 10^{-3}$ N·m⁻¹.[12] Based on γ_S, the surface tension and the contact angle of various compounds on AAO, the interfacial energy at T = 298 K was calculated from the Eq. (S1) and listed in **Table S1.**

This procedure was applied using at first the software recommended by the provider for the Kruess tensiometer, GmbH, Germany included in DSA 100S software, and then it was repeated independently taking into account: water, ethylene glycol, diiodomethane and bromobenzene. Finally, only two from these liquids were taken into account: water and ethylene glycol (with a stable and repeatable contact angle values on AAO), since for diiodomethane and bromobenzene contact angle on alumina was around 0°. We did not regard glycerol due to a similar ratio of a dispersive and non-dispersive part in the surface tension to ethylene glycol. We believe that taking more liquids for calibration can also cause some calculations problems as was referred by Jańczuk et al.[5] and Hejda et al.[7]. Moreover, it should be mentioned that for all samples (there were all in a liquid state) the difference between the advancing and receding contact angles was below the estimated uncertainty of the contact angle measurements; thus, for all calculations, the mean value was taken into account.

Table S1. Contact angle (θ), surface tension (γ_L) and interfacial energy (γ_{SL}) of indicated substances at T = 298 K. [a]Data for oligostyrene (n=3) were taken from Ref.13.

sample	θ [°]	γ_L [mN·m⁻¹]	γ_{SL} [mN·m⁻¹]
methyl methacrylate (MMA)	0	24±0.1	35±1
1-vinyl-2-pirolidone (VP)	7±1.6	38±0.1	21±1
1-methyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide ([MVIM][NTf₂])	46.5 ±3.3	37±0.1	33±1
oligostyrene (n=3)[a]	25	35	3
water	45	71.7	-
ethylene glycol	40.1	47.1	-

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