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Statgels and dynagels

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This article is dedicated to Jean-Marie Lehn, whose lectures and articles on dynamers (Lehn, 2005) were an inspiration.

Abstract
Gels are often described as colloidal systems made of a liquid phase in a continuous solid phase. But this definition is ambiguous because the same word "gel" applies to very different systems, either non connected such as the parenchyma of plant tissues (assuming that the cytosol is a liquid), or connected, such as jams. Using the "disperse system formalism" (DSF), it is possible to envision systematically all kinds of gels of one kind that was called statgels. All possible structures can also be dynamic, generating dynagels, whose original bioactivities can be explored.

Résumé
La dénomination « gel » s'applique, trop largement, aux systèmes colloïdaux composés d'une phase liquide et d'une phase solide. Cette définition est ambiguë, parce que le même mot est utilisé pour la désignation de systèmes aussi différents que les gels « non connectés », tels le parenchyme du tissu végétal (en supposant le cytosol liquide), ou des gels connectés telles les confitures. A l'aide du formalisme des systèmes dispersés (DSF), on peut envisager systématiquement des gels de nombreuses sortes, notamment des gels dynamiques, ou dynagels, dont on explore la bioactivité.

Keywords
Gel, statgel, dynagel, bioactivity, DSF

Mots clés
Gel, statgel, dynagel, bioactivité, DSF

Introduction

Using the formal language called "Disperse System Formalism" (DSF) (This, 2007 ; 2009), it is possible to describe the physical structure of existing colloidal systems, and also to predict the existence of systems that were not envisioned before and whose physical and chemical properties are original. Among colloids, gels attract much interest for their potential as intriguing materials (Terech and Weiss, 1997;

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Abdallah and Weiss, 2000) and as substrates for biomedical applications (Qiu and Park, 2001; Hofmann, 2002).

In particular, hydrogels formed from low-molecular-weight compounds that respond to pH can be used for oral drug delivery as well as for biosensor technology, especially when biochemical components are involved. Hydrogels have also been shown to respond to ligand-receptor molecular recognition (Zhang *et al.*, 2003, 2004) and redox stimuli (Kawano *et al*., 2004).

More generally, gels can have important applications in all "formulation" activities, including food, as studied by molecular gastronomy. Indeed, gels owe their properties to the dispersion of bioactive compounds, *i.e.* compounds that can interact with receptors in the body of living beings, abbreviated "bc" in the following text (This, 2013a). Such compounds can be dispersed in the various phases making up gels, and their particular dispersion leads to very different dynamic "bioactivities", that is a characterization of the release of bc. This is a result of "matrix effects", or how much a system traps compounds. In particular, understanding the bioactivity of new kinds of gels could be important for note-by-note cooking, *i.e.* the food preparation technique based on using pure compounds instead of plant and animal tissues (This, 2011 ; 2013b).

According to the International Union of Pure and Applied Chemistry, gels are defined as physical systems made of a liquid phase dispersed into a continuous solid phase (IUPAC, 2001). This definition is very broad, as it does not give any precision about the kind of dispersion. Following the definition, the gel category encompasses the parenchyma of plant tissues, muscular tissues of animals, gelatin gels, jams, water-filled sponges as well as the accumulation of silica particles in chromatography columns used for chemical analysis and product separation/purification. However, the development of the DSF showed that the operator "/", describing the random dispersion of a phase into another, does not apply to all gels. This operator can describe emulsions, with an aqueous solution (W, for water) and an

"oil" solution (O), with the two possibilities, namely water into oil (W/O) or oil into water (O/W), and it can also describe foams, with gas (G) dispersed in another phase (G/W, G/O, G/S), suspensions (S/O, S/W, S1/S2), aerosols (W/G, O/G, S/G) and finally some gels made of liquid droplets dispersed in a solid (Figure 1). However, it does not describe some gels such as gelatin aqueous gels, for example, where two phases, respectively liquid and solid, are both continuous and three-dimensional.

For this reason, the formal language called "complex disperse system/non periodical organization of space" (CDS/NPOS) that was first proposed in 2002 (This, 2005) had to be later improved with the introduction of the operator "x", which designates the imbrication of two continuous phases. The new name DSF was given to the improved formal language (This, 2013d).

In particular, the WxS formula corresponds to gels with a continuous three-dimensional aqueous phase W and a continuous three-dimensional solid network S (Figure 2). Because of the continuity of the liquid phase W, such gels are said to be "connected", which means that a solute in the liquid phase can diffuse throughout the whole system.

How many kinds of gels actually exist? Here, after this question is theoretically discussed, a distinction will be made between fixed gels, or "statgels", with strong forces between the subunits that make the solid network, and dynamic gels, or "dynagels", when the assembly of network's subunits is of supramolecular nature.

Simple gels as described using DSF formulas

Gels are particular colloids, *i.e.* systems in which the molecules or polymolecular particles dispersed in a medium have at least in one direction a dimension roughly between 1 nm and 1 µm, or that in a system discontinuities are found at distances of this order of length (IUPAC, 2001). It is not necessary for all three

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Figure 1. The simplest disperse systems for which one phase is randomly dispersed in another phase. The operator "/" indicates the random dispersion. The letters G, O, S, and W respectively stand for gas, oil, solid and water. Under each system, the traditional name is given. Formula such as W_1/W_2 or O_1/O_2 are meaningless, because the can be reduced to W or O respectively, and they are no disperse systems.

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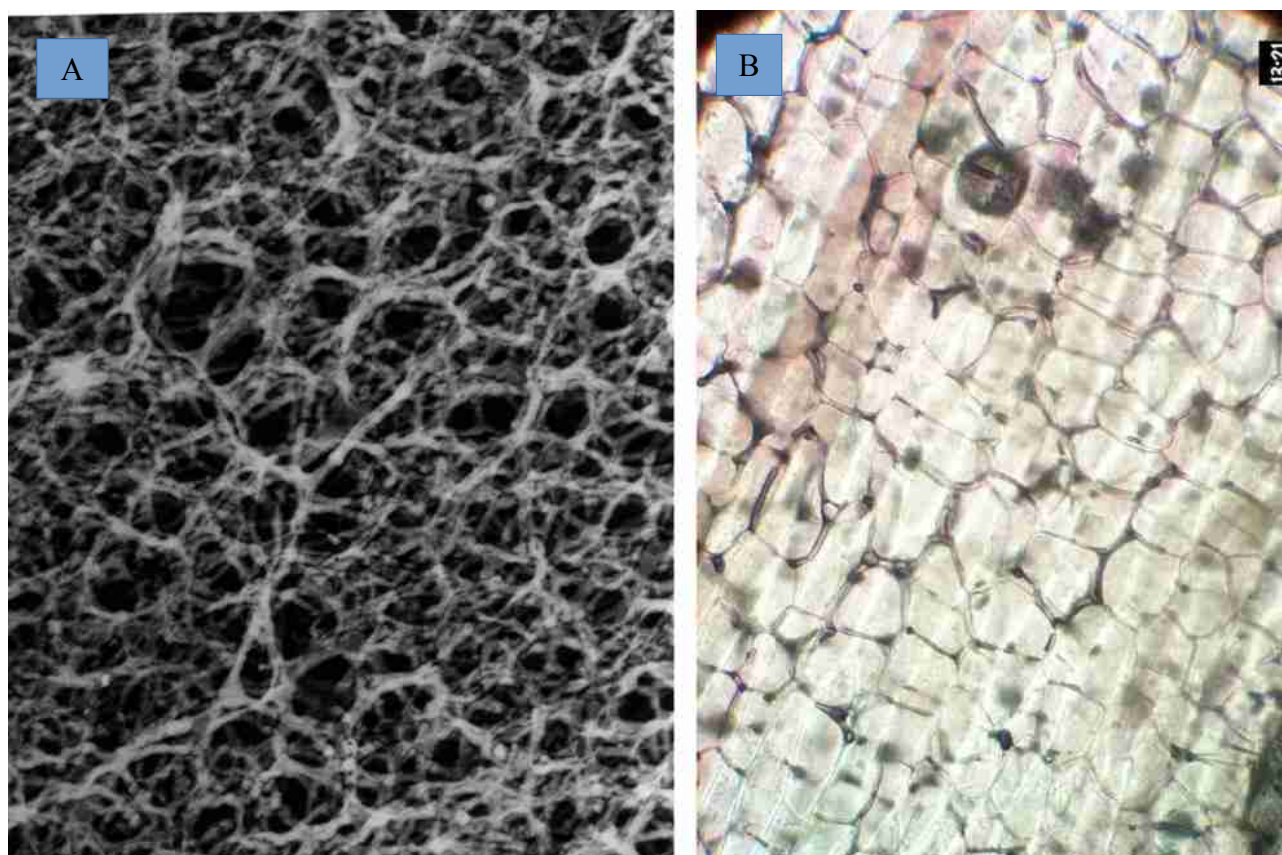*(N3AF)*

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Figure 2. Gelatin gels (A, electronic microscopy) and plant tissues such as the parenchyma of Allium cepa *L. (B, optical microscopy) are both "gels", according to IUPAC. However, their physical structures and their DSF formula are different : respectively WxS for A, and W/S for B .*

dimensions to be in the colloidal range: fibers in which only two dimensions are in the 1 nm/1 µm range, and thin films, in which one dimension is in this range, may also be classified as colloidal. Nor is it necessary for the units of a colloidal system to be discrete: continuous network structures, the basic units of which are of colloidal dimensions, also fall in this class (*e.g.* porous solids, gels and foams).

In order to envision all kinds of "simple" gels, *i.e.* gels including only one liquid phase and one solid phase, it is not difficult to write some lines of computer program producing systematically all DSF formulas. Programs for such purpose have to include the three phases O, S, W (alphabetic order), the three operators "/", "x", "@" (where

"@" describes inclusion, as recommended by IUPAC), and the four possibilities for the dimensions of objects D_0, D_1, D_2, D_3, respectively for objects of dimension zero, one, two and three. The solid continuous network has necessarily three dimensions, and it has to be used as the last term of the formula, in spite of DSF using preferably the alphabetic order (Figure 3).

The list of all possibilities is then: $D_0(O)/D_3(S)$, $D_0(W)/D_3(S)$, $D_1(O)/D_3(S)$, $D_1(W)/D_3(S)$, $D_2(O)/D_3(S)$, $D_2(W)/D_3(S)$, $D_1(O)xD_3(S)$, $D_1(W)xD_3(S)$, $D_2(O)xD_3(S)$, $D_2(W)xD_3(S)$, $D_3(O)xD_3(S)$, $D_3(W)xD_3(S)$, $D_1(O)@D_3(S)$, $D_1(W)@D_3(S)$, $D_2(O)@D_3(S)$, $D_2(W)@D_3(S)$.

Formula can be written, but do these systems

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Computer program for the calculation of all possible gels (no simplification):

phase := [W, O, S];
dimension := [D0, D1, D2, D3];
operateur := ["X","/", "@", "&sigma;"];
formule := "";
graine := "";
for dim1 to 4 do
        for phas1 to 3 do
                for ope to 4 do
                        for dim2 to 4 do
                                for phas2 to 3 do
if phas1 <> phas2 then formule := cat(graine, dimension[dim1], "(", phase[phas1], ")", operateur[ope],
dimension[dim2], "(", phase[phas2], ")")
end if
                                end do
                        end do
                end do
        end do
end do
```

Figure 3. A simple computer program can generate all possible gels of any "class". Here the program for generating all gels of class 2. After an initialization step creating an empty formula, the various phases and operators are added in imbricated loops, so that all combinations are determined. With such a simple program, the list has to be cleaned manually of all impossible systems. For example, it is not possible to disperse randomly (/) structures of dimension 3 in a structure of lower dimension.

exist? Envisioning all of them one after the other would be tedious, but the two following examples show that the issue is only of practice, and not of theory. The first formula of the list $(D_0(O)/D_3(S))$, for example, corresponds to a random dispersion of oil droplets in a continuous solid. This sounds new, but it can be obtained by various processes, including freezing at a temperature below 0 °C a O/W emulsion, for which the "oil" is a compound that would not be miscible to water and would solidify at temperature below 0 °C (for example carbon disulfide, for which the freezing point is -111.5 °C). Another system is obtained using the formula $D_3(O)xD_3(S)$: when one first makes a O/W emulsion, with proteins containing cysteine residues dissolved in the liquid aqueous phase, the heating of the system leads to protein coagulation, so that the system is now described by $D_3(O)/[D_3(W)xD_3(S)]$; drying this gelled emulsion, called a "gibbs" (This, 2009), can lead to the desired gel, called a "graham". "Natural" systems already exist having this formula, such as white chocolate at a temperature between 34 °C and 37 °C, as a liquid continuous "oil" phase is dispersed in a continuous solid network (Loisel *et al*., 1997).

The various gels associated with the formula of the previous list could be named using natural language. To this end, it is proposed to rank the information by order of importance: the name "gel" is added by the indication on connection, such as connected or non-connected. When the liquid phase is organized as structures of one or of two dimensions, the indication "with channels"

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or "with sheets" can be given, depending on the dimension of dispersed objects.

When objects of zero dimension are used, it is proposed not to give any particular indication because the formula correspond then to familiar systems. Finally, the nature of the dispersed objects, such as aqueous solution or oil is given. For examples, sponges with open pores would be described as connected systems with channels, and oleogels could also be envisioned, but it should be observed that not only edible phases can be considered; other systems with other organic liquids can be described as well, using other letters than the two O and W.

More complex gels (more than two phases)

This first list being made, it has to be observed that more than one phase, "water" or "oil", can be included in the three dimensional, continuous, solid phase. This leads to envisioning connected or non-connected gels with a disperse phase that is itself a colloidal system, such as an emulsion, or a suspension, etc. When only one phase is dispersed, the gels are said to be of "class 1", and the systems are of "class k" (k being an integer) when k phases are dispersed in the continuous solid network.

Because the number k can have any integer value, the whole list of all possible gels is infinite, including, for example: connected gels with sponge water-oil phase, non connected gels with sponge water-oil phase (Wadsten *et al.,* 2006), connected gels of aqueous channels, non-connected gels of aqueous channels, connected or non-connected gels with liquid channels, connected or non-connected gels with oil channels... Sometimes very long names such as "non connected gel of liquid suspensions in oil sheets" are needed.

Such names based on natural language are cumbersome. The DSF makes it easier to envision possible gels: another small computer program building DSF formula can produce all possibilities for the successive classes of gels. For two phases, the program first creates an
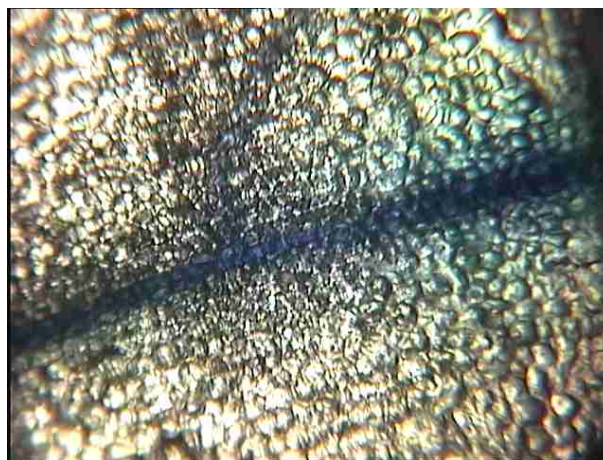

Figure 4. This plant tissue is a part of the root of Daucus carota *L. It includes parenchymatous tissue and connective tissue (xylem, phloem), colored in blue, so that the system has the formula $[[D_0(W_1)/]+[D_1(W_2)x]]D_3(S)$. The whole picture is 3 mm wide.*

empty DSF formula, then it performs imbricated loops, adding a dimension, then a phase, then an operator, then again a dimension, and then again a phase, taking care of parentheses. At the end of the formula, the part "$D_3(S)$"is added, in order to make a gel.

For example, the complex name given above ("non-connected gel of liquid suspensions in oil sheets") corresponds to the formula $[D_0(S)/D_2(O)]/D_3(S)$. The simplest program does not reject impossible formulas (such as $D_0(S)xD_3(W)$, with a phase of zero dimension that would extend in all three dimensional space), but it is easy to filter manually the possible solutions.

After such simplification, by increasing order of classes, the list can be used to envision complex gels, which can be identified in natural objects: for example, a sample of plant tissue, *e.g.* a part of the root of *Daucus carota* L. (Figure 4) is made of parenchymatous tissue and of connective tissue (xylem, phloem), so that the system has the formula $[[D_0(W_1)/]+$

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$[D_1(W_2)x]]D_3(S)$. In this formula, both "$D_0(W_1)/$" and "$D_1(W_2)x$" operate on the same $D_3(S)$. It is assumed that the cytosol is a liquid (W1), but if it is more realistically preferred to consider that it is itself a gel, then W_1/S' could be used instead of W_1 (Cazor *et al*., 2006).

Moreover, new gels can be produced using the formulas as guides: for example, the gel $D_1(W)/[D_3(W)XD_3(S)]$ can be made by dispersing cylinders of an aqueous gelatin gel in an agar-agar gel where protease enzymes (EC 3.4) are dissolved: after gelling of agar-agar, enzymes diffuse toward the gelatin gel, and they destroy the solid network, leaving liquid channels in the agar-agar gel. Another example is the use of "chaotic mixers" (Tabeling *et al*., 2004) where two solutions would be injected: one aqueous solution, and one solution of a gelling agent; after dispersion and gelling, the result is a multisheet gel. Of course, each particular gel has specific bioactive properties.

Indeed, making new gels is only a first step. It is also interesting to characterize them chemically, physically, biologically. It was proposed to use a general description called "bioactivity", along with the definition of a "matrix effect" (This, 2011, 2013a, 2013c).

Gels are often used in technology, in particular for formulation activities, because compounds dissolved in the liquid phase can diffuse toward the environment and *vice versa*. When released compounds interact with biological receptors, they have been called "bioactive". In some cases, a physical binding is needed to trigger physiological effects: olfaction, sapiction, trigeminal effects, calcium perception, perception of unsaturated fatty acids (Martin *et al*., 2011; Tordoff *et al*., 2012). But for vision the effect is indirect, and for receptors inside tissues, a transfer into the blood system is needed, sometimes after modifications during digestion. Here let us remark that even compounds that would be trapped by the swallowed bits of food are encompassed by the given definition, such as tasty ions adhering surfaces, complexed salivary proteins on some compounds in food.

Theoretical and experimental determinations of bioactivities have to be analysed specifically. For example, supramolecular interactions such as van der Waals forces, hydrophobic pseudo forces, hydrogen bonds, disulfide bridges... between the solvent and the solid network of gels can reduce the self-diffusion coefficient of the solvent molecules or of the dissolved bc, so that the release of bc would be delayed (Matsukawa and Ando, 1996). Also various compartments can release differently bc, such as plant tissues, modeled as $D_1(W)XD_3(S) +D_0(W)/D_3(S)$, for which it was shown that the release of solutes in the sap is fastest than from parenchyma cells (This, 2013a).

More complex systems: more than two phases, dynagels/statgels

In the previous sections, we considered gels with only two phases, but many food systems are more complex disperse systems, with other phases than only solid and liquid. Such systems can also be easily envisioned using DSF. Using the same formalism and the same programming technique for building formulas (Figure 3), one can calculate a wealth of disperse systems that were not envisioned formerly. For example, one can make connected solid foams with aqueous sheets, or emulsions with non-connected sheets, etc. For all such systems, bioactivity can also be interpreted in terms of diffusion but also of weak (supramolecular) and strong (molecular) chemical forces between molecular species.

However, such analyses are considering only "static" gels, where solutes and solvent could diffuse in liquid compartments since diffusion in the solid parts would be much slower. They do not take into account the fact that another analytical frame can introduce new phenomena, and different mechanisms. Indeed, the analysis of "culinary systems" shows that there are "physical gels", with a solid network made from the reversible assembly of constituent molecules, such as gelatin gels, and "chemical gels", with a fixed structure (This, 1996). The examination of the diffusion of bc in a fixed gel is

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like the Born-Oppenheimer assumption for the calculation of molecular orbitals (McQuarrie, 2007), but one can also have a more dynamical approach, in particular when the thermal energy is of the same order of magnitude as the binding energy of the "monomers" (subunits) that can make the solid, "polymeric" network.

Here the words "monomer" and "polymer" call for a comparison with dynamers, dynamic polymer that can reorganize, because their subunits are linked by supramolecular forces (Lehn, 2010). Dynamers are defined as constitutional dynamic polymers, *i.e.* polymeric entities whose monomeric components are linked through reversible connections and have therefore the capacity to modify their constitution by exchange and reshuffling of their components. They may be either of supramolecular or molecular nature depending on whether the connections are non-covalent interactions or reversible covalent bonds (Lehn, 2010).

For gels, "dynagels" and "statgels" can be proposed as well. As for dynamers, dynagels can be defined as constitutional dynamic gels, *i.e.* gels whose monomeric components of the solid network are linked through reversible connections and have therefore the capacity to modify their constitution by exchange and reshuffling of their components. They may be either of supramolecular or molecular nature depending on whether the connections are non-covalent interactions or reversible covalent bonds.

Dynamers can be chemically dynamic, involving a reversible chemical reaction, and physically dynamic, based on physical non covalent interactions; the same idea holds for dynagels, as their solid network is often a polymer. However, in this case, the description is made more complex as the solvent, and possible solutes, can interact with the solid network and with the released units.

One example of dynagels is gelatin gels at a temperature close to the critical melting point. Of course, gelling of gelatin depends on the particular chemical composition of the aqueous solvent in which gelatin is dissolved (Bellini *et al.*, 2015), but a simple thermodynamical description can be made. Let us assume, for example, that

the continuous solid network is obtained by the linking of a certain number *n* of subunits at each node (for gelatin gels, *n* = 3) (Djabourov *et al.*, 1988), with a constant binding energy *E* for each subunit. In the assumption of the Boltzmann distribution, the proportion $p(b,f)$ of subunits being bound (b) on one end and free (f) at the other at a certain absolute temperature *T* would be $p(b,f) = K . \exp(- E / k_B T)$, k_B being the Boltzmann constant, and *K* a normalization constant.

If the binding or release of a particular end of a subunit does not depend on the state of the other end (linked or free), then the probability for a subunit to be entirely free $p(f,f)$ is simply proportional to $\exp(- 2 E / k_B T)$. The sharp exponential variation of this proportion with temperature explains why gelatin gel can be dynamic only within a narrow range of temperatures.

For example, when the temperature is equal to 2 $E / 0.693 k_B$, half the subunits would be free, with considerable changes of the mechanical properties of the gel (as for a 5 % gelatin gel compared to a 10 % gel). Moreover, the bioactivity of statgels and dynagels having the same DSF formula, *i.e.* the same physical organization, can be very different, even with constant binding energy between the solutes or the solvent, on one hand, and the solid network, on the other hand, because of a new component of diffusion of monomers (along with their surrounding of solute and solvent molecules) in the constantly reorganizing system.

As for dynamers, dynagels can exist by nature or by intent. For both, there are "internal" and "external" questions.

Internal questions concern the physical structure, with the determination of the physical properties: mechanical, optical, electrical, etc. Of course, the dynamic structure of the gel can change the diffusion of solutes in the liquid phase, but also solutes that have specific chemical affinities for the monomers of the gel matrix could change the equilibrium of monomer association-dissociation, allowing some control of the gel matrix, such as when effectors can

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change the equilibrium of dynamers (Lehn, 2005). About external questions, the interaction of the dynagel and the environment is concerned, such as how the dynamic reorganization of dynagels changes the self-diffusion coefficient of solutes?

Dynagels, as well as dynamers, are particular cases of dynamic materials ("dynamats") (Lehn, 1999a), these systems being defined as materials whose constituents are linked through reversible connections, either non-covalent or covalent, and are able to continuously reorganize through assembly/disassembly processes and exchange of components in a given set of conditions, usually under thermodynamic control (Lehn, 1999b), but eventually involving kinetic bottlenecks or traps.

As dynamers, dynagels are adaptable and self-assembling systems (Lehn, 1995, 2002; Philp and Stoddart, 1996; Atwood *et al*., 2002), capable of selecting in principle their components in response to external stimuli or to environmental factors, so that they behave as adaptive materials (Lehn, 1999a,b, 2002a,b).

As supramolecular dynamers, supramolecular dynagels are defined as the entities whose solid network is generated by the polyassociation of molecular monomers bearing complementary binding groups capable of connecting through the usual non-covalent interactions implemented in supramolecular chemistry: electrostatic, hydrogen bonding, donor–acceptor, van der Waals as well as metal ion coordination.

Of course, the building of the solid network of dynagels is imposing some particular characteristics to supramonomers, as for dynamers, and in particular the presence of more than two binding sites. Otherwise, the suprapolymer would be linear. Molecular dynagels, as molecular dynamers, are reversible covalent systems which open a range of perspectives to polymer chemical physics.

Finally, as for double dynamic polymers, one can envision double dynagels, combining monomers that bear complementary non-covalent interaction units as well as complementary reversible functional groups. This allows the generation of polygels presenting double dynamic behavior, gels that are dynamic on both molecular and supramolecular levels.

In conclusion, the operation of the various new kinds of gels in chemical physics, and more generally in materials science, confers to the gel entities new physical and chemical characteristics. In particular, dynagels can have many of the properties of dynamers, including the ability to respond to external stimuli and to environmental conditions, *i.e.* adaptability, a major tenet of constitutional dynamic chemistry, which enables the development of adaptive chemistry (Lehn, 2002a,b). The further exploration of these features may be expected to open wide perspectives for basic research in colloidal science as well as to give access to a range of novel properties and applications in colloid technology.

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Note de recherche

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