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Supramolecular Interactions in Chitosan Gels

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Chitosan gel particles show selective size changes with a large variety of effector compounds. Swelling induced by protonation of the chitosan amino groups is counteracted by non-covalent cross-linking with anions, depending on the structure of the acids. Thus, contraction amounts to 30 % with malonic acid, but to <1 % with the homologuous succinic acid, to 60 % with tartaric acid and to 51 % with 2,4-dinitrophenol. With acetic acid expansion starts at around pH 6, whereas with, for example, hydrochloric acid swelling occurs at around pH 4. All size changes are essentially due to changes in water content. Basic amino acids, such as His, Lys and Arg, induce significantly enhanced expansion only in the presence of other acids as cofactors, therefore performing as logic AND gates. Enantioselective size changes are large with dibenzoyltartaric acid derivatives. Reducing the size of the gel particles allows the speed of size change to increase significantly; a similar sensitivity increase is achieved by the accompanying compartmentalization effect.

Introduction

Chitosan is a readily available material from biological sources and has a considerable potential for a manifold of applications.[1] Chitosan, which is a polymer with 2-aminoglucose as the monomer, as well as its biological precursor, chitin, is used in separation technology, in particular in the form of membranes,[1,2] due to its special binding capacity for metal ions.[3,4] In the presence of simple inorganic or organic acids chitosan (Scheme 1) forms a hydrogel,[5] although in the absence of a cross-linker[6] the material slowly dissolves under acidic conditions.[7] Chemical modification[1,8] expands the applicability of chitosan, in particular for drug and gene delivery,[1,9] and also in combination with cyclodextrins.[10] The unique features of chitosan and its derivatives also make it a versatile material for the food industry[11] and in particular for medicine,[12] for example, as nano-DNA carriers,[13] as a bioadhesive or as an absorption enhancer.[14] Chitosan can also be imprinted with effector molecules, such as xylene,[15] or can be used in carbon nanotube fibres.[16]

The use of chitosan as a chemomechanical material has until now essentially been restricted to relatively unspecific effects of pH,[17,18] temperature[17,18] and salt changes. Thus, chitosan-polyacrylic acid gels exhibit three maximum expansions at pH 3, 6 and 8.[19] The swelling of chitosan gels by carboxylic acids has been found to be dependent on their pK and chain length.[20] Usually one observes increased swelling at lower pH, also with, for example, chitosan-polyacrylamide derivatives,[21] but for xanthan-chitosan gels swelling was observed at pH 10 as well as at pH 0.[22] The volume contraction observed with polyvalent phosphoric acid can be ascribed to ionic cross-linking counteracting the expansion.[23]

The major aim of this work was to clarify the dependence of volume changes on the nature of effector anions, mostly organic anions of different structures. In addition, we wanted to see if biologically important effectors such as amino acids can trigger motions in these hydrogels, and also in combination with cooperatively working second effector molecules. Corresponding logic gate effects have been found with other hydrogels and have already been shown to be very promising.[24]

Results and Discussion

Volume Changes Triggered by Different Acids and Solvation Water

Figure 1 and the data in Table 1 demonstrate that size changes of the chitosan gel are not only a function of pH, but also of the structure of the different acids. Free acids lead to expansion, depending on their pK_a values. The presence of anions at a higher pH, however, leads to contraction by non-covalent cross-linking between the anions and the chitosan nitrogen centres, which, with pK_a values[25] of about 6.5, are protonated (see Scheme 1, c). Benzoic and cyclohexanoic acids behave like acetic acid, whereas dicarboxylic acids exhibit a dependence on the chain length sep-

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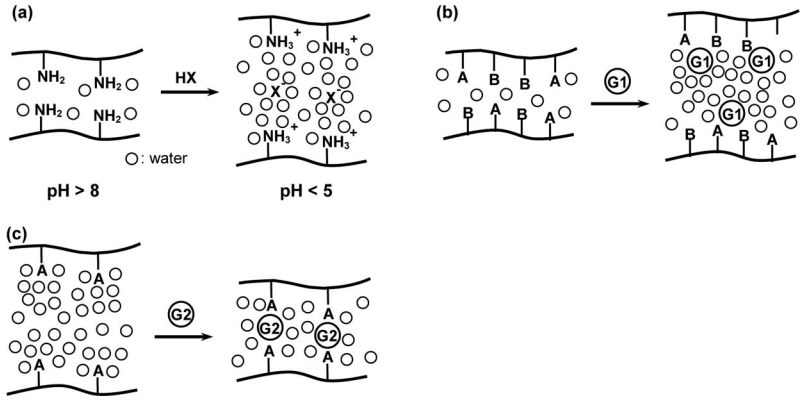


Scheme 1. Chitosan structure and a) water uptake as result of pH change with concomitant charge increase, b) water uptake as result of complexation with guest **G1** and c) water release as result of, for example, ionic cross-linking with guest anion **G2**.

Table 1. Expansion factors (EF, by changing the pH from 7.0 ± 0.3 to the given pH) with different acids.[a]

Acid[b]	pK_a	pH	EF (%)	Acid[d]	pK_a	pH	EF (%)
Hydrochloric	–	2.0	135 ± 1.0	Benzoic (20 mM)	4.19	5.0	95 ± 2.7
		4.0	0.0 ± 0.8				
		6.0	–0.3 ± 0.6	Cyclohexanoic (50 mM)	–	5.0	114 ± 1.1
Acetic	4.75	4.3	131 ± 0.9	Oxalic (10 mM)	1.23, 4.19	5.0	1.0 ± 0.5
		5.7	99 ± 0.2				
		6.4	4.9 ± 0.6	Malonic (10 mM)	2.83, 5.69	5.0	12 ± 1.0
Phosphoric	2.12, 7.21, 12.7	1.6	28 ± 0.4	Succinic (10 mM)	4.16, 5.16	5.0	105 ± 1.0
		5.2	0.7 ± 0.2				
		5.8	–0.6 ± 0.2	Glutaric (10 mM)	4.34, 5.41	5.0	107 ± 0.9
Sulfuric[c]	1.92	5.0	0.8 ± 0.4	Tartaric (10 mM)	2.98, 4.34	5.0	8.4 ± 1.4

[a] EF as a % of size change in one direction. EF = 0% for the gel at pH 7 in the absence of additional salts, unless noted otherwise. Errors/deviations (in ±%) from an average of three measurements. [b] The total concentration of the anion at the given pH is adjusted with the corresponding sodium salts. [c] Measured in the presence of additional 30 mM phosphate buffer. [d] The pH was adjusted by adding NaOH.

arating the carboxylic groups: glutaric and succinic acids, which have similar pK_a values to the monoacids, have the same effect as the monoacids. In contrast, oxalic, tartaric and malonic acids, which have low pK_a values due to the proximity of the carboxy groups, lead to reduced chemomechanical effects, in analogy to phosphate in which cross-linking with the anions counteracts expansion. The full deprotonation of phosphoric acid occurs only at a higher pH, but even the monoanion acts as a very efficient cross-linker due to the four oxygen interaction sites. Surprisingly, swelling by acetic acid starts at around pH 6, whereas with hydrochloric acid the expansion occurs at around pH 4 (Figure 1). This suggests that ionic cross-linking, which counteracts the swelling, is less effective with acetate anions. This may be due to the particular propensity of carboxylic acids to intermolecular hydrogen-bonding, which can lead to the uptake of more effector molecules and accompanying water.

Solvation and desolvation at the ionic sites and the possible replacement of water molecules by cross-linking with anions has a distinct effect on the gel volume changes. The essential role of changes in the water content of chitosan-derived hydrogels has been characterized, for example, for

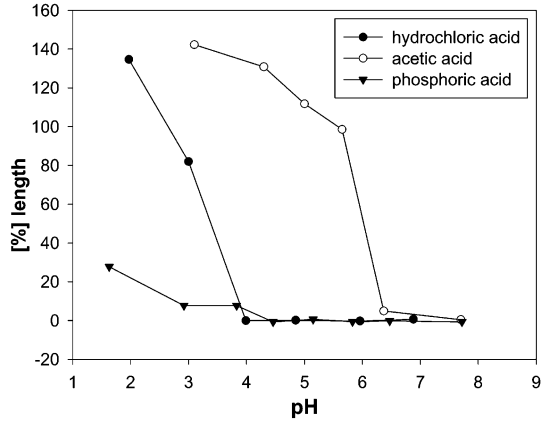


Figure 1. pH profiles of the expansion of a chitosan film in the presence of different acids. Total concentration of acid and the corresponding salt: 0.1 M; ratio of acid to salt as required for the given pH.

pH-triggered variations by differential scanning calorimetry (DSC)[18] and for heat-induced volume changes by adiabatic vacuum calorimetry, which also allows differentiation be-

tween free and bound water.[26] We used gravimetric measurements to determine water content, which showed swelling in the presence of 0.1 M acetic acid and 50 mM L-histidine with a 10.7-fold increase in water. The corresponding volume increased by a factor of 9.5. This indicates that most of the size change is due to the differences in water content. UV measurements allowed us to determine the amount of histidine in the swollen gel; a ratio of the chitosan monomer unit to histidine of approximately 1:2 was measured. Hence the weight increase by the guest histidine contributes little to the size expansion in comparison with the water uptake. Scheme 1 summarizes the steps that are responsible for the size changes. Protonation of polyamines usually leads to swelling due to charge repulsion and solvation of both the cationic sites and the simultaneously imported guest anions G1 by water (steps a and b). In chitosan gels this swelling effect is reduced due to a smaller charge density in comparison with, for example, polyethyleneimine[27,28] or polyallylamine.[29] The protonation-induced swelling is with chitosan gels significantly counteracted by non-covalent cross-linking, which is most efficient with the multidentate guest anions G2, such as sulfate or phosphate (step c). In line with this, the expansion decreases with increasing concentration of phosphate (Figure 2). Metal ions, such as copper(II) ions, induce only small changes, for example, $15 \pm 2\%$ with 50 mM copper(II) acetate, compared with other polyamine gels.[30] The efficient binding of metal salts to the chitosan gel is apparent from the blue colour of the gel particles that forms upon treatment with Cu^{II} salt solution.

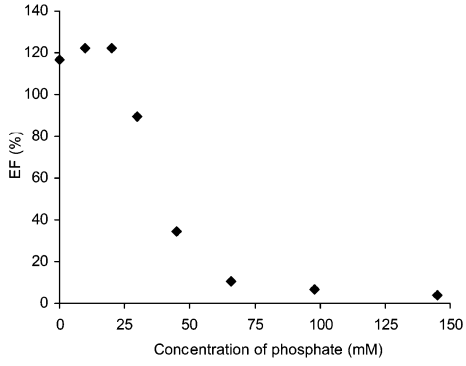


Figure 2. Profile of the expansion (EF) of a chitosan film versus phosphate concentration at pH 5 in the presence of AcOH + NaOAc. Total concentration: 0.1 M; ratio as required for pH 5.

Organic Effectors on Gels Prepared with Acetic Acid as Conditioner

As acetic acid showed a large expansion at higher pH (Figure 1), we explored the size changes caused by many effectors with gels treated first with 50 mM acetic acid as "conditioner" at the same pH as used for immersion into the effector solution. The starting size for experiments with this conditioner thus refers to gel particles containing acetic acid, but NMR spectra show that the acetic acid conditioner is expelled on immersion into the effector solution. No significant chemomechanical motions were observed in the presence of molecules that have efficient hydrogen-bonding donors or acceptors, such as malonamide, sugars or hydroquinone, but lack an anionic function (Scheme S1 in the Supporting Information). Several organic effectors bearing anionic groups, which were largely tested in the search for chiral recognition, trigger size changes that can be largely understood by the above-mentioned arguments. Large contractions, which counter the expansion induced by the acetic acid, are observed with, for example, tartaric acid at pH 5, as the exceedingly low pK of that acid and the presence of two carboxylate groups make it a perfect cross-linker. The small effects of, for example, the nitrobenzoic acids are in line with the same effect of benzoic acid, which behaves similarly to the acetic acid in the starting gel. The small contraction by naphthalenesulfonate, in comparison with sulfate, which is a good cross-linker (Table 1), can be ascribed to steric hindrance. The large contractions caused by the 2,4-dinitrophenol and the anthraquinone acids may be related, respectively, to the simultaneous interactions of the two nitro or carbonyl groups with the chitosan functional groups, and thus better cross-linking. Porphyrin-tetrakis(phenylsulfonate) triggers a relatively large contraction even at 0.5 mM, which can be explained by the many mutual salt bridges possible with this cross-linker.

Difference with Enantiomeric Effectors

The presence of chiral centres in chitosan renders these gels promising candidates for enantioselective motions, which indeed have been found for the first time with these intelligent materials by using a variety of optical active compounds as possible effectors[31] (see Table S1 of the Supporting Information). The difference between tartaric acid derivatives such as *O*,*O*′-dibenzoyltartaric acid (DBTA) or *O*,*O*′-di-*p*-toluoyltartaric acid (DTTA) as effectors at pH 3.5 seems to be large (Table S1), but results essentially from very abrupt changes in the concentration profiles (see Figure S1). The differences between the enantiomers with benzoic or *o*-nitrobenzoic acid instead of acetic acid as conditioner are similar to those obtained with acetic acid (Table S1). Simultaneous action of DBTA and other compounds such a Phe or Trp did not show any changes compared with DBTA alone (Table S2). Enantiomeric amino acids showed no significant size change differences, and neither did the presence of additional phenyl rings in the Z-protected derivatives (see Scheme S1). Only with His was there a moderate enantioselectivity in the presence of acetic acid as cofactor (Table S3). As already described in our preliminary communication,[31] the most dramatic enantioselectivity is reached with tartaric acid derivatives in which phenyl moieties provide for significant cation–π interactions with the protonated nitrogen centres of chitosan. The corresponding mode of interaction was corroborated by MAS-NMR spectra, with quite selective ring-current effects of the effector phenyl groups on the aminoglucose protons of the polymer.

Cooperativity between Amino Acids and Organic Effectors/ Logic AND Gate Functions

Only basic amino acids such as His, Lys or Arg show a remarkably enhanced expansion if used in combination with some other acids as cofactor (Table 2). Thus, the expansion factor EF (always given in one dimension) induced by His increases from zero in combination with phosphoric acid to 30% with hydrochloric and to 60% with benzoic acid. Phosphoric and sulfuric acids are, for the reasons discussed above, such strong ionic cross-linkers that the amino acid cannot compete. Chloride competes less, and with benzoate an additional factor must be responsible for the greatly enhanced expansion with the His effector. As with related chemomechanical polymers, one can explain this by the formation of a less tight network upon binding of a larger cofactor, which then allows better binding of a substrate such as His (Scheme 2). Positive cooperativity, reminiscent of the logic gate functions observed with other chemomechanical polymers,[24] is also seen with Arg and Lys, but to a smaller degree. This can be understood on the basis of the more basic amino acid side-chain (pK = 9–11), which renders at pH 5 a protonated nitrogen centre, diminishing the cross-linking effect of the anionic site of the amino acid. In contrast, His with a side-chain pK of only 6 barely interferes with the ionic cross-linking.

Table 2. Expansion factors (EF) with amino acids and phosphate buffer at pH 5.0.[a]

Cofactor	L-His	L-Arg	L-Lys	Control[b]
0.07 M HCl	30 ± 3.0	2.5 ± 0.7	3.4 ± 0.3	(12.6) ± 0.4
0.1 M AcOH	23 ± 1.4	19 ± 1.0	15.5 ± 2.7	(90) ± 1.7
0.1 M H_3PO_4	–1.4 ± 0.7	–1.6 ± 0.4	–1.9 ± 0.4	(0.3) ± 0.1
0.1 M H_2SO_4	–2.0 ± 0.1	–3.1 ± 0.5	–2.6 ± 0.9	(6.8) ± 0.3
0.08 M PhCOOH	60 ± 1.7	47 ± 2.8	43 ± 4.4	(61) ± 0.3

[a] See footnotes to Table 1. The net effects of amino acid are given as difference between the total expansion and the control. Amino acid concentration: 50 mM. Measurements were made in the presence of 30 mM phosphate buffer; neutral amino acids, such as Ala, showed <3% expansion. [b] Control: effect in the absence of amino acid.

Response Velocity and Sensitivity Increase by Reducing the Size of Polymer Particles

For many applications, for example, in the sensor field, it is desirable to enhance the sensitivity and the reaction speed of chemomechanical materials. It has been shown that the use of smaller polymer particles allows the use of more dilute effector solutions as long as the binding affinity towards the polymer functions is sufficiently large.[30] This compartmentalization effect allows a ten-fold sensitivity increase of the chitosan gel.[31] For example, the same contraction occurs at a 1 mM DBTA effector concentration at a particle volume of about 7 mm^3 as at 0.1 mM with a gel piece of about 0.2 mm^3 (Table S4). The chemomechanical response velocity can also be increased significantly if, with smaller gel particles, the surface to volume ratio (S/V) is increased. Thus, the approximate "half-life" time ($t_{1/2}$) for 50% of the maximum expansion decreases from $t_{1/2}$ = 42 min with S/V = 10.0 to 3 min with S/V = 35 (Figure 3).

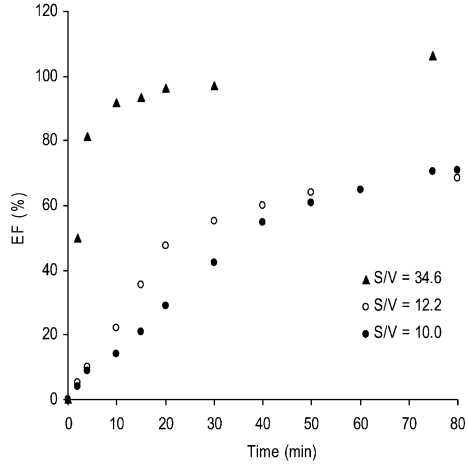
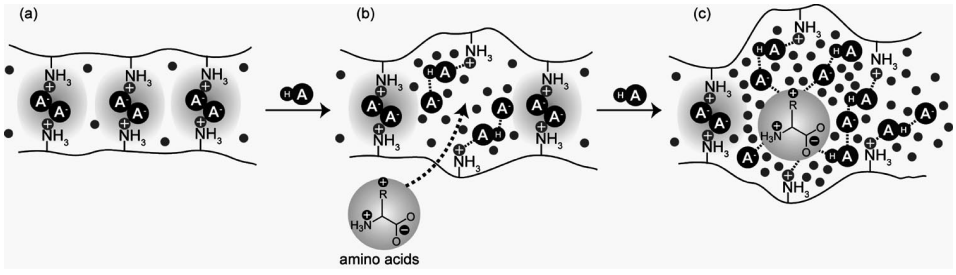


Figure 3. Expansion kinetics and surface to volume (S/V) effects for chitosan; elongation induced by 50 mM L-histidine and 0.1 M acetic acid in 30 mM phosphate buffer at pH 5.0. Approximate "half-life" time ($t_{1/2}$) for 50% of the maximum expansion: $t_{1/2}$ = 42, 32 and 3 min for S/V = 10.0, 12.2 and 34.6, respectively.



Scheme 2. Cooperativity and logical gate function model. (a) Tight polymer network due to ionic cross-linking with anions such as phosphate. (b) Swelling occurs on uptake of more effector AH and water moleucles, with liberation primarily of bound anions A. The looser network then provides for better binding of guest molecules such as basic amino acids, so that (c) the polymer swells with the uptake of more solvation water.

Experimental Section

Preparation of the Polymer Gel: Chitosan (medium molecular weight; M_w = 190000–310000) was purchased from Aldrich. According to NMR spectroscopy, the degree of deacetylation was 86%. Chitosan flakes (1.00 g) were dissolved in 0.8 wt.-% of acetic acid (100 mL). The solution was placed in Petri dishes of 90 mm diameter and left at room temperature in air for the solvent to slowly evaporate. After 2 weeks, a homogeneous film had formed and was heated in an oven at 60 °C for 3 days, then vacuum-dried in a desiccator at 20 mbar for a week to remove further water and acetic acid. The resulting film was immersed in a 1 M sodium hydroxide solution with stirring for 24 h to neutralize any remaining acetic acid. The film was washed with deionized water and then stirred in deionized water for 2 weeks, changing the water frequently. The thickness of the resulting gel film was 0.4 ± 0.04 mm.

Measurement of Size Changes: The polymer gel film was cut into small square pieces with volumes of approximately 0.2–0.3 mm^3 (in the case of swelling measurements) and 5–6 mm^3 (in the case of contraction measurements). The sizes of these particles were measured as described previously.[32] Then the pieces were immersed in 1.0 mL of different effector solutions (for examples, see Figure S2, a,b,c).

After usually 18 h, the sizes of the polymer pieces were measured to determine the expansion factor (EF): $EF = (l_f - l_i)/l_i \times 100$ (%) (l_i = initial length, l_f = final length)

The lengths were the average of four measured edges; the thicknesses changed in a similar way, but could not be measured as accurately. The EF value was the average of at least three experiments; the mean deviations were usually less than 2% and are indicated in the tables.

NMR Measurements: Bruker DRX 500 spectrometer. MAS NMR of the gels spectra also showed the disappearance of the AcOH conditioner signals upon reaction with other acids or anions as effector.

Determination of Water Content: Gravimetric measurements were performed as described previously[32] by weight differences before and after drying gel pieces in vacuo at 70 °C. Three individual gel pieces were used and the average was taken. The deviations from three experiments were within ±1%.

Supporting Information (see also the footnote on the first page of this article): Detailed data on the expansions and contractions of chitosan hydrogel particles, concentration profiles with different tartaric acid derivatives and photographic illustration of size changes with several effectors.

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