Supplementary information

Effect of Solvent Properties on the Critical Solution Temperature of Thermoresponsive Polymers

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**Table S1.** Critical solution temperatures of differently concentrated PNiPAm and PiPOx (21 kDa) dispersions prepared in H2O and D2O measured with DLS and DSC, respectively.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **PNiPAm (DLS)** | **H2O** | **D2O** | **PNiPAm (DSC)** | **H2O** | **D2O** |
| *ρ* [mg ml-1] | ***T* [°C]** | | *ρ* [mg ml-1] | ***T* [°C]** | |
| 10-1 | 45.0 | 43.4 | 10-1 | 46.49 | 44.52 |
| 100 | 40.0 | 41.0 | 100 | 43.54 | 42.32 |
| 101 | 35.4 | 36.6 | 101 | 39.94 | 38.67 |
| **PiPOx (DLS)** | **H2O** | **D2O** | **PiPOx (DSC)** | **H2O** | **D2O** |
| *ρ* [mg ml-1] | ***T* [°C]** | | *ρ* [mg ml-1] | ***T* [°C]** | |
| 10-1 | 45.0 | 43.8 | 10-1 | 46.39 | 45.27 |
| 100 | 42.0 | 40.6 | 100 | 43.29 | 42.57 |
| 101 | 38.6 | 37.8 | 101 | 40.27 | 39.55 |

**Table S2.** Comparison of onset and peak temperature values [°C] in DSC thermograms of PNiPAm and PiPOx dispersions (21 kDa polymers; 10-1 mg ml-1, 100 mg ml-1 and 101 mg ml-1) in H2O and D2O.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **PNiPAm** | **H2O** | | | **D2O** | | |
| *ρ* [mg ml-1] | *T*onset | *T*peak | **Δ*T*** | *T*onset | *T*peak | **Δ*T*** |
| 10-1 | 43.94 | 46.49 | **2.55** | 39.27 | 44.52 | **5.25** |
| 100 | 41.34 | 43.54 | **2.20** | 40.04 | 42.32 | **2.28** |
| 101 | 37.83 | 39.94 | **2.11** | 38.11 | 38.67 | **0.56** |
| **PiPOx** | **H2O** | | | **D2O** | | |
| *ρ* [mg ml-1] | *T*onset | *T*peak | **Δ*T*** | *T*onset | *T*peak | **Δ*T*** |
| 10-1 | 43.08 | 46.39 | **3.31** | 40.58 | 45.27 | **4.69** |
| 100 | 41.3 | 43.29 | **1.99** | 40.63 | 42.57 | **1.94** |
| 101 | 39.19 | 40.27 | **1.08** | 38.58 | 39.55 | **0.97** |

**Table S3.** Critical solution temperatures of PNiPAm and PiPOx (21 kDa; 1 mg ml-1) in Hofmeister series salt solutions prepared in H2O and D2O from 1 mM to physiological ionic strength measured with DLS and DSC, respectively.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **PNiPAm** | **1 mM salts** | | **10 mM salts** | | **160 mM salts** | |
| **DLS** | ***T*H2O** | ***T*D2O** | ***T*H2O** | ***T*D2O** | ***T*H2O** | ***T*D2O** |
| No salt | 40.2 (0 mM) | 41.0 (0 mM) | - | - | - | - |
| K2SO4 | 40.4 | 40.2 | 39.4 | 39.4 | 31.2 | 32.0 |
| K2HPO4 | 40.6 | 40.4 | 39.8 | 39.8 | 28.8 | 31.8 |
| KCl | 40.4 | 40.4 | 40.2 | 40.2 | 37.0 | 36.8 |
| KSCN | 40.4 | 40.4 | 40.4 | 40.4 | 39.2 | 42.6 |
| **PNiPAm** | **1 mM salts** | | **10 mM salts** | | **160 mM salts** | |
| **DSC** | ***T*H2O** | ***T*D2O** | ***T*H2O** | ***T*D2O** | ***T*H2O** | ***T*D2O** |
| No salt | 43.54 (0 mM) | 42.32 (0 mM) | - | - | - | - |
| K2SO4 | 43.1 | 43.61 | 42.11 | 42.01 | 34.42 | 35.16 |
| K2HPO4 | 43.9 | 44.08 | 43.75 | 43.71 | 34.57 | 35.73 |
| KCl | 42.83 | 43.6 | 42.68 | 42.32 | 39.84 | 40.45 |
| KSCN | 43.00 | 43.73 | 42.73 | 42.93 | 44.29 | 44.87 |
| **PiPOx** | **1 mM salts** | | **10 mM salts** | | **160 mM salts** | |
| **DLS** | ***T*H2O** | ***T*D2O** | ***T*H2O** | ***T*D2O** | ***T*H2O** | ***T*D2O** |
| No salt | 42.2 (0 mM) | 40.2 (0 mM) | - | - | - | - |
| K2SO4 | 41.8 | 40.8 | 40.6 | 39.8 | 32.0 | 31.4 |
| K2HPO4 | 41.2 | 40.2 | 40.4 | 39.4 | 31.4 | 31.2 |
| KCl | 41.4 | 40.6 | 41.2 | 39.6 | 39.2 | 35.6 |
| KSCN | 41.2 | 40.0 | 40.8 | 41.2 | 52.8 | 51.8 |
| **PiPOx** | **1 mM salts** | | **10 mM salts** | | **160 mM salts** | |
| **DSC** | ***T*H2O** | ***T*D2O** | ***T*H2O** | ***T*D2O** | ***T*H2O** | ***T*D2O** |
| No salt | 43.29 (0 mM) | 42.57 (0 mM) | - | - | - | - |
| K2SO4 | 43.45 | 42.61 | 43.22 | 42.09 | 35.39 | 35.41 |
| K2HPO4 | 43.12 | 42.36 | 42.32 | 41.1 | 34.35 | 34.23 |
| KCl | 43.51 | 42.65 | 43.53 | 42.06 | 41.9 | 41.69 |
| KSCN | 43.03 | 42.15 | 43.07 | 42.98 | 52.75 | 53.35 |

|  |  |
| --- | --- |
|  |  |
| (**a**) | (**b**) |
|  |  |
| **(c)** | **(d)** |
|  |  |
| **(e)** | **(f)** |

**Figure S1**. DSC-recorded thermograms of PNiPAm (21 kDa; 1 mg ml-1) in H2O and D2O. Red: K2SO4, blue: K2HPO4, pink: KCl, green: KSCN; polymer dispersed in solutions of (a) 1 mM salts in H2O; (b) 1 mM salts in D2O; (c) 10 mM salts in H2O; (d) 10 mM salts in D2O; (e) 160 mM salts in H2O and (f) 160 mM salts in D2O.

**Table S4.** DSC-derived transition enthalpies per monomer unit of PNiPAm and PiPOx (21kDa) in differently concentrated salt solutions prepared in H2O and D2O.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **PNiPAm** | **Δ*H*monomer [J mol-1]** | | | | | | |
| **H2O** | **1 mM salt** | **10 mM salt** | **160 mM salt** | **D2O** | **1 mM salt** | **10 mM salt** | **160 mM salt** |
| No salt | 5568 (0 mM) | - | - | No salt | 11459 (0 mM) | - | - |
| K2SO4 | 5676 | 5946 | 5838 | K2SO4 | 5892 | 7135 | 6703 |
| K2HPO4 | 4968 | 5730 | 5514 | K2HPO4 | 6432 | 6324 | 5838 |
| KCl | 5375 | 5676 | 5730 | KCl | 5946 | 6973 | 5892 |
| KSCN | 5514 | 6270 | 5195 | KSCN | 6649 | 6162 | 4243 |
| **PiPOx** | **Δ*H*monomer [J mol-1]** | | | | | | |
| **H2O** | **1 mM salts** | **10 mM salts** | **160 mM salts** | **D2O** | **1 mM salts** | **10 mM salts** | **160 mM salts** |
| No salt | 4719 (0 mM) | - | - | No salt | 4470 (0 mM) | - | - |
| K2SO4 | 5189 | 4227 | 5568 | K2SO4 | 5368 | 4222 | 6703 |
| K2HPO4 | 5286 | 3357 | 5027 | K2HPO4 | 5011 | 5514 | 6162 |
| KCl | 4859 | 4541 | 9135 | KCl | 5676 | 5459 | 9514 |
| KSCN | 4730 | 7838 | 15459 | KSCN | 5784 | 12865 | 18000 |

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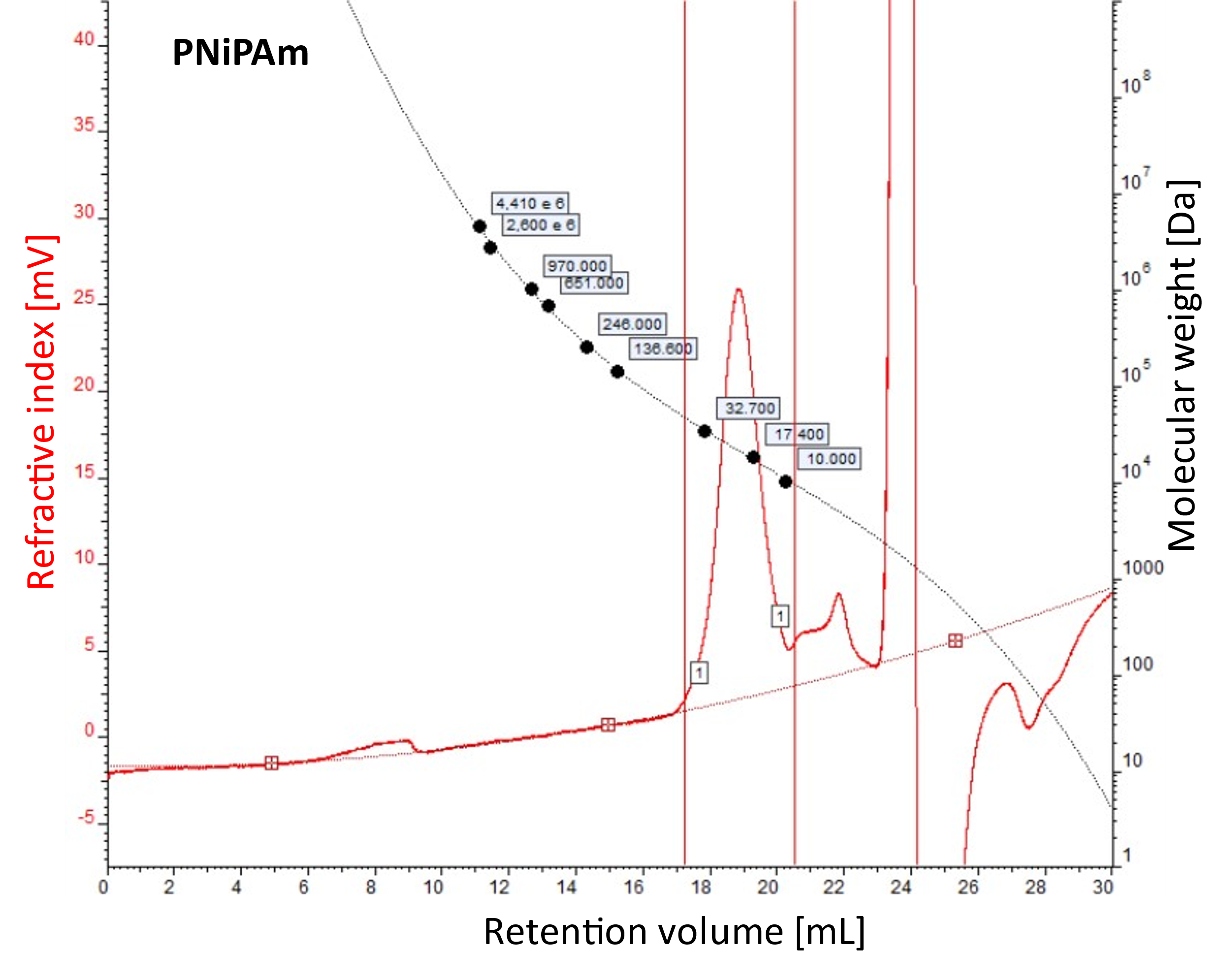
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**Figure S2.** 1H NMR spectrum for PNiPAm in CDCl3 at 300 MHz. Normalised intensity is plotted against chemical shifts relative to TMS (0 ppm). Structural components and corresponding peaks are marked with letters **a** to **d**. PNiPAm: δH(300 MHz, CDCl3, ppm) 4.02 (s, 1H), 2.14 (s, 1H), 1.66 (d, 2H), 1.15 (d, 6H)

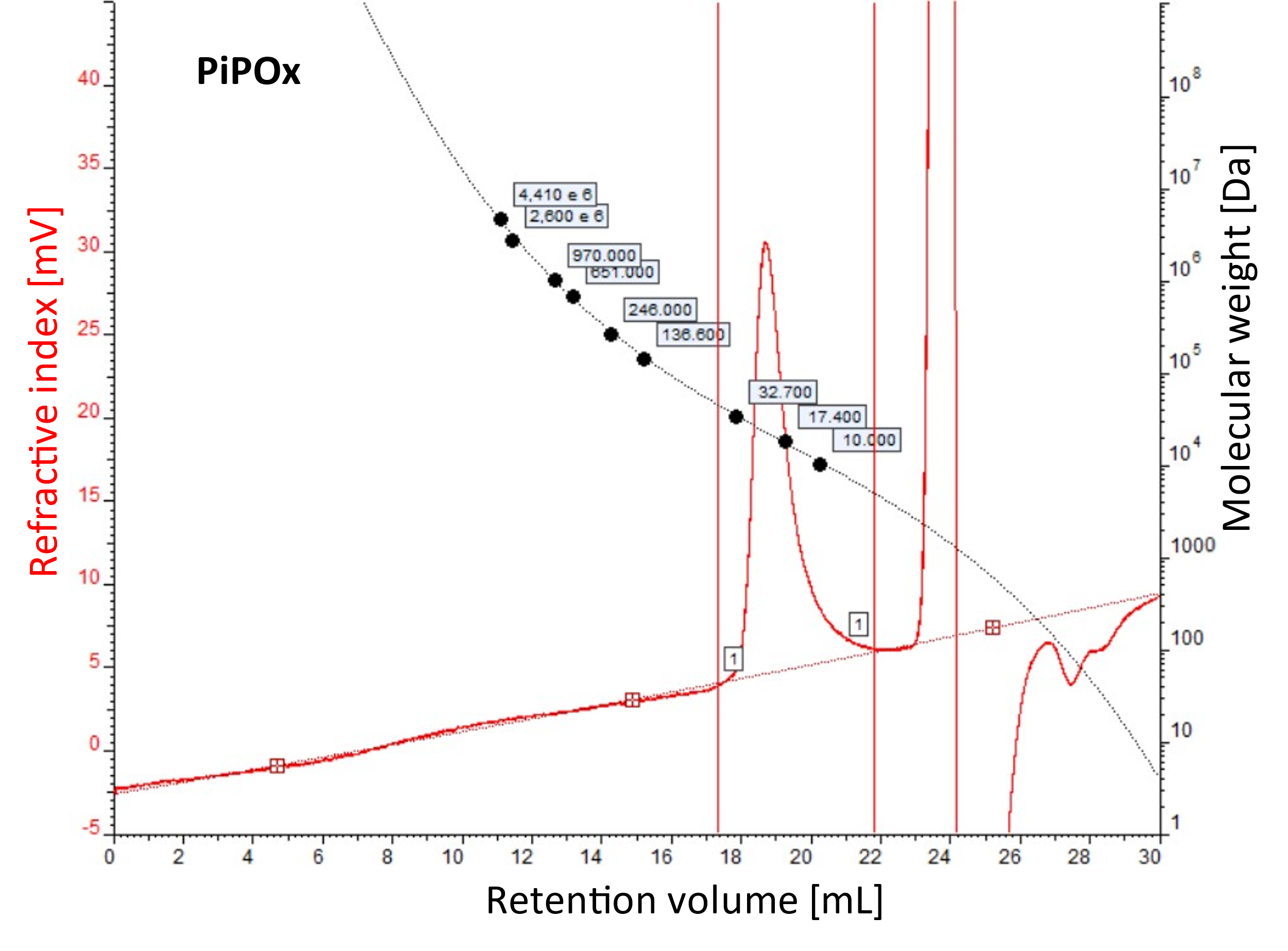
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**Figure S3.** 1H NMR spectrum for PiPOx in CDCl3 at 300 MHz. Normalised intensity is plotted against chemical shifts relative to TMS (0 ppm). Structural components and corresponding peaks are marked with letters **a** to **d**. PiPOx: δH(300 MHz, CDCl3, ppm) 3.46 (d, 2H), 3.00 (s, 3H), 2.77 (d, 1H), 1.10 (s, 6H).



**Figure S4.** Gel permeation chromatography of PNiPAm based on its RG against a standard of polystyrene in N,N-dimethylformamide (DMF). 3.5 mg polymer were dissolved in 1 ml DMF containing 0.05 mol l-1 lithium bromide. 50 µl of sample were measured at a flow rate of 9.5 ml min-1 at 60 °C.



**Figure S5.** Gel permeation chromatography of PiPOx based on its RG against a standard of polystyrene in N,N-dimethylformamide (DMF). 3.5 mg polymer were dissolved in 1 ml DMF containing 0.05 mol l-1 lithium bromide. 50 µl of sample were measured at a flow rate of 9.5 ml min-1 at 60 °C.

**Table S5.** Polymer weight and polydispersity derived from GPC.

|  |  |  |
| --- | --- | --- |
| Polymer | **PNiPAm** | **PiPOx** |
| Linear Formula | CH3(C6H11NO)nOH | CH3(C6H11NO)nOH |
| *M*w [kDa] | 21.368 | 21.119 |
| *M*n [kDa] | 20.379 | 20.341 |
| PDI | 1.049 | 1.038 |

|  |  |
| --- | --- |
|  | Eq. S1 |