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Synthesis of poly(tartar amides) as bio-inspired antifreeze additives

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Materials and methods: All reagents if not specified were obtained from Sigma Aldrich with purity of more than 96%, and used without further purification.

Materials: L-(+)-Tartaric acid dimethylester (99%), 3,3′-diamino-*N*-methyldipropylamine (96%), 2,2′-(ethylenedioxy)diethylamine (99%). Polyethylenglycol (PEG-6: $\overline{M}_w^{app}$ =6000, $\overline{M}_w^{app}/\overline{M}_n^{app}$ = 1.025) from PSS-Ticker, polyglyceroles (PG-5; $\overline{M}_n^{app}$ =5000, $\overline{M}_w^{app}/\overline{M}_n^{app}$ 1.5 and PG-2 ($\overline{M}_n^{app}$ =2000, $\overline{M}_w^{app}/\overline{M}_n^{app}$ 1.5) from Hyperpolymers, Germany.

Methods: ^{1}H NMR measurements were carried out at room temperature on a Bruker DPX-400 spectrometer operating at 400.1 MHz. ^{13}C-NMR was recorder on the same instrument at 100.6 MHz. Gel permeation chromatography (GPC) was performed at 70 °C, using *N*-methyl pyrolidone (NMP) as eluent with a flow rate of 0.8 mL/min. The column set consists of two 300×8 mm PSS GRAM columns with 7 μ, 10^2 and 10^3 Å (PSS GmbH, Mainz, Germany). A refractive index (RI) detector as well as a UV detector was used and the calibration was performed relative to linear polystyrene standards (PSS GmbH). Fourier transform infrared (FT-IR) spectroscopy measurements were performed using a BioRad 6000 FT-IR spectrometer equipped with a single reflection diamond ATR-bridge. Wide angle X-Ray (WAXS) scattering was made with a Bruker-PDS 120 with $\mathrm{Cu}_{\mathrm{K}\alpha}$ radiation. Standard differential scanning calorimetry (DSC) measurements were run with a Netzsch DSC 204 Phoenix (cryo protocol is given below). Optical microscopy was carried out with a Leika DMRB polarization microscope and a Linkam TMS 600 cooling stage attached.

Synthesis of 2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate dimethylester (I):

In a round bottom flask a solution of dimethyl-L-tartarate (1 eq., 1.0 g, 5.6 mmol) in 20 mL acetone, 2,2-dimethoxypropane (10 eq., 6 g, 57 mmol) and *p*-toluene sulfonic acid monohydrate (PTSA) (0.02 g, 0.1 mmol) were mixed at 0° C and stirred for about 4 h. After additional stirring at room temperature over night the solvent was distilled off under reduced pressure. The obtained crude product was dissolved in chloroform, extracted three times with water to remove the remaining PTSA. Fractional distillation under reduced pressure yielded **I** as slightly yellow oil. ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 1.42$ (s, 6H, O-C$\underline{H}_3$); 3,73 (s, 6H, -C-C$\underline{H}_3$); 4.70 (s, 2H, -C$\underline{H}$-O-) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 26.1$ ($\underline{C}H_3$-C-O), 52.5 (O-$\underline{C}H_3$), 76.8 ($\underline{C}$H-O), 113.6 (CH-O-$\underline{C}$-CH_3) ppm.

General polymerization procedure: The polymers were synthesized by an ester-amidation polycondensation of the dimethyl diester of hydroxyl protected tartaric acid (**I**) and a corresponding diamine.

Poly(tartar amido 3-amino diamino-N-methyldipropylamine) ***(P1)***: **I** (1 g, 4.6 mmol) was mixed with 3,3-diamino-*N*-methyl dipropylamine (**II**) (0.66 g, 4.6 mmol) in 20 mL of chloroform and stirred at room temperature for 5 days. After removal of solvent by distillation under reduced pressure, the polymer was obtained as a viscous. ^{1}H NMR (400.1 MHz, $CDCl_3$) $\delta = 1.43$ (s, 6H, O-C-C$\underline{H}_3$), 1.75 (s, 4H, CH_2-C$\underline{H}_2$-CH_2), 2.27 (s, 3H, 1N-C$\underline{H}_3$), 2.6 (s, 4H, CH_3-N-C$\underline{H}_2$), 3.35 (s, 4H, CH2-C$\underline{H}$2-NH), 4.50 (s, 2H, CH) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 25.2$ ($\underline{C}H_3$-C-O), 26.7 (NH-CH_2-$\underline{C}H_2$), 37.8

(O=C-NH-$\underline{C}H_2$), 41.3 (N-$\underline{C}H_3$), 52.5 ($\underline{C}H_3$-N-CH_2), 76.8 ($\underline{C}$H-O), 113.6 (O-$\underline{C}$-CH_3), 177.13 ($\underline{C}$=O) ppm. FT-IR: υ = 3286, 2931, 2851, 1649, 1521, 1445, 1076 cm^{-1}. GPC analysis of P1: $\overline{M}_n^{app} = 4400$, $\overline{M}_w^{app} / \overline{M}_n^{app} = 1.6$. The synthesis of the *poly(tartar amido ethyl 2,2'-(ethylenedioxy)ethylamine)* ***(P2)*** was performed by polycondenzation of **I** (1 g, 4.6 mmol) and 2,2′-(ethylenedioxy)-diethylamine (**III**) (0.67 g, 4.7 mmol) in 30 mL of toluene. The polymerization was performed for 120 hours in a round bottom flask at 50° C under continuous removal of methanol. The workup procedure was performed according to the protocol described above, yielding **P2** in as colorless, viscous oil.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.42 (s, 6H, O-C-$C\underline{H}_3$); 3.46 (br, 4H; CH_2-$C\underline{H}_2$-NH); 3.62-3.69 (br, 8H, -O-$C\underline{H}_2$-$C\underline{H}_2$-O, O-$C\underline{H}_2$-CH_2-NH) 4.90 (s, 2H, CH-O) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 25.1 ($\underline{C}H_3$), 39.7 ($\underline{C}H_2$-NH), 69.7 ($\underline{C}H_2$-O), 77.5 ($\underline{C}$H-O), 112.0 (O-$\underline{C}$-CH_3), 171.4 ($\underline{C}$=O) ppm. FT-IR: υ = 3303, 2931, 2867, 1657, 1523, 1453, 1210, 1076 cm^{-1}. GPC analysis of **P2**; $\overline{M}_n^{app} = 4.600$ mol, $\overline{M}_w^{app} / \overline{M}_n^{app} = 1.9$.

The crude polymer P1 and P2 were further used to remove the 1,2-diol protecting groups, without isolation from residual monomers.

Deprotection and final purification of the polymers: The ketal protection group for the 1,2-diol structure in **P1** and **P2** was removed by the treatment with strongly acidic ion exchange resign (1 g polymer, 1 g Dowex 50-200 in 5 mL methanol, refluxed for 24 h). In the case of incomplete deprotection, the polymer solution was treated with trifluoroacidic acid (1 g polymer in 40 mL THF and 40 mL of TFA/H_2O (75 vol.%)) The polymers **P1'** and **P2'** were obtained in 40% and 48% yield respectively after distilling of the solvents and dialyzed against Millipore water.

P1': ^{1}H NMR (400.1 MHz, D_2O) $\delta = 1.75$ (s, 4H, CH_2-$C\underline{H}_2$-CH_2), 2.27 (s, 3H, N-$C\underline{H}_3$), 2.60 (s, 4H, CH_3-N-$C\underline{H}_2$), 3.35 (s, 4H, CH2-C$\underline{H}$2-NH), 4.51 (s, 2H, CH-O) ppm. ^{13}C NMR (100.6 MHz, D_2O) $\delta = 26.7$ (NH-CH2-$\underline{C}$H2), 37.8 ($\underline{C}$-NH), 41.3 (N-$\underline{C}H_3$), 52.5 ($\underline{C}$H2-N-CH_3), 76.8 ($\underline{C}$-OH), 177.1 ($\underline{C}$=O) ppm. FT-IR: $\upsilon = 3280$, 2931, 2851, 1649 , 1445, 1076 cm^{-1}. GPC analysis of **P1':** $\overline{M}_n^{app}$ = 5.000, $\overline{M}_w^{app}/\overline{M}_n^{app}$ = 1.4.

P2': ^{1}H NMR (400 MHz, D_2O): $\delta = 3.46$ (br, 4H; CH_2-$C\underline{H}_2$-NH), 3.62-3.69 (br, 8H, -O-$C\underline{H}_2$-$C\underline{H}_2$-O and O-$C\underline{H}_2$-CH_2-NH), 4.93 (s, 2H, CH-O) ppm. ^{13}C NMR (100.6 MHz, D_2O): $\delta = 38.6$ ($\underline{C}H_2$-NH), 69.4 ($\underline{C}H_2$-O), 72.3 ($\underline{C}$-OH), 171.4 ($\underline{C}$=O) ppm. FT-IR: $\upsilon =$ 3300, 2931, 2867, 1657, 1523, 1453, 1210, 1076 cm^{-1}. GPC analysis of **P2':** $\overline{M}_n^{app}$ = 4000, $\overline{M}_w^{app}/\overline{M}_n^{app}$ = 1.7.