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Large macroscopic size changes in chemomechanical polymers with binding sites for metal ions

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A flexible polymer based on the reaction of polyacrylate with diethylenetriamine shows, under the control of transition metal ions in the external aqueous medium, size expansion or contraction by up to 200% (corresponding to 400% volume change); the macroscopic movements, which are fully reversible, show a distinct maximum at a certain metal salt concentration, and vary significantly with the addition of second effector compounds such as sodium chloride or benzoate.

The chemo-mechanical polymers known to date are actuated mostly by changes of pH, of temperature, of solvent composition, or by light, magnetic fields, or external voltage.[1] Implementation of supramolecular binding sites into flexible polymers allows for the first time selective molecular recognition in artificial systems to be translated into large macroscopic actions.[2] Such systems hold much promise for the development of new actuators, molecular machines, or sensors. Ethylene diamine units are traditional binding sites, in particular for transition metal ions, and these we incorporated into hydrogels by reaction of polymethyl(methyl)acrylate with excess diethylenetriamine. The resulting hydrogel films showed large, fully reversible shape changes as functions of different metal ions.

In contrast to related changes with organic effectors such as AMP, where we always observed expansion,[2] the interaction of the polymer films with metal salts in water produced both expansion or contraction (Fig. 1). Larger ions such as lead(II) led to particularly large expansion, reaching 190% in size (length × width of a polymer film piece), or 390% in volume. It should be emphasized that the size changes were always measured after the polymers had taken up, under swelling, the maximum possible amount of water (85 ± 5 %, in the absence of salts such as phosphate buffer). The swollen film pieces were then immersed in aqueous solutions of the corresponding metal acetates; these were used in order to overcome solubility and hydrolysis problems with *e.g.* halide salts at the chosen pH values, which were as far as possible close to neutral. The speed of the expansion was similar to that observed with organic substrates;[2] the size and the transparent color, which was typical for the corresponding metal–ene complexes, did not change in the first hour, and underwent only slow degradation over the following several weeks. During the experiment the pH of the supernatant metal salt solutions changed by 0.3 to 1.0 units on average; in view of the known expansion pH profile of the same polymer[2] these pH changes at points close to neutral cannot be responsible for the larger size changes produced by interaction with the metal ions. The polymer films upon exposure to the different transition metal ions showed colors characteristic for the corresponding ene complexes.

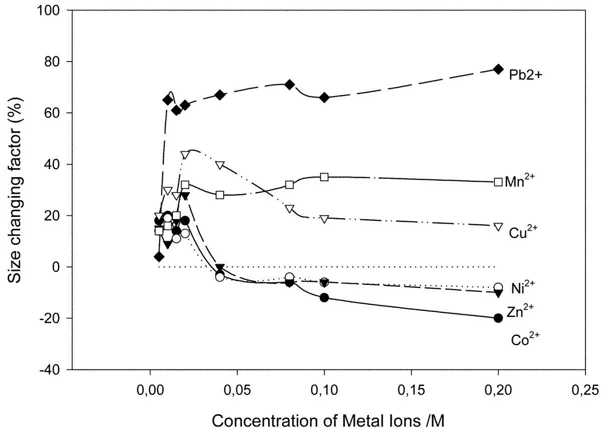

Fig. 1 Size changes of the polymer film with different metal ions. Changes given as length increase or decrease (50% length change, *e.g.*, corresponds to 125% square size, or 237% volume change).

Strikingly, the metal induced size changes are not smooth functions of the effector concentrations, in sharp contrast to the effects of organic substrates.[2] The profiles with metal ions (Fig. 1) show a pronounced maximum of expansion, which occurs at about 0.02 M metal salt concentration if the film particle used is always of the same size (about 2 × 5 mm in the experiments illustrated in the figures). That the size change becomes smaller upon adding more of the metal salt suggests, that at higher effector concentrations a second, much weaker binding site becomes occupied, which can result in a reverse size change. The second binding may be the result of enhanced association of the accompanying anions with protonated nitrogen atoms in the polymeric receptor, or of a weak association of metal ions at a second site.

Capacity measurement showed that polymer particles of the same size as those used in the shape change experiments indeed contained the amount of metal ions corresponding (within the error) to a 0.02 M solution, after taking the particles out of solutions containing excess metal salt. Thus, complexometric titrations with metal salts liberated from such a polymer piece (about 6 mg dry weight) by washing with excess aqueous HCl showed with Cu(II) and Ni(II) the presence of an average 2×10^{-5} Mol metal, which corresponds to the maximum expansion observed with the 2 ml of a 0.02 M metal salt solution used. Related expansion maxima have been found with the same chemo-mechanical polymer in experiments with organic effectors, where a maximum effect was reached if certain second effector compounds were present at 0.02 M concentration; this is the basis of a new macroscopic logical gate function.[3]

The metal induced size changes can also dramatically depend on the presence of a second effector. This is illustrated in Figs. 2a–d, where the expansion by interaction with *e.g.* Zn(II) is converted even to a contraction in the presence of either sodium benzoate or sodium chloride (Fig. 2a). Similarly, with Cu $(OAc)_2$ one observes large a negative cooperativity effect in the presence of NaCl or $NaNO_3$ (Fig. 2b). With Ni(II) the 20% length expansion (corresponding to 73% volume increase) is even converted to 30% contraction (120% by volume) by the presence of sodium benzoate (Fig. 2c). Only with the large lead ion is the effect of the additional salt small, and even converted to a small positive cooperativity (Fig. 2d). The results can be rationalized by partially competitive, but weaker binding of the alkali salt anions (which are present in much higher concentration than the strongly bound transition metal ions) to protonated nitrogen atoms in the polymeric receptor units. Noticeably, the alkali salts themselves produce only negligible expansion or contraction of the polymers.

The metal induced dimension changes occur within a few minutes, and are completely reversible. The reversal of the movements can be initiated by removing the bound metal ions either with excess acidic solutions, or more effectively by adding

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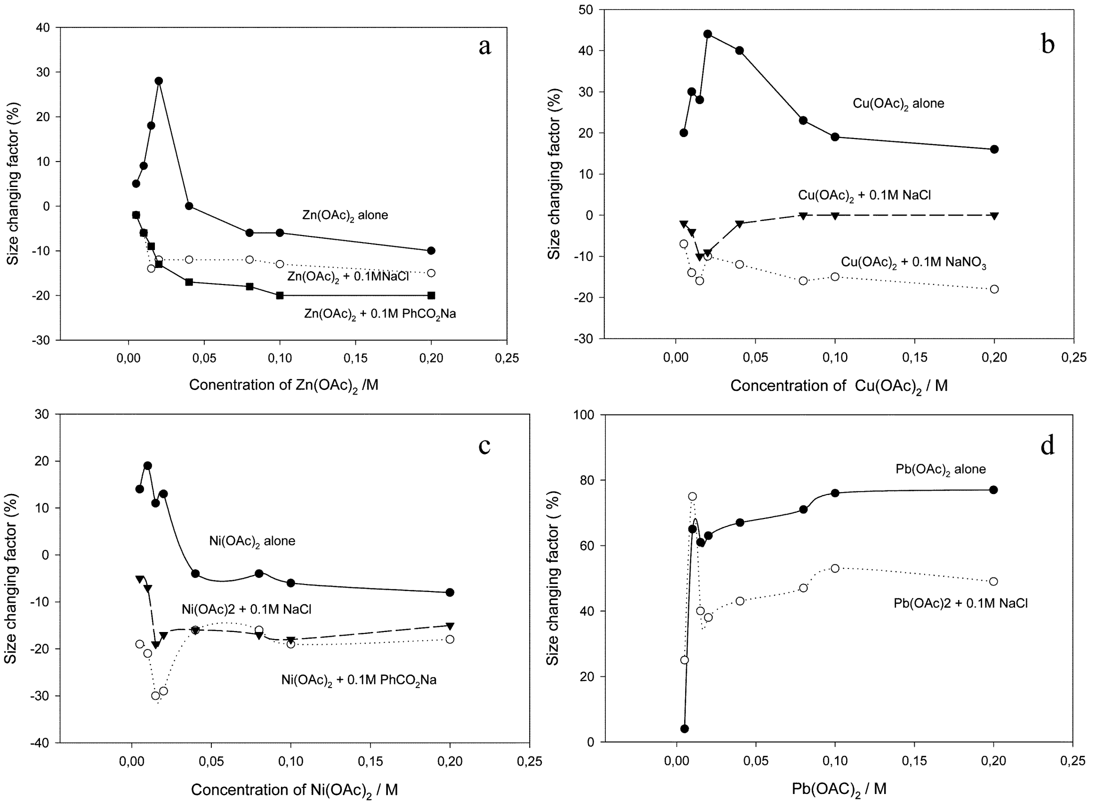

Fig. 2 Effects of a second substrate on size change induced by metal ions. (Size change given as length increase or decrease; 50% length change, *e.g.*, corresponds to 125% square size, or 237% volume change).

strong complexation agents such as EDTA to the supernatant solution.

Supramolecular chemo-mechanical systems like that reported here[4] can lead to *e.g.* macroscopic valves, where substances are released or taken up as function of certain metal ion levels, or to other metal-induced actuators. Metal ions have been used extensively as essential components in ingenious molecular machines,[5] which, however, until now cannot directly communicate to the outside world.

Notes and references

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