Supporting Information for the manuscript

Temperature Dependent Behavior of Isotactic and Atactic Poly(Methacrylic Acid) in the Presence of $MgCl_2$ and $CaCl_2$

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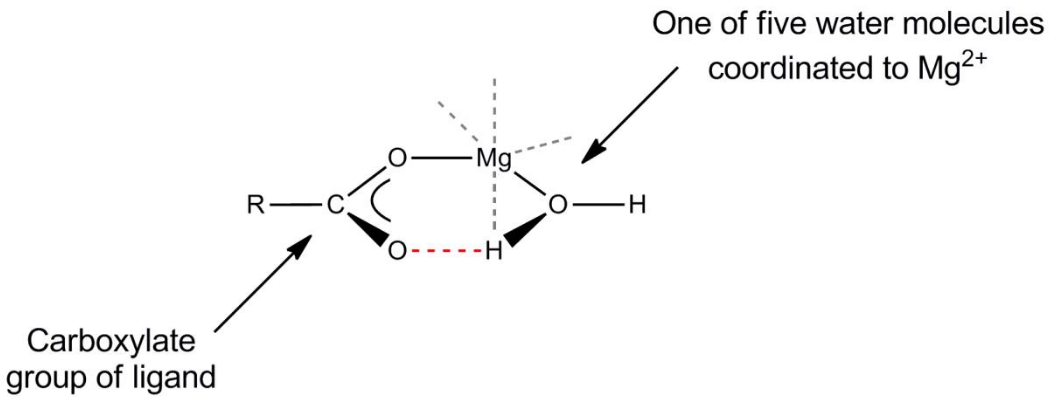
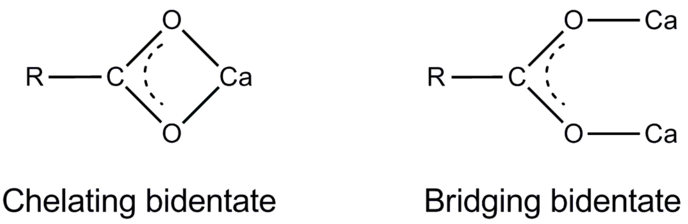
a) Monodentate binding of Mg^{2+}



b) Bidentate binding of Ca^{2+}



Scheme S1. Schematic presentation of the a) monodentate binding of Mg^{2+} to COO^- and b) two possible bidentate binding modes of Ca^{2+} to COO^-, chelate and bridging.

Experimental

Materials

Isotactic poly(methyl methacrylate) (iPMMA) was converted into the acid form by hydrolysis in oxygen-free 96% H_2SO_4, followed by hydrolysis in 1 M NaOH. For this purpose, 3 g of iPMMA were added to 150 mL of H_2SO_4 at room temperature and stirred for 24 hours under constant flow of N_2. The temperature was raised to 60 °C. After 5 hours at 60 °C, when the polymer completely dissolved, the solution was cooled to 0 °C and poured into 3 L of ice-cold distilled water. The lightly yellow precipitated polymer was filtered and dissolved in water by adding solid NaOH until the pH of the solution was around 9. After heating the polymer at 60 °C for approximately 30 minutes, isotactic poly(methacrylic acid) (iPMA) was precipitated by a drop-wise addition of concentrated H_2SO_4. For further purification of iPMA, the dialysis was used. The polymer was first dialyzed against 0.02 M HCl to to exchange Na^+ for H^+. For $\alpha_N < 0.2$, iPMA precipitated from the solution. Further dialysis was performed against single and triple distilled water in order to thoroughly remove all low molar mass impurities. The obtained precipitate was filtered and dried by lyophilization (using Heto HETOSTATIC, Type CD 2.5; Heto-Holten A/S, Allerød, Denmark).

Preparation of Solutions

Added salt concentrations (c_s) and the corresponding ionic strengths (I) in a- and iPMA solutions are reported in Table S1.

Table S1. Concentrations (c_s) of added metal chlorides ($MgCl_2$ and $CaCl_2$) and the final ionic strengths (I) (all at 25 °C) of aqueous iPMA (c_p = 0.022 mol L^{-1}; α_N is given in the Table) and aPMA (c_p = 0.023 mol L^{-1}, α_N = 0) solutions used for UV-Vis, visual, fluorimetric and pH measurements.

	iPMA			aPMA	
Added salt	I / mol L^{-1}	c_s / mol L^{-1}	α_N	I / mol L^{-1}	c_s / mol L^{-1}
$MgCl_2$	0.01	0.0033	0.20	0.1	0.0333
	0.02	0.0067	0.20	0.2	0.0667
$CaCl_2$	0.01	0.0033	0.20	0.1	0.0333
	0.02	0.0067	0.63	0.2	0.0667

Methods

Visual observations

Photographs of aPMA and iPMA samples in $MgCl_2$ and $CaCl_2$ during heating and cooling are collected in Tables S2−S4.

Table S2. Visual observations of aPMA (c_p = 0.023 mol L^{-1}, α_N = 0) samples in the presence of $MgCl_2$ and CaC_2 during heating in a water bath. For taking photos, samples were briefly taken from the water bath and photographed immediately.

***T* / °C**	**aPMA in 0.0333 M $MgCl_2$**	**aPMA in 0.0333 M $CaCl_2$**
15		
25		
45		

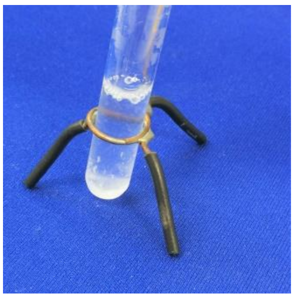
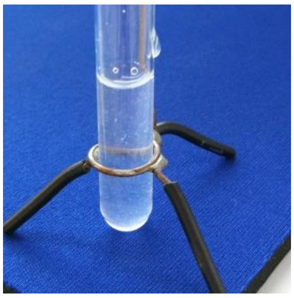
T / °C	aPMA in 0.0333 M $MgCl_2$	aPMA in 0.0333 M $CaCl_2$
55		
65		
75		
85		
95		

Table S3. Visual observations of aPMA (c_p = 0.023 mol L^{-1}, α_N = 0) samples in the presence of $MgCl_2$ and $CaCl_2$ during cooling in a water bath. For taking photos, samples were briefly taken from the water bath and photographed immediately.

***T* / °C**	**aPMA in 0.0333 M $MgCl_2$**	**aPMA in 0.0333 M $CaCl_2$**
85		
75		
65		
55		

T / °C	aPMA in 0.0333 M $MgCl_2$	aPMA in 0.0333 M $CaCl_2$
45		
25		
15		

Table S4. Visual observations of iPMA (c_p = 0.022 mol L^{-1}, α_N = 0.20) samples in the presence of $MgCl_2$ and $CaCl_2$ at 25 °C.

T / °C	iPMA in 0.0033 M $MgCl_2$	iPMA in 0.0033 M $CaCl_2$
25		

UV Spectroscopy

Heating and cooling temperature programs of a- and iPMA solutions are reported in Table S5.

Table S5. Temperature program for heating and cooling of a- and iPMA solutions.

	iPMA		**aPMA**	
Heating / Cooling	**Temperature range / °C**	**Rate / °C min^{-1}**	**Temperature range / °C**	**Rate / °C min^{-1}**
Heating	0−95	1	0−95	1
Cooling	95−15	1	95−0	1
Cooling	15−0	1	/	/

Light Scattering

Examples of calculated hydrodynamic radii (R_h) distributions for iPMA (α_N = 0.2) in $CaCl_2$ solution with I = 0.01 mol L^{-1} and for aPMA (α_N = 0) solution in $CaCl_2$ with a ten-times higher I (I = 0.1 mol L^{-1}) are shown on Figure S1.

a) b)

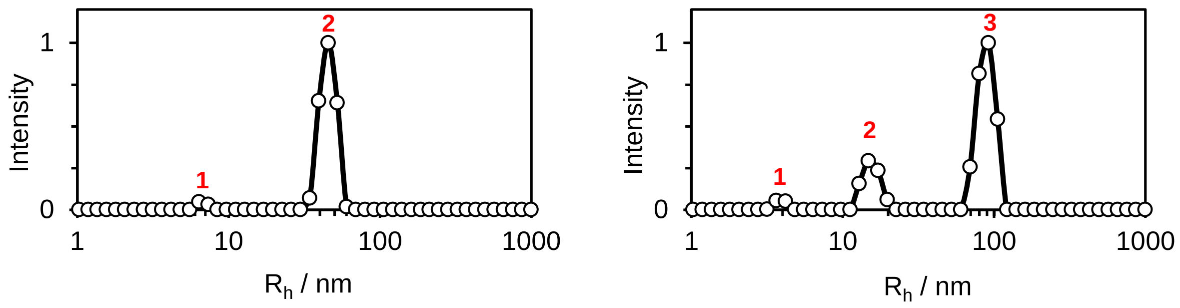


Figure S1. Size distributions of particles in aqueous solutions of a) iPMA (c_p = 0.022 mol L^{-1}, α_N = 0.20) and b) aPMA (c_p = 0.023 mol L^{-1}, α_N = 0) in $CaCl_2$ with I = 0.1 mol L^{-1} at θ = 120°. In the iPMA case, peak 1 corresponds to small particles and peak 2 to associates (with $R_{h,ass}$). In the aPMA case, peaks 1 and 2 correspond to individual chains and smaller associates, while peak 3 applies to larger aggregates with $R_{h,ass}$.

Results

UV Spectroscopy

Figure S1 demonstrates the determination of LCST and UCST values in aPMA and iPMA solutions, respectively. The obtained temperatures for aPMA and iPMA solutions in $MgCl_2$ and $CaCl_2$ with different *I* are reported in Table S6 and S7.

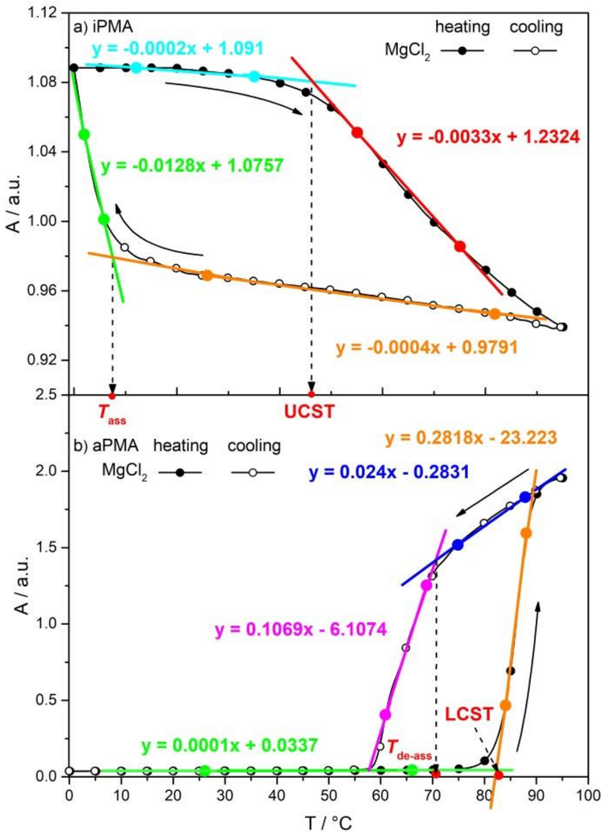


Figure S2. The method of determination of a) UCST for iPMA in $MgCl_2$ with I = 0.01 mol L^{-1} and b) LCST for aPMA in $MgCl_2$ with I = 0.1 mol L^{-1}.

Table S6. LCST and $T_{de\text{-}ass}$ obtained from UV spectra of aPMA (c_p = 0.023 mol L^{-1}, α_N = 0) solutions in $MgCl_2$ and in $CaCl_2$ with I = 0.1, 0.2, 0.3, 0.4 and 0.5 mol L^{-1}.

I **/ mol L^{-1}**	***c*$_s$ / mol L^{-1}**	**LCST / °C**		***T*$_{de\text{-}ass}$ / °C**	
		$MgCl_2$	$CaCl_2$	$MgCl_2$	$CaCl_2$
0.1	0.0333	81	75	59	58
0.2	0.0667	73	69	52	50
0.3	0.1	68	65	47	45
0.4	0.1333	65	63	43	40
0.5	0.1667	63	61	37	35

Table S7. UCST and T_{ass} obtained from UV spectra of iPMA (c_p = 0.022 mol L^{-1}, α_N = 0.20) solutions in $MgCl_2$ and $CaCl_2$ with I = 0.01 mol L^{-1}.

Added salt	***α*$_N$**	**UCST / °C**	***T*$_{ass}$ / °C**
$MgCl_2$	0.19	48	7
$CaCl_2$	0.19	35	/*

*could not be otained from the UV spectrum

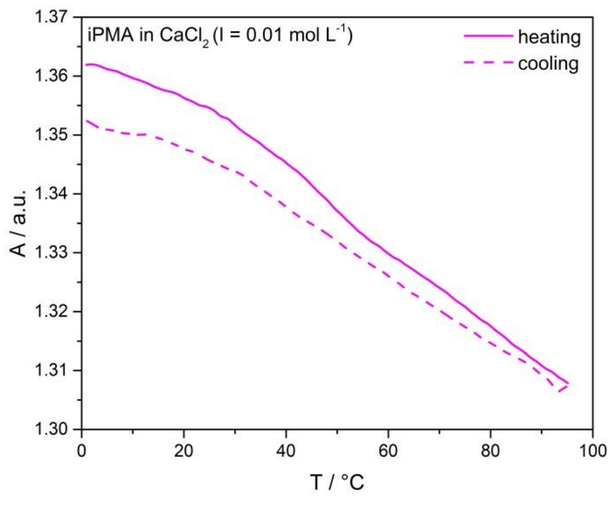


Figure S3. The enlarged plot of the temperature dependence of the UV absorbance (A) at 280 nm for iPMA (c_p = 0.022 mol L^{-1}, α_N = 0.20) solution in $CaCl_2$ with I = 0.01 mol L^{-1}.

Fluorescence measurements

In Figure S4 pyrene fluorescence emission spectra are shown for iPMA and aPMA solutions in $MgCl_2$ and $CaCl_2$, while the calculated I_1/I_3 values are reported in Table S8.

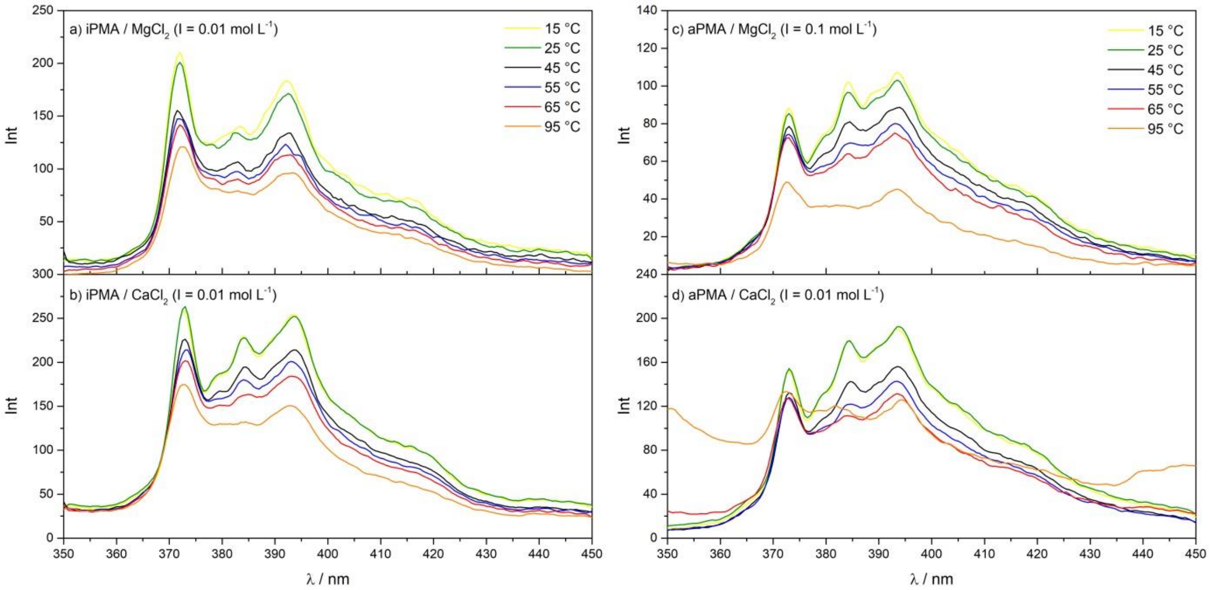


Figure S4. Emission spectra of pyrene for iPMA (c_p = 0.022 mol L^{-1}, α_N = 0.20) solutions in a) $MgCl_2$ and b) $CaCl_2$ (both with I = 0.01 mol L^{-1}) and for aPMA (c_p = 0.023 mol L^{-1}, α_N = 0) solutions in c) $MgCl_2$ and d) $CaCl_2$ (both with I = 0.1 mol L^{-1}).

Table S8. Effect of temperature on the intensity ratio I_1/I_3 of the first and third vibrational peaks in the pyrene fluorescence emission spectra for iPMA (c_p = 0.022 mol L^{-1}, α_N = 0.20) in aqueous $MgCl_2$ and $CaCl_2$ with I = 0.01 mol L^{-1} and for aPMA (c_p = 0.023 mol L^{-1}, α_N = 0) in aqueous $MgCl_2$ and $CaCl_2$ with I = 0.1 mol L^{-1}.

	I_1/I_3 (iPMA)		I_1/I_3 (aPMA)	
T / °C	0.0033 M $MgCl_2$	0.0033 M $CaCl_2$	0.0333 M $MgCl_2$	0.0333 M $CaCl_2$
15	1.50	1.13	0.86	0.85
25	1.49	1.16	0.88	0.86
45	1.46	1.16	0.97	0.93
55	1.52	1.19	1.07	1.05
65	1.57	1.23	1.13	1.14
95	1.53	1.32	1.34	/

Table S9. The pyrene intensity ratio I_1/I_3 in iPMA (c_p = 0.022 mol L^{-1}, α_N reported is reported in the Table) and aPMA (c_p = 0.023 mol L^{-1}, α_N = 0) with added $MgCl_2$ and $CaCl_2$ in solutions with different ionic strength I and at 25°C.

	iPMA			aPMA	
Added salt	***I* / mol L^{-1}**	α_N	I_1/I_3	***I* / mol L^{-1}**	I_1/I_3
$MgCl_2$	0.01	0.20	1.49	0.1	0.89
	0.02	0.20	1.51	0.2	0.91
$CaCl_2$	0.01	0.20	1.16	0.1	0.89
	0.02	0.63	/*	0.2	0.88

* a very turbid solution.

pH measurements

The measured pH and the calculated α_i values are reported in Table S10.

Table S10. The measured pH and calculated *I* values for iPMA (c_p = 0.022 mol L^{-1}, α_N = 0.20) and aPMA (c_p = 0.023 mol L^{-1}, α_N = 0) in aqueous $MgCl_2$ and $CaCl_2$ solutions with different $_I$.

iPMA					**aPMA**			
Added salt	***I* / mol L^{-1}**	α_N	**pH**	α_i	**Added salt**	***I* / mol L^{-1}**	**pH**	α_i
/	/	0.20	5.820	0.190	/	/	3.56	0.012
$MgCl_2$	0.01	0.20	5.680	0.190	$MgCl_2$	0.1	3.52	0.013
	0.02	0.20	5.590	0.190		0.2	3.45	0.015
$CaCl_2$	0.01	0.20	5.610	0.190		0.3	3.42	0.016
	0.02	0.63	/	/		0.4	3.42	0.016
						0.5	3.44	0.016
					$CaCl_2$	0.1	3.36	0.019
						0.2	3.22	0.026
						0.3	3.17	0.029
						0.4	3.13	0.032
						0.5	3.08	0.036