Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Figure S1. Scanning Electron micrographs of synthesised calcite.

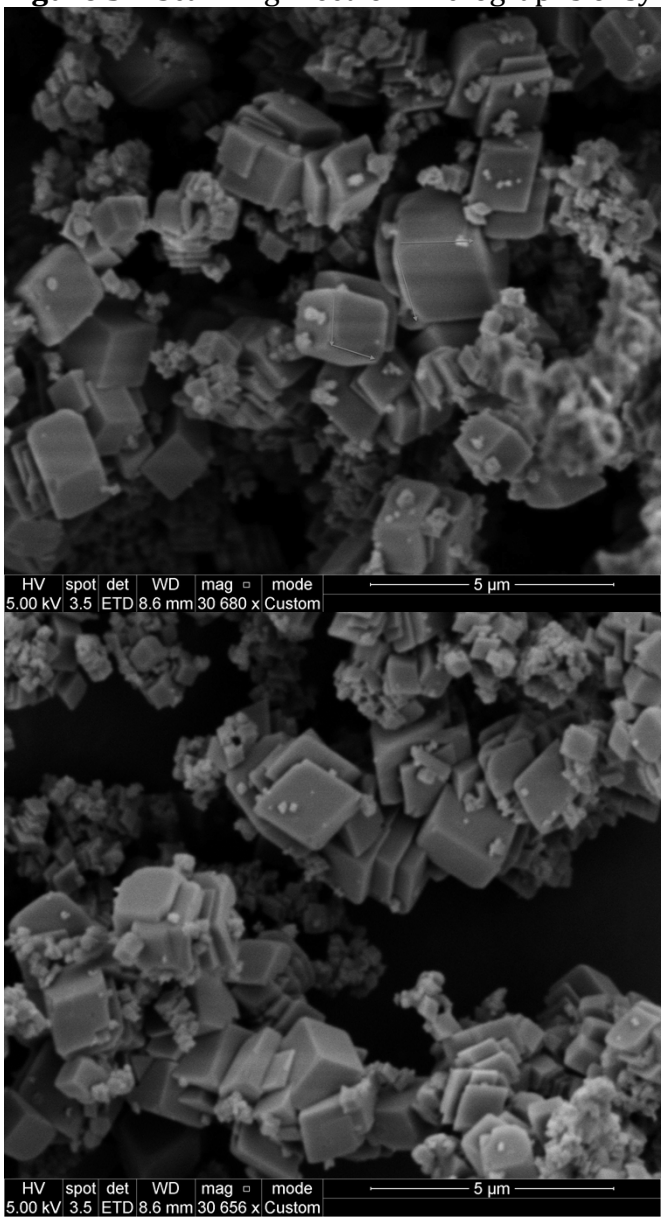


Figure S2. Powder XRD profile for the calcite particles.

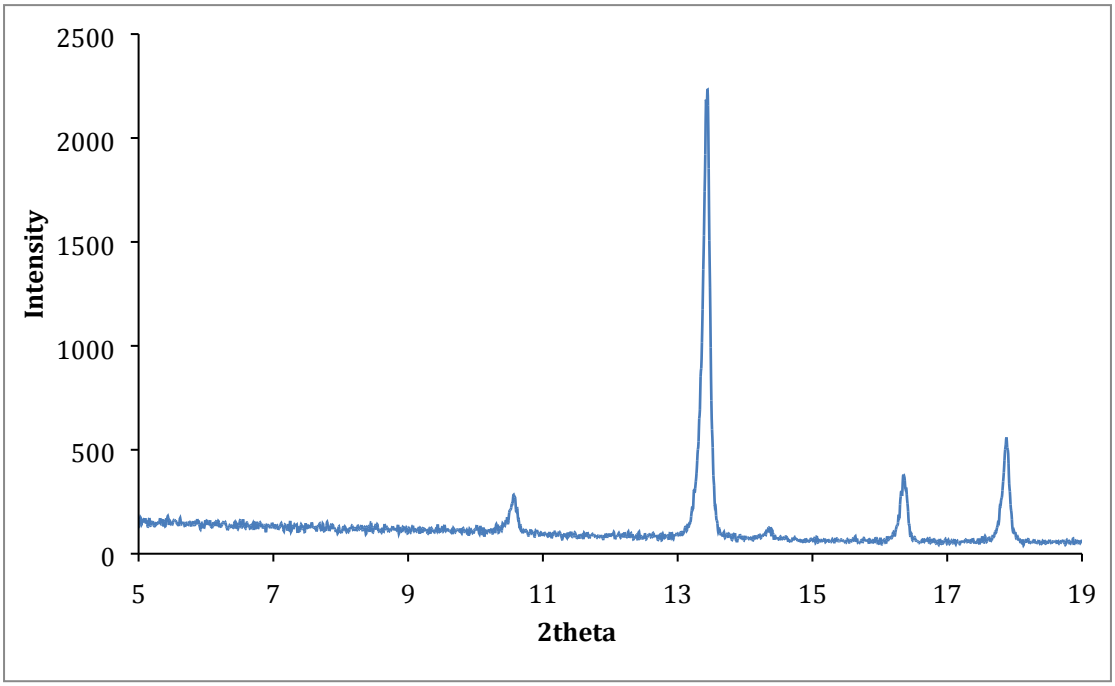


Table S1. Relative intensities of calcite Bragg peaks and comparison with a pure calcite reference

hkl	0 12	1 04	0 06	1 10	1 13
dÅ calcite	3.850	3.031	2.839	2.494	2.282
Intensity	12	100	6	17	25

Figure S3. Zeta potential of a 10%wt calcite solution as a function of pH

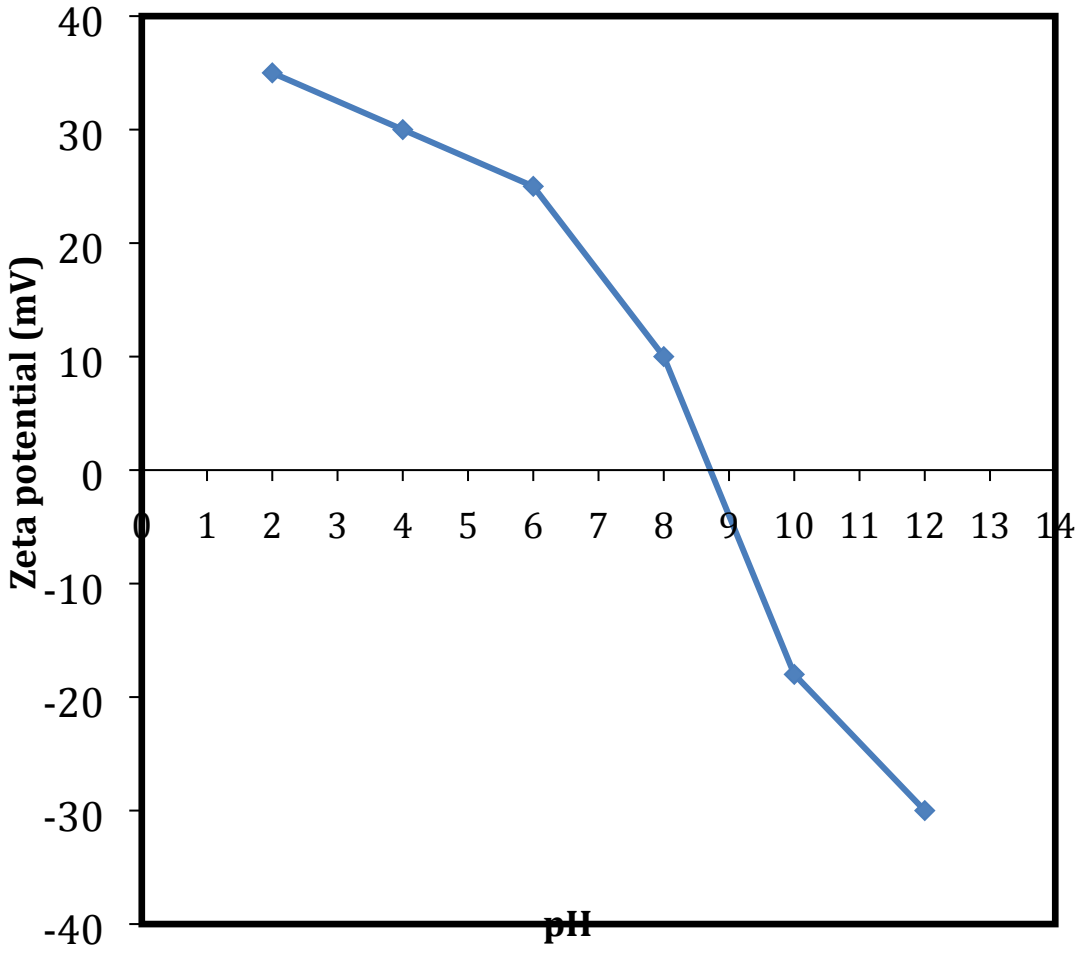
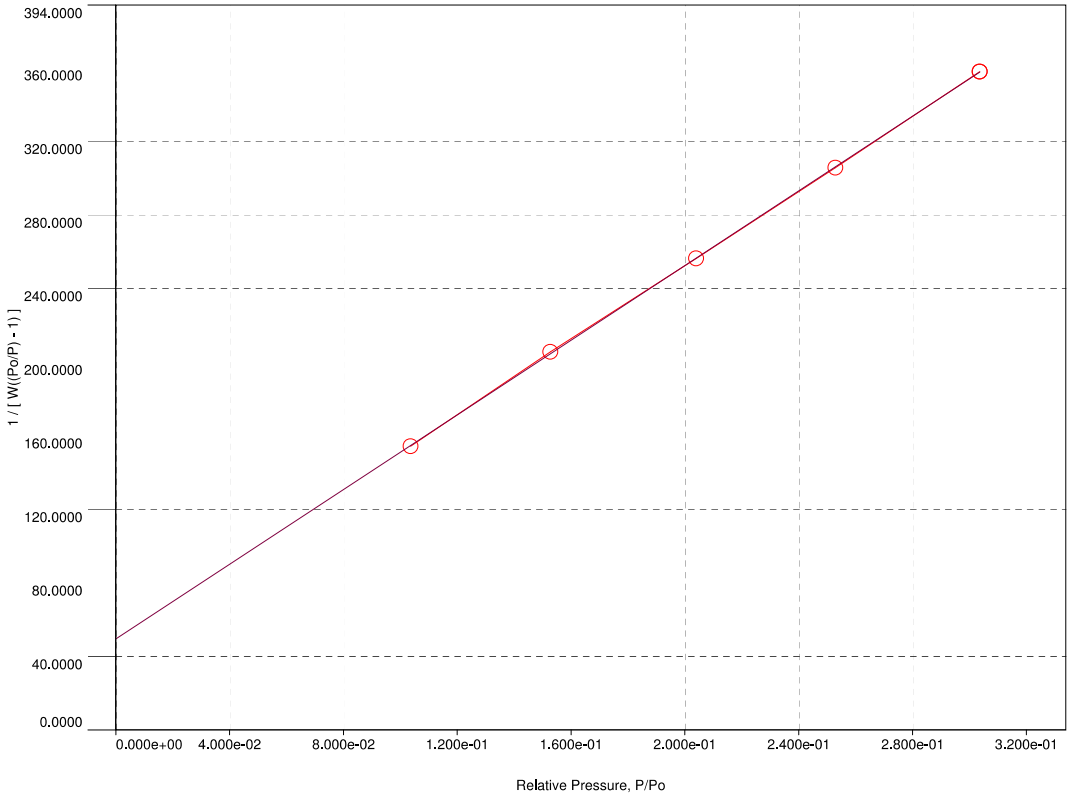


Figure S4. BET surface area by gas sorption and average surface area for the calcite sample



BET summary

Slope =	1014.546
Intercept =	4.941e+01
Correlation coefficient, r =	0.999968
C constant=	21.534
Surface Area =	3.273 m^2/g

Figure S5. Particle size distribution for the calcite sample

Sample ref.	: CaCO3 /5
Produkt	: Calcium Carbonate
Kunde	: University of Sheffield
Comments	:
Liquid	: VE-Wasser
Dispersing agent	:
Operator	: BD
Company	: Quantachrome GmbH
Location	: 85235 Odelzhausen
Date : 14.07.2015	Time : 13:56:18
Index meas.	: 3065
Database name	: CilasDB1

Ultrasounds	: 60	s (+during)
Obscuration	: 22 %	
Diameter at 10%	: 0.78	µm
Diameter at 50%	: 2.84	µm
Diameter at 90%	: 5.60	µm
Mean diameter	: 3.03	µm
Fraunhofer		
Density/Factor	---------	
Specific surface	----------	
Automatic dilution	: No / No	
Meas./Rins.	: 30s/60s/3	
SOP name	: 1090L 5.00	

Customer defined classes — in volume / undersize

x	0.02	0.10	0.50	1.00	2.00	3.20	4.00	6.00	8.00	10.00
Q3	0.20	0.37	4.50	15.70	35.70	56.46	70.50	92.75	99.07	100.00

x	15.00	20.00	32.00	45.00	63.00	112.0	140.0	224.0	315.0	500.0
Q3	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

x : diameter / µm Q3 : cumulative value / % q3 : density distribution

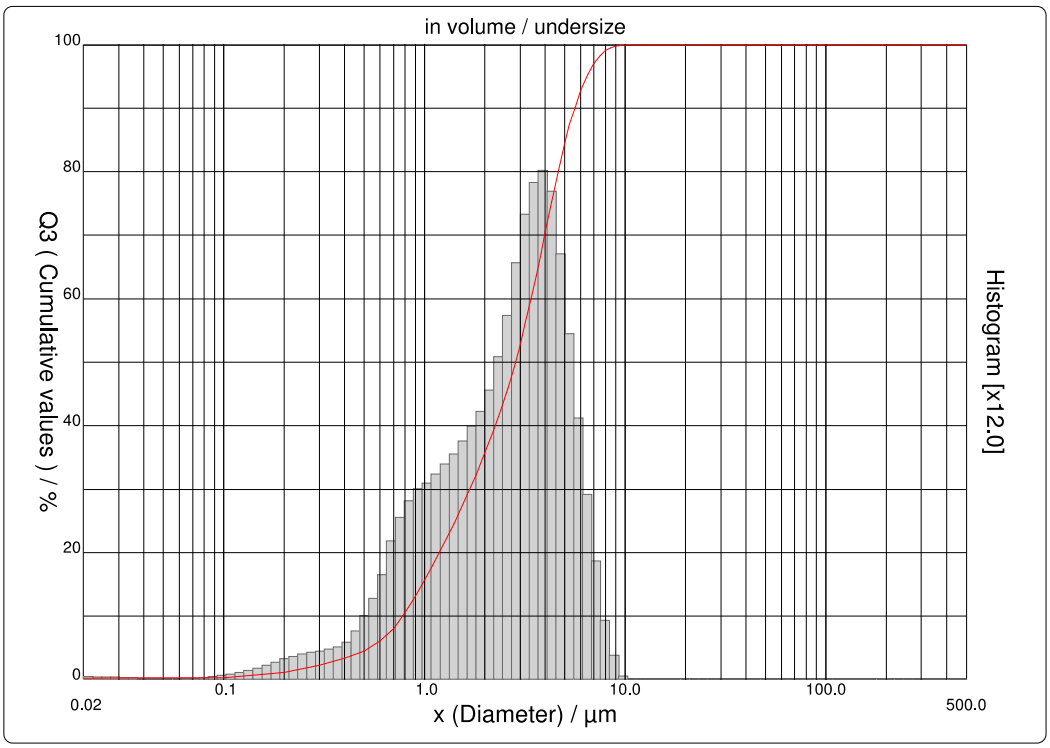


Figure S6 (a). Decay of anisotropy, r(t), of ACE-labelled PAA in aqueous solution at pH 2, and the associated single-exponential fit with the distribution of residuals.

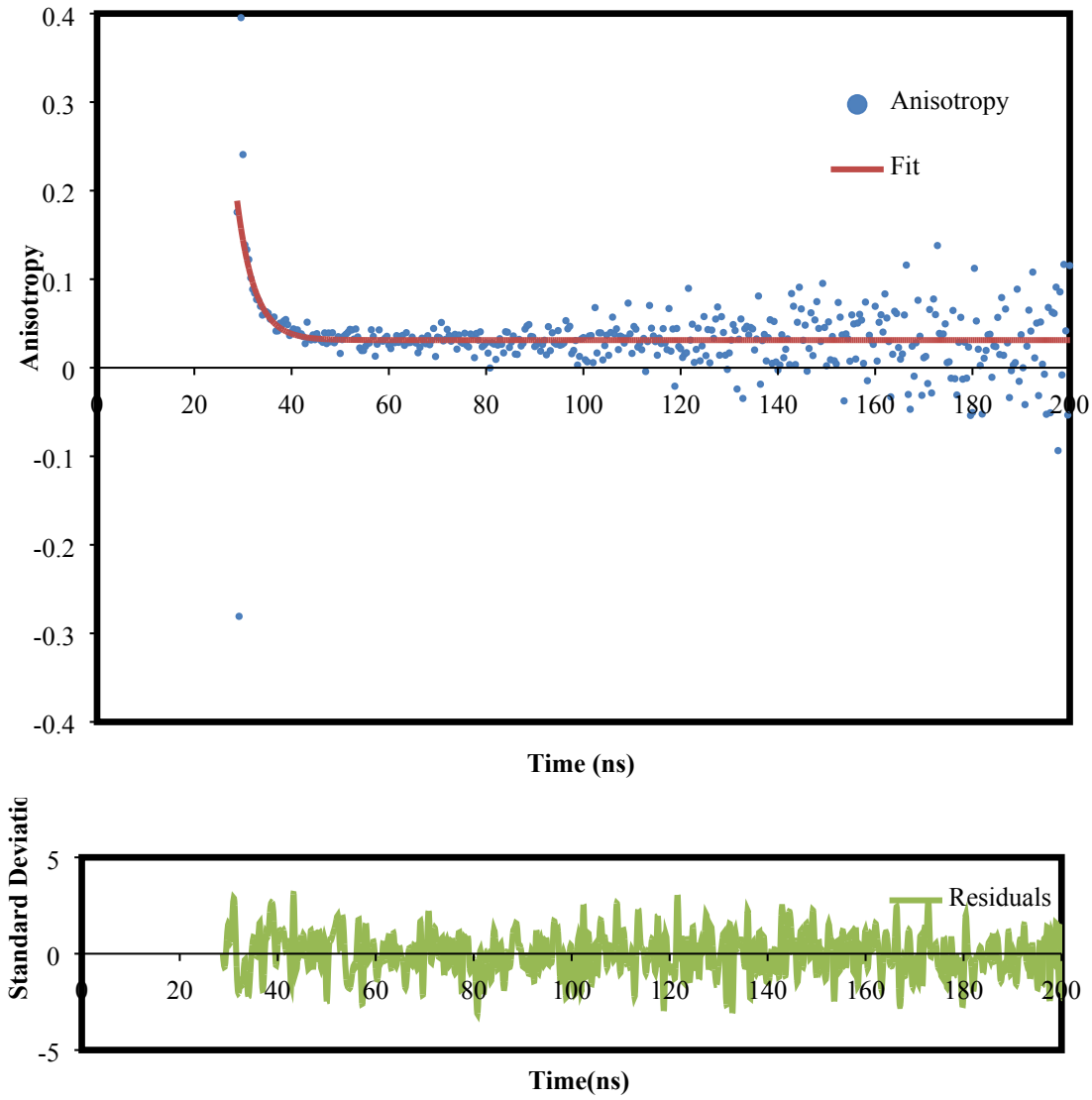


Figure S6 (b). Decay of anisotropy, r(t), of ACE-labelled PAA in aqueous solution at pH 12, and the associated single-exponential fit with the distribution of residuals.

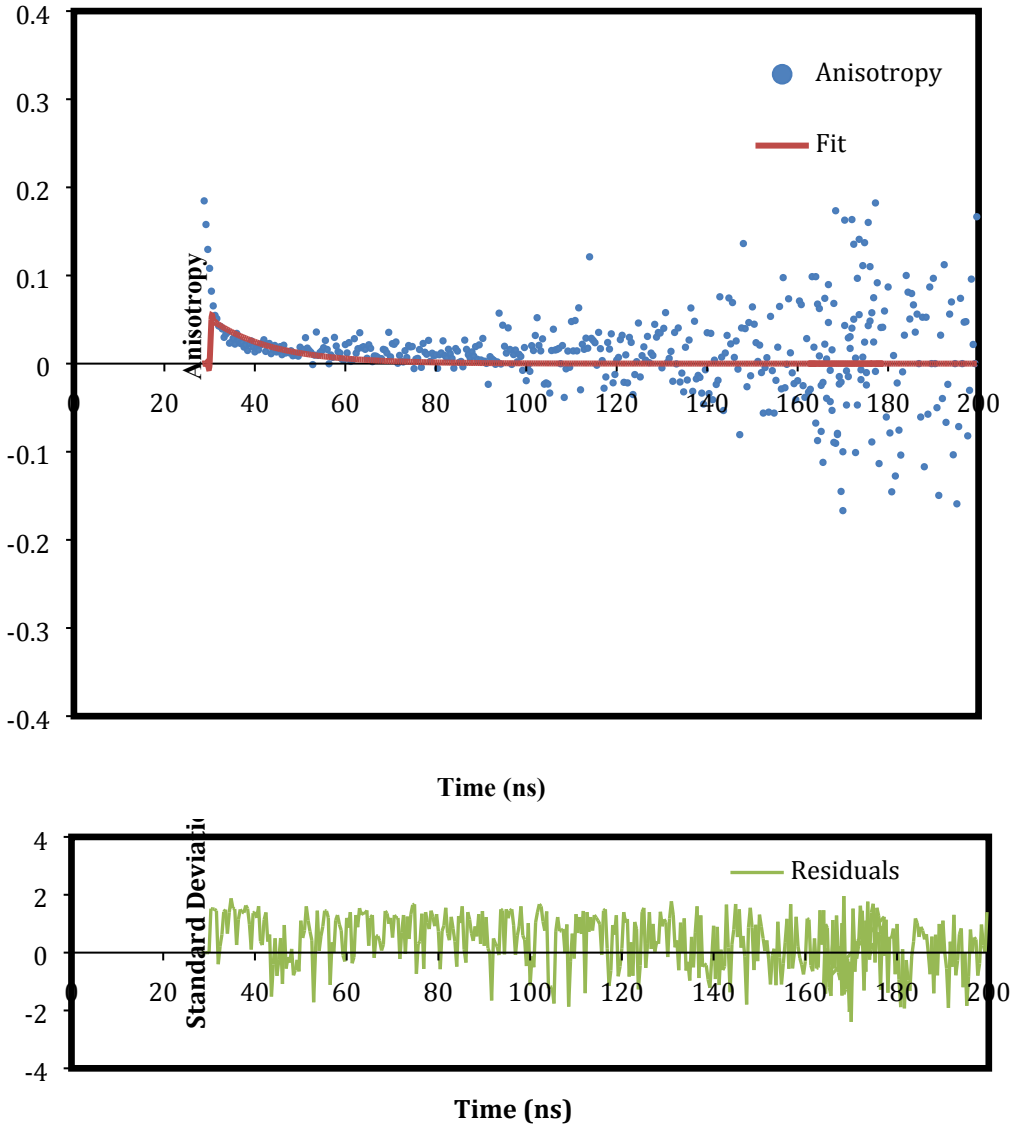


Figure S6 (c). Decay of anisotropy, r(t), of AmNS-labelled PAA in aqueous solution at pH 2, and the associated single-exponential fit with the distribution of residuals.

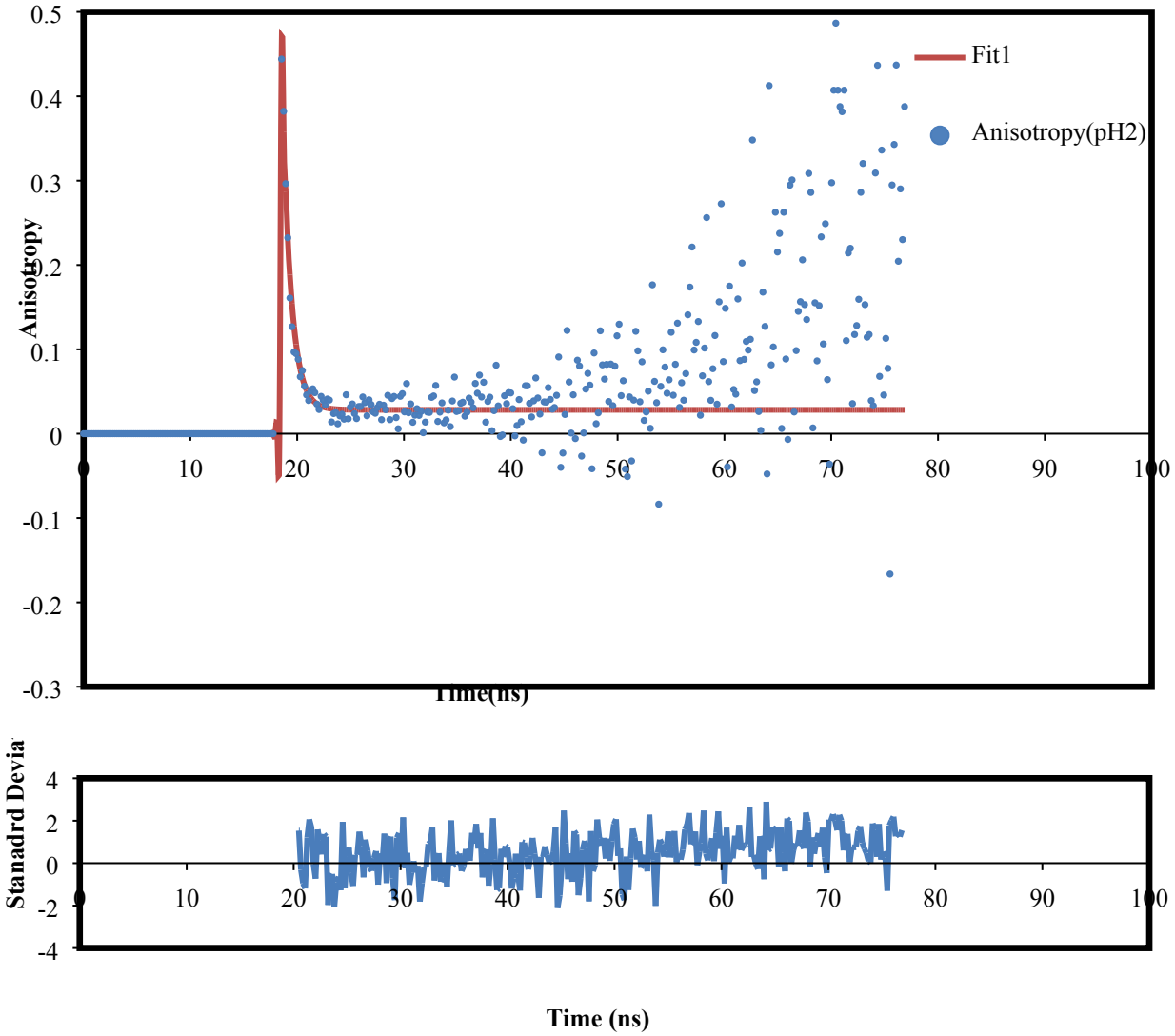


Figure S6 (d). Decay of anisotropy, r(t), of AmNS-labelled PAA in aqueous solution at pH 12, and the associated single-exponential fit with the distribution of residuals.

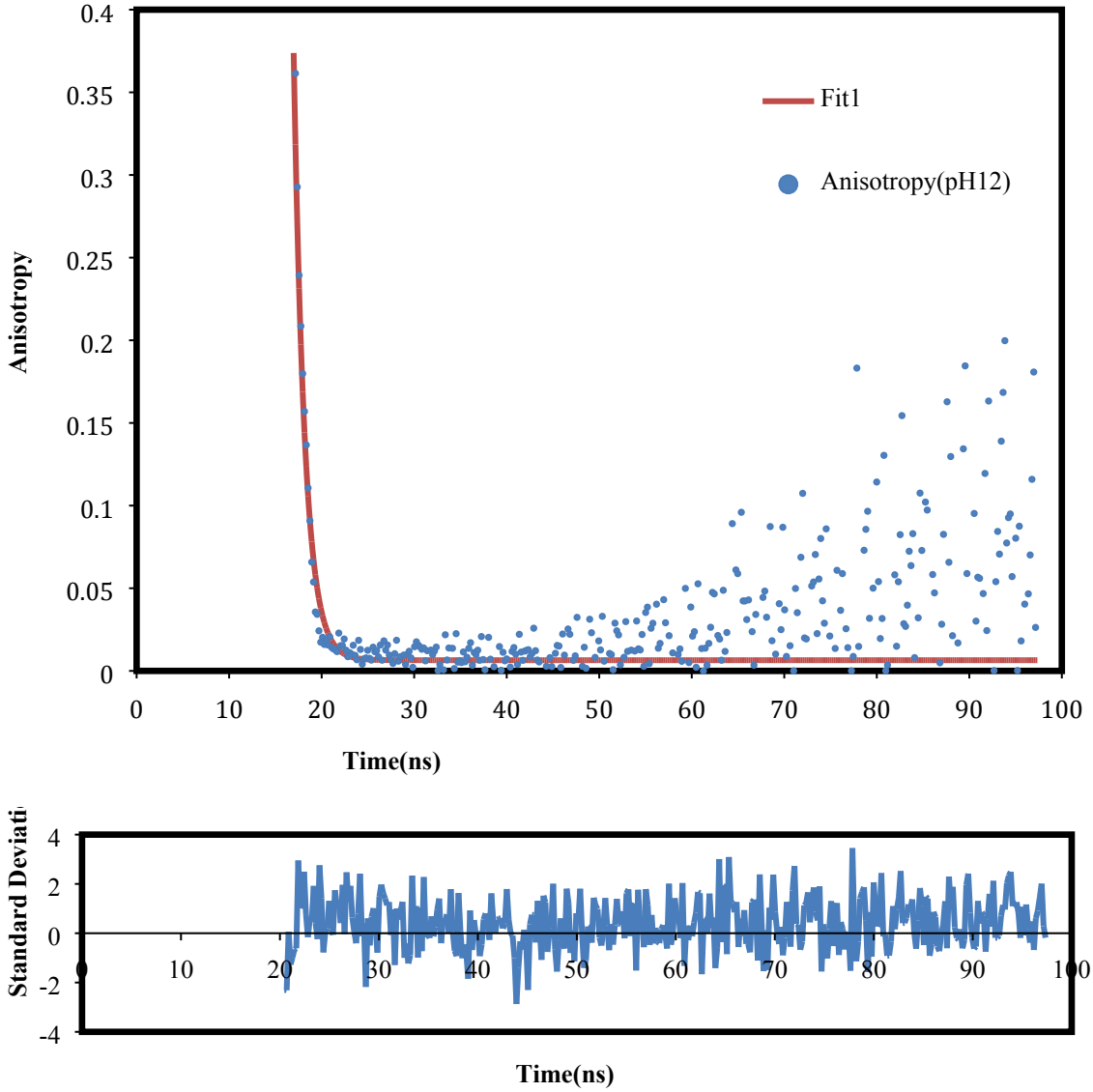


Figure S6 (e). Decay of anisotropy, r(t), of AmNS-labelled PAA in 1 wt% calcite at pH 7, and the associated single-exponential fit with the distribution of residuals.

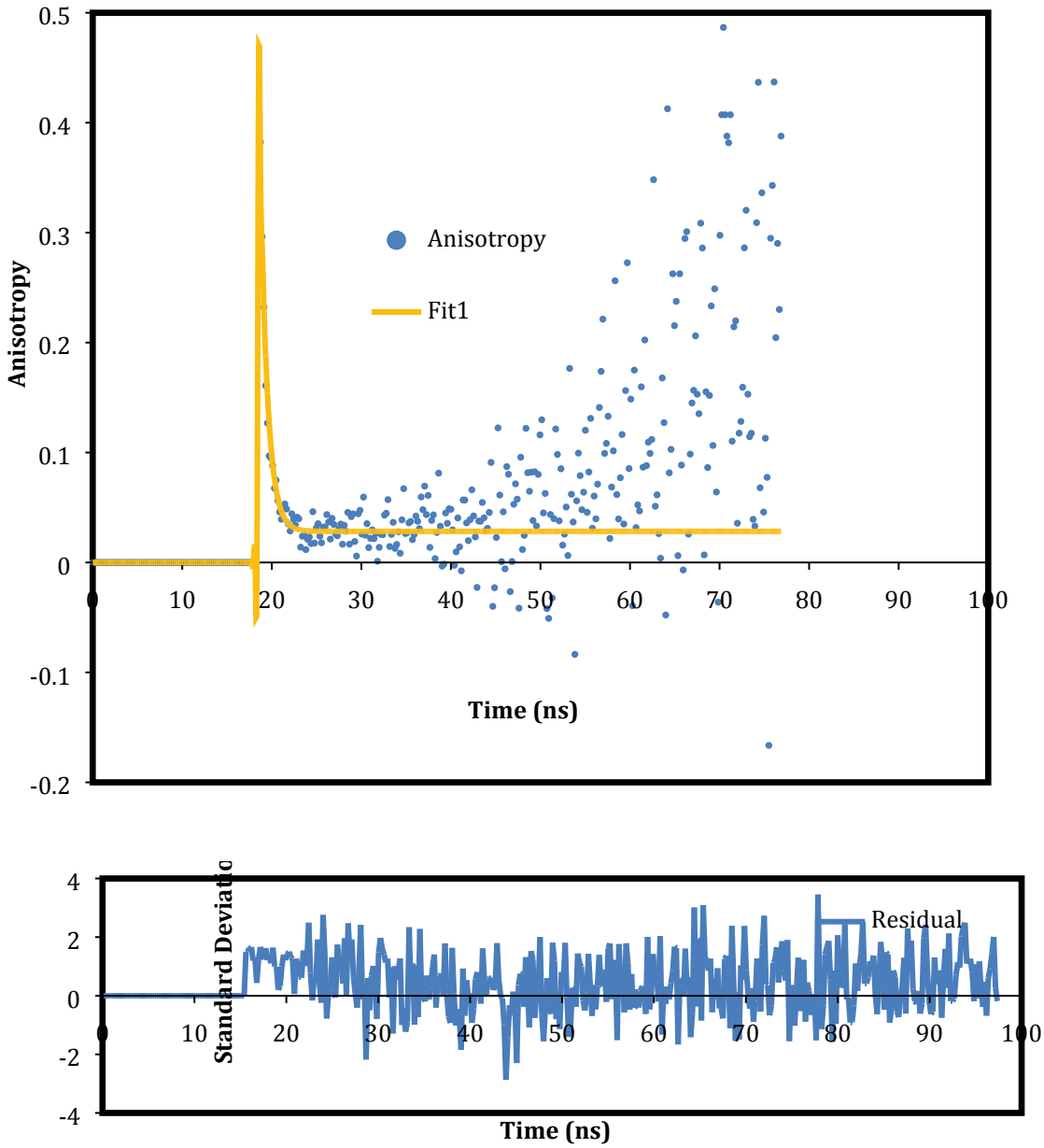


Figure S6 (f). Decay of anisotropy, r(t), of AmNS-labelled PAA in 1 wt% calcite at pH 11, and the associated single-exponential fit with the distribution of residuals.

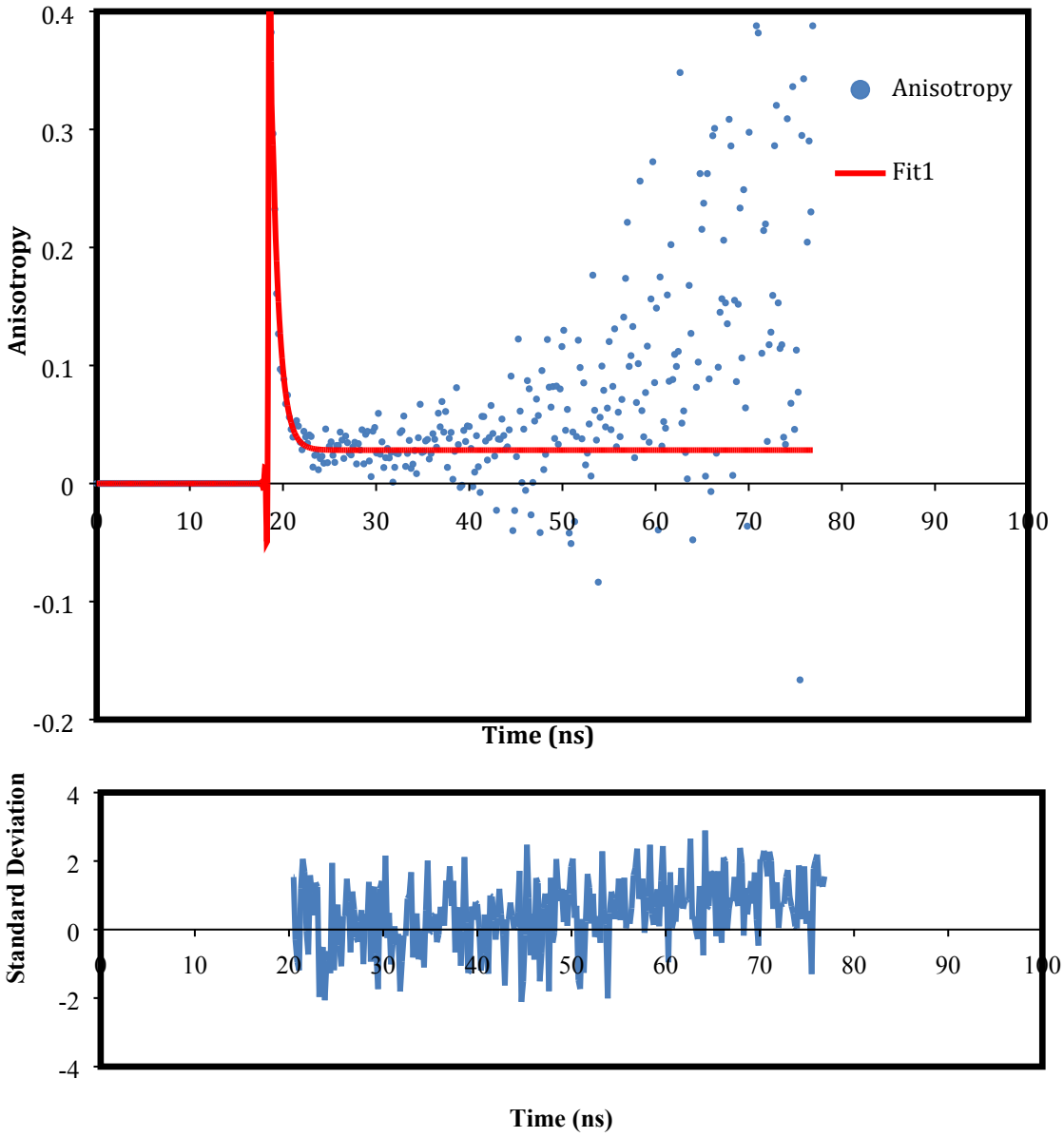


Figure S7 (a) Anisotropy decays of 10^{-5} M ACE in water at different pH values. (It displays an extremely short correlation time to reach up to 0.10 ns at pH 3, 7 and 11. And, all decays are superimposable on each other; this supposes that the anisotropy of free fluorophore is not affected by the pH change)

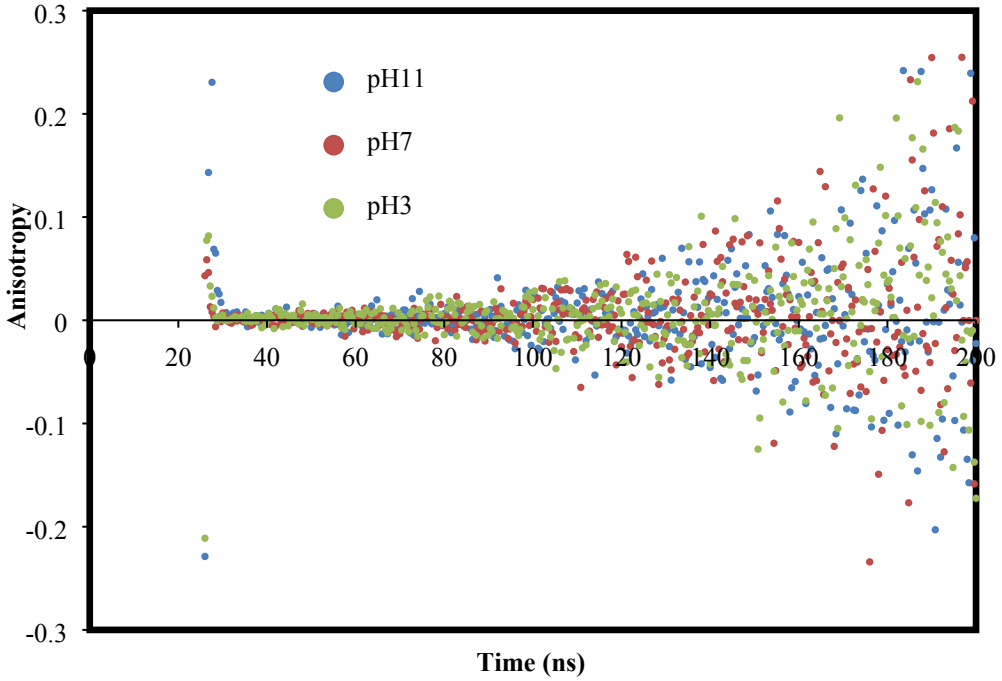
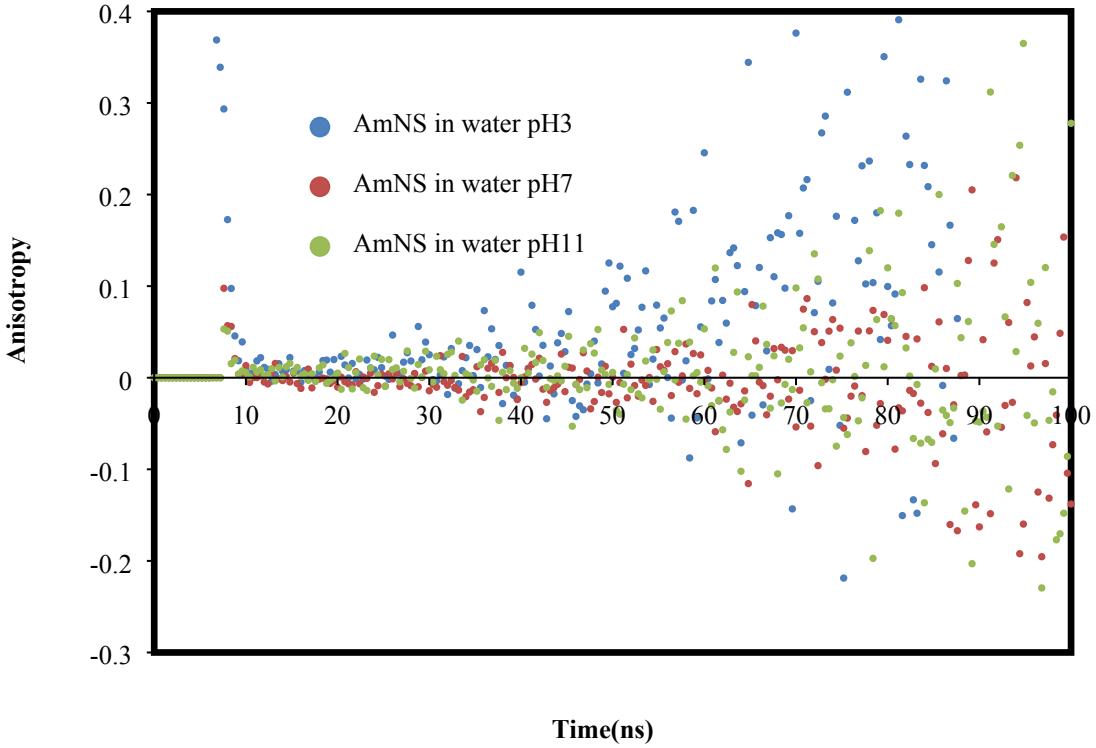


Figure S7 (b). Anisotropy decays of 10^{-5} M AmNS in water at different pH values, τ_c = ~0.1ns



Fundamental basis of TRAMS

The basis of time-resolved anisotropy measurements (TRAMS) is as follows: A degree of anisotropy (r) with respect to the vertical plane can be created in a random distribution of fluorophores by using vertically polarized pulsed light. Information regarding molecular motion of this photo- selected population can subsequently be derived by analyses of the decay of anisotropy,

$$r(t), \quad r(t) = \frac{i_{\parallel}(t) - G i_{\perp}(t)}{i_{\parallel}(t) + 2G i_{\perp}(t)} \quad (3)$$

following measurement of the time-resolved fluorescence emission via a rotatable polariser orientated in the parallel [$i_{\parallel}$ (t)] and perpendicular [$i_{\perp}$ (t)] planes. G is a factor which corrects for the bias in the detection of radiation polarized in different planes, and was determined as 1.0 for the current experimental set-up by measuring $i_{\parallel}$ (t) and $i_{\perp}$ (t) with horizontally polarized excitation light. If a single relaxation occurs in the system then the anisotropy will decay via a mono exponential function

$$r(t) = r_o \exp(-t/\tau_c) \quad (4)$$

where r_o is the intrinsic anisotropy and τ_c is the correlation time which characterizes the motion of the fluorophore of interest. If the fluorophore is covalently attached to a polymer either during or after synthesis then information concerning macromolecular conformations can be obtained via TRAMS and the resultant τ_c. For example, a short τ_c would be associated with an expanded flexible chain while a large τ_c would be consistent with a collapsed slow moving globular structure.