REVISTA DE LA REAL ACADEMIA DE CIENCIAS

REVISTA DE LA REAL ACADEMIA DE CIENCIAS Exactas Físicas Químicas y Naturales DE ZARAGOZA

Serie 2.ª
Volumen 79

2024

REVISTA DE LA REAL ACADEMIA DE CIENCIAS
Exactas, Físicas, Químicas y Naturales
DE ZARAGOZA
Serie 2.ª. Volumen 79
2024

Revista de la Real Academia de Ciencias Exactas, Físicas, Químicas y Naturales de Zaragoza es una revista anual, editada por la Real Academia de Ciencias Exactas, Físicas, Químicas y Naturales de Zaragoza, y editada y distribuida a través de Prensas de la Universidad de Zaragoza. Calle Pedro Cerbuna, 12. 50009 Zaragoza (España). Tel +34 976761330 puz@unizar.es http://puz.unizar.es/

La Real Academia de Ciencias de Zaragoza agradece el apoyo de la Facultad de Ciencias de la Universidad de Zaragoza.

Depósito legal: Z 218-1960
ISSN: 0370-3207

Edita: Prensas de la Universidad de Zaragoza
Imprime: Servicio de Publicaciones. Universidad de Zaragoza

ÍNDICE DE MATERIAS

Rev. Real Academia de Ciencias. Zaragoza. **79:** 7–52, (2024). ISSN: 0370-3207

Designing polymer materials with dynamic bonds

Jesús del Barrio Lasheras

Instituto de Nanociencia y Materiales de Aragón (INMA)
CSIC-Universidad de Zaragoza
50009 Zaragoza, España
Departamento de Química Orgánica
Universidad de Zaragoza, 50009 Zaragoza, Spain
jdb529@unizar.es

Premio a la Investigación de la Academia 2024. Sección de Químicas

Abstract

Polymeric materials have revolutionized modern life, from electronics to biomedical devices, thanks to breakthroughs in synthesis and engineering. Yet, traditional polymers –built on covalent static networks– pose challenges in, for example, degradation and energy-intensive recycling. Now, interest in dynamic chemistries has enabled reconfigurable polymer systems that respond to external stimuli, supporting applications such as chemical recycling and adaptive materials. Dynamic bonds, including supramolecular and dynamic covalent interactions, provide tools for designing responsive materials with tailored and reversible structures, allowing controlled adaptations in response to environmental changes. This article summarizes key design strategies for integrating dynamic bonds into polymeric materials, and highlights major advancements and emerging trends in this field.

1 Introduction

The development and use of polymeric materials, driven by advancements in their synthesis, engineering, and manufacturing, have profoundly transformed modern society.[1] Since H. Staudinger's Macromolecular Hypothesis in 1920,[2] polymers have evolved into one of the largest segments of the materials industry, finding diverse applications across a number of fields from low-cost electronics to implantable biomedical devices, and lightweight parts for vehicles and airplanes. However, many *conventional* polymers rely on high-molecular-weight *static* networks, which can sometimes result in issues such as undesirable or uncontrolled degradation and the requirement of energy-intensive processes for their recycling and reprocessing. In other words, common *traditional* polymers are frequently designed as passive structures, focusing on enhancing their mechanical, thermal, or electronic properties. These *traditional* polymeric materials typically exhibit permanent non-reconfigurable covalent bonds, with efforts concentrated on preventing the breakage of these bonds under operating conditions, as such, breakage usually results in an undesirable decline in the properties and performance of the material.

Over the past few decades, there has been renewed interest in dynamic chemistries, where specific bonds or interactions can be broken, reformed, or reconfigured upon exposure to certain environmental factors.[3,4] The ability of dynamic bonds to isomerize, rearrange, break and reform allows the creation of structurally distinct dynamic polymer systems that can adapt their structure or composition and potentially demonstrate a controlled macroscopic response to external stimuli. The use of dynamic or reconfigurable *bond-making chemistries* also represents an opportunity to revise current strategies for designing and constructing polymeric materials, with a view towards addressing critical challenges in, for example, chemical recycling and innovative biomedical materials.

The history of reversible processes within polymer science is extensive and diverse, and encompasses phenomena such as ring-chain equilibria and the utilization of dynamic equilibria between propagating radicals and dormant species in controlled radical polymerizations.[5] A number of reversible covalent and non-covalent interactions (as well as isomerizable or rearrangeable functional moieties), have been successfully integrated with diverse organic build-

ing blocks –of low and high molecular weight– to create adaptive and stimuli-responsive materials (Figure 1). Some examples of these building blocks include end-functionalized oligomers and polymers, block-copolymers, polymer network precursors and reactive liquid crystals (LCs) to name just a few. Surely, the reader will recognize that a wide range of materials inherently possess the ability to exhibit stimuli-responsive behavior through various mechanisms. Indeed, phase segregation and phase transitions, including the glass transition and the isotropization of LCs, are central to numerous applications such as actuators, adaptive surfaces, re-healable materials and substance delivery systems.[6,7] Unlike the previous examples, the main idea behind polymeric materials exhibiting a dynamic architecture, as discussed in this brief revision, is that their subcomponents can rearrange due to the responsive nature of specific dynamic bonds. This rearrangement leads to changes in structure or connectivity, resulting in a controlled macroscopic response. Therefore, the careful selection of dynamic bonds and specific (macro)molecular building blocks enables the creation of materials with tailored responses for particular applications.

In this Review, a *dynamic* bond is defined as any type of bond capable breaking and reforming, or rearranging, typically under equilibrium conditions. Consequently, the term *dynamic* includes two broad families of bonds: supramolecular (i) and dynamic covalent interactions (ii). Supramolecular or non-covalent bonds typically include hydrogen bonding, π–π stacking, metal-ligand coordination, macrocyclic host-guest complexation and halogen bonding. A dynamic covalent bond, in contrast, can be viewed as a reversible covalent bond that breaks and reforms cleanly, without causing any significant side reaction. Therefore, replacing a covalent bond that connects specific subcomponents or monomeric units within a larger macromolecular construct by a dynamic bond may produce a structurally dynamic material capable of exhibiting stimuli-responsive behavior (Table 1). The two broad families (i) and (ii) of dynamic bonds share some common characteristics such as the ability to exchange, and the fact that their end-state composition can be influenced to some extent by external factors such as temperature, concentration, etc. Supramolecular interactions (ii) are generally in equilibrium, while dynamic covalent bonds (i) typically require the presence of a catalyst or specific stimulation to revert.

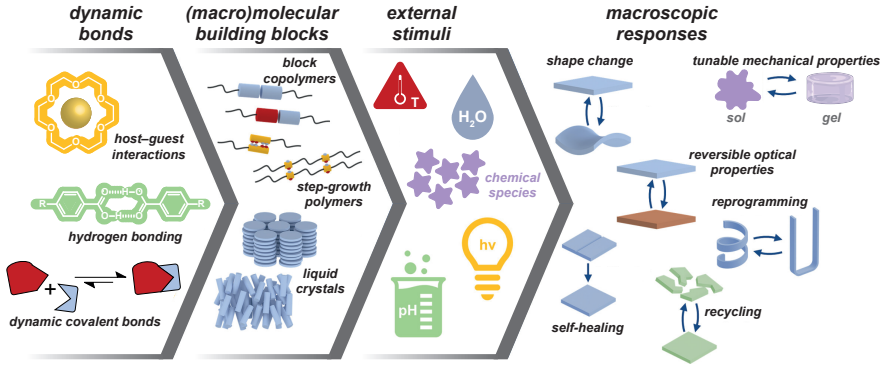


Figure 1: Rationale for pursuing the integration of dynamic bonds into (macro)molecular materials. Adapted from ref. 6 Copyright 2021 The Authors.

For the materials scientist, the molecular toolbox available for designing stimuli-responsive materials is broad and varied (Figure 1). The dynamic bond serves as a crucial element within this toolkit, enabling the adjustment of specific thermodynamic and kinetic parameters that ultimately dictate the macroscopic behavior of structurally dynamic polymers.[8] Of course, other factors must be considered when selecting the appropriate dynamic bond for a specific materials application such as the directionality of the complementary components and the solubility of the binding motifs. These aspects, along with other design features related to incorporating dynamic bonds into (macro)molecular architectures will be discussed in the following sections.

1.1 Supramolecular non-covalent interactions

In order to look at the characteristics of polymeric structures incorporating dynamic non-covalent bonds (i.e. supramolecular polymers), certain considerations are necessarily required for their definition. Meijer *et al.* has proposed the following.[9]

Supramolecular polymers are defined as polymeric arrays of monomeric units that are brought together by reversible and directional secondary interactions, resulting in polymeric properties in dilute and concentrated solutions, as well as in the bulk. The monomeric units of the supramolecular polymers themselves do not possess a repetition of chemical fragments.

dynamic bond	**binding motif**	**(macro)molecular architecture**	**conditions**	**material property/ application**	**ref.**
hydrogen bonding	carboxylic acid dimer	liquid crystal network	solvent-free ambient temp.	controlled deformation in response to moisture	[180]
dynamic covalent	arylboronate–diol	star tetra-PEG network	aqueous ambient temp.	glucose responsive hydrogels for therapeutic encapsulation and release	[154]
host-guest complexation	CB[8]–viologen–naphthyl ternary complex	supramolecular amphiphilic block copolymer	aqueous ambient temp.	multi-responsive micellar encapsulats for therapeutic transport and release	[66]
dynamic covalent	Zn catalyzed transesterification	epoxy/acid and epoxy/anhydride polymer network	solvent-free $100 - 250\,^{\circ}\mathrm{C}$	maleable and reparable crosslinked polymer networks	[103]

Table 1: Selected examples of structurally dynamic polymer materials.

The directionality and strength of the supramolecular bonding are important features of systems that can be regarded as polymers and that behave according to well-established theories of polymer physics.

This definition focuses exclusively on behavior typical of supramolecular polymers from relatively low molecular weight subcomponents (Figure 2d), but macromer-based supramolecular systems should also be considered. Examples of these materials include telechelic macromonomers reversibly bound within the main chain of a larger supramolecular polymeric species (Figure 2f), or block copolymers where disparate blocks are connected through non-covalent interactions (Figure 2e). These examples employ the same specific interactions as small molecule monomers and can potentially be described using similar established theories.

With this definition in hand, it is possible to review some of the general aspects associated with the incorporation of supramolecular bonds into (macro)molecular structures. In the simplest scenario, useful monomers, either small molecules or macromers, leading to linear structures are necessarily bis-functional and the linking can be of self-complementary or complementary in nature. Self-complementary motifs are capable of binding either through an A:A or A:B motif. The latter generally consists of molecules capable of associating through a double-sided functional structures (e.g. urea stacking promoted by hydrogen bonding and π–π stacking). Comparatively, complementary interactions can be either two-component binding through an A:B motif, or even three-component (for example A:B:A, whereby component B is required for association of components A).

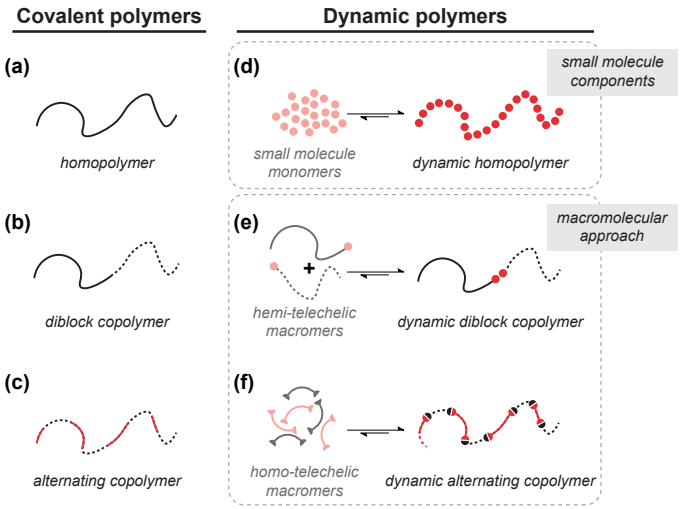


Figure 2: Schematic representation of a covalent homopolymer (a), block copolymer (b), alternating copolymer (c), and their dynamic counterparts (d–f).

Following the traditional condensation polymerization model all known structures of traditional polymers, including linear homo- and block copolymers, crosslinked networks, graft copolymers, comb and (hyper)branched polymers are accessible in supramolecular polymers.[10] With linear supramolecular polymers specifically the degree of polymerization, DP, is associated with the stability or strength of the non-covalent interactions employed between monomeric units and the concentration.[11] If non-cooperativity in the supramolecular polymerization is assumed and the association constant (K_a) between the monomers is known, it is possible to calculate the theoretical DP of a supramolecular polymer according to the Carother's equation.[12,13] The DP is significantly influenced by K_a and the concentration. According to a theoretical framework by Ciferri,[10,14] a relatively high association

constant (e.g., $K_a > 10^5\,\mathrm{M}^{-1}$) between monomers in solution is essential for obtaining polymers with high molecular weight when monomer concentrations are in the hundreds of millimolar to molar range. This high molecular weight is crucial for achieving significant mechanical properties or stimuli-responsive behavior.

Another important characteristic of the dynamic supramolecular bond is the timescale on which the bond exists, defined by the rate of monomer association (k_{on}) and dissociation (k_{off}). These kinetic parameters, related to the equilibrium constant ($K_a = k_{\mathrm{on}} \cdot k_{\mathrm{off}}^{-1}$), are crucial in determining, for example, the speed at which the material responds to specific stimulation. True dynamic supramolecular materials must be reversible on experimental time scales. A physical model developed by Cates in the late 1980s for worm-like micellar systems predicts the viscoelastic properties of supramolecular polymers by accounting for both the stability and kinetics of non-covalent interactions between monomers.[15,16] Such a model has been shown to effectively describe the behavior of a broad range of non-covalent crosslinked materials, including the viscoelastic behavior of reversible self-complementary 2-ureido-4[1*H*]-pyrimidinones UPy-based supramolecular polymers.[17] Together, the thermodynamics and kinetics of the dynamic bond significantly influence both the mechanical properties of the supramolecular polymer system and its ability to produce a macroscopic response.

The toolkit of non-covalent dynamic bonds encompasses a variety of interactions including, but not limited to, π–π stacking, hydrogen bonding, halogen bonding, metal-ligand coordination and macrocyclic host-guest complexation (Figure 3). These relatively weak dynamic bonds are typically in equilibrium and, therefore, they are highly responsive to thermal conditions, solvents, reagents, and concentration. Such factors can indeed be leveraged to create dynamic materials that are sensitive to various stimuli.

Hydrogen bonding is crucial in many natural and manmade supramolecular materials. Such an interaction is key to the three-dimensional structure and assembly of both DNA and RNA, where its directionality, specificity and ability to work in a concerted fashion are of fundamental importance –indeed, the combination of multiple base pairs and π–π stacking enables the system to overcome the competition by water molecules. These bonds are certainly not the strongest of the non-covalent interactions (Figure 3), however, due to

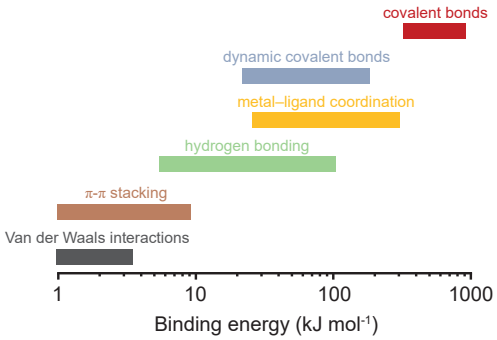


Figure 3: Typical binding energies for different types of bonds and interactions. Adapted with permission from ref 4. Copyright 2021 American Chemical Society.

their directionality and specificity, it is possible to readily design binding motifs capable of accepting and donating, or both, multiple hydrogen bonds simultaneously, which greatly enhances their stability (i.e. K_a).[18] As with single hydrogen bonds, the strength of the resulting interaction is affected by several factors: (i) the nature of the donor, D, and acceptor, A (i.e. angle between D and A, for example), (ii) the solvent, and (iii) the configuration of the donor and acceptor sites (e.g. a different binding strength will be provided by an array of DAAD *vs.* that of DADA). When designing multiple hydrogen bonding units it is important to take into consideration secondary attraction and repulsion between neighboring interactions. As demonstrated in Figure 4, these secondary interactions can greatly alter the K_a leading to a difference of more than two orders of magnitude between the ADA-DAD motif (Figure 4a) and the AAA-DDD motif (Figure 4c).[19]

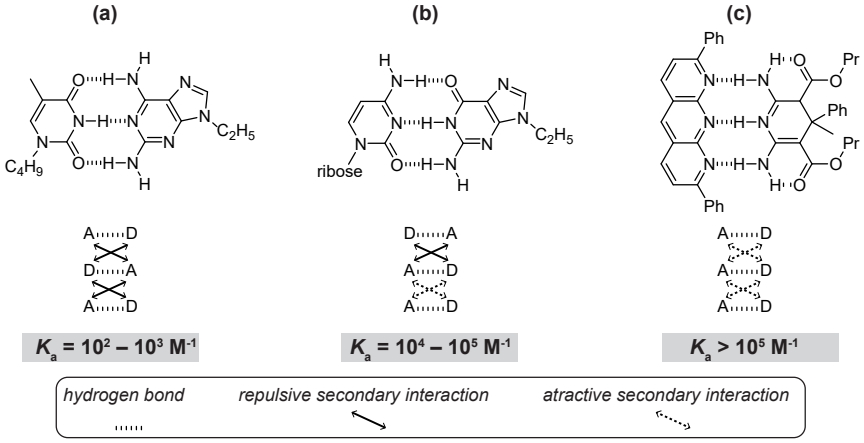


Figure 4: Selected examples of multiple hydrogen bonding motifs.

There have been a large number of multiple-hydrogen bonding arrays reported in the literature over the past three decades.[9,10,20] Each has their own characteristics, ranging from the quintessential quadruple hydrogen bonding unit UPy, an AADD self-complementary array synthesized in a simple one-step process from commercially available isocytosines,[21] which exhibits relatively high dimerization (ca. $10^7 - 10^8\,\mathrm{M}^{-1}$) constants in chloroform, to the more complex pairs produced by Gong and co-workers, which show exceptionally high stability in organic solvents,[22,23] and, in some recent cases, even in aqueous media.[24]

Perhaps the most studied and applied hydrogen bonding unit is that of the UPy-derived family of polymers. Meijer and co-workers have produced a large volume of research in UPy dimerization and its tautomerization to selectively form an A:B complementary binding pair with 2,7-diamido-1,8-napthyridine, NaPy.[25] They demonstrated the assembly of UPy-telechelic poly(ethylene-co-butylene), pEB, prepared *via* post-polymerization functionalization of hydroxy-telechelic pEB (Figure 5).[26] The assembly of these low molecular weight polymers drastically alters the materials properties, converting the starting material from a viscous liquid to an elastic solid after the functionalization with UPy motifs. This demonstrates the versatility of supramolecular polymers as they exhibit properties akin to traditional covalent macromolecules while providing the facile processability from the low melt viscosities of oligomers.

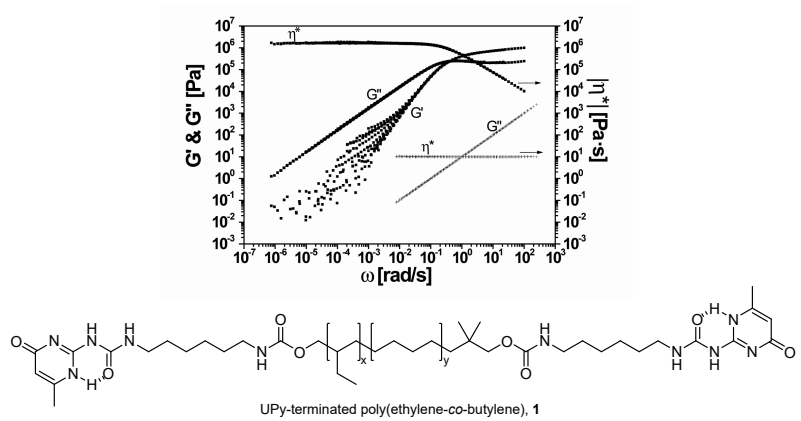


Figure 5: Master curves (top) of dynamic melt viscosity (η^*), storage (G') and loss (G'') moduli corresponding to UPy-pEB-UPy (black squares) and hydroxyl-telechelic pEB (gray crosses), and chemical structure of UPy-pEB-UPy (bottom). Adapted with permission from ref 26. Copyright 2000 John Wiley & Sons, Inc.

In another study Meijer and co-workers investigated the self-assembly of UPy- and NaPy-telechelic poly(octene) macromonomers which were prepared by ring opening methathesis polymerization, ROMP, using bis-functional chain transfer agents, CTAs.[27] They demonstrated the development of a facile method for the preparation of a range of polymers with end-group fidelity of exactly two that can form supramolecular homo- and block-copolymers using controlled polymerization and simple functional CTAs. They also demonstrated the importance of end-group fidelity as this system exhibited a high dependence of specific viscosity on concentration, comparable to small molecule supramolecular polymers. Interestingly, the materials in the previous examples exhibited much lower dependencies (on concentration, for example), which is due to the presence of some unfunctionalized end-groups leading to chain stoppers that drastically decrease the apparent DP.

Despite the impressive K_a values reported for many of the previous systems and their utility in forming supramolecular materials, their exceptional self-assembly behavior is perhaps restricted to non-polar solvents or the hydrophobic domains within compartmentalized structures. This is because K_a values decrease significantly in polar solvents due to competition from solvent hydrogen bonding. In contrast, metal-ligand coordination has been used in aqueous as well as organic media in a variety of systems. The dynamic nature of these interactions is highly variable. Some metal-ligand coordination –for example, certain cases of Ru(II)-based systems– do not show reversibility on experimental timescales and,[28] therefore cannot be considered dynamic in the definition used above. This feature, nevertheless is interesting as it enables the creation of materials that closely resemble traditional polymers but with latent, chemically responsive capabilities. Particularly with this type of interaction, it is crucial to make careful choices when designing a system, as the selection of metal ion and ligand significantly impacts the stability of the bond and its responsiveness due to varying binding energies (Figure 3).

Some of the most frequently used metal ions include Fe, Ru, Mn, Os, Pt, Ir, Co, Ni, Zn and Cd, and these are normally used in their low oxidation states. Schubert and co-workers reported that diblock homopolymers made from terpyridine ligands and Fe(II) exhibit higher thermal stability than those based on Ru(II).[29] The same group exploited later the terpyridine-based complexation and noted that diblock homopolymers complexed with Zn(II)

degrade readily in both acidic and basic conditions, whereas analogous polymers complexed with Ni(II) remain unaffected by pH changes.[30] Taking these ideas into account, a comprehensive library of metallo-supramolecular systems was later developed, which included small molecules, and semi-telechelic and telechelic macromers, all featuring terpyridine ligands as end-groups.[30] One particularly interesting case involved the post-polymerization assembly of terpyridine-functionalized semi-telechelic polyethylene oxide (pEO) and pEB macromers, which resulted in the formation of metallo-supramolecular block copolymers. Schubert and co-workers further advanced this field by developing a terpyridine-functionalized initiator for nitroxide-mediated polymerization (NMP), yielding semi-telechelic polystyrene. Additionally, they devised a method to synthesize telechelic polymers by reacting the nitroxide end-group with a maleimide-functionalized terpyridine unit in a post-polymerization process.[31] Despite the proven efficacy of the dynamic metal-ligand coordination bond for the preparation of linear supramolecular polymers, the formation of these structures is still under statistical control. In the formation of AB diblock copolymers, a two-step approach is used. First, the metal of choice is complexed with the end-group of the first block, A. Then, the second block, B, is complexed with the remaining metal binding sites to form the final diblock copolymer. The presence of terpyridine units on both blocks introduces statistical control to these systems, resulting in some inevitable contamination by A and B diblock homopolymers, though likely in minimal amounts.

Recent developments in dynamic organo- and hydrogels based on metal-ligand coordination have significantly enhanced the understanding of the thermodynamics and kinetics of these dynamic bonds and their impact on the viscoelasticity of polymer networks. Such dynamic systems exploit the binding capabilities of, for example, histidine, catechol and bisphosphonate ligands which in many occasions have been incorporated to the chain ends of multi-arm star polyethylene glycol, PEG, leading to polymer network precursors of well-defined functionality and molecular weight.[32] A particular limiting aspect of metal-ligand coordination is associated with the use of metal ions themselves. While the previous materials have been successfully formed in water and can even assemble into higher-order structures like micelles, the presence of metal ions restricts their application in many aqueous systems where low toxicity is a common factor.

Macrocyclic host-guest complexation is another interesting and extensively utilized approach for achieving dynamic covalent bonding. In the context of this review, such a complex or bond occurs when a guest molecule is trapped within the structure of a host. The latter usually features external functional groups that interact with solvent molecules, while its internal structures facilitate guest binding through a specific shape or a favorable environment. This is especially true for highly stable host-guest complexes where a hydrophobic guest is encapsulated into the hydrophobic cavity of a particular host, such as cyclodextrins (α-, β- and γ-CD) and cucurbit[n]urils, CB[n] ($n = 5 - 8$ and 10), in water through favorable solvophobic interactions (Figure 6). The macrocyclic-based host-guest complexation associated with flexible crown ethers typically exhibit K_a values ranging from 10^2 to 10^4 M^{-1} in polar organic solvents.[33] The CD host family displays relatively high K_a values, reaching up to 10^5 M^{-1} in water.[34,35] Remarkably, some members of the CB[n] host family have demonstrated even higher K_a values, in some cases up to 10^{12} M^{-1} in water.[36,37] Dynamic bonding *via* macrocyclic host-guest complexation is highly tunable based on the architecture, size and structural features of both the host and guest molecules, as well as dipole-dipole and ion-dipole interactions between them –given that the guest is often a charged species. Relevant cavity-bearing molecules include crown ethers, CDs, CB[n], and pillar[n]arenes among others (Figure 6).

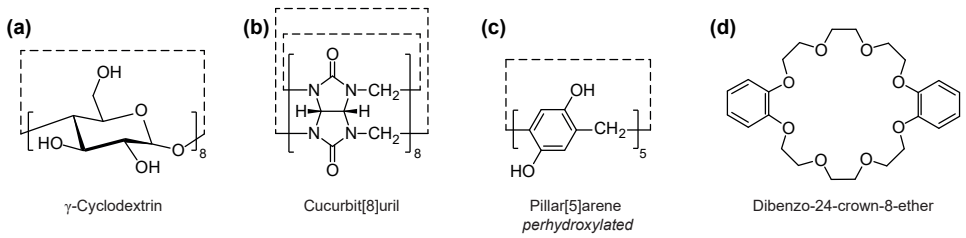


Figure 6: Structures of selected macrocycles.

Each type of macrocyclic host possesses unique characteristics, making the selection of the appropriate host for a specific reconfigurable system or polymeric materials dependent on the desired behavior of the final dynamic material. As will be discussed later, there are many opportunities to fine-tune the responsiveness of dynamic materials through host-guest complex formation.

A number of crown ethers varying in size have been prepared including bis(*p*-phenylene)-34-crown-10 (BPP34C10), bis(*m*-phenylene)-32-crown-10 (BMP32C10), dibenzo-24-crown-8 (DB24C8), and benzo-21-crown-7 (B21C7). While crown ethers exhibit relatively low K_a values, they have been exploited to produce a wide variety of structurally dynamic materials.[38,39] In general, the ring sizes of crown ethers can significantly affect the binding affinity for specific guest molecules. BPP34C10 and its derivatives can form a 1:1 threaded structure with 4,4'-bipyridinium derivatives (**2** in Figure 7b, for example),[40] a binding ability which inspired the development of a large family of catenanes and other mechanically interlocked systems based on cyclobis(paraquat-*p*-phenylene), $CBPQT^{4+}$.[41] BPP34C10 also exhibits relatively strong binding affinity for other dicationic species and more electron-deficient guests, such as 2,7-diazapyrenium derivatives (such as **3** in Figure 7b).[42] Owing to their molecular structure, BMP32C10 and its derivatives can interact with 4,4'-bipyridinium-containing guests, forming sandwich-like or threaded host-guest complexes.[43] DB24C8 and dibenzylammonium salts spontaneously form 1:1 host-guest complexes. Additionally, DB24C8 exhibits a 1:1 complexation stoichiometry with 4,4'-bipyridinium derivatives, though with a weaker binding affinity.[44] B21C7, the smallest benzo crown ether, forms host-guest complexes with secondary ammonium salts, showing a relatively high K_a.[45] On account of the outstanding host-guest binding capabilities of crown ethers, a broad array of crown ether-based dynamic bonds have been utilized to create supramolecular polymers characterized by diverse structural architectures including poly[*c*2]daisy linear structures, hyperbranched polymers, crosslinked networks, dendrimers, and star-shaped polymers.[38,46]

CDs are some of the most extensively studied and well-developed macrocyclic hosts, largely due to their straightforward synthesis and the ease with which the hydroxyl groups at the portal and periphery of their cavity can be functionalized.[35] Consequently, this facilitates their integration into various molecular systems, including polymeric materials. CD is easily synthesized through the enzymatic degradation of starch, making it commercially affordable and promising for industrial and biological applications. A key limitation of CD systems, however, is their relatively low affinity for specific guest molecules, which constrains the performance of their associated supramolecular materials. A wide range of dynamic hydrogels,

stimuli-responsive coatings, and functional biomaterials have been developed utilizing CD host-guest interactions as dynamic bonds, with further details available in comprehensive reviews.[34,35,47,48]

Calixarene and pillararene derivatives generally exhibit much higher binding affinities with specific molecular guests compared to crown ethers and CDs.[49,50] They are also relatively easy to synthesize and functionalize. However, their strong association is primarily limited to certain metal ions. While these macrocycles have been integrated into sensing devices and polymer networks, the narrow range of stable host-guest complexes may limit their broader application in other fields.[51]

The CB[n] family shows significantly higher association levels in aqueous media compared to earlier macrocycles, making them highly promising for developing materials with exceptional physical properties.[36,37] However, a major drawback has been the limited functionalization methods and the difficulties in separation and purification. Recent advancements, though, have simplified the functionalization of CB[n],[52,53] marking a potential paradigm shift in its applications and unlocking opportunities to create materials with unprecedented properties.[54]

The basic structure of CB[n] is depicted in Figure 7a. It is a symmetric, barrel-shaped cyclic oligomer of glycoluril containing between 5 and 10 repeat units –other larger CB[n]s, including CB[14], have been identified but the CB[n] series with $n = 5 - 8$ and $n = 10$ are the most commonly used hosts. The tunable size of its hydrophobic cavity along with its polar carbonyl portals lead to exceptional encapsulation capabilities (*vide infra*). The CB[n] family shows distinct solubility trends that follow an odd-even pattern, which may be linked to changes in the arrangement of hydrogen-bonded water clusters around the homologues in water. CB[5] and CB[7] have relatively high solubilities of 20–30 mM in neutral water, whereas CB[6] and CB[8] display much lower solubilities of ca. 0.01–0.02 mM. Due to these properties, each member of the CB[n] family requires distinct approaches for separation and use in chemical reactions and molecular recognition. Methods for synthesizing, separating, and purifying CB[n] and its derivatives are still evolving, with recent efforts focused on isolating and scaling up functionalized CB[n] analogues, including both cyclic and open-chain species.[55,56] Since Mock and co-workers first demonstrated the ability of CB[6] to bind a

series of alkylammonium and alkydiammonium ions in aqueous formic acid,[57,58] interest in the area of CB[n] complexation has grown significantly. Combining the fundamentals of CB[n] host-guest chemistry with the dimensional diversity within this macrocycle family has revealed a vast, previously unexplored realm of supramolecular chemistry.

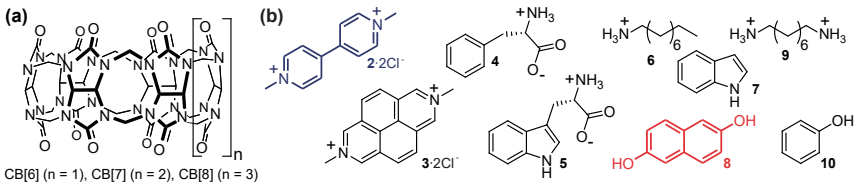


Figure 7: Structures of CB[6–8] (a) and selected guests **2**–**10** (b) including a common complementary pair of guest molecules, methyl viologen dichloride (**2**) and 2,6-dihydroxynaphthalene (**8**), leading to CB[8] heteroternary complexation.

In CB[5] to CB[7], only a single molecular species can be encapsulated. However, in CB[8] and larger homologues, the significantly larger cavity sizes enable the simultaneous binding of two guests (Figure 8a). This ability to form ternary inclusion complexes expands the possibilities for molecular recognition and interaction. CB[8], in particular, has been widely studied for its specific molecular recognition capabilities.[59] It exhibits strong affinities for small, flat aromatic guests, especially in three-component systems (i.e. ternary complex), where two guests are accommodated simultaneously inside the CB[8] cavity.[60,61] The guest-binding mechanism of CB[8] occurs in a stepwise manner. First, a 1:1 binary complex forms between CB[8] and an electron-deficient aromatic molecule (**2** or **3** in Figure 7b, for example), characterized by a relatively high association constant (K_a ca. $10^5 - 10^7\,\mathrm{M}^{-1}$). This is followed by a second binding event with an electron-rich, flat aromatic molecule (**7**, **8** and **10** in Figure 7b, for example). While the formation of the ternary complex has a slightly lower association strength, it still results in a thermodynamically stable three-component system with a high overall association constant (Figure 8a). A wide range of guest molecules involved in this or similar processes has been extensively studied by several research groups, including those led by Professors Kim, Nau, Isaacs, Scherman, Brunsveld, Buschmann, and Urbach.[62] A key focus within the CB[n] research community has been to understand CB[8] complex formation in water, as it is essential for creating dynamic materials with versatile, real-world applications.[63]

The initial exploration of ternary CB[8] complexation in supramolecular polymer chemistry was conducted by Scherman and co-workers. Their work focused on preparing end-functional polymers that incorporated specific complementary guests for CB[8].[64,65] Subsequently, the use of this macrocycle as the mediating linker, a hierarchy of self-assembling structures was produced (Figure 8). Diblock copolymers were successfully assembled by combining a polymer bearing a single first guest with CB[8] and an analogous polymer with a second guest (Figure 8c).[64,66] Furthermore, if the block lengths are designed strategically, taking into account the balance of hydrophobicity and hydrophilicity, it becomes possible to achieve higher-order structures such as cylindrical micelles and polymer vesicles. Another example is the use of functional side-chain homopolymers to produce dynamic hydrogels.[67,68] In this approach, complementary polymer chains with pendant guest molecules were prepared. Specifically, two polymers were synthesized: one with first guest moieties and the other with second guest moieties (Figure 8d). When these polymers are combined in specific ratios with CB[8], they form a three-dimensional crosslinked hydrogel that can retain significant amounts of water, with some hydrogels achieving water content as high as 99.95%.[69] This exceptional water retention reduces the required amount of hydrogelator while also providing shear-thinning and self-healing characteristics. Other reconfigurable materials exploiting the binding capabilities of CB[8] include microcapsules and polymer micelles as substance delivery systems,[70] crystalline two-dimensional fibers,[71] stimuli-responsive colloids,[72] and protein hybrids,[73] among others.

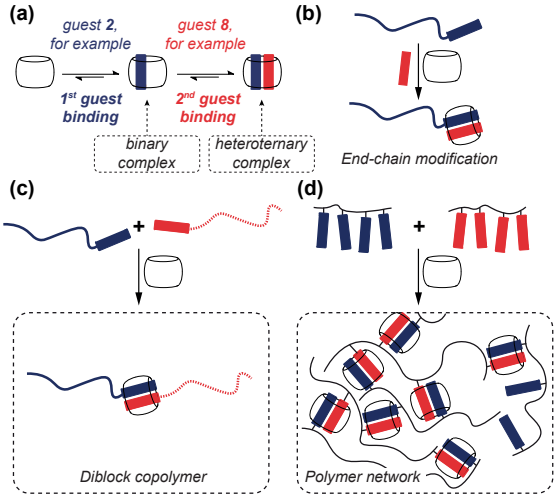


Figure 8: Schematic representation of the formation a CB[8] heteroternary complex (a) and a series of structurally dynamic polymer constructs based on CB[8] complexation: end-modified linear homopolymer (b), diblock copolymer (c) and polymer network (d).

The progress in supramolecular chemistry has allowed for the development of materials forming robust yet dynamic non-covalent materials. It is apparent that a new research area has solidified a place in the field of polymer science, as the materials that have been produced possess many of the important and well-known properties of traditional covalent polymers, yet offer the opportunity for responsiveness to external stimuli.

1.2 Dynamic covalent interactions

Dynamic covalent chemistry can be seen as a synthetic strategy that combines the robustness of covalent bonds with the adaptability of dynamic interactions. Indeed, it involves the reversible formation and breaking of covalent bonds leading to the creation of molecular systems that can respond to changes in their environment in a predictable manner.[74,75] Most traditional covalent synthetic transformations pursue the formation of new bonds which are created to be static and permanent under normal standard conditions. Conversely, dynamic covalent chemistry relies on covalent bonds that can form and dissociate reversibly. Such a process is usually achieved through the equilibrium between different molecular states, and it is typically governed by thermodynamic control, meaning that the system tends to reach the most thermodynamically stable state.[76] Indeed, this feature allows the system to (i) adapt in response to external stimuli –including pH and temperature changes, or the presence of specific chemical species– and (ii) even self-heal after damage (*vide infra*).

Examples of reversible covalent bonds in dynamic covalent chemistry include imine bonds, boronic esters, and hydrazones, among others (Figure 9). Like the previously mentioned non-covalent interactions (see Section 1.1), these dynamic covalent bonds have been integrated with various organic building blocks to develop materials for applications such as tissue regeneration, drug delivery, and sensors among others.[77]

While thermodynamic control is crucial, the kinetics of bond formation and breaking also play a significant role. Some dynamic covalent bonds can exchange at ambient temperatures, but many exhibit exchange rates that are extremely slow, resulting in, for example thermally gated stress relaxation behaviour (*vide infra*). For some systems, it has been

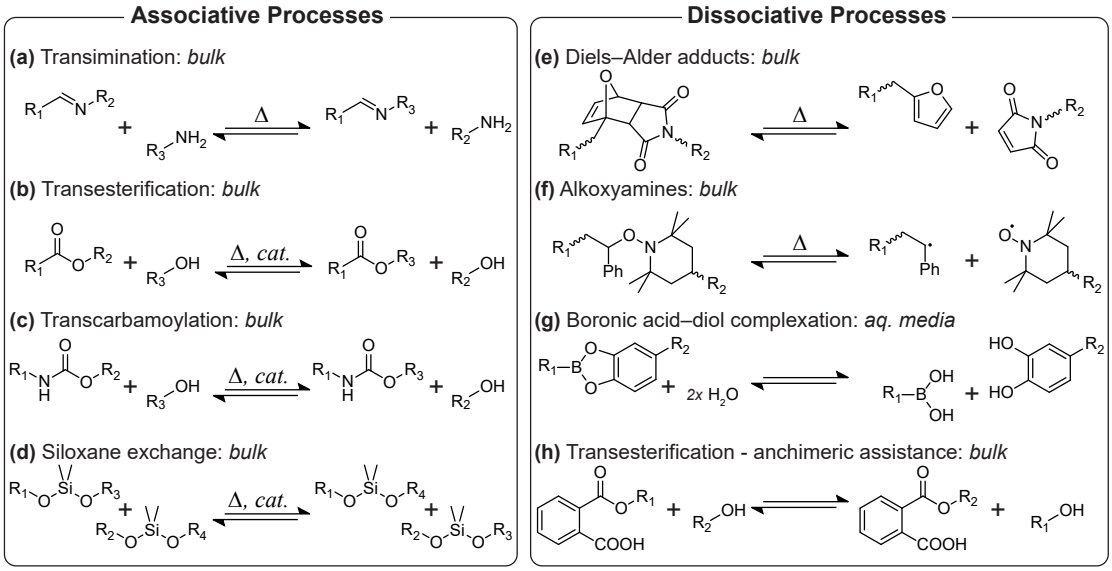


Figure 9: Selected examples of associative and dissociative dynamic covalent interactions.

suggested that bond lifetimes between 1 millisecond and 1 minute provide connections that are stable and detectable with most analytical methods, while still being dynamic enough to enable rapid adaptation.[78] This results in equilibrium times ranging from hours to days for large dynamic systems. Concerning the practical applications of (macro)molecular materials that incorporate dynamic covalent bonds, the maximum equilibration time is related to the stability of the system, as equilibrium must be achieved before any significant uncontrolled degradation occurs. Since covalent connections are in general more stable than supramolecular interactions, dynamic covalent bonds tend to be more robust but also exchange more slowly compared to their non-covalent counterparts. Therefore, most dynamic covalent bonds necessitate elevated temperature and/or the presence of a catalyst to facilitate exchange (Figure 9).

In the context of dynamic covalent materials, mild reaction conditions are beneficial for preserving bond integrity and maintaining sensitive non-covalent interactions within the system. The specific dynamic covalent bond must also align with the intended application, with resistance to moisture and oxygen being generally crucial. In biological applications, a dynamic covalent bond should exchange readily in water (Figure 9g, for example); however, only a few bonds that meet these criteria have been identified.

It is important to note that, quite often, there is a trade-off between stability and equilibration rates, as more reactive dynamic covalent bonds typically result in decreased system stability and *vice versa*. Indeed, the use of a catalyst to facilitate equilibration is quite common in dynamic covalent materials. The catalytic species can be manipulated to halt equilibration before analysis or to selectively toggle the exchange on or off. A diverse array of bond exchange catalysts has been employed with dynamic covalent materials, ranging from simple buffered acid or base solutions to complex multicomponent catalytic systems. Several of these approaches will be discussed in the following sections. The list of chemistries that have been used in dynamic covalent materials formation is broad, and include transesterification, Diels-Alder cycloaddition, boronic ester complexation, etc. These dynamic covalent molecular systems continuously break and reform bonds in response to physical or chemical cues such as mechanical loading, pH, or temperature. This adaptability leads to the development of highly processable, self-healing materials with frequency-dependent mechanical properties. For instance, disulfide motifs were recognized early on as reversible.[79] More recently, the reversible formation and cleavage of disulfide bonds in response to light and pH was utilized to create dynamic hydrogels.[80,81] Another common strategy to produce dynamic covalent materials involves the incorporation of acylhydrazone binding motifs in dynamic linear polyamides to reversibly exchange repeating monomers.[82] Schiff's base chemistry has also been utilized to create crosslinkable and self-healable polymer networks through imine or hydrazine bond formation in aqueous media. For instance, Wei and co-workers reported an injectable hydrogel suitable as a biocompatible carrier for specific cell therapy applications.[83] Alternatively, boronic ester formation takes place under mild conditions in aqueous media, notably without requiring a catalyst (see Figure 9g). Indeed, boronic ester exchange is possible even under physiological conditions.[84] Additionally, the reactivity of boronic acids with diol species can be modified through various strategies, such as neighboring group effects, enabling the preparation of materials with tunable mechanical properties (Figure 10).[85,86]

Overall, the chemistries and strategies for preparing dynamic covalent polymeric materials are diverse, each with its own thermodynamics and kinetics, resulting in varying macroscopic responses to external stimulation.[87,88] A few selected examples of such strategies have been presented in this section, with additional information available in recent com-

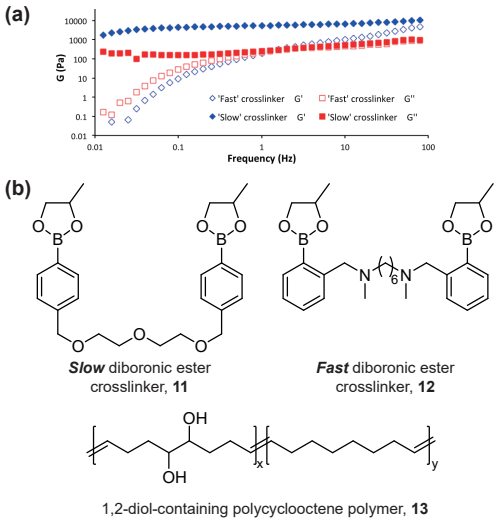


Figure 10: Rheological behavior (a), G' (diamonds) and G" (squares), of samples of polymer **13** (b) crosslinked with diboronic esters **12** (open symbols) and **11** (closed symbols). Adapted with permission from ref 86. Copyright 2015 American Chemical Society.

prehensive reviews.[89,90] The following sections focus on the implications of incorporating dynamic bonds into polymer materials, their sensitivity to external stimuli and recent trends.

2 Thermally-responsive structurally dynamic polymers

Many stimuli-responsive materials with dynamic bonds, particularly those utilizing non-covalent binding motifs, inherently exhibit thermoresponsive behavior due to the relative weakness of these interactions. The sensitivity to thermal stimuli depends on factors such as the type of dynamic bond integrated into polymeric systems and whether it is part of the main chain or acts as a side-chain crosslinking moiety. These strategies, commonly used to facilitate heat-driven reorganization of polymer structures after synthesis, have been extensively studied to impart properties like self-healing, improved processability, and controlled viscoelasticity.[91]

One interesting supramolecular polymer network exhibiting self-healing behavior relies on multiple donor–acceptor π–π stacking interactions.[92,93] Such material is comprised of a physical mixture of a polyamide equipped with terminal pyrene groups and a copolyimide

bearing π-electron-deficient diimide moieties in the main chain of the polymer. The mixture of these two polymer results in a physical blend capable of producing free-standing films with remarkable tensile modulus of up to 1 MPa at 30 °C. The enhanced mechanical properties of the blend are attributed to the intercalation of the terminal electron-rich pyrene moieties of the polyamide into the chain folds of the polyimine containing multiple electron-deficient diimide moieties. The association of these complementary components is thermally reversible, allowing the material to heal itself (Figure 11). In fact, damaged films can be restored and regain their original tensile modulus by briefly heating to 80 °C. This healing capacity is reproducible across multiple cycles without a loss of efficiency.

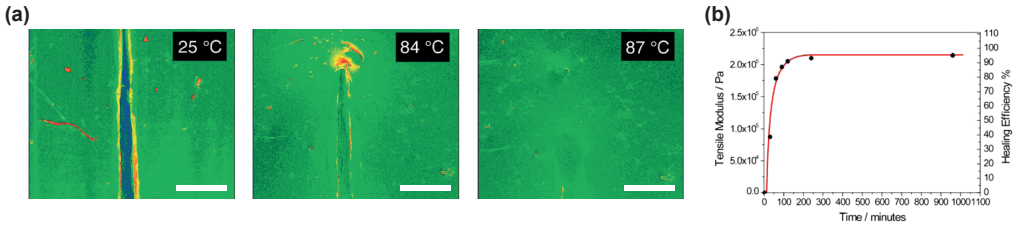


Figure 11: SEM images (scale bars: 300 μm) demonstrating the thermally-induced self-healing behavior of a supramolecular polymeric material (a) and recovery of tensile modulus as a function of healing time (b). Adapted with permission from ref 93. Copyright 2010 American Chemical Society.

In addition to donor–acceptor π–π stacking interactions, hydrogen bonding and other types of non-covalent interactions,[94,95] a wide variety of healable materials have been implemented by exploiting reversible covalent bonds including Diels-Alder adducts,[96] dynamic covalent alkoxyamine bonds[97] and disulfides[98,99] to name just a few. Indeed, in the past decade, the field of thermoresponsive dynamically reconfigurable materials has experienced substantial growth, leading to the emergence of a new materials, among which covalent adaptable networks, CANs, stand out prominently. CANs combine the advantageous properties of thermosets and thermoplastics. They exhibit the mechanical strength and solvent resistance of thermosets while maintaining the ability to be reprocessed and reshaped like thermoplastics. This unique combination is enabled by the presence of dynamic bonds, usually dynamic covalent bonds, which, similar to earlier examples, can break and reform under specific conditions, enabling the polymer network to rearrange without compromising its integrity.

Tobolsky and co-workers identified stress relaxation in covalent polymer networks in the 1940s during their investigations into the viscoelastic behavior of polysulfide rubbers and other polymeric materials.[79,100] At that time, the stress relaxation behavior was tentatively associated with the exchange of disulfide bonds. However, the concept of chemically induced stress relaxation remained largely unexplored for several decades until the 1990s and early 2000s, when it gained renewed interest with a focus on reprocessable and recyclable thermoset materials.[101,102] One important milestone in reprocessable materials is the introduction of vitrimers,[103] as one new family of CANs, by Leibler and co-workers in 2011.[104] The first vitrimer materials applied a zinc catalyst to introduce dynamic covalent transesterification into classical thermosetting epoxy–acid and epoxy–anhydride systems. At room temperature, the materials behave like standard thermosets and do not flow. However, thanks to the catalyst-accelerated transesterification of β-hydroxy esters present in the network, the system can change its topology through bond reshuffling above a characteristic temperature. Solubility tests conducted at high temperature demonstrated that the network is essentially insoluble even after prolonged immersion in a good solvent, thus confirming the *associative* nature of the exchange –in contrast to a *dissociative* mechanism (*vide infra*). Such associative reaction mechanism involves bond exchange reactions where a new bond forms before the old bond breaks, maintaining the crosslinked structure throughout the process (Figure 12a). These materials can flow above a second glass transition temperature, coined T_v, which can be seen as a topology freezing transition temperature. Creep-recovery and stress relaxation experiments indicate that these materials exhibit Arrhenius-like behavior regarding their viscosity. Such a behavior is controlled by dynamic covalent exchange reactions and can be tuned by varying the type and amount of catalyst. The materials proposed by Leibler and co-workers are readily repairable and can be reshaped by localized heating to achieve a new equilibrium shape, provided the duration of the application of stress exceeds the relaxation time at the specified temperature.[105,106]

Another type of CAN, introduced by Drockenmuller and co-workers, involves dynamic covalent transalkylation exchange of C–N bonds.[107] In this case, poly(1,2,3-triazole)-containing networks were generated *via* the addition of an azide-alkyne monomer and a dibromo aliphatic species, without the use of solvent or catalyst. At elevated temperatures, the exchange between pendant halide functionalities and triazole rings enables complete stress

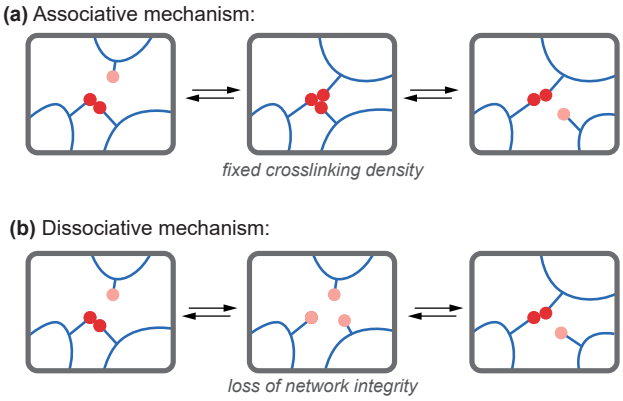


Figure 12: Schematic representations of associative (a) and dissociative (b) exchange reactions in structurally dynamic polymer networks.

relaxation. It was shown that the material can be reprocessed a number of cycles through a grinding compression molding process and even maintained its conducting properties after the reprocessing.

Leibler and co-workers have recently demonstrated that crosslinked polybutadiene can be turned into a material with vitrimer-like behavior by addition of a relatively low amount of Grubbs' second generation Ru catalyst.[108] Initially, an insoluble network was formed *via* radical-induced crosslinking of polybutadiene. The material was subsequently swollen in a good solvent to remove residual small molecule impurities through washing. After drying, the material was re-swollen in a Grubbs' catalyst solution. A control experiment was run whereby the catalyst was loaded into the material after being deactivated through cross-metathesis with an excess of vinyl ether, and both systems were investigated for their dynamic behavior. The authors demonstrated that the C−C metathesis catalyst facilitated exchange between the alkylidene catalyst and the double bonds in the polymer backbone, allowing for macroscopic flow. In cyclic creep-recovery experiments, the material exhibited continuous creep, with higher catalyst concentrations accelerating this phenomenon. Similar trends were observed at elevated temperatures and in stress relaxation experiments. In contrast, the control material with the deactivated catalyst showed no signs of creep or stress relaxation, confirming that the dynamic polymer reorganization is facilitated by the catalyst-mediated C−C metathesis. Recently, it has been demonstrated that dioxaborolane metathesis can be used to create vitrimers from commodity polymers including

poly(methyl methacrylate), polystyrene, and high-density polyethylene. Despite being permanently crosslinked, the final polymer networks can be reprocessed multiple times through extrusion or injection molding.[109]

CANs are also capable of undergoing structural reorganization *via* a dissociative mechanism (Figure 12). Such a mechanism involve the temporary breaking of bonds within the network, leading to a transient decrease in crosslink density. Upon reformation of the bonds, the network is restored. Dissociative polymer networks have been reported using a variety of reversible covalent bonds such as Diels-Alder adducts, thioesters, dynamic urea bonds, Schiff's bases, boronic esters and boroxines.[90,91] Wudl and co-workers developed a thermally remendable crosslinked polymeric material that behaves like traditional epoxy resins at standard operating temperatures. However, it can restore its properties after fracturing when heated to elevated temperatures.[110,111] Wudl's material takes advantage of the relatively mild temperature and rapid equilibrium of the maleimide–furane Diels-Alder dynamic bond. Indeed, at 120 °C the degree of inactive crosslinks was determined to be around 30%. Upon cooling, the system was shown to recover its initial crosslinking degree. Similar materials, produced using a solvent-free method, were reported to achieve healing efficiencies exceeding 80%. An alternative approach were reported by Lehn and co-workers exploiting a bifunctional dicyanofumarate in the presence of ethylene glycol based bifunctional fulvenes.[112] This method generated dynamic polymers, ultimately leading to self-healing materials through the introduction of fulvene crosslinkers. The reader is referred to recent reviews for more details on CANs exhibiting a dissociative mechanism.[90,91,113]

In summary, structurally dynamic polymers have made use of a wide variety of thermally activated reversible bonds. Among the materials presented (*vide supra*), CANs represent a significant advancement in polymer science, offering a unique combination of properties from both thermosets and thermoplastics. Whether based on associative or dissociative mechanisms, reconfigurable polymer networks lead to materials with< dynamic, adaptable properties. As research progresses, the potential of CANs and other dynamic polymer networks continues to expand, paving the way for new innovations in materials science.[114]

3 Beyond thermoresponsive materials: Light- and chemoresponsive behaviors in structurally dynamic polymers

In addition to the thermally triggered behavior seen in structurally dynamic polymers (Section 2), these materials may also respond to chemical species or stimuli that alter the stability of dynamic bonds. Several dynamic bonds, such as Schiff's base chemistry, macrocyclic host-guest complexation, boronic esters, and disulfides have been utilized to create materials that respond to, for example, pH changes, redox stimuli or the presence of specific chemical species (Figure 1). In this context, light –in combination, many times, with specific photoswitches– serves as an efficient and clean stimulus that can act non-invasively, offering excellent spatiotemporal control through modulation of properties like wavelength, intensity, and polarization.[115] Using light to trigger the reorganization of polymeric structures eliminates the risks associated with undesirable thermally initiated processes, such as irreversible degradation of the polymer backbone. Additionally, light demonstrates a high degree of orthogonality with various chemical species and functionalities.[116] Light excitation can also induce the reversible formation of new covalent bonds, particularly through cyclization reactions –a phenomenon that has been extensively utilized for the patterning and structuring of polymeric systems.[117,118]

Reversible cycloaddition reactions represent a prominent category of bond-forming processes widely used in polymer chemistry and materials science. Among these, the $[2 + 2]$ photodimerization of cinnamates (Figure 13a) is one of the most commonly employed cyclization reactions. This reaction is frequently utilized to produce insoluble crosslinked systems, rendering these materials suitable for applications like photoresists. Over the past few decades, the area of cinnamate-functionalized materials has significantly expanded, and crosslinked cinnamate-containing polymers have been applied in a variety of fields including photoalignment layers for LCs,[119] stimuli-responsive hydrogels,[120] and reconfigurable –via a dissociative mechanism– polymer networks and elastomeric materials.[121]

Another light-induced bond formation reaction is the $[2+2]$ photodimerization of coumarin derivatives. This process produces the corresponding cyclobutane dimer upon irradiation with light of $\lambda > 300$ nm, and can be reversed using UV light with a shorter

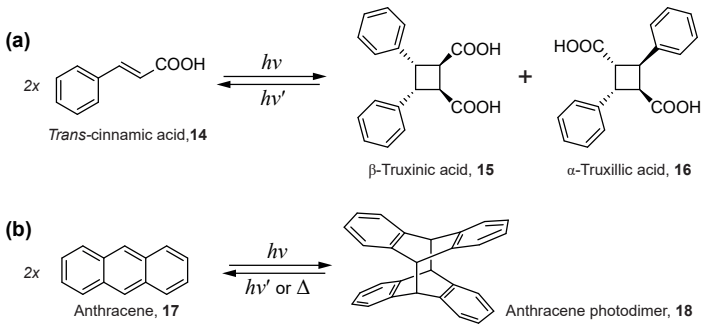


Figure 13: Examples of photoinduced cycloaddition reactions include *trans*-cinnamic acid (a) and anthracene (b). Figure illustrates two of the possible isomers formed from the photoinduced dimerization of *trans*-cinnamic acid.

wavelength. Similarly to cinnamate materials, coumarin-containing polymers have been used in LC photo-alignment,[122] and the development of a wide variety of patterned surfaces and stimuli-responsive materials,[123,124] including reconfigurable polymer networks.[125] In a recent study, Wu and colleagues demonstrated the use of the photodimerization of a coumarin derivative as a dynamic bond, creating a hydrogel by copolymerizing a coumarin-functionalized methacrylate monomer with acrylic acid in the presence of hexadecyltrimethylammonium chloride (CTAC) micelles (Figure 14).[126]

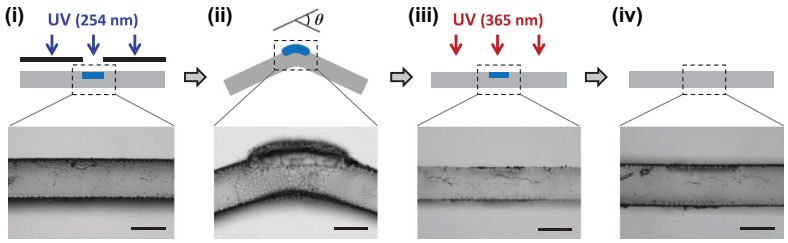


Figure 14: Schematic representation and images (i–iv) illustrating the reversible folding of a hydrogel strip controlled by light (scale bars: 500 μm). The sample is structured *via* a through-thickness light-induced sensitization process gradient with the aid of a photomask. Adapted with permission from ref 126. Copyright 2021 John Wiley & Sons, Inc.

The hydrogel exhibited a rewritable gradient structure owing to the presence of the photoresponsive coumarin functional moieties. The weakly charged poly(acrylic acid) formed a series of polyelectrolyte–surfactant complexes with CTAC, which increased the local concentration of coumarin moieties and, consequently, enhanced the dimerization efficiency. In addition, the polyelectrolyte–surfactant complexes served as physical crosslinkers to improve the mechanical performance of the hydrogel. Upon irradiation with 254 nm UV light, the coumarin dimers in the hydrogel cleaved, resulting in a swollen gel with a Young's mod-

ulus of 30 kPa. It was shown that the hydrogel can return to its original, more robust state, by first being exposed to an acidic aqueous solution and then irradiated with 365 nm UV light.

The photodimerization of anthracene is another well-established strategy for reversibly breaking and reforming covalent bonds through a photochemical reaction, following a dissociative mechanism similar to the previous examples in this section (Figure 13b). Many anthracene derivatives have the ability to photodimerize *via* a $[4 + 4]$ cycloaddition under excitation with UV light (λ of *ca.* 366 nm).[127] The resulting dimers, which increase the crosslinking degree of the antharacene-containing network, can be reverted thermally at relatively high temperatures (typically above 180 °C) or photochemically with UV light irradiation of $\lambda < 300$ nm. This phenomenon has been exploited to impart self-healing, recycling, and shape-memory behaviors in various polymer systems.[128] It is important to note that the reduced conjugated system and contorted geometry of the dimeric motifs –in comparison to the monomeric anthracene moieties– can per se significantly impact the photochromic and mechanical properties of the polymeric architecture they are incorporated to.[129]

In addition to the previous reactions, other photoinduced processes to reversibly reconfigure the structure of a polymer network at the molecular level include the photo-triggered radical mediated addition-fragmentation chain transfer (AFT), which is particularly attractive because of its relatively fast reaction kinetics. Similar to traditional reversible addition-fragmentation chain transfer (RAFT) reactions, AFT chemistry involving allyl sulfides combines the stability of covalent bonds with the reactivity typical of radical processes.[130,131] During this light-triggered process, each absorbed photon can initiate a series of bond exchanges, leading to rearrangement within the polymer network. However, the total number of cleaved bonds at any given moment remains relatively low. Bowman and co-workers have produced a series of polymer networks, *via* thiol–ene Click Chemistry, through the use of mixtures of di- and tetra-functional thiols and a reactive allyl sulfide derivative.[132] The resulting networks showed creep-recovery behavior upon irradiation with light of different wavelengths and demonstrated that AFT of allyl sulfides can be exploited to obtain dynamic materials. This concept has been further exploited for stress-managing in polymer glasses, composites and coatings.[133,134]

Matyjaszweski and co-workers have utilized trithiocarbonate and thiuram disulfide binding motifs to impart photoinduced dynamic behavior into a series of polymer networks (Figure 15).[135,136] Similar to processes in RAFT polymerization, both trithiocarbonate and thiuram disulfide groups can undergo reshuffling under UV and visible light irradiation, respectively, resulting in reversible bond rearrangement. Although trithiocarbonate-based materials exhibit self-healing properties, their applications may be limited due to the low stability of intermediate carbon radical species in air and at high temperatures, along with potential undesired recombination or termination processes. In contrast, thiuram disulfide materials demonstrate enhanced oxygen-tolerant self-healing capabilities.

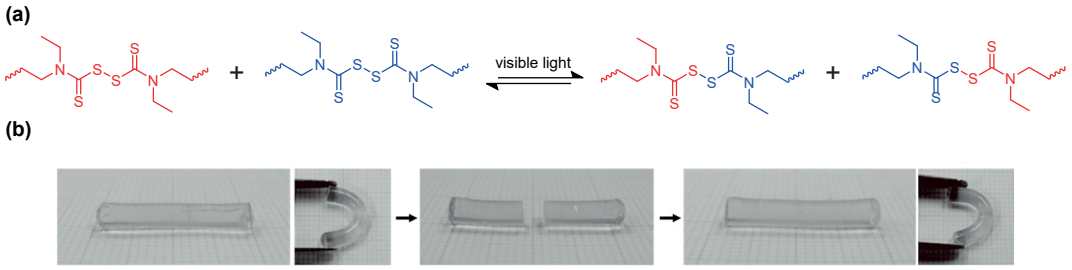


Figure 15: Visible light triggered shuffling of thiuram disulfide moieties (a) and self-healing (b). Adapted with permission from ref 136. Copyright 2012 John Wiley & Sons, Inc.

An alternative strategy for achieving photocontrol over structurally dynamic polymers involves the use of azobenzenes and other photoisomerizable moieties. Azobenzene is probably the most widely used class of photoswitches,[137] owing to its simple structure, rapid and straightforward synthesis, and robust and efficient photochemistry.[138,139] The photoinduced reversible isomerization of azobenzene derivatives results in significant changes in molecular geometry and polarity.[140] This phenomenon forms the basis for a wide variety of applications, ranging from optical data storage to photo-triggered substance release.[141,142] Indeed, azobenzene-containing materials, particularly liquid crystalline elastomers (LCEs) and networks, have been extensively studied over the past four decades for their use in light-controlled actuators and photodeformable materials.[7,143] In this regard, azobenzene converts light stimulation into specific deformations through a combination of photothermal and photochemical processes,[144] or primarily photochemical processes in some cases,[145] without the need for bond reshuffling. In some other cases, the isomerization of azobenzene is accompanied by a significant change in the connectivity of specific polymeric architectures. For instance, the complexation of CDs by azobenzene guests has proven highly

valuable, as the binding constants of the E and Z isomers toward the macrocycle differ significantly (Figure16a).[146] Such a phenomenon has been exploited to produce, for example, photoresponsive CD-containing hydrogel actuators and light-responsive adhesives.[147,148]

In CB[n] systems, as previously introduced (Section 1.1), azobenzene derivatives have primarily been used as second guests in heteroternary complexes by attaching to a water-soluble moiety or polymer.[149,150] There is a report in which azobenzene derivatives, substituted with two quaternized amines, serve as first guests for CB[8].[151] The binding mode of these doubly charged derivatives to CB[8] is determined by the nature of the cationic group. Trimethylammonium substituents induce 1:1 complexation and allow for the uptake of a second guest (Figure 16b), while a pyridinium substituents induce a 2:2 binding mode (Figure 16c). Upon isomerization to the Z form, both molecules take a 1:1 binding mode and do not allow for the uptake of another guest, likely due to the larger volume occupied by this isomer. This represents and alternative strategy to remotely control the connectivity of polymeric systems by means of light irradiation. In the context of boronic ester complexation, Kalow and co-workers have recently demonstrated that ortho-azobenzene boronic acids exhibit isomerism-dependent binding equilibria with diols (Figure 16d).[152] Small differences in the binding affinity to diols significantly impact the dynamic boronic ester bonds that hold together polymeric networks (organogels). Indeed, the viscoelasticity of the gels can be remotely controlled with visible light, including red light. As our understanding of the isomerization of azobenzenes and other photoswitches expands, it is essential to comprehend how specific phototriggered isomerization processes occur in both solution and bulk materials, or in the presence of specific host molecules, as significant differences can exist in the photoresponsive behavior of a given photoswitch. This knowledge will help identify new opportunities for controlling the structure of soft materials, such as polymer networks, gels, and LCs, using light.

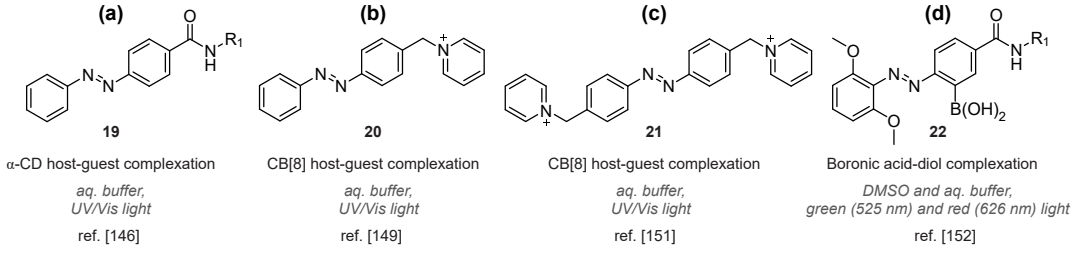


Figure 16: Examples of incorporating azobenzenes into polymer constructs that result in light-responsive, structurally dynamic materials.

In addition to the thermal- and light-induced responsive behavior, another possible stimulation is the triggering associated with the chemical composition of the environment. In contrast to previously introduced examples, chemical stimulation offers unique advantages in terms of specificity, mild operating conditions, and versatility, particularly in complex and sensitive environments like biological systems.[153] While thermal and light stimuli are valuable for their ability to be externally applied and controlled, chemical stimuli excel in applications requiring selective, reversible, and energy-efficient responses. Their speed can range from fast (seconds to minutes) to slow (hours) depending on the kinetics of chemical reaction involved, the concentration and diffusion rates of the triggering species, and the polymer architecture among other aspects. Nonetheless, chemical responses are generally slower than the typical rapid reactions triggered by light in dynamic polymeric materials. As already mentioned, the triggering associated with changes in pH is indeed quite frequent, as pH sensitivity is inherent to many dynamic bonds including imines and Coulombic interactions.[83] Beyond pH, disulfide bonds, for example, can undergo reversible exchange reactions under redox conditions.[98] In the presence of a reducing agent, such as glutathione, disulfide bonds switch to thiols, which can revert back to disulfides bond under oxidative conditions. Additionally, boronic acids can react with diols to form boronic esters, and this reaction is reversible depending on the pH and the presence of competing diols (for example, specific monosaccharides such as glucose).[154] These transformations occur under thermodynamic control, ensuring that the dynamic bonds respond appropriately to changes in the environment.

One less explored mechanism in chemoresponsive structurally dynamic polymers is the induction of specific conformational changes through the reversible formation and cleavage of dynamic binding motifs. A notable example of this is an LCE developed by Rowan and co-workers that incorporates metal ion-binding sites derived from 2,6-bis(2-benzimidazolyl)pyridine (Bip).[155] In the absence of metal ions, the Bip-derived binding motifs adopt a rod-like conformation and, overall, the crosslinked material exhibits liquid crystal (LC) behavior. In the presence of metal ions (Fe^{2+}), however, the Bip-derived binding motifs form metal-ligand complexes causing a large rearrangement of the polymer network and the loss of the LC properties. Such a LC-to-isotropic transition upon metal ion binding, in well-aligned monolithic samples, forms the basis for actuation, and enables functions such as weight lifting. It was also demonstrated that various metal ions, including

those from transition metals and lanthanide salts, can serve as effective actuation triggers. These actuation mechanisms could be utilized in controlled substance delivery systems and sensing devices for parameters such as humidity, metal ions, and pH.

4 Outlook and conclusions

Our capability to develop dynamic binding chemistries and apply them in polymer science with ease and precision is crucial for creating innovative materials that can respond predictably to specific stimuli, self-heal, adapt, or even be programmed to perform multiple tasks. Such properties are highly relevant in a number of contexts including chemical recyclability,[156] soft robotics,[157] and energy conversion and storage.[158] Breakthroughs in these areas will of course be the result of a multidisciplinary collaboration among chemists, physicists, and engineers each contributing to the complex puzzle of materials innovation. Progress will be driven by both industrial and societal demands –such as the need to rethink polymer design and manufacturing for effective reuse, waste collection, and recycling– as well as by curiosity-driven research. As the field of structurally dynamic polymers continues to evolve, it is essential to deepen and strengthen our fundamental understanding of the complex behavior of dynamic bonds, CANs and supramolecular materials –a know-<ledge that not only underpins existing technologies,[159,160] but also drives the development of new applications and materials.[161] A notable example is the broad family of "flowable" crosslinked polymers (Section 2). These materials behave like conventional thermosets under serving (or operating) conditions but can be reprocessed like thermoplastics when a chemical reaction, such as bond exchange, is activated (primarily by heat). Nevertheless, for practical industrial applications, bond exchange should be a highly activated and rapid reaction during polymer processing to prevent degradation –at temperatures of 200 to 250 °C typically– while, at the same time, remain sufficiently slow, or even dormant, under normal operating conditions to suppress creep. Such a challenge, already recognized in pioneering reports,[162] has been at the focus of substantial theoretical and experimental research effort for the last 50 years. Examples of creep resistant yet dynamic polymer networks are beginning to appear (see Section 2). Some of them achieve their properties by managing the availability of catalysts or additives that are external to the composition of

the polymer networks. Additionally, the presence of common functional groups within the polymer architecture, located in spatial proximity to specific dynamic or covalent bonds, can significantly influence chemical exchange. This phenomenon, known in organic chemistry as neighboring group participation (NGP),[163] has become an exciting design concept for tuning reactive bonds and controlling the dynamic behavior of dynamic covalent networks.[104] Our group has exploited in the past the benefits of NGP effects to develop a diverse range of LC materials.[164,165] Currently, one of our main focuses is the reversible condensation of *ortho*-substituted aryl aldehydes/ketones boronic acids (Figure 17a) and amines, and α-effect amines (nucleophiles including hydrazides and aminooxy derivatives). Quantitative condensation takes place in aqueous media, at mM concentrations and neutral pH, when a boronic acid group is in close proximity (*ortho* position) to the carbonyl group of the electrophile.[166,167] The remarkable stability of these adducts is associated with specific interactions between the electron-rich imine nitrogen and the electron deficient boron. The imine adduct **23** depicted in Figure 17b exhibits a K_d (observed) of ca. 10 mM in aqueous media (pH 7.0). In contrast, the imine formed from the condensation of 2-methoxy-1-ethanamine and 3-formylphenylboronic acid –analogous to **23**, but without any NGP effects– exhibits a much higher K_d of about 5 M, indicating significantly lower stability.[168] Since the association constants (K_a values fall in the $10^2 - 10^7\,\mathrm{M}^{-1}$ range depending on the pair of nucleophile and electrophile, see adducts **23**–**25** in Figure 17) and kinetics (typical k_{on} values in the $10^2 - 10^3\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ range) of boron-stabilized imine adducts at physiological pH cover a wide spectrum range, we believe the potential for material properties tunability is exceptional. Our aim is to explore this dynamic bond for the development of tunable viscoelastic hydrogel –designed for use as injectable local drug delivery systems and adaptable cell niches– as well as polymeric micelles and DNA-polymer hybrid materials.

Expanding our fundamental understanding of dynamic bond behavior, whether in aqueous media or in bulk –with the former being especially relevant for biomedical applications– will be essential for improving the design of dynamic polymer materials and tackling challenges in, for example, biomedicine[169,170] and plastic recycling.[156] Indeed, it has been shown that commodity polymers can be modified with dynamic covalent bonds to enable reprocessing, enhance upcycling of waste products, or recover the material value of individual plastics with ease.[109,171,172]

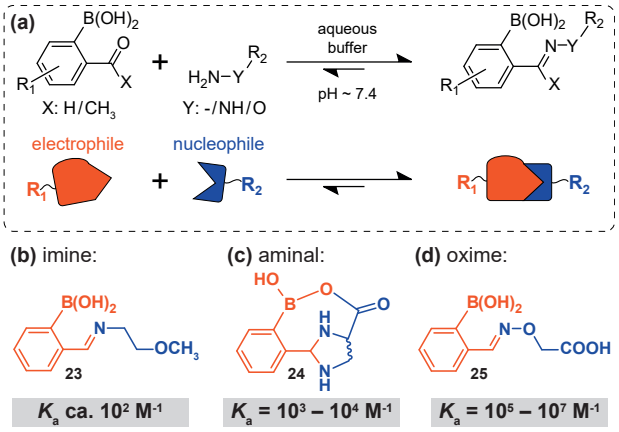


Figure 17: Ortho-substituted aryl aldehyde boronic acids react rapidly (k_{on} ca. $10^2 - 10^3$ $M^{-1}s^{-1}$) with amine-based nucleophiles in neutral aqueous media (a) to yield stable yet reversible adducts (b–d).

In addressing biomedical challenges, the integration of both dynamic bonds (such as host-guest complexation) and reactive bonds (e.g., acrylate groups) within the same polymeric structure presents a particularly promising strategy for creating synthetic surrogates of the natural extracellular matrix or viscoelastic inks for 3D printing in tissue engineering.[173] Polymer networks incorporating covalent and dynamic bonds –supramolecular or dynamic covalent– have also proven particularly valuable in creating hydrogels with extreme toughness,[174] as well as glassy gels that are transparent and rigid like Plexiglas® while also being stretchy, adhesive, self-healing, and electrically conductive.[175,176] Such crosslinked networks could become significant in energy storage and soft robotics, where there is a demand for robust, dynamic, and multifunctional materials.[177] Additional areas that could benefit from the use of structurally dynamic polymers include underwater adhesives and sealants,[178] responsive coatings,[179,180] haptics,[181] additive manufacturing,[182,183] smart textiles,[184] and more.

A key takeaway is that the thoughtful integration of dynamic bonds into polymeric constructs, such as networks, block copolymers and polymeric micelles, creates valuable structurally dynamic materials. This concept is illustrated in this brief review through selected examples and research projects, including several conducted in Zaragoza. While some aspects and trends –such as the use orthogonal binding chemistries,[185] transient dynamic binding in non-equilibrium systems,[186] and the development of dynamic polymers activated by mild stimuli like visible or near-infrared (NIR) light,[187,188] which are essential for biological and medical applications– are only briefly discussed, the selected examples high-

light significant progress in the field over the past few years and underscore the crucial role that the dynamic bonds will continue to play in advancing future materials and polymer technologies.

Acknowledgements

I would like to sincerely thank the Real Academia de Ciencias de Zaragoza for selecting me as the recipient of the Premio de Investigación 2024 en la Sección de Químicas. Although this award is individual, it reflects the contributions of many who have played a key role in my education and a significant part of the research outlined in this review. I feel fortunate to work alongside such talented and dedicated individuals. I am indebted to Luis Oriol, Carlos Sánchez and Oren Scherman, for their mentoring and support throughout my PhD, postdoctoral, and senior research stages, as well as sparking my interest in polymer chemistry and self-assembly. I extend my thanks to my PhD students Enrique Guerreiro, Alejandro Postigo, Mehrzad Javadzadeh, Joseba Ruiz, Rahul Singh Yadav, Santiago Sarasa and María Sofía Navarrete for their effort and commitment. Additionally, I am thankful to the Liquid Crystals and Polymers group for their continued support, with special appreciation to Silvia Hernández, whose contributions have been deeply enriching and extend far beyond our scientific collaboration.

I would like to thank my host research institutions in Spain, including Universidad de Zaragoza and Instituto de Nanociencia y Materiales de Aragón, INMA (CSIC- Universidad de Zaragoza). I also thank the support from Gobierno de Aragón and Ministerio de Ciencia, Innovación y Universidades, as well as from my industrial partners, Schlumberger and Certest Biotec. Over the past seven years, my research activity in Zaragoza has been made possible through various projects: RYC-2015-18471, CTQ2017-84087-R, PID2020-113003GB-I00, CNS2022-135887, PCI2023-143390 and the Marie Skłodowska-Curie Innovative Training Network STORM-BOTS.

References

[1] C.S. Brazel, S.L. Rosen, *Fundamental Principles of Polymeric Materials*, Wiley, 2012.

[2] H. Staudinger, *Ber. Dtsch. Chem. Ges.* 1920, **53**, 1073–1085.

[3] W. Zhang, Y. Jin, Dynamic Covalent Chemistry: *Principles, Reactions, and Applications*, Wiley, Hoboken, 2017

[4] S. Samanta, S. Kim, T. Saito, A.P. Sokolov, *J. Phys. Chem. B* 2021, **125**, 9389–9401.

[5] S.J. Rowan, S.J. Cantrill, G.R.L. Cousins, J.K.M. Sanders and J.F. Stoddart, *Angew. Chem., Int. Ed.*, 2002, **41**, 898–952.

[6] S.J.D. Lugger, S.J.A. Houben, Y. Foelen, M.G. Debije, A.P.H.J. Schenning, D.J. Mulder.*Chem. Rev.* 2022, **122**, 4946–4975.

[7] T. White, D. Broer, *Nat. Mater.* 2015, **14**, 1087–1098

[8] R.J. Wojtecki, M.A. Meador, S.J. Rowan, *Nat. Mater.* 2011, **10**, 14–27.

[9] L. Brunsveld, B.J.B. Folmer, E.W. Meijer, R.P. Sijbesma, *Chem. Rev.* 2001, **101**, 4071–4097.

[10] A. Ciferri, *Supramolecular Polymers*, Taylor and Francis Group: New York, 2005

[11] R.B. Martin, *Chem. Rev.* 1996, **96**, 3043–3064.

[12] P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, 1953.

[13] C.G. Odian, *Principles of Polymerization*, Wiley: New York, 2004.

[14] A. Ciferri, *Macromol. Rapid. Commun.* 2002, **23**, 5111–529.

[15] M.E. Cates, *Macromolecules* 1987, **20**, 2289–2296.

[16] M. . Cates, *J. Phys. Chem.* 1990, **94**, 371–375.

[17] R.P. Sijbesma, F. H.Beijer, L. Brunsveld, B. J.B. Folmer, J.H.K.K. Hirschberg, R.F.M. Lange, J.K.L. Lowe, E.W. Meijer, *Science* 1997, **278**, 1601–1604.

[18] M.J. Krische, J.-M. Lehn, *The Utilization of Persistent H-Bonding Motifs in the Self-Assembly of Supramolecular Architectures*, Springer, 2000.

[19] R.P. Sijbesma, E.W. Meijer, *Chem. Commun.* 2003, **1**, 5–16.

[20] E.A. Appel, J. del Barrio, X.J. Loh, O.A. Scherman, *Chem. Soc. Rev.* 2012, **41**, 6195–6214.

[21] S.H.M. Söntjens., R.P. Sijbesma, M.H.P. van Genderen, E.W. Meijer *J. Am. Chem. Soc.* 2000, **122**, 7487–7493.

[22] X. Yang, F. Hua, K. Yamato, E. Ruckenstein, B. Gong, W. Kim, C. Y. Ryu, C.Y. *Angew. Chem. Int. Ed.* 2004, **43**, 6471–6474.

[23] D.A. Leigh, C.C. Robertson, A.M.Z. Slawin, P.I.T. Thomson, *J. Am. Chem. Soc.* 2013, **135**, 9939–9943.

[24] Y. Sun, J. Gu, H. Wang, J.L. Sessler, P. Thordarson, Y.-J. Lin, H. Gong, *J. Am. Chem. Soc.* 2019, **141**, 20146–20154.

[25] R.F.M. Lange, M.V. Gurp and E.W. Meijer, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 3657–3670.

[26] B.J.B. Folmer, R.P. Sijbesma, R.M. Versteegen, J.A.J. van der Rijt, E.W. Meijer, E.W. *Adv. Mater.* 2000, **12**, 874–878.

[27] O.A. Scherman, G.B.W. Ligthart, H. Ohkawa, R.P. Sijbesma, E.W. Meijer, E.W. *Proc. Natl. Acad. Sci. U.S.A.* 2006, **103**, 11850–11855.

[28] R. Hogg, R.G. Wilkins, *J. Chem. Soc.* 1962, 341–350.

[29] M. Heller and U.S. Schubert, *Macromol. Rapid Commun.* 2001, **22**, 1358–1363.

[30] B.G.G. Lohmeijer, U.S. Schubert, *J. Polym. Sci., Part A: Polym. Chem.* 2003, **41**, 1413–1427.

[31] B.G.G. Lohmeijer, U.S. Schubert, *J. Polym. Sci., Part A: Polym. Chem.* 2004, **42**, 4016–4027.

[32] L. Shi, P. Ding, Y. Wang, Y. Zhang, D. Ossipov, J. Hilborn, *Macromol. Rapid Commun.* 2019, **40**, 1800837

[33] G.W. Gokel, W.M. Leevy, M.E. Weber, *Chem. Rev.* 2004, **104**, 2723–2750.

[34] K.A. Connors, *Chem. Rev.* 1997, **97**, 1325–1358.

[35] M.V. Rekharsky, Y. Inoue, *Chem. Rev.* 1998, **98**, 1875–1918.

[36] J. Lagona, P. Mukhopadhyay, S. Chakrabarti, L. Isaacs, *Angew. Chem. Int. Ed.* 2005, **44**, 4844–4870

[37] S.J. Barrow, S. Kasera, M. J. Rowland, J. del Barrio, O.A. Scherman *Chem. Rev.* 2015, 115, 12320-12406.

[38] B. Zheng, F. Wang, S. Donga, F. Huang, *Chem. Soc. Rev.* 2012, **41**, 1621–1636.

[39] Z. Duan, F. Xu, X. Huang, Y. Qian, H. Li, W. Tian, *Macromol. Rapid Commun.* 2022, **43**, 2100775.

[40] B.L. Allwood, N. Spencer, H. Shahriari-Zavareh, J.F. Stoddart and D.J. Williams, *J. Chem. Soc., Chem. Commun.* 1987, 1064–1066.

[41] P.R. Ashton, T.T. Goodnow, A.E. Kaifer, M.V. Reddington, A.M.Z. Slawin, N. Spencer, J.F. Stoddart, C. Vicent and D.J. Williams, *Angew. Chem., Int. Ed. Engl.* 1989, **28**, 1396–1399.

[42] M. Liu, X. Yan, M. Hu, X. Chen, M. Zhang, B. Zheng, X. Hu, S. Shao, F. Huang, *Org. Lett.* 2010, **12**, 2558–2561.

[43] C. Yao, J. Zhang, M. Cheng, Q. Sun, Y. Pan, J. Jiang, L. Wang, *Macromol. Rapid Commun.* 2018, **39**, 1700218.

[44] S. Dong, Y. Luo, X. Yan, B. Zheng, X. Ding, Y. Yu, Z. Ma, Q. Zhao, F. Huang, *Angew. Chem. Int. Ed.* 2011, **50**, 1905–1909.

[45] J. Chen, X. Yan, X. Chi, X. Wu, M. Zhang, C. Han, B. Hu, Y. Yu, F. Huang, *Polym. Chem.* 2012, **3**, 3175–3179.

[46] Q. Chena, K. Zhu, *Chem. Soc. Rev.* 2024, **53**, 5677–5703.

[47] E.M. Martin del Valle, *Process Biochem.* 2004, **39**, 1033–1046.

[48] Z. Liu, Y. Liu, *Chem. Soc. Rev.* 2022, **51**, 4786–4827.

[49] A. F. D. de Namor, R. M. Cleverley, M. L. Zapata-Ormachea, *Chem. Rev.* 1998, 98, 2495-2526.

[50] T. Ogoshi, T. Yamagishi, Y. Nakamoto, *Chem. Rev.* 2016, **116**, 7937–8002.

[51] D. Xia, P. Wang, X. Ji, N.M. Khashab, J.L. Sessler, F. Huang, *Chem. Rev.* 2020, **120**, 6070–6123.

[52] D. Lucas, T. Minami, G. Iannuzzi, L. Cao, J. B. Wittenberg, P. Anzenbacher Jr., L. Isaacs, *J. Am. Chem. Soc.* 2011, **133**, 17966–17976.

[53] M. M. Ayhan, H. Karoui, M. Hardy, A. Rockenbauer, L. Charles, R. Rosas, K. Udachin, P. Tordo, D. Bardelang, O. Ouari, *J. Am. Chem. Soc.* 2015, **137**, 10238–10245.

[54] H. Yin, Q. Cheng, D. Bardelang, R. Wang, *JACS Au* 2023, **3**, 2356–2377.

[55] B. Vinciguerra, L. Cao, J. R. Cannon, P. Y. Zavalij, C. Fenselau, L. Isaacs, *J. Am. Chem. Soc.* 2012, **134**, 13133–13140.

[56] L. Isaacs, *Acc. Chem. Res.* 2014, **47**, 2052–2062.

[57] W.L. Mock, N.Y. Shih, *J. Org. Chem.* 1983, **48**, 3618–3619.

[58] P. Balaram, *ACS Omega* 2024, **9**, 4162–4165.

[59] K. Kim, *Chem. Soc. Rev.* 2002, **31**, 96–107.

[60] H.-J. Kim, J. Heo, W. S. Jeon, E. Lee, J. Kim, S. Sakamoto, K. Yamaguchi, K. Kim, K. *Angew. Chem. Int. Ed.* 2001, **40**, 1526–1529.

[61] M.E. Bush, N.D. Bouley, A.R. Urbach, *J. Am. Chem. Soc.* 2005, **127**, 14511–14517.

[62] E. Masson, X. Ling, R. Joseph, L. Kyeremeh-Mensaha, X. Lu, *RSC Adv.* 2012, **2**, 1213–1247.

[63] J. Murray, K. Kim, T. Ogoshi, W. Yao, B.C. Gibb, *Chem. Soc. Rev.* 2017, **46**, 2479–2496.

[64] U. Rauwald, O.A. Scherman, *Angew. Chem. Int. Ed.* 2008, **47**, 3950–3953.

[65] U. Rauwald, J. del Barrio, X.J. Loh, O.A. Scherman, *Chem. Commun.* 2011, **47**, 6000–6002.

[66] X.J. Loh, J. del Barrio, P.P.C. Toh, T.-C. Lee, D. Jiao, U. Rauwald, E.A. Appel, O.A. Scherman, *Biomacromolecules* 2012, **13**, 84–91.

[67] E.A. Appel, F. Biedermann, U. Rauwald, S.T. Jones, J.M. Zayed, O.A. Scherman, *J. Am. Chem. Soc.* 2010, **132**, 14251–14260.

[68] C.S.Y. Tan, J. del Barrio, J. Liu, O.A. Scherman, *Polym. Chem.* 2015, **6**, 7652–7657.

[69] E.A. Appel, X J. Loh, S.T. Jones, F. Biedermann, C.A. Dreiss, O.A. Scherman, *J. Am. Chem. Soc.* 2012, *134*, 11767–11773.

[70] J. Zhang, J.; R.J. Coulston, S.T. Jones, J. Geng, O.A. Scherman, C. Abell, *Science* 2012, **335**, 690–694

[71] J. del Barrio, J. Liu, R.A. Brady, C.S.Y. Tan, S. Chiodini, M. Ricci, R. Fernández-Leiro, C.-J. Tsai, P. Vasileiadi, L. Di Michele, D. Lairez, C. Toprakcioglu, O.A. Scherman, *J. Am. Chem. Soc.* 2019, **141**, 14021–14025.

[72] Y. Lan, Y. Wu, A. Fox, O.A. Scherman, *Angew. Chem. Int. Ed.* 2014, **53**, 2166–2169.

[73] H.D. Nguyen, D.T. Dang, J.L.J. van Dongen, L. Brunsveld, *Angew. Chem. Int. Ed.* 2010, **49**, 895–898.

[74] S. J. Rowan, S.J. Cantrill, G.R. Cousins, J.K. Sanders, J.F. Stoddart, *Angew. Chem., Int. Ed.* 2002, **41**, 898–952

[75] F.B.L. Cougnon, A.R. Stefankiewicz, S. Ulrich, *Chem. Sci.* 2024, **15**, 879–895.

[76] P.T. Corbett, J. Leclaire, L. Vial, K.R. West, J.-L. Wietor, J.K.M. Sanders, S. Otto, *Chem. Rev.* 2006, **106**, 3652–3711.

[77] Y. Jin, C. Yu, R.J. Denman, W. Zhang, *Chem. Soc. Rev.* 2013, **42**, 6634–6654

[78] Y. Zhu, H. Yang, Y. Jin, W. Zhang, *Chem. Mater.* 2013, **25**, 3718–3723.

[79] M.D. Stern, A.V. Tobolsky *J. Chem. Phys.* 1946, **14**, 93–100.

[80] B.D. Fairbanks, S.P. Singh, C.N. Bowman, K.S. Anseth, *Macromolecules* 2011, **44**, 2444–2450.

[81] K.N. Plunkett, M.L. Kraft, Q. Yu, J.S. Moore, *Macromolecules* 2003 **36**, 3960–3966

[82] W.G. Skene, J.-M.P. Lehn, *Proc. Natl. Acad. Sci.* 2004, **101**, 8270–8275.

[83] B. Yang, Y. Zhang, X. Zhang, L. Tao, S. Li, Y. Wei, *Polym. Chem.* 2012, **3**, 3235–3238.

[84] J.N. Cambre, B.S. Sumerlin, *Polymer* 2011, **52**, 4631–4643.

[85] B. Marco-Dufort, M.W. Tibbitt, *Mater. Today Chem.*, 2019, **12**, 16–33.

[86] O.R. Cromwell, J. Chung, Z. Guan, *J. Am. Chem. Soc.* 2015 **137**, 6492–6495.

[87] P. Chakma, D. Konkolewicz, *Angew. Chem. Int. Ed.* 2019, **58**, 9682–9695.

[88] F. García, M.M.J. Smulders, *J. Polym. Sci. Part A: Polym. Chem.* 2016, **54**, 3551–3577.

[89] W.K. Zou, J.T. Dong, Y.W. Luo, Q. Zhao, T. Xie, *Adv. Mater.* 2017, **29**, 1606100.

[90] Z. Lei, H. Chen, S. Huang, L.J. Wayment, Q. Xu, W. Zhang *Chem. Rev.* 2024, **124**, 7829–7906.

[91] N. Zheng, Y. Xu, Q. Zhao, T. Xie, *Chem. Rev.* 2021, **121**, 1716-1745.

[92] S. Burattini, H.M. Colquhoun, J.D. Fox, D. Friedmann, B.W. Greenland, P.J.F. Harris, W. Hayes, M.E. Mackay, S.J. Rowan, *Chem. Commun.* 2009, 6717–6719.

[93] S. Burattini, B.W. Greenland, D. Hermida Merino, W. Weng, J. Seppala, H.M. Colquhoun, W. Hayes, M.E. Mackay, I.W. Hamley, S.J. Rowan *J. Am. Chem. Soc.* 2010 **132**, 12051–12058.

[94] L. Lewis, K. Stewart, M. Anthamatten, *Macromolecules* 2014, 47, 729-740.

[95] Y. Liu, L. Wang, L. Zhao, Y. Zhang, Z.-T. Li, F. Huang, *Chem. Soc. Rev.* 2024, 53, 1592-1623.

[96] B.J. Adzima, H.A. Aguirre, C.J. Kloxin, T.F. Scott, C.N. Bowman, *Macromolecules* 2008, 41, 9112–9117.

[97] H. Otsuka, K. Aotani, Y. Higaki, Y. Amamoto, A. Takahara, *Macromolecules* 2007, **40**, 1429–1434.

[98] R. Martin, A. Rekondo, A.R. de Luzuriaga, G. Cabanero, H.J. Grande, I. Odriozola, *J. Mater. Chem. A*, 2014, **2**, 5710–5715.

[99] C. King-Poole, H. Thérien-Aubin, *Adv. Funct. Mater.* 2024, 2405608.

[100] A.V. Tobolsky, *J. Appl. Phys.* 1956, **27**, 673–685.

[101] L. Leibler, M. Rubinstein, R.H. Colby, *J. Phys. II France* 1993, **3**, 1581–1590.

[102] T. Maeda, H. Otsuka, A. Takahara, *Prog. Polym. Sci.* 2009, **34**, 581–604.

[103] D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler, *Science* 2011, **334**, 965–968.

[104] M. Guerre, C. Taplan, J.M. Winne, F.E. Du Prez, *Chem. Sci.* 2020, **11**, 4855–4870.

[105] M. Capelot, M.M. Unterlass, F. Tournilhac, L. Leibler, *ACS Macro Lett.*, 2012, **1**, 789–792

[106] M. Capelot, D. Montarnal, F. Tournilhac, L. Leibler, *J. Am. Chem. Soc.*, 2012, **134**, 7664–7667

[107] M.M. Obadia, B.P. Mudraboyina, A. Serghei, D. Montarnal, E. Drockenmuller, *J. Am. Chem. Soc.* 2015, **37**, 6078–6083.

[108] Y.-X. Lu, F. Tournilhac, L. Leibler, Z. Guan, *J. Am. Chem. Soc.* 2012, **134**, 8424–8427

[109] M. Röttger, T. Domenech, R. van der Weegen, A. Breuillac, R. Nicoläy, L. Leibler, *Science* 2017, **356**, 62–65.

[110] X. Chen, M.A. Dam, K. Ono, A. Mal, H. Shen, S.R. Nutt, K. Sheran, F. Wudl, *Science* 2002, **295**, 1698–1702

[111] X. Chen, F. Wudl, A.K. Mal, H. Shen, S.R. Nutt, *Macromolecules* 2003, **36**, 1802–1807.

[112] P. Reutenauer, E. Buhler, P.J. Boul, S.J. Candau, J.M. Lehn, *Chem. Eur. J.* 2009, **15**, 1893–1900.

[113] L. Li, X. Peng, D. Zhu, J. Zhang, P. Xiao, *Macromol. Chem. Phys.* 2023, **224**, 2300224.

[114] V. Zhang, B. Kang, J.V. Accardo, J.A. Kalow, *J. Am. Chem. Soc.*, 2022, **144**, 22358–22377

[115] M.-M. Russew, S. Hecht, *Adv. Mater.* 2010, **22**, 3348–3360.

[116] A. Goulet-Hanssens, F. Eisenreich, S. Hecht, *Adv. Mater.* 2020, **32**, 1905966.

[117] J. del Barrio, C. Sánchez-Somolinos, *Adv. Opt. Mater.* 2019, **7**, 1900598.

[118] T. Hughes, G.P. Simon, K. Saito, *Mater. Horiz.* 2019, **6**, 1762–1773.

[119] N. Kawatsuki, K. Goto, T. Kawakami, T. Yamamoto, *Macromolecules* 2002, **35**, 706–713.

[120] K. Takada, *Polym. J.* 2023, **55**, 1023–1033.

[121] H. Masai, T. Nakagawa, J. Terao, *Polym. J.* 2024, **56**, 297–307.

[122] M. Obi, S. Morino, K. Ichimura, *Macromol. Rapid Commun.* 1998, **19**, 643.

[123] A. Concellon, A.P.H.J. Schenning, P. Romero, M. Marcos, J.L. Serrano, *Macromolecules* 2018, **51**, 2349–2358.

[124] A. Concellón, P. Romero, M. Marcos, J. Barberá, C. Sánchez-Somolinos, M. Mizobata, T. Ogoshi, J.L. Serrano, J. del Barrio, *J. Org. Chem.* 2020, **85**, 8944–8951.

[125] S.A. Safavi-Mirmahalleh, M. Golshan, B. Gheitarani, M.S. Hosseini, M. Salami-Kalajahi, *Eur. Polym. J.* 2023, **198**, 112430.

[126] C.N. Zhu, C.Y. Li, H. Wang, W. Hong, F. Huang, Q. Zheng, Z.L. Wu, *Adv. Mater.* 2021, **33**, 2008057.

[127] H. Bouas-Laurent, J.-P. Desvergne, A. Castellan, R. Lapouyade, *Chem. Soc. Rev.* 2000, **29**, 43–55.

[128] J. Van Damme, F. Du Prez, *Prog. Polym. Sci.* 2018, **82**, 92–119.

[129] K.A. Günay, T.L. Ceccato, J.S. Silver, K.L. Bannister, O.J. Bednarski, L.A. Leinwand, K.S. Anseth, *Angew. Chem. Int. Ed.* 2019, **58**, 9912–9916.

[130] C.J. Kloxin, T.F. Scott, C.N. Bowman, *Macromolecules* 2009, **42**, 2551–2556.

[131] C.R. Fenoli, C.N. Bowman, *Polym. Chem.* 2014, **5**, 62–68.

[132] T.F. Scott, A.D. Schneider, W.D. Cook, C.N. Bowman, *Science* 2005, **308**, 1615–1617.

[133] T.F. Scott, R.B. Draughon, C.N. Bowman, *Adv. Mater.* 2006, **18**, 2128–2132.

[134] A.M. Mineo, M.E. Buck, R. Katsumata, *J. Polym. Sci.* 2021, **59**, 2719–2729.

[135] Y. Amamoto, J. Kamada, H. Otsuka, A. Takahara, K. Matyjaszewski, *Angew. Chem., Int. Ed.* 2011, **50**, 1660–1663.

[136] Y. Amamoto, H. Otsuka, A. Takahara, K. Matyjaszewski, *Adv. Mater.* 2012, **24**, 3975–3980

[137] F.A. Jerca, V.V. Jerca, R. Hoogenboom, *Nat. Rev. Chem.* 2022, **6**, 51–69.

[138] J.A. Delaire, K. Nakatani, *Chem. Rev.* 2000, **100**, 1817–1846.

[139] A. Natansohn, P. Rochon, *Chem. Rev.* 2002, **102**, 4139–4176.

[140] M. Sato, T. Kinoshita, A. Takizawa, Y. Tsujita, *Macromolecules* 1988, **21**, 1612–1616.

[141] S. Hvilsted, C. Sánchez, R. Alcalá, *J. Mater. Chem.* 2009, **19**, 6641–6648.

[142] J. del Barrio, L. Oriol, C. Sánchez, J.L. Serrano, A. Di Cicco, P. Keller, M.-H. Li, *J. Am. Chem. Soc.* 2010, **132**, 3762–3769.

[143] H.K. Bisoyi, Q.L. *Chem. Rev.* 2016, **116**, 15089–15166.

[144] A. Gelebart, A.D. Jan Mulder, M. Varga, A. Konya, G. Vantomme, E.W. Meijer, R.L.B. Selinger, D.J. Broer, *Nature* 2017, **546**, 632–636.

[145] P. Sartori, R.S. Yadav, J. del Barrio, A. DeSimone, C. Sánchez-Somolinos, *Adv. Sci.* 2024, **11**, 2308561.

[146] I. Tomatsu, A. Hashidzume, A. Harada, *J. Am. Chem. Soc.* 2006, **128**, 2226–2227.

[147] K. Iwaso, Y. Takashima, A. Harada, *Nat. Chem.* 2016, **8**, 625–632.

[148] A. Harada, Y. Takashima, M. Nakahata, *Acc. Chem. Res.* 2014, **47**, 2128–2140.

[149] J. del Barrio, P.N. Horton, D. Lairez, G.O. Lloyd, C. Toprakcioglu, O.A. Scherman, *J. Am. Chem. Soc.* 2013, **135**, 11760–11763.

[150] C.S.Y. Tan, J. del Barrio, J. Liu, O.A. Scherman, *Polym. Chem.* 2015, **6**, 7652–7657.

[151] J. del Barrio, S.T.J. Ryan, P.G. Jambrina, E. Rosta, O.A. Scherman, *J. Am. Chem. Soc.* 2016, **138**, 5745–5748.

[152] J.V. Accardo, E.R. McClure, M.A. Mosquera, J.A. Kalow, *J. Am. Chem. Soc.* 2020, **142**, 19969–19979.

[153] M. Gosecka, M. Gosecki, *Acta Biomater.* 2020, **116**, 32–66.

[154] V. Yesilyurt, M.J. Webber, E.A. Appel, C. Godwin, R. Langer, D.G. Anderson, *Adv. Mater.* 2016, **28**, 86–91.

[155] B.T. Michal, B M. McKenzie, S. . Felder, S.J. Rowan, *Macromolecules* 2015, **48**, 3239–3246

[156] M. Jiang, N. Mahmud, C.B. Koelbl, D. Herr, J.C. Worch, *J. Polym. Sci.* 2024, **62**, 3562–3583.

[157] Y. Chi, Y. Li, Y. Zhao, Y. Hong, Y. Tang, J. Yin, *Adv. Mater.* 2022, **34**, 2110384

[158] R. Liu, Z. L. Wang, K. Fukuda, T. Someya, *Nat. Rev. Mater.* 2022, **7**, 870–886.

[159] S.J. Harris, M.A. McKervey, D.P. Melody, J. Woods, J.M. Rooney, *Instant adhesive composition utilizing calixarene accelerators*, US 4556700 A, 1985.

[160] J. del Barrio, R.S. Hartshorne, T.L. Hughes, A. Meredith, *Viscosification of aqueous solutions*, US 11248162 B2, 2022.

[161] Note from the author: Both large multinational companies and smaller ventures, such as *SupraPolix B.V.*, *Cycladex Ltd.* and *Aqdot Ltd.*, which specialize in supramolecular materials, have demonstrated a keen interest in structurally dynamic polymers.

[162] P.C. Colodny, A.V. Tobolsky, *J. Am. Chem. Soc.* 1957, **79**, 4320–4323.

[163] B. Capon, Q. Rev., *Chem. Soc.*, 1964, **18**, 45–111.

[164] P. Cerrada, M. Marcos, J.L. Serrano, *Mol. Cryst. Liq. Cryst.* 1989, **170**, 79–87.

[165] M. Marcos, F. Navarro, L. Oriol, J.L. Serrano, *Makromol. Chem.* 1989, **190**, 305–311.

[166] P.M. Cal, J.B. Vicente, E. Pires, A.V. Coelho, L.F. Veiros, C. Cordeiro, P.M. Gois, *J. Am. Chem. Soc.* 2012, **134**, 10299–10305.

[167] P. Schmidt, C. Stress, D. Gillingham, *Chem. Sci.* 2015, **6**, 3329–3333.

[168] N.J. Gutiérrez-Moreno, F. Medrano, A.K. Yatsimirsky, *Org. Biomol. Chem.* 2012, **10**, 6960–6972

[169] A. Chrisnandy, D. Blondel, S. Rezakhani, N. Broguiere, M.P. Lutolf, *Nat. Mater.* 2022, **21**, 479–487.

[170] B.L. LeSavage, D. Zhang, C. Huerta-López, A.E. Gilchrist, B. A. Krajina, K. Karlsson, A.R. Smith, K. Karagyozova, K.C. Klett, M.S. Huang, C. Long, G. Kaber, C.M. Madl, P.L. Bollyky, C. Curtis, C.J. Kuo, S.C. Heilshorn, *Nat. Mater.* 2024, **23**, 1138-1149.

[171] E.G. Morado, M.L. Paterson, D.G. Ivanoff, H.-C. Wang, A. Johnson, D. Daniels, A. Rizvi, N.R. Sottos, S.C. Zimmerman, *Nat. Chem.* 2023, **15**, 569–577.

[172] R. W. Clarke, T. Sandmeier, K.A. Franklin, D. Reich, X. Zhang, N. Vengallur, T.K. Patra, R. J. Tannenbaum, S. Adhikari, S.K. Kumar, T. Rovis, E.Y.-X. Chen, *Nature* 2023, **616**, 731–739.

[173] A.P. Dhand, M.D. Davidson, J.H. Galarraga, T.H. Qazi, R.C. Locke, R.L. Mauck, J.A. Burdick, *Adv. Mater.* 2022, **34**, 2202261.

[174] X. Li, J.P. Gong, *Nat. Rev. Mater.* 2024, **9**, 380–398.

[175] Z. Huang, X. Chen, S. J.K. O'Neill, G. Wu, D.J. Whitaker, J. Li, J.A. McCune, O.A. Scherman, *Nat. Mater.* 2022, **21**, 103–109.

[176] M. Wang, X. Xiao, S. Siddika, M. Shamsi, E. Frey, W. Qian, W. Bai, B.T. O'Connor, M.D. Dickey, *Nature* 2024, **631**, 313–318.

[177] X. Liu, M. Gao, J. Chen, S. Guo, W. Zhu, L. Bai, W. Zhai, H. Du, H. Wu, C. Yan, Y. Shi, J. Gu, H.J. Qi, K. Zhou, *Adv. Funct. Mater.* 2022, **32**, 2203323.

[178] K. Kikkawa, Y. Sumiya, K. Okazawa, K. Yoshizawa, Y. Itoh, T. Aida, *J. Am. Chem. Soc.* 2024, **146**, 21168–21175.

[179] J. Sokjorhor, T. Yimyai, R. Thiramanas, D. Crespy, *J. Mater. Chem. B*, 2024, **12**, 6827–6839.

[180] K.D. Harris, C.W.M. Bastiaansen, J. Lub, D.J. Broer, *Nano Letters* 2005, **5**, 1857–1860.

[181] A. Gerald, S. Russo, *Nat. Rev. Mater.* 2024, **9**, 86–88.

[182] K. Yang, J.C. Grant, P. Lamey, A. Joshi-Imre, B.R. Lund, R.A. Smaldone, W. Voit, *Adv. Funct. Mater.* 2017, **27**, 1700318.

[183] D.J. Bischoff, M.E. Mackay, *ACS Appl. Polym. Mater.* 2024, 6, 3335–3341.

[184] H. Tan, L. Sun, H. Huang, L. Zhang, R.E. Neisiany, X. Ma, Z. You, *Adv. Mater.* 2024, **36**, 2310020.

[185] M.D. Preuss, T. Schnitzer, S.A.H. Jansen, S.C.J. Meskers, T.H.R. Kuster, X. Lou, E.W. Meijer, G. Vantomme, *Angew. Chem. Int. Ed.* 2024, **63**, e202402644

[186] A. Sorrenti, J. Leira-Iglesias, A.J. Markvoort, T.F. A. de Greef, T.M. Hermans, *Chem. Soc. Rev.* 2017, **46**, 5476–5490.

[187] A. Roche, E. Terriac, R.M. Tejedor, L. Oriol, A. del Campo, M. Piñol, *Eur. Polym. J.* 2020, **126**, 109561.

[188] D. Hoenders, S. Ludwanowski, C. Barner-Kowollik, A. Walther, *Angew. Chem. Int. Ed.* 2024, **63**, e202405582.

Rev. Real Academia de Ciencias. Zaragoza. **79:** 53–68, (2024). ISSN: 0370-3207

Orbit propagation with Lie-Deprit methods in satellite dynamics

A. Abad and A. Elipe

IUMA. Universidad de Zaragoza. Zaragoza. Spain

Abstract

In this paper we generate an analytical theory for the motion of the artificial satellite in which the tesseral model of the planetary potential is considered. We integrate the problem by applying the Lie-Deprit method with three consecutive canonical transformations: the elimination of the parallax, the Delaunay normalization and a final double normalization to eliminate the perigee and the node. We apply this theory to the 2×2, 4×4, and 5×5 tesseral models and we propagate the motion of the satellite, and also, we present the error of this analytical propagation versus the numerical propagation for a wide range of initial conditions.

1 Introduction

Analytical theories have been widely used in the study of the motion of an artificial satellite. Among the advantages of using analytical theories we may extract that they are very fast to evaluate since they consists of explicit functions of time, which results in a very useful tool in mission analysis where a fast orbit propagator is needed because it is necessary to integrate the orbit for many sets of initial conditions. Besides, analytical theories provide a good understanding of the qualitative dynamics as well as the effects of the perturbation terms [1, 2, 10, 23]. The search of frozen orbits is a good example of how the analytical theories help in the analysis of certain systems [9, 5].

On the contrary, the main difficulty of analytical theories is that it is quite complex to derive the final formulas and also to have them with the less terms as possible, although as the order of the theory increases, it is frequent to cope with millions of terms [14]. However,

computers are becoming faster and cheaper, and also there are many commercial software packages that allow the construction of analytical theories of order high enough even with desk computers [4].

Due to the difficulties in building a convenient analytical theory for the satellite when tesseral harmonics are included, most of the related works have been applied to the zonal problem. The most common theories use Deprit's integration method [11] by applying a battery of canonical transformations (the elimination of the parallax [12], the elimination of the perigee [8], the Delaunay normalization [13], the Krylov-Bogoliubov method [7], etc.). In Abad *et al.* [3] an analytical tool (ATESAT) to make analytical integrations of the zonal problem of the satellite is presented. ATESAT obtains not only the analytical expressions of the transformation but the code of the software to propagate the satellite with such theory. Using ATESAT, a third order theory of the motion of an orbiter about Mars [19] was generated using a zonal model of sixth degree. The numerical results of this theory for a wide range of initial condition give an error less than 400 meters after a month.

The Coriolis term of the Hamiltonian cannot be avoided in the tesseral problem because of the appearance of the node in the expression of the potential. This, together with the size of the expression, makes very involved the analytical integration. Several attempts to handle this problem have been made. Let us mention here the works of Kaula [16], Wnuk [24, 25] based on series expansions in the eccentricity of the potential function, or the solution of Segerman and Coffey [20], that uses the relegation algorithm of Deprit *et al.* [15], or the more recent paper of Palacián [17].

In this communication we use a way presented by Serrano [21] to integrate the tesseral problem. In this method, three transformation are applied: the relegation algorithm to simplify the problem, the Delaunay normalization to eliminatete the mean anomaly and, finally, a double normalization to eliminate simultaneously the perigee and the node. We use a modern version, coded in C++ instead of C, of our old Poisson Series processor PSPC [6] to generate an analytical theory of several orders of the 2×2, 4×4 and 5×5 tesseral models. Lastly, with the C codes automatically generated by the Poisson Series Processor we propagate a big set of initial conditions during a month, and we present the errors of the analytical theory compared with the numerical integration.

2 The tesseral model of the satellite

The Hamiltonian of the tesseral $N \times N$ model of the satellite, expressed in polar-nodal variables $(r, \theta, \nu, R, \Theta, N)$, may be written as the sum of the Keplerian term, the Coriolis term, the Main Problem term and the rest of zonal and tesseral terms as

$$\mathcal{H} = \mathcal{H}_k + \mathcal{H}_c + \mathcal{H}_m + \mathcal{H}_r,$$

where we have

$$\begin{aligned} \mathcal{H}_k &= \frac{1}{2}\left(R^2 + \frac{\Theta^2}{r^2}\right) - \frac{\mu}{r}, \\ \mathcal{H}_c &= -\omega N, \\ \mathcal{H}_m &= \frac{\mu}{r}\left(\frac{\alpha}{r}\right)^2 J_2 P_2(\sin i \sin\theta), \\ \mathcal{H}_t &= \sum_{n=2}^{N} \mathcal{H}_n^t, \end{aligned} \tag{1}$$

where μ is the gravitational constant, α the equatorial Earth's radius, ω is the Earth's angular velocity, P_2 is the Legendre polynomial of order 2, and i is the inclination of the orbit.

The expression of the tesseral part can be decomposed into

$$\begin{aligned} \mathcal{H}_2^t &= -\frac{\mu}{r}\left(\frac{\alpha}{r}\right)^2 \sum_{j=1}^{2} \left(C_{2,j}\cos j\lambda + S_{2,j}\sin j\lambda\right) P_{2,j}(\sin i \sin\theta), \\ \mathcal{H}_n^t &= -\frac{\mu}{r}\left(\frac{\alpha}{r}\right)^n \sum_{j=0}^{n} \left(C_{n,j}\cos j\lambda + S_{n,j}\sin j\lambda\right) P_{n,j}(\sin i \sin\theta), \end{aligned} \tag{2}$$

with $P_{n,j}$ the associated Legendre polynomials, and $C_{n,j}$ and $S_{n,j}$ are the tesseral coefficients of the planet gravitational potential. For details, the reader is addressed to [16].

The relative order of the terms of the Hamiltonian has been extensively studied by Serrano [22]. Taking into consideration the relative value of the mean motion of the satellite with respect to the rotation angular velocity of the planet, Serrano [22] suggests to scale the Hamiltonian in the following way

$$\mathcal{H} = \mathcal{H}_0 + \epsilon\mathcal{H}_1 + \frac{\epsilon^2}{2!}\mathcal{H}_2 + \frac{\epsilon^4}{4!}\mathcal{H}_4,$$

where

$$\mathcal{H}_0 = \mathcal{H}_k,$$

$$\mathcal{H}_1 = \frac{\mathcal{H}_k}{\epsilon} = -\omega^* N,$$

$$\mathcal{H}_2 = \frac{2!\,\mathcal{H}_m}{\epsilon^2} = \frac{\mu}{r}\left(\frac{\alpha}{r}\right)^2 J_2^* P_2(\sin i \sin\theta), \tag{3}$$

$$\mathcal{H}_4 = \frac{4!\,\mathcal{H}_r}{\epsilon^4} = -\frac{\mu}{r}\left(\frac{\alpha}{r}\right)^2 \sum_{j=1}^{2}\left(C_{2,j}^* \cos j\lambda + S_{2,j}^* \sin j\lambda\right) P_{2,j}(\sin i \sin\theta)$$
$$-\frac{\mu}{r}\sum_{n=3}^{6}\left(\frac{\alpha}{r}\right)^n \sum_{j=0}^{n}\left(C_{n,j}^* \cos j\lambda + S_{n,j}^* \sin j\lambda\right) P_{n,j}(\sin i \sin\theta).$$

Note that we introduce a fictitious small parameter ϵ as the order of the Coriolis term with respect to the Keplerian Hamiltonian,

$$\epsilon = \frac{|\mathcal{H}_c|}{|\mathcal{H}_k|} = \frac{\omega\sqrt{\mu a(1-e^2)}\cos i}{\mu/2a} \tag{4}$$

and we rewrite the constants in the form

$$\omega = \epsilon\,\omega^*, \quad J_2 = \frac{\epsilon^2}{2!}J_2^*, \quad C_{i,j} = \frac{\epsilon^4}{4!}C_{i,j}^*.$$

Figure 1 represents the level curves of the function $\epsilon = \epsilon(a, i)$ given by Eq. (4). The horizontal axis represents the semi major-axis (a), with a range between 1 and the semi major axis of a geostationary orbit (we take the equatorial radius as unit of distance), whereas the vertical axis is for the inclination (i) with a range between 0º and 180º. Out of the yellow area the value of ϵ increases and consequently, the proposed scaling is not adequate for these regions.

3 Lie-Deprit method

The well known Lie-Deprit method [11] consists of finding a canonical Lie transformation of generator

$$W(\boldsymbol{x}, \boldsymbol{X}; \epsilon) = \sum_{n\geq 0} \frac{\epsilon^n}{n!} W_n(\boldsymbol{x}, \boldsymbol{X}),$$

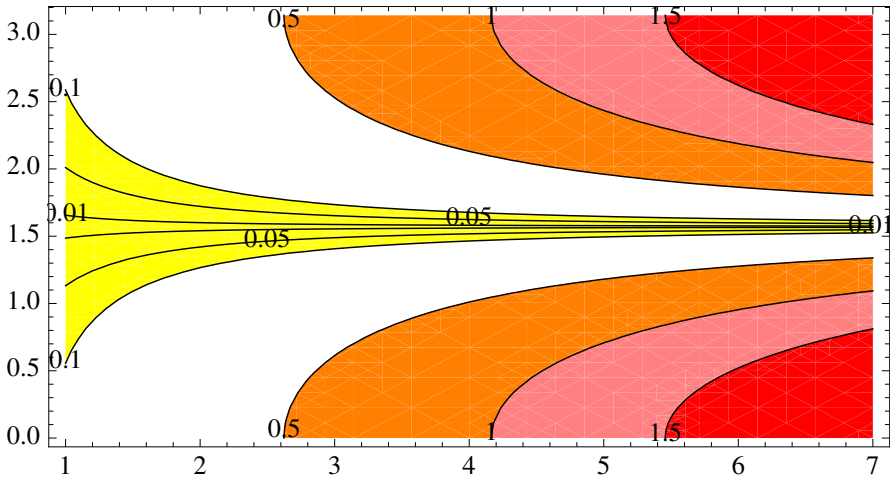


Figure 1: Level curves of the function $\epsilon = \epsilon(a, i)$. Yellow area corresponds to the smaller values of ϵ.

that transforms the original Hamiltonian

$$\mathcal{H}(\boldsymbol{x}, \boldsymbol{X}; \epsilon) = \sum_{n \geq 0} \frac{\epsilon^n}{n!} \mathcal{H}_n(\boldsymbol{x}, \boldsymbol{X}),$$

of a given dynamical system, into a new Hamiltonian

$$\mathcal{K}(\boldsymbol{y}, \boldsymbol{Y}; \epsilon) = \sum_{n \geq 0} \frac{\epsilon^n}{n!} \mathcal{K}_n(\boldsymbol{y}, \boldsymbol{Y}),$$

enjoying certain properties.

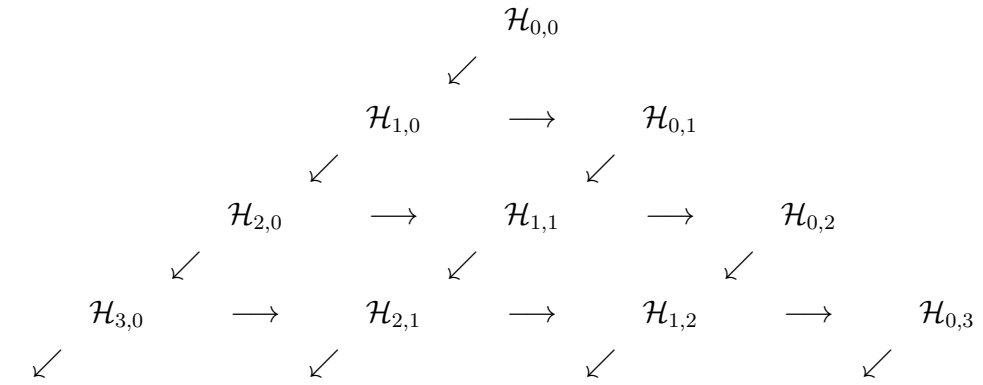
By changing the notation as $\mathcal{H}_{n,0} = \mathcal{H}_n, \quad \mathcal{H}_{0,n} = \mathcal{K}_n$, we may write the relation among the old and new Hamiltonians and the generator of the transformation by means of the so-called Lie triangle algorithm

$$\mathcal{H}_{i,j} = \mathcal{H}_{i+1,j-1} + \sum_{k=0}^{i} \binom{i}{k} \left(\mathcal{H}_{i-k,j-1}, W_{k+1}\right). \tag{5}$$

where (f, g) stands for the Poisson bracket, defined as

$$(f, g) = \sum_{i}^{3} \left(\frac{\partial f}{\partial X_i} \frac{\partial g}{\partial x_i} - \frac{\partial f}{\partial x_i} \frac{\partial g}{\partial X_i} \right).$$

To compute the transformed Hamiltonian we apply an iterative process showed in the following scheme (for details, see the original paper of Deprit [11]):



At order n (from $n=1$), we compute the line $\mathcal{H}_{i,j}$, with $i+j=n$, and $i=n-1,\ldots,0$, from the element $\mathcal{H}_{n,0}$, the terms $\mathcal{H}_{i,j}$, of the previous lines, and the elements W_i, $(i \leq n)$. Hence

$$
\begin{array}{lcll}
\mathcal{H}_{n-1,1} & = & \mathcal{H}_{n,0} & +\ldots+k_{12}(\mathcal{H}_{20},W_{n-2})+k_{11}(\mathcal{H}_{10},W_{n-1})+(\mathcal{H}_{00},W_n) \\
\mathcal{H}_{n-2,2} & = & \mathcal{H}_{n-1,1} & +\ldots+k_{22}(\mathcal{H}_{11},W_{n-2})+\quad(\mathcal{H}_{01},W_{n-1}) \\
\mathcal{H}_{n-3,3} & = & \mathcal{H}_{n-2,2} & +\ldots+\quad(\mathcal{H}_{02},W_{n-2}) \\
\ldots & = & \ldots & \\
\mathcal{H}_{0,n} & = & \ldots &
\end{array}
\tag{6}
$$

where the k_{ij} coefficients are

$$k_{12}=\binom{n-1}{n-3}=\frac{1}{2}(n-1)(n-2),\quad k_{11}=\binom{n-1}{n-2}=(n-1),\quad k_{22}=\binom{n-2}{n-3}=(n-2).$$

From these relations we may define the tilde elements by the expression

$$\mathcal{H}_{i,j}=\widetilde{\mathcal{H}}_{i,j}+(\mathcal{H}_{00},W_n)=\widetilde{\mathcal{H}}_{i,j}-\mathcal{L}_0W_n,\quad i<n.$$

where the so-called Lie operator $\mathcal{L}_0$ is defined as the Poisson bracket $\mathcal{L}_0(F)=(H_{0,0},F)$.

Deprit's method tries to compute, iteratively, line by line, the elements W_n. Let us suppose we have completed the $n-1$ first lines of the Lie triangle and the elements $W_1,\ldots W_{n-1}$ are known; then we may compute the tilde elements in line n by the formulas

$$
\begin{array}{lcllllll}
\widetilde{\mathcal{H}}_{n,0} & = & \mathcal{H}_{n,0} & & & & & \\
\widetilde{\mathcal{H}}_{n-1,1} & = & \widetilde{\mathcal{H}}_{n,0} & +\ldots+ & k_{12}(\mathcal{H}_{20},W_{n-2}) & + & k_{11}(\mathcal{H}_{10},W_{n-1}), \\
\widetilde{\mathcal{H}}_{n-2,2} & = & \widetilde{\mathcal{H}}_{n-1,1} & +\ldots+ & k_{22}(\widetilde{\mathcal{H}}_{11},W_{n-2}) & + & (\widetilde{\mathcal{H}}_{01},W_{n-1}), \\
\widetilde{\mathcal{H}}_{n-3,3} & = & \widetilde{\mathcal{H}}_{n-2,2} & +\ldots+ & (\widetilde{\mathcal{H}}_{02},W_{n-2}) & , & & \\
\ldots & = & \ldots & & & & & \\
\widetilde{\mathcal{H}}_{0,n} & = & \ldots & & & & &
\end{array}
$$

and, finally, we obtain the element W_n by solving the homological equation

$$\widetilde{\mathcal{H}}_{0,n} = \mathcal{H}_{0,n} + \mathcal{L}_0 W_n. \tag{7}$$

The usual way to apply the Deprit's method is to split the tilde element $\widetilde{\mathcal{H}}_{0,n}$ into two parts

$$\widetilde{\mathcal{H}}_{0,n} = \mathcal{H}^{(1)}_{0,n} + \mathcal{H}^{(2)}_{0,n},$$

in such a way that we easily find a first integral of the partial differential equation

$$\mathcal{L}_0 W_n = \mathcal{H}^{(2)}_{0,n},$$

and we take $\mathcal{H}^{(1)}_{0,n}$ as the order n of the new Hamiltonian

$$\mathcal{H}_{0,n} = \mathcal{H}^{(1)}_{0,n}.$$

4 Solving the tesseral problem of the satellite

An analytical theory for the motion of the artificial satellite, using the Lie-Deprit method, consists of applying several Lie canonical transformations until we are able to integrate the problem. As it is easy to imagine, there are several choices. We can integrate the problem by applying only one transformation, the *Delaunay normalization* [13], which requires to have the Hamiltonian of the problems expressed in terms of the Delaunay variables, and then, we need to replace the powers $(1/r)^n$ into power series of the eccentricity, which reduces the valididy of the theory to only quite small eccentricities. In order to avoid such series expansions of the eccentricity, more than one transformation must be applied.

To integrate the zonal problem of the satellite [3, 7, 18] we apply first the *elimination of the parallax* [12]. The elimination of the parallax is a classical Lie canonical transformation that reduces the complexity of the Hamiltonian, expressed in polar-nodal variables, by reducing the terms proportional to $1/r^n$, $(n \geq 2)$ into terms only proportional to $1/r^2$. Once we apply the elimination of the parallax transformation, we obtain a new Hamiltonian depending on the mean anomaly ℓ and the perigee g. The *elimination of the perigee* transformation [8] eliminates the perigee angle of the expression of the Hamiltonian. Finally, a Delaunay normalization eliminates the mean anomaly and makes the final Hamiltonian independent of the coordinates, then, the problem becomes trivially integrable.

The previous method cannot be applied to the tesseral problem because the node angle ν explicitly appears in the Hamiltonian. A new method to integrate this problem has been proposed by Serrano [21]. This method is based on three Lie canonical transformations, namely, a modified version of the elimination of the parallax that includes the node; a Delaunay normalization to eliminate the mean anomaly and, finally, a double normalization to eliminate simultaneously the perigee and the node.

4.1 Elimination of the parallax

The original elimination of the parallax algorithm cannot be directly applied to the tesseral problem since the variable ν appears in the expressions; however we may change slightly the algorithm in order to simplify the Hamiltonian.

The elimination of the parallax is based on the expression of the operator $\mathcal{L}_0$ in polar–nodal variables

$$\mathcal{L}_0 = R\frac{\partial}{\partial r} - \left(\frac{\mu}{r^2} - \frac{\Theta^2}{r^3}\right)\frac{\partial}{\partial R} + \frac{\Theta}{r^2}\frac{\partial}{\partial \theta}. \tag{8}$$

Let us suppose we are dealing with expressions of the form

$$\mathcal{F}^0_m = \Gamma^c_k \cos(j\nu) + \Gamma^s_k \sin(j\nu), \quad \mathcal{F}^\theta_m = \Gamma^c_k \cos(i\theta + j\nu) + \Gamma^s_k \sin(i\theta + j\nu), \tag{9}$$

where the script m in $\mathcal{F}$ represents a triad of elements i, j, k, and Γ^c_k, Γ^s_k belong to the kernel of $\mathcal{L}_0$, i.e. $\mathcal{L}_0\Gamma^c_k = 0$, $\mathcal{L}_0\Gamma^s_k = 0$.

For $\mathcal{F}^\theta_m$ we may write

$$\mathcal{L}_0\mathcal{W}^\theta_m = \frac{\Theta}{r^2}\mathcal{F}^\theta_m, \quad \text{with} \quad \mathcal{W}^\theta_m = \frac{\Gamma^c_k}{i}\sin(i\theta + j\nu) + \frac{-\Gamma^s_k}{i}\cos(i\theta + j\nu). \tag{10}$$

In order to apply the Lie-Deprit method let us suppose that we know the expression of $\widetilde{\mathcal{H}}_{0,n}$, in which two kind of terms appear:

- terms $\widetilde{\mathcal{H}}^r_{0,n}$ with the factor $1/r^n$, $n \geq 2$,
- terms $\widetilde{\mathcal{H}}^*_{0,n}$ in which the variable r does not appear. These terms come from the computation of the Poisson bracket $(\mathcal{H}_{0,1}, W_n)$ because r does not appear neither in W_n (see the next step) nor in $\mathcal{H}_{0,1} = \mathcal{H}_{1,0}$.

Taking into account the relations

$$\frac{1}{r} = \frac{\mu}{\Theta^2}\left(1 + C\cos\theta + S\sin\theta\right), \quad C = e\cos g, \quad S = e\sin g,$$

where C and S are the *state functions* that belong to the kernel, we may reduce the exponent of r in $\widetilde{\mathcal{H}}^r_{0,n}$ changing $1/r^n$ by

$$\frac{1}{r^n} = \frac{1}{r^2}\left(\frac{\mu}{\Theta^2}\left(1 + C\cos\theta + S\sin\theta\right)\right)^{n-2}.$$

Then, expanding the expression of $\widetilde{\mathcal{H}}^r_{0,n}$ we obtain an expression of the form

$$\widetilde{\mathcal{H}}^r_{0,n} = \widetilde{\mathcal{H}}^0_{0,n} + \widetilde{\mathcal{H}}^\theta_{0,n}, \quad \widetilde{\mathcal{H}}^0_{0,n} = \sum_m \frac{\Theta}{r^2}\mathcal{F}^0_m, \quad \widetilde{\mathcal{H}}^\theta_{0,n} = \sum_m \frac{\Theta}{r^2}\mathcal{F}^\theta_m. \tag{11}$$

Finally we may choose the expression of the new Hamiltonian

$$\mathcal{H}_{0,n} = \widetilde{\mathcal{H}}^*_{0,n} + \widetilde{\mathcal{H}}^0_{0,n}, \tag{12}$$

and $\mathcal{L}_0 W_n$ (needful to refresh the diagonal) will be

$$\mathcal{L}_0 W_n = \widetilde{\mathcal{H}}_{0,n} - \mathcal{H}_{0,n} = \widetilde{\mathcal{H}}^\theta_{0,n}. \tag{13}$$

Finally, since $\mathcal{L}_0 W_n = \widetilde{\mathcal{H}}^\theta_{0,n}$ has the form $(\Theta/r^2)\sum_m \mathcal{F}^\theta_m$, then, taking into account (10) the generator, W_n can be obtained by the expression

$$W_n = \sum_m \mathcal{W}^\theta_m. \tag{14}$$

4.2 Delaunay Normalization

Since Delaunay's normalization consists of eliminating the mean anomaly ℓ from the Hamiltonian, first, let us change the Hamiltonian from Polar–Nodal to Delaunay variables, then the Keplerian Hamiltonian becomes

$$\mathcal{H}_K = -\frac{\mu^2}{2L^2},$$

and the Lie operator $\mathcal{L}_0$ is

$$\mathcal{L}_0 = \frac{\mu^2}{L^3}\frac{\partial}{\partial \ell} \tag{15}$$

To obtain the n-th order of the transformation we start with the value of $\widetilde{\mathcal{H}}_{0,n}$ previously computed at the order $(n-1)$-th.

Then, choose as the new Hamiltonian the average over ℓ of the term $\widetilde{\mathcal{H}}_{0,n}$

$$\mathcal{H}_{0,n} = \frac{1}{2\pi}\int_0^{2\pi} \widetilde{\mathcal{H}}_{0,n}\, d\ell, \tag{16}$$

and the n-th term of the generating function will be obtained, from the homological equation, by the quadrature

$$W_n = \frac{L^3}{\mu^2}\int \left(\widetilde{\mathcal{H}}_{0,n} - \mathcal{H}_{0,n}\right)\, d\ell, \tag{17}$$

4.3 Double normalization

After Delaunay normalization the first three orders of the Hamiltonian

$$\mathcal{H}_{0,0} = \mathcal{H}_{0,0}(L), \quad \mathcal{H}_{1,0} = \mathcal{H}_{1,0}(H), \quad \mathcal{H}_{2,0} = \mathcal{H}_{2,0}(L,G,H),$$

depend, respectively, on the moments L, H and (L, G, H), whereas the rest of terms are of the form $\mathcal{H}_{n,0} = \mathcal{H}_{20}(\_, g, h, L, G, H)$. From these expressions we deduce the following Lie-derivatives

$$\mathcal{L}_0 = \frac{\mu^2}{L^3}\frac{\partial}{\partial \ell}, \quad \mathcal{L}_1 = -\omega\frac{\partial}{\partial h}, \quad \mathcal{L}_2 = L^*\frac{\partial}{\partial \ell} + G^*\frac{\partial}{\partial g} + H^*\frac{\partial}{\partial h},$$

where L^*, G^*, H^* are functions of the momenta L, G, H.

With this, we decompose the generator W_n in three parts

$$W_n = W_n^\ell(\ell, g, h, L, G, H) + W_n^h(\_, g, h, L, G, H) + W_n^g(\_, g, \_, L, G, H),$$

then, we have

$$\mathcal{L}_0 W_n = \mathcal{L}_0 W_n^\ell, \quad \mathcal{L}_1 W_n = \mathcal{L}_1 W_n^h, \quad \mathcal{L}_2 W_n = \mathcal{L}_2 W_n^g.$$

The objective of the *Double normalization* transformation is to eliminate simultaneously both variables g and h. Since these variables do not appear in the first three orders of the Hamiltonian, then we choose

$$\mathcal{H}_{01} = \mathcal{H}_{10}, \quad \mathcal{H}_{02} = \mathcal{H}_{20}.$$

With these requirements, the equation (6) leads to a value of $W_1^{(h)} = 0$ whereas $W_1^{(g)}$ remains undetermined.

The homological equation, in this case, can be expressed in the form

$$\widetilde{\mathcal{H}}_{n0} = \mathcal{H}_{0n} + \frac{1}{2}n(n-1)\mathcal{L}_2 W_{n-2}^{(g)} + n\mathcal{L}_1 W_{n-1}^{(h)}.$$

To solve the order $n \geq 3$ we split $\widetilde{\mathcal{H}}_{n,0}$ in three terms

$$\widetilde{\mathcal{H}}_{n,0} = \widetilde{\mathcal{H}}_{n,0}^{\emptyset}(\_,\_,\_,L,G,H) + \widetilde{\mathcal{H}}_{n,0}^{g}(\_,g,\_,L,G,H) + \widetilde{\mathcal{H}}_{n,0}^{h}(\_,g,h,L,G,H),$$

where

- $\widetilde{\mathcal{H}}_{n,0}^{\emptyset} \in \ker(\mathcal{L}_1) \cap \ker(\mathcal{L}_2)$, i.e. the terms does not depend of g and h.
- $\widetilde{\mathcal{H}}_{n,0}^{g} \in \ker(\mathcal{L}_1)$, i.e. terms that depend only on g, but not on h.
- $\widetilde{\mathcal{H}}_{n,0}^{h}$ are the terms depending on h. The variable g may appear on these terms, but it is not mandatory.

With these assumptions we write

$$\begin{aligned} \mathcal{H}_{0n} &= \widetilde{\mathcal{H}}_{n,0}^{\emptyset}, \\ \tfrac{1}{2}n(n-1)\mathcal{L}_2 W_{n-2}^{(g)} = \widetilde{\mathcal{H}}_{n0}^{g}, \;&\Longrightarrow\; W_{n-2}^{(g)} = \frac{2}{n(n-1)G^*}\int \widetilde{\mathcal{H}}_{n0}^{g}\, dg, \\ n\mathcal{L}_1 W_{n-1}^{(h)} = \widetilde{\mathcal{H}}_{n0}^{h}, \;&\Longrightarrow\; W_{n-1}^{(h)} = -\frac{1}{n\,\omega}\int \widetilde{\mathcal{H}}_{n0}^{h}\, dh. \end{aligned} \tag{18}$$

and in this way, we complete the generator at order $n-2$ and besides we compute one term of the generator at order $n-1$.

5 Application of the theory to the orbit propagation

To check the use of this analytical integration of the artificial satellite problem as an orbit propagator, the first task is to construct the analytical theory by using a Poisson Series processor. We do that with a modern version, coded in C++ instead of C, of our old Poisson Series processor PSPC [6].

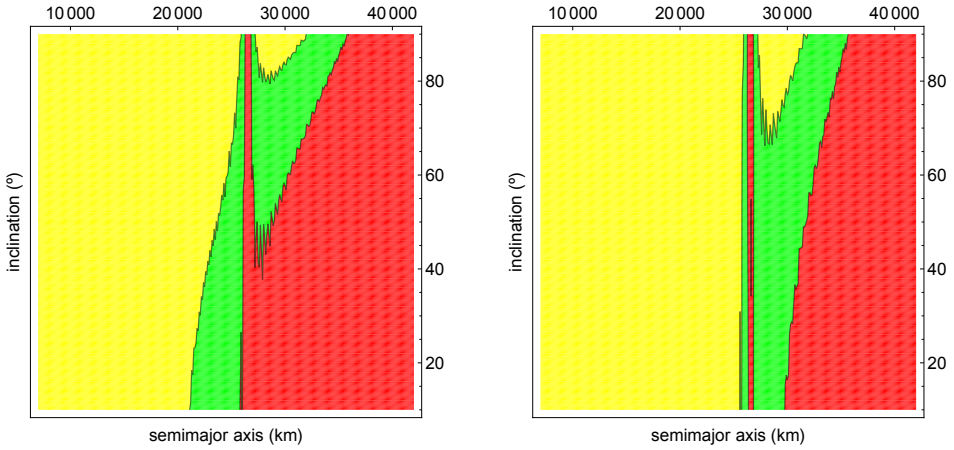


Figure 2: Differences between analytical and numerical integrations for the (2×2) -tesseral model. Left) results for a 6th-order theory. Right) same model and a 7th-order theory. Horizontal axis is the semi-major axis $a \in [7000, 42000]$ km (from low orbits till geostationary orbits), and vertical axis represents the inclination $i \in [0^o, 90^o]$. Initial conditions (a, i) inside the yellow region provide an error less than one km after one month of propagating the orbit. Green area give errors between one and two km. Red area represents errors greater than two km after the propagation of the orbit for one month.

We build up the theory for the models (2×2), (4×4) and (5×5) of the potential. In the two first cases we obtain a 6-th and 7-th order theory. In the model (5×5) we obtain only the 6-th order theory because of an *out of memory* error when we try to make the 7-th order with a computer of 32 GB of total memory.

The `C` code to propagate the orbit has been automatically written by the Poisson series processor from the direct and inverse expressions of the three transformations.

To check this program we compare it with a propagation of the same model obtained by using `dopri853`, a Runge-Kutta method of order 8(5,3) due to E. Hairer (see `http://www.unige.ch/ hairer/software.html`).

We begin, in both cases, from a set of initial conditions that cover a wide range of semimajor-axis (from low to geostationary orbits) and inclinations (from 0^o to 90^o). We propagate the orbit during a month and, finally, we compare the position obtained with the numerical integration with the one obtained with the analytical integration.

Figures 2 and 3 represent the results of these comparisons. In these figures the horizontal axis stands for the semi major axis a, from 7000 to 42000 km. The vertical axis represents the inclination i, in degrees.

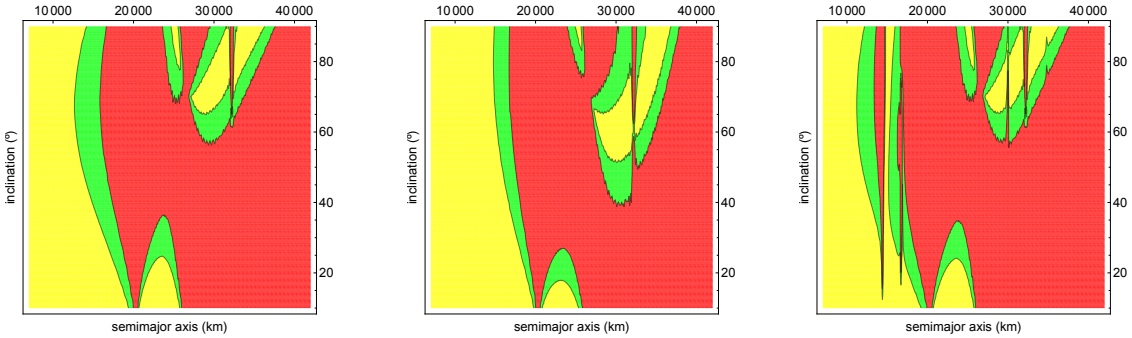


Figure 3: Differences between analytical and numerical integrations for the (4×4)-model: Left) a 6th order theory; Center) a 7th order theory. Right) The same analysis, but now for the (5×5)-model and a 6th order theory. Horizontal axis is the semi-major axis $a \in [7000, 42000]$ km (from low orbits till geostationary orbits), and vertical axis represents the inclination $i \in [0^o, 90^o]$. Initial conditions (a, i) inside the yellow region provide an error less than one km after one month of propagating the orbit. Green area give errors between one and two km. Red area represents errors greater than two km after the propagation of the orbit for one month.

The left part of the Figure 2 represents the comparison between a 6-th order theory of the model 2×2 with respect to the numerical integration of the same mode. The right part is the comparison of the 7-th order theory of the same model with respect to the numerical integration of this model.

Figure 3 contains the comparison of the 6-th and 7-order of the (4×4)-model (left and middle plots respectively) and the 6-th order of the (5×5)-model (right plot). The yellow area of these figures contains initial conditions (a, i) which give an error less than one km after propagating the orbit during one month. Green area represents error between one and two km. Red area corresponds to initial conditions giving errors greater than two km after one month. We can see that the analytical propagation gives good results for small values of the semi major axis, which agree with the relation of the small parameter of the theory and the semi major axis.

Acknowledgements

This work has been supported by Grant PID2020-117066-GB-I00 funded by MCIN/AEI/ 10.13039/501100011033, and by the Aragon Government and European Social Fund (group E24_23R). Authors are indebted to the reviewer comments that improved the final version of the manuscript.

References

[1] Abad, A., Calvo, M. and Elipe, A. (2020). Integration of Deprit's radial intermediary, *Acta Astronautica* **173**, 19–21.

[2] Abad, A., Calvo, M. and Elipe, A. (2021). On the integration of Cid's radial intermediary", *Acta Astronautica* **179**, 519–524.

[3] Abad, A., Elipe, A., Palacián, J. and San-Juan, J.F. (1998). ATESAT: A symbolic processor for artificial satellite theory. *Mathematics and Computers in Simulation*, **45**, 497–510.

[4] Abad, A., Elipe, A., San-Juan, J.F. and Serrano, S. (2004). Is Symbolic Integration better than Numerical Integration in Satellite Dynamics? *Applied Mathematics Letters*, **17**, 59–63.

[5] Abad, A., Elipe, A. and Tresaco, E. (2009). Analytical Model to Find Frozen Orbits for a Lunar Orbiter. *Journal of Guidance and Control and Dynamics*, **32 (3)**, 888–898.

[6] Abad, A. and San-Juan, J.F. (1994). PSPC: A Poisson Series Processor coded in C. In: *Dynamics and Astrometry of Natural and Artificial Celestial Bodies*. (K. Kurzynska, F. Barlier, P.K. Seidelmann, and I. Wytrzyszczak, eds.). Adam Mickiewicz University, Pozńan. 383–387.

[7] Abad, A., San-Juan, J.F. and Gavín, A. (2001). Short time evolution of artificial satellites. *Celestial Mechanics and Dynamical Astronomy*, **79**, 277–296.

[8] Alfriend, K.T. and Coffey, S.L. (1984). Elimination of the perigee in satellite problem. *Celestial Mechanics*, **32**, 163–172.

[9] Coffey, S.L., Deprit, A. and Deprit, E. (1994). Frozen orbits for satellites close to an Earth-like planet. *Celestial Mechanics and Dynamical Astronomy*, **59**, 37–72.

[10] Coffey, S.L., Deprit, A., Deprit, E. and Healy, L. (1990). Painting the phase space portrait of an integrable dynamical system. *Science*, **247**, 833–836.

[11] Deprit, A. (1969). Canonical transformations depending on a small parameter. *Celestial Mechanics*, **1**, 12–30.

[12] Deprit, A. (1981). The elimination of the parallax in satellite theory. *Celestial Mechanics*, **24**, 111–153.

[13] Deprit, A. (1982). Delaunay normalisations. *Celestial Mechanics*, **26**, 9–21.

[14] Deprit, A. and Miller, B. (1989). Simplify or Perish. *Celestial Mechanics*, **45**, 189–200.

[15] Deprit, A., Palacián, J. and Deprit, E. (2001). The relegation algorithm. *Celestial Mechanics and Dynamical Astronomy*, **79**, 157–182.

[16] Kaula, W. (1966). *Theory of Satellite Geodesy*. Blaisdell: Waitham, Mass.

[17] Palacián, J. (2007). Dynamics of a satellite orbiting a planet with an inhomogeneous gravitational field. *Celestial Mechanics and Dynamical Astronomy*, **98**, 219–249.

[18] San Juan, J. F. (1996). *Manipulación algebraica de series de Poisson. Aplicación a la teoría del satélite artificial*, Ph. D. Thesis, University of Zaragoza, Zaragoza.

[19] San Juan, J.F., Serrano, S. and Abad, A. (2004). Analytical Theory of Motion of a Mars Orbiter. *Lecture notes in Computer Science*, **3039**, 327–334.

[20] Segerman, A.M. and Coffey, S.L. (2000). An analytical theory for tesseral gravitational harmonics. *Celestial Mechanics and Dynamical Astronomy*, **73**, 139–156.

[21] Serrano, S. (2003). *Teorías analíticas del movimiento de un satélite artificial alrededor de un planeta. Ordenación asintótica del potencial en el espacio fásico*, Ph. D. Thesis, University of Zaragoza, Zaragoza.

[22] Serrano, S. (2009). Asymptotic ordination of artificial satellite Hamiltonian. *Applied Mathematics and Computation*, **215 (3)**, 1124–1134.

[23] Tresaco, E., Carvalho, J.P.S., Elipe, A., Prado, A.F.B.A. and R. Vilhena de Moraes, R. (2018). Averaged model to study long-term dynamics of a probe about Mercury. *Celestial Mechanics and Dynamical Astronomy* **130**: 9.

[24] Wnuk, E. (1988). Tesseral harmonic perturbations for high order and degree harmonics. *Celestial Mechanics and Dynamical Astronomy*, **44**, 179–191.

[25] Wnuk, E. and Breiter, S. (1990). Tesseral harmonic perturbations in radial transverse and binormal components. *Celestial Mechanics and Dynamical Astronomy*, **48**, 375–385.

Rev. Real Academia de Ciencias. Zaragoza. **79:** 69–73, (2024). ISSN: 0370-3207

IN MEMORIAM
Ilma. Sra. Dña. María Victoria Arruga Laviña

Caridad Sánchez Acedo

Presidenta de la Sección de Naturales

Perdiguera 17-10-1948 — Zaragoza 10-6-2024

Con profunda tristeza, cumplo el honroso cometido de recordar la insigne figura de una gran mujer, sin otro mérito por mi parte que la amistad que nos unía y que ha dejado un recuerdo imborrable y una imperecedera huella en mi corazón.

Compartimos durante muchos años en la Facultad de Veterinaria de nuestra Universidad, y posteriormente en esta Academia, proyectos, quehaceres, inquietudes, sueños, penas, y alegrías con una amistad sincera, leal, verdadera e incondicional.

Su legado es un ejemplo de entrega vocacional, sentido del deber, compromiso social, afán de servicio, rectitud, humildad y generosa humanidad, porque en el camino de su vida ha dejado una estela luminosa de bien y de bondad cargada de buenas acciones. Su rápida y prematura partida nos ha conmovido y ha dejado un profundo vacío en los que disfrutamos de su generosa amistad.

Conservo como un preciado recuerdo los mensajes que intercambiamos durante su enfermedad y transcribo su despedida como muestra de generosidad, fortaleza, y fe profunda e inquebrantable: "*Muchas gracias por tu amistad buena amiga. Aquí estoy para que Dios haga su voluntad*".

María Victoria Arruga Laviña nació en Perdiguera, localidad situada al pie de la Sierra de Alcubierre, el 17 de octubre de 1948 en el seno de una familia dedicada a la agricultura, que inculcó en sus tres hijos el sentido del deber, la perseverancia, el esfuerzo, la responsabilidad y un gran espíritu de superación que constituyeron el fundamento de su vida.

Realizó los estudios primarios y secundarios en la escuela de esta localidad, donde descubrió su vocación e ilusión por aprender. De esta etapa conservó vivo el recuerdo de sus maestras que dejaron una huella perenne en su formación.

Cursó como alumna destacada, con las máximas calificaciones el bachillerato en el Instituto Miguel Servet de Zaragoza. En 1970 ingresó en la Facultad de Ciencias de la Universidad de Zaragoza para cursar el Selectivo de Ciencias y en 1975, obtuvo brillantemente el título de Licenciada en Ciencias Biológicas en la Universidad de Navarra.

A partir de este momento, becada por el Ministerio de Educación y Ciencia, inició una intensa y fructífera actividad docente e investigadora en el departamento de Genética de la Facultad de Veterinaria de nuestra Universidad. En 1980 obtuvo el título de doctora en Ciencias Biológicas en la Universidad de Barcelona, con la calificación de Sobresaliente *cum laude*.

Su extensa y fructífera actividad académica ha estado avalada por una excelente formación, como profesora ayudante (1976), profesora titular en 1984 y catedrática de Genética (2010) en el departamento de Anatomía, Embriología y Genética de la Facultad de Veterinaria hasta su jubilación el año 2013.

A lo largo de su amplia labor académica, transmitió sus profundos conocimientos y su pasión por la Ciencia con calor y entusiasmo, como universitaria vocacional y excelente docente. Sus alumnos loan su magisterio realizado con rigor, honestidad y gran humanidad.

Buen ejemplo de ello es la dirección de 14 Tesis doctorales junto con numerosos Trabajos fin de Máster, Trabajos fin de Grado y Tesinas de Licenciatura. Impartió cursos de posgrado, Máster y Conferencias en la Academia polaca de Jarzebin, en el Instituto Agronómico Mediterráneo y en las Universidades de Montevideo, Córdoba, Islas Baleares, Complutense de Madrid y San Jorge de Zaragoza.

La profesora Arruga fue una persona emprendedora, trabajadora incansable que desarrolló una intensa actividad investigadora en las Universidades de Valencia, Milán, Budapest, Massachussets, Upsala, Reading, en el *Institut National de Recherche pour l'Agriculture, l'Alimentation et l'Environnement* de Jouy-en-Josas (París), en la *Bristol Veterinary School* y en el *Hammersemith Hospital* de Londres.

Los resultados de su gran capacidad de trabajo y férrea voluntad se reflejan en un extraordinario curriculum con más de 200 publicaciones sobre Epigenética, Citogenética y Patologías de origen genético en revistas indexadas y recopiladas en bases de datos internacionales, junto con capítulos de libros, ponencias y numerosas comunicaciones en Congresos.

Dirigió más de 100 proyectos de investigación, contratos y convenios con instituciones nacionales e internacionales y hasta su jubilación coordinó el grupo de investigación GENPATVET reconocido por la Diputación General de Aragón.

Su ingente labor investigadora ha sido reconocida, como miembro del Comité de las revistas de mayor impacto en su especialidad. Desarrolló una extensa labor como evaluadora en organismos dedicados a la financiación de proyectos de investigación nacionales e internacionales de la Unión Europea, Suecia, Francia, Argentina, Uruguay y en las agencias para la calidad del sistema universitario de Valencia, Castilla y León, Aragón y en la nacional ANECA.

Ingresó en esta Real Academia de Ciencias (10-12-2015) con la medalla número 34, para ocupar la vacante producida por el fallecimiento del doctor D. Manuel Tamparillas Salvador. Su extenso discurso sobre *Epigenética. ¿somos únicamente la expresión de nuestro genotipo o hay otras intereacciones entre los genes y factores externos que modifiquen nuestro fenotipo?* ratifica la profundidad de sus conocimientos.

De su actividad en esta Academia, como presidenta de la sección de Naturales desde el año 2016 hasta su fallecimiento, cabe señalar su encomiable labor realizada con responsabilidad y entrega como persona afable, conciliadora, coherente con sus ideas, sencilla y abierta al diálogo a la vez que rigurosa y honesta.

Su brillante trayectoria científica ha sido ampliamente reconocida y galardonada, con el nombramiento de Docente honoraria por la Universidad de Montevideo, Miembro del Comité de Expertos del Instituto de Genética de Polonia, Coordinadora de la Comisión europea del Ministerio de Economía y Empresa, Miembro de la Comisión europea para la estandarización del cariotipo en diversas especies animales y con el premio Félix Azara 2012 concedido por la Diputación de Huesca.

A estas distinciones hay que añadir su ingreso como Académica correspondiente de la Real Academia de Medicina de Zaragoza (26-10-2023). Su magnífico discurso sobre el *Pangenoma y sus posibles aplicaciones en la medicina personalizada*, evidencia la solidez de sus argumentos y su formación científica.

Debo añadir que este acto tiene un especial significado para mí, ya que tuve el honor de pronunciar el discurso de recepción y glosar su actividad científica y su calidad humana, sin poder imaginar que en un breve período de tiempo escribiría esta nota necrológica cargada de emoción y sentimiento.

Días antes de su fallecimiento recibió el nombramiento de *Hija predilecta de Perdiguera*, por su destacada trayectoria académica y constante dedicación al progreso y bienestar de la Sociedad.

A través de estas líneas, escritas con profundo afecto y admiración, transmito en nombre de esta Academia y en el mío propio, mis sentimientos de condolencia a su esposo José Ignacio Bonafonte Zaragozano, discípulo, compañero y entrañable amigo. A sus hijos Elena y Nacho, a sus nietas Almudena y María y a toda su familia.

María Victoria creó una familia de la que se sentía orgullosa y le aportaba según sus propias palabras “felicidad sosegada y esperanza de vida, facilitándole la inspiración y el empeño en su trabajo”.

Hoy nos queda su recuerdo tras una trayectoria llena de méritos y, sobre todo, de una gran humanidad. Supo conjugar su fe profunda con la razón y la Ciencia. Su recuerdo permanecerá para siempre, ya que supo despertar admiración y afecto en el corazón de los que la conocimos.

Que brille para ella la luz perpetua, que viajó a la eternidad, allá donde la muerte es vida y la alegría infinita. Descanse en paz.

Actividades de la Real Academia de Ciencias Exactas, Físicas, Químicas y Naturales de Zaragoza durante el año 2024

Sesiones y actividades corporativas

La Real Academia de Ciencias Exactas, Físicas, Químicas y Naturales de Zaragoza (en adelante Academia) ha celebrado durante el año 2024, seis sesiones plenarias, cuatro de ellas ordinarias y dos extraordinarias.

Las sesiones ordinarias tuvieron lugar los días que se indican a continuación, con una breve exposición de los puntos más relevantes tratados:

- 17 de abril, en la que se dio recepción al discurso de ingreso de Doña María Luisa Sarsa Sarsa, designando al académico Manuel Asorey para dar el discurso de contestación; se aprobó la propuesta de nuevos académicos de la Sección de Naturales: doña Berta Sáez Gutiérrez, don José Luis Peña Monné y don José Manuel Nicolau Ibarra; y se aprobó la propuesta de nuevo académico correspondiente de la Sección de Químicas, don Carlos Genzor Asín.

- 3 de julio, en la que se aprobó la propuesta de nuevo académico de la Sección de Físicas: don Conrado Rillo Millán; y la propuesta de nuevos académicos correspondientes de la Sección de Naturales: don Eduardo Martínez de Pisón Stampa, don Gregorio Montero González y doña María Patrocinio Morrondo Pelayo.

- 21 de noviembre, en la que se dio recepción al trabajo correspondiente al Premio de Investigación 2024, relativo a la Sección de Químicas (don Jesús del Barrio Lasheras). El premio correspondiente a la Sección de Naturales quedó desierto. Así mismo, se aprobó remitir el escrito "*Consideraciones sobre el tratamiento de la Geología y los mapas de riesgos naturales en el PGOU de Teruel*", elaborado por el académico José Luis Simón.

- 17 de diciembre, en la que se aprobaron las propuestas de las Secciones de Exactas y Físicas para los Premios de Investigación 2025: doña Carmen Rodrigo Cardiel y don Jesús Carrete Montaña; se aprobó la propuesta de nuevo académico correspondiente de la Sección de Exactas: don Ernesto Estrada; aprobándose, por último, la adhesión de la Academia a la Red Panhispánica de Lenguaje Claro y Accesible.

Las sesiones extraordinarias se celebraron en la Sala de Grados de la Facultad de Ciencias:

- 18 de septiembre: Ingreso de la nueva académica María Luisa Sarsa Sarsa.

- 21 de noviembre: Entrega del Premio de Investigación 2024 al investigador propuesto por la Sección de Químicas: don Jesús del Barrio Lasheras.

Altas y bajas de académicos numerarios, de honor y correspondientes

Bajas, por fallecimiento, de académicos numerarios:

Doña María Victoria Arruga Laviña, fallecida el 10 de junio, quien fue académica numeraria desde su ingreso en la Academia el 10 de diciembre de 2015 hasta su fallecimiento, ocupando la medalla número 34.

Ingreso de académicos numerarios:

El 18 de septiembre la académica electa doña María Luisa Sarsa Sarsa presentó su discurso de ingreso "*Haciendo visible lo invisible*", recibiendo la medalla número 40, siendo contestado su discurso por el académico Manuel Asorey Carballeira.

Nombramiento de académicos numerarios:

En la sesión ordinaria del 17 de abril se aprobó la propuesta de nuevos académicos de la Sección de Naturales: doña Berta Sáez Gutiérrez, don José Luis Peña Monné y don José Manuel Nicolau Ibarra.
En la sesión ordinaria del 3 de julio se aprobó la propuesta de nuevo académico de la Sección de Físicas: don Conrado Rillo Millán.

Nombramiento de académicos correspondientes:

En la sesión ordinaria del 17 de abril se aprobó la propuesta de nuevo académico correspondiente de la Sección de Químicas: don Carlos Genzor Asín.
En la sesión ordinaria del 3 de julio se aprobó la propuesta de nuevos académicos correspondientes de la Sección de Naturales: don Eduardo Martínez de Pisón Stampa, don Gregorio Montero González y doña María Patrocinio Morrondo Pelayo.
En la sesión ordinaria del 17 de diciembre se aprobó la propuesta de nuevo académico correspondiente de la Sección de Exactas: don Ernesto Estrada.

Firma de convenios

El 26 de abril la Academia firmó un convenio de colaboración con la Fundación Ibercaja para colaborar en el desarrollo de los ciclos de conferencias que organiza la Academia en el Patio de la Infanta.

Publicaciones de la Academia

Se ha publicado el volumen 78 de la Revista de la Academia de Ciencias de Zaragoza, correspondiente a 2023.
Asímismo, se ha publicado el discurso de ingreso de la académica doña María Luisa Sarsa Sarsa, junto al correspondiente discurso de contestación por el académico don Manuel Asorey Carballeira.

Organización de conferencias y eventos

La Academia durante 2024 ha organizado dos ciclos de divulgación científica de tres conferencias cada uno, que se desarrollaron en primavera y otoño, en las instalaciones de la Obra social de Ibercaja del Patio de la Infanta, c/ San Ignacio de Loyola 16, a las 19 horas. y que contaron con una excelente acogida de público.

Ciclo de conferencias: "Retos y oportunidades de la inteligencia artificial"

Organizado por la Sección de Físicas, el ciclo de primavera se desarrolló con los títulos de conferencias y protagonistas siguientes:

6 de marzo: *Inteligencia artificial hoy: cómo funciona y qué podemos hacer con ella*, impartida por Luis Martín Moreno (Instituto de Nanociencia y Materiales de Aragón, CSIC-Universidad de Zaragoza).

13 de marzo: *Ética e inteligencia artificial*, impartida por José Ignacio Latorre (Centro para las tecnologías cuánticas, Singapur).

20 de marzo: *Mecanismos físicos de la inteligencia natural*, impartida por Jordi García Ojalvo, (Universidad Pompeu Fabra, Barcelona).

Ciclo de conferencias: "Impactos del cambio climático: el reto de la adaptación"

Organizado por la Sección de Naturales, el ciclo de otoño se desarrolló con los títulos de conferencias y protagonistas siguientes:

16 de octubre: *¿Vamos a tener menos agua?*, impartida por Miguel García Vera, doctor en Hidrogeología, Jefe de Planificación Hidrológica de la Confederación Hidrográfica del Ebro.

23 de octubre: *Calentamiento global: ¿Habrá más riesgos para nuestros montes?*, impartida por Rafael Calama Sainz, doctor Ingeniero de Montes, Investigador del Instituto Nacional de Investigación y Tecnología Agraria y Alimentaria (INIA-CSIC). Esta conferencia contó con la colaboración del Colegio Oficial de Ingenieros de Montes en Aragón.

30 de octubre: *El cambio climático y el incremento de enfermedades infecciosas emergentes*, impartida por Caridad Sánchez Acedo, doctora en Veterinaria, Catedrática emérita de la Universidad de Zaragoza y académica de número de las Reales Academias de Ciencias y de Medicina de Zaragoza.

Otras actividades

El 13 de marzo se cursó una visita a la empresa CERTEST, en San Mateo de Gállego, organizada por el académico Carlos Gómez-Moreno, siendo muy bien recibidos por los fundadores, Óscar Landeta y Carlos Genzor, quienes explicaron las características de la empresa, su evolución, proyectos que desarrollan y planes de futuro, para luego proceder a visitar los laboratorios, donde trabajan muchos antiguos alumnos de la Universidad de Zaragoza y, por ende, de alguno de los académicos.
El 20 de marzo, por iniciativa del Senatus Científico, se visitó la remodelada Facultad de Filosofía y Letras.
En los últimos meses del año, el académico José Luis Simón elaboró el informe "*Consideraciones sobre el tratamiento de la Geología y los mapas de riesgos naturales en el PGOU de Teruel*", que la Academia remitió al Ayuntamiento de Teruel.

Premios de investigación de la Academia

Al igual que en los años previos, el premios de investigación de la Academia han contado con el apoyo económico de la Fundación San Valero, fruto del convenio existente entre ambas instituciones.
Cumplidos los trámites exigidos de entrega de un artículo de su ámbito y especialidad para su publicación en la Revista de la Academia, en la sesión extraordinaria de 27 de noviembre se procedió a la exposición del trabajo y a la entrega del Premios de investigación de la Real Academia de 2024 que correspondió, por la Sección de Químicas, a don Jesús del Barrio Lasheras, profesor contratado doctor del Departamento de Química Orgánica de la Universidad de Zaragoza, que presentó su trabajo "*Designing polymer materials with dynamic bonds*".
El premio correspondiente a la Sección de Naturales quedó desierto.

Honores, distinciones y nombramientos a académicos

El Sr. Presidente, Antonio Elipe Sánchez, fue nombrado académico de la "*International Academy of Astronautics*", en su comisión "*Engineering Sciences*", a la que pertenecía como académico correspondiente desde 2019.

La académica Sra. Dña. María Victoria Arruga fue nombrada hija predilecta de Perdiguera.

Se ha publicado un volumen de revista en celebración del 75 aniversario del académico Sr. D. Juan Bartolomé Sanjoaquín: *Prof. Juan Bartolomé: A brief scientific profile.*, Fiz. Nizk. Temp. **50** (2024), 475-476/Low Temperature Physics **50** (2024), 429-430. doi:10.1063/10.0026055/

El académico Sr. D. Manuel Doblaré Castellano ha sido elegido:

- profesor distinguido de la Universidad Nanjing Tech en Nanjing (China),
- *Fellow* de la *Asia-Pacific Artificial Intelligence Association* (AAIA),
- *Associate Member* de *Stanford Sigma Xi scientific association.*

El académico Sr. D. Manuel Ricardo Ibarra García ha sido nombrado "*Fellow*" de la "*European Physical Society*" y "Alumni Distinguido" de la Universidad de Granada.

El académico Sr. D. Fernando Luis Vitalla ha sido nombrado

- coordinador de la sub-área "Física Cuántica y de la Materia" de la Agencia Estatal de Investigación,
- miembro del comité C5 ("*Low Temperature Physics*") de la "*International Union for Pure and Applied Physics* (IUPAP)".

Participación en la organización de conferencias y congresos

El académico Sr. D. Manuel Doblaré Castellano ha organizado el congreso "DIAMOOC *Workshop: Integrated AI Design and Engineering of 3D Bioprinted Multi-Organoids on Chip for Tumor Diagnosis and Therapy*", celebrado en Zaragoza los días 24 y 25 de mayo.

El académico Sr. D. Fernando Luis Vitalla ha co-organizado el simposio "QT04-*Molecular Quantum Systems*", en el marco del congreso internacional "2024 *Fall Meeting of the Materials Research Society* (MRS24)", Boston (USA), 1-5 de diciembre y ha sido miembro del "*International Scientific Committee*" de la "*Quantum Matter International Conference & Expo*", San Sebastián, 6-10 mayo.

El académico Sr. D. Luis Martín Moreno ha co-organizado el encuentro "*Nanolight* 2024", en el Centro de Ciencias de Benasque, del 25 de febrero al 2 de marzo.

El académico Sr. D. Ignacio Pérez-Soba Diez del Corral ha sido Miembro del comité organizador de la V Reunión del Grupo de Trabajo de Hidrología Forestal de la Sociedad Española de Ciencias Forestales (SECF), celebrada del 16 al 18 de octubre en Canfranc (Huesca), y ha sido designado miembro del comité científico del IX Congreso Forestal Español, organizado por la SECF y a realizar del 16 al 20 de junio de 2025 en Gijón (Asturias). Igualmente, fue coordinador y presentador de la *Jornada sobre planificación y ejecución de aprovechamientos de madera. Bases para una Gestión Forestal Activa y Sostenible*, organizada en Cedrillas (Teruel), el 28 de febrero, por el Departamento de Medio Ambiente y Turismo del Gobierno de Aragón, el Colegio Oficial de Ingenieros de Montes en Aragón y los Ayuntamientos de Cedrillas y de Monteagudo del Castillo.
También ha sido el presentador y moderador del debate posterior de las siguientes conferencias:

- *Construcción con madera: frente a los tópicos, tecnología, sostenibilidad y oportunidades*, impartida por el Doctor Ingeniero de Montes Sr. D. Miguel Esteban Herrero, en el Ateneo de la Escuela de Ingeniería y Arquitectura (EINA) de la Universidad de Zaragoza el 6 de noviembre.
- *Calentamiento global: ¿Habrá más riesgos en nuestros montes?*, impartida por el Doctor Ingeniero de Montes Sr. D. Rafael Calama Sanz, y organizada por la Real Academia de Ciencias de Zaragoza, la Fundación Ibercaja y el Colegio Oficial de Ingenieros de Montes en Aragón en el Patio de la Infanta de Zaragoza, el 23 de octubre.

Además, ha sido (por tercer año consecutivo) miembro del Jurado de los Premios del Concurso nacional "R7 por el planeta", concedidos por la Fundación Ibercaja para premiar iniciativas de centros educativos para el desarrollo sostenible de la sociedad y de su entorno, y para reconocer actitudes y valores en el ámbito de la protección del medio ambiente.

La académica Sra. Dña. María Luisa Sarsa Sarsa ha sido miembro de los comités organizadores de los siguientes eventos:

- *Primera reunión de los planes complementarios astroHEP, Plan de Recuperación, transformación y Resiliencia-MRR*, en Zaragoza, del 5 al 7 de junio.
- *XXXV edición de la Olimpiada Aragonesa de Física*, celebrada en la Facultad de Ciencias de la Universidad de Zaragoza el 23 de febrero.

El académico Sr. D. José Luis Simón Gómez ha participado en los siguientes eventos:

- Organización, junto a Carlos Liesa y Eduardo Espílez (Fundación Dinópolis), de la jornada divulgativa *Geolodía 24–Teruel. Un altiplano que conserva el paisaje del Turoliense, Ababuj-El Pobo (Teruel)*. Geolodía es una actividad de divulgación de la geología a nivel nacional que se celebra simultáneamente en todas las provincias

españolas, coordinada por la Sociedad Geológica de España.
- Visita guiada y coordinación del acto de celebración, el 7 de septiembre, en el Parque Geológico de Aliaga, con motivo de la inclusión de sus estructuras de superposición de pliegues en la lista de los "Segundos 100 Lugares" del patrimonio geológico de interés mundial por la "*International Union of Geological Sciences*'' (IUGS).
- Coordinación de la Jornada de Encuentro en torno al Patrimonio Natural de Teruel, organizada en colaboración con el Instituto de Estudios Turolenses, celebrada el 23 de noviembre en el salón de actos de la Cámara de Comercio de Teruel.

Conferencias y cursos impartidos por nuestros académicos

El Sr. Presidente, Antonio Elipe Sánchez, ha impartido la conferencia invitada titulada *An oxymoron: Generalized Restricted Three Body Problem*, en el "Astronomical Observatory", de la "Adam Mickiewicz University", en Poznań, Polonia, el 9 de abril.

El académico Sr. D. Enrique Artal ha impartido las siguientes conferencias:
- *Orbifolds and line arrangements*. Conferencia invitada en la Sesión Especial "Algebra-Geometry" del "Seventeenth International Conference Zaragoza-Pau on Mathematics and its Applications", celebrada en Jaca, septiembre de 2024. Además ha sido miembro del Comité Científico del Congreso.
- *Intersections of ellipsoids and singularities II*. Conferencia plenaria en el "International Congress on Complex Geometry, Singularities and Dynamics: In honor of José Seade", celebrado en Cuernavaca (México), junio 2024.
- *Intersecciones singulares de cuádricas coaxiales*. Conferencia invitada en la Sesión Especial de la Red Española de Topología del Congreso Bienal RSME2024, Pamplona, enero de 2024. Además ha sido organizador de esta sesión y de la Sesión Especial de la Red de Geometría Algebraica y Singularidades.
- *Algebraic, geometric and topological properties of complex projective plane curves*. Conferencia en el "Topology & Geometry Seminar NUS", en Singapur, octubre de 2024, durante una estancia de investigación.

El académico Sr. D. José Cariñena Marzo ha impartido la conferencia *El concepto de Simetría y su contribución al desarrollo de la ciencia*, conferencia inaugural del Programa de Doctorado de la Universitat Jaume I , en Castelló, el 28 de Noviembre.
También ha participado en los congresos "XXV Encuentro de Invierno", en Zaragoza, del 18 al 19 de enero, en el "Workshop on the quantum future", en Zaragoza, el 13 de marzo, y en el "Acte en record al professor Miguel Muñoz", en la UPC, Barcelona, el 7 de junio.

El académico Sr. D. Manuel Doblaré Castellano ha impartido las siguientes conferencias:

– *On modeling cell pasticity in contiumm mathematical biology*, conferencia semiplenaria en la "2024 Eccomass Conference" at Lisbon.
– *Homeostasis and epigenetic adpatation, concept, modeling, and examples*, conferencia invitada en el "2024 International Workshop on The coupled nonlinear continuum theory horizon", celebrado en Castro Urdiales, del 1 al 5 de julio.

El académico Sr. D. Alberto Elduque ha impartido las siguientes conferencias:
– *The extended Freudenthal magic square via tensor categories*, conferencia invitada en el congreso "Symmetric Tensor Categories and Representation Theory", celebrada en el "Institute of Pure and Applied Math (IPAM)", University of California Los Angeles, USA; 8–12 de enero.
– *From the Albert Algebra to Kac's Jordan superalgebra via tensor categories*, conferencia invitada en el congreso "XVI Jornadas de Álgebra No Conmutativa", celebrado en la Universidad de Granada, 4–5 de abril.
– *From the Albert Algebra to Kac's Jordan superalgebra via tensor categories*, conferencia en el Seminario del Departamento de Matemáticas de la Universidad de California-Berkeley, 29 de abril.
– *Gradings by root systems and S-structures on Lie algebras*, conferencia invitada en el congreso "Advances in Lie Theory, Representation Theory, and Combinatorics: Inspired by the work of Georgia M. Benkart", celebrado en el "Simons Laufer Mathematical Sciences Institute", Berkeley, USA, 1–3 de mayo.
– *From algebras to superalgebras via tensor categories*, curso de 4 horas en la escuela de verano "Álgebras de Hopf y Categorías Tensoriales", celebrada en la Universidad de Almería, 8–12 de julio.
– *Gradings on simple Lie algebras: old and new*, conferencia plenaria en el congreso "XXVII Brazilian Algebra Meeting", celebrado en el "Inst. Mathematics and Statistics", Uniersidade de São Paulo, Brasil, 15–19 de julio.
– *A few exceptional algebras*, conferencia en la sesión especial "Fifty Years of Communications in Algebra" en el congreso 'Joint Meeting of the NZMS, AustMS and AMS", celebrado en la University of Auckland, Nueva Zelanda, 9–13 de diciembre.

El académico Sr. D. Manuel Ricardo Ibarra García ha impartido las siguientes conferencias:
– *Ultrasonic effects due to the interaction of electromagnetic radiation with magnetic nanoparticles*, conferencia Plenaria en el Congreso Internacional "Nanomaterials Applied to Life Science" (NALS-2024), celebrado en Granada.
– *Magnetic nanofibers for degradation of organic pollutants*, impartida en la "Hong Kong University of Science and Technology".

El académico Sr. D. Fernando Luis Vitalla ha impartido las siguientes conferencias invitadas:

- *Wiring up molecular spin qubits with superconducting circuits*, en la Escuela Nacional de Materiales Moleculares (ENMM24), Almuñécar (España), el 14 de marzo.
- *Circuit-QED with molecular spin qudits* en la "International Conference on Superconductivity and Magnetism", Fethiye (Turquía), 29 de abril.
- *Wiring up molecular spin qubits with superconducting circuits*, en el simposio "Molecular Quantum Technologies" del "EurChemS Chemistry Congress", Dublín (Irlanda), 10 de julio.
- *Wiring up molecular spin qudits with superconducting circuits*, en la "European Conference on Molecular Magnetism (ECMM24)", Cracovia (Polonia), 17 de julio.
- *Wiring up molecular spin qudits with superconducting circuits*, en la "International Conference on Modern Trends in Molecular Magnetism (MTMM24)", Bangalore (India), 7 de noviembre.
- *Circuit-QED with molecular spin qudits*, en el "3rd workshop on Molecular Quantum Technology (MQT 2024)", Puerto Varas (Chile), 17 de diciembre.

El académico Sr. D. Luis Martín Moreno ha impartido las siguientes conferencias invitadas:

- *An overview of applications of Deep Learning in Science*, en el "XI International Conference BIFI 2024: Artificial Intelligence at theCrossroads of Interdisciplinary Science", en Zaragoza, el 17 de enero.
- *Retos y oportunidades de la inteligencia artificial*, en el Ciclo de Conferencias de Primavera, de la Academia de Ciencias de Zaragoza, en Zaragoza, el 24 de marzo.
- *Strong Light Matter Coupling in Ultra-Small Volumes*, en la Bienal de la Real Sociedad Española de Física, en San Sebastián, el 17 de julio.

El académico Sr. D. Luis Oro Giral ha impartido las siguientes conferencias:

- *Química, descarbonización y energías renovables*, en la Universidad de la Experiencia, Campus de Caspe, el 15 de octubre.
- *Química, descarbonización y energías renovables*, en el campus de Huesca de la Universidad de Zaragoza, el 12 de diciembre.

El académico Sr. D. Ignacio Pérez-Soba Diez del Corral ha impartido las siguientes conferencias y cursos:

- 12 horas de docencia en el *XVIII Diploma de Especialización en Derecho Local de Aragón*, organizado por la Universidad de Zaragoza y el Departamento de Presidencia, Interior y Cultura del Gobierno de Aragón, y convocado por la Orden PIC/1714/2023, de 16 de noviembre (BOA n.º 226, de 23 de noviembre). Fueron

tres sesiones de 4 horas cada una, dos en Zaragoza (29 de abril y 21 de octubre) y una en Huesca (14 de octubre), que se dedicaron a la protección legal de los montes municipales aragoneses, con especial referencia a los declarados de utilidad pública.

- Impartió, como profesor único, dos ediciones del curso *Protección y regulación legal de los montes en la Comunidad Autónoma de Aragón*, organizado por el Departamento de Medio Ambiente y Turismo del Gobierno de Aragón (Huesca, del 23 al 25 de enero; Zaragoza, del 12 al 14 de febrero). 22 horas lectivas en total.
- Impartió, como profesor único, tres ediciones del curso *Incendios forestales y su regulación legal*, organizado por el Instituto Aragonés de Administración Pública (Zaragoza, 9 de abril; Huesca, 18 de abril y Teruel, 30 de abril). 15 horas lectivas en total.
- Impartió, como profesor único, cuatro webinars de formación para la Red Estatal de Montes Públicos (REMP), coordinada por la Fundación Centro de Servicios y Promoción Forestal y de su Industria de Castilla y León (CESEFOR), todos ellos impartidos por videoconferencia, sumando 12 horas lectivas: *Clasificación legal y naturaleza jurídica de los montes públicos en España* (24 de julio), *El régimen jurídico de defensa y de uso de los montes de utilidad pública* (25 de septiembre), *Deslinde y amojonamiento de montes de utilidad pública* (19 de noviembre) y *Régimen jurídico de los aprovechamientos forestales en montes de utilidad pública* (17 de diciembre).
- *La defensa contra aludes en áreas de montaña*, en la Jornada sobre recuperación de daños provocados por catástrofes naturales, organizada por la Fundación del Colegio de Ingenieros de Caminos, Canales y Puertos. Madrid, 1 de febrero.
- *Aprovechar madera y gestionar ecosistemas: dos caras de una moneda*, en la Jornada "Los aprovechamientos de madera en los montes públicos de Aragón", organizada por el Departamento de Medio Ambiente y Turismo del Gobierno de Aragón, el Centro Público Integrado de Formación Profesional "San Blas" y el Colegio Oficial de Ingenieros de Montes en Aragón. Barrio de San Blas, Teruel, 2 de mayo.
- *El cambio climático: certezas e incertidumbres*, en la Jornada "Los mitos de la emergencia climática. Una visión humanista del medio ambiente", organizada por el Grupo parlamentario Vox de las Cortes de Aragón. Zaragoza, 24 de mayo.
- *Actualización y puesta en valor del Catálogo de Montes de Utilidad Pública. La experiencia de la provincia de Zaragoza*, en la Jornada de presentación del proyecto REMP (Red Estatal de Montes Públicos), organizada por la Dirección General de Biodiversidad, Bosques y Desertificación del Ministerio para la Transición Ecológica y el Reto Demográfico y la Fundación CESEFOR. Madrid, 11 de junio.
- *Manuel Silva, historiador y filósofo de la ingeniería española*, en la Sesión In Memoriam del académico Excmo. Sr. D. Manuel Silva Suárez, organizada por la Real Academia de Ingeniería. Madrid, 18 de junio.

- *La restauración hidrológico-forestal de los Arañones y del torrente de los Meses*. Ponencia invitada en la V Reunión del Grupo de Hidrología Forestal de la Sociedad Española de Ciencias Forestales. Canfranc (Huesca), 16 de octubre.
- *El agua no sale de los ríos. La restauración hidrológico-forestal, herramienta para la gestión integral del ciclo hidrológico*, en las XXXI Jornadas Forestales de Gran Canaria, Paraninfo de la Universidad de Las Palmas de Gran Canaria, 14 de noviembre.
- *Falsos mitos sobre incendios forestales*, en la Jornada técnica "Incendios forestales: interconexiones", organizada por la Asociación Española de Lucha contra el Fuego (ASELF) en colaboración con la Dirección General de Protección Civil y Emergencias del Ministerio del Interior. Escuela Nacional de Protección Civil y Emergencias, Rivas-Vaciamadrid (Madrid), 21 de noviembre.

Igualmente, fue miembro de la mesa redonda *La subversión del humor, la humanidad y la cordura: 150 años de G.K. Chesterton*, organizada por el Centro Pignatelli de la Compañía de Jesús y la Fundación Cultural Ángel Herrera Oria. Zaragoza, 4 de junio.

La académica Sra. Dña. María Luisa Sarsa Sarsa ha impartido conferencias invitadas en los congresos:

- *Invisibles Data Days*, celebrado en el MPPP Garching, Munich, Alemania, del 6 al 7 de mayo.
- *SUSY2024: theory meets experiment*, celebrado en el IFT, Madrid, del 10 al 14 de junio.
- *RENATA and 21st MultiDark Joint Meeting*, celebrado en Santander, del 8 al 11 de octubre.

Además, ha actuado como integrante del grupo RISArchers con el monólogo "L@s Físic@s de Partículas y los dinosaurios", el 24 de febrero, en "El show de los monólogos científicos, Ciclo solidario de artes escénicas 2024", en el centro cívico Teodoro Sánchez Punter, Zaragoza.

El académico Sr. D. Javier San Román Saldaña ha impartido las siguientes conferencias:

- *El estado del río Aguasvivas*, en la localidad de Blesa (Teruel), el 22 de junio.
- *El cambio climático*, en la localidad de Jasa (Huesca), el 28 de septiembre.

El académico Sr. D. José Luis Simón Gómez ha impartido las siguientes conferencias:

- *Geología y desastres naturales: el espacio concreto, el tiempo profundo*, en la festividad de San Alberto Magno de la Facultad de Ciencias de la Universidad de Zaragoza, el 13 de noviembre.
- *Geología: una ciencia cargada de futuro*, en la jornada especial de educación ambiental "Historias de la Tierra", organizada por el IUCA y celebrada en el Campus

Universitario de Teruel el 25 de enero.

- *El terremoto de Used y las fallas activas de la Cordillera Ibérica central*, en el X Curso de Didáctica de la Geología, organizado por el Centro de Profesorado de Calatayud, y celebrada en Used (Zaragoza) el 24 de febrero.
- *Las cuatro caras de las catástrofes naturales*, en el IES Pilar Lorengar de Zaragoza, el 25 de marzo.
- *El impacto humano en el Planeta desde una Sociedad del desconocimiento*, dentro de la Semana de la Ciencia "Margarita Salas", organizada por el Club de la Prensa Asturiana, celebrada en Oviedo el 16 de abril.
- *¿Emergencia o cambio? ¿Climático, global o civilizatorio?*, organizada por el Círculo de Recreo-Casino de Teruel, celebrada en Teruel el 16 de mayo.
- *Pensamiento mágico y pensamiento racional ante los desastres naturales*, dentro del ciclo "Encuentros con la Ciencia", del Ámbito Cultural de El Corte Inglés, Zaragoza, 17 de octubre.

Además ha participado como ponente en mesa redonda "Energías renovables en Aragón", organizada por el Consejo de Protección de la Naturaleza de Aragón (CPNA), celebrada en el Centro Joaquín Roncal de Zaragoza el 23 de septiembre, así como en la . jornada "Riesgo sísmico y gestión de la emergencia en la Comunidad Autónoma de Aragón", organizada por la Dirección General de Protección Civil y Emergencias del Ministerio del Interior, impartiendo la conferencia *Fallas activas en Aragón y su implicación en la peligrosidad sísmica*, celebrada en la Subdelegación del Gobierno en Zaragoza el 13 de mayo.

El académico Sr. D. José S. Urieta Navarro impartió el seminario *Escalado del proceso electroquímico. Del laboratorio a la producción industrial*, los días 18,19 y 20 de marzo, dentro de las actividades complementarias del Máster de Química Industrial de la Universidad de Zaragoza.

Otras contribuciones relevantes de nuestros académicos

El académico Sr. D. Alberto Elduque organiza la XX temporada del *Taller de Talento Matemático*, actividad dirigida a estudiantes de secundaria, desde 3º de ESO hasta 2º de Bachillerato, así como la *Fase Aragonesa de la Olimpiada Matemática Española.*
También ha organizado la Fase Final de la LX Olimpiada Matemática Española, celebrada en Calatayud, del 13 al 17 de marzo.

El académico Sr. D. Manuel Ricardo Ibarra García ha realizado estancias como profesor invitado en las siguientes universidades:

- Universidad de Granada, como "Visiting Scholar" en el marco del Programa Propio de la UGR,

- AGH University Krakow (Poland),
- Hong Kong University Science and Technology, Clearwater, Kowloon Hong Kong,
- University of Science and Technology HKUST Guangzhou, China.

El académico Sr. D. Ignacio Pérez-Soba Diez del Corral ha sido:

- Decano del Colegio Oficial de Ingenieros de Montes en Aragón.
- Presidente de la Comisión Deontológica Nacional del Colegio Oficial de Ingenieros de Montes.
- Patrono de la Fundación "Capital Natural".
- Miembro del Comité Forestal de Aragón (órgano consultivo técnico del Gobierno de Aragón).

La académica Sra. Dña. María Luisa Sarsa Sarsa ha sido

- Co-IP del proyecto "ANAIS-112 Y ANAIS+: Detectores avanzados de ioduro de sodio para la búsqueda de materia oscura e I+D en otras técnicas basadas en centelleo", financiado por la Agencia Estatal de Investigación. Ref. PID2022-138357NB-C21. Periodo de ejecución del 1 de septiembre de 2023 hasta el 30 de agosto de 2026.
- Coordinadora del nodo en la Universidad de Zaragoza de la Red Temática "MultiDark", financiada por el Ministerio de Ciencia e Innovación/Agencia Estatal de Investigación. Ref: RED2022-134411-T. IP Miguel Ángel Sánchez Conde (Universidad Autónoma de Madrid). Duración de la red: desde el 1 de junio de 2023 hasta el 31 de mayo de 2025.
- Miembro del equipo investigador del proyecto LA5.A3. Búsquedas directas de materia oscura (ANAIS+: mejoras en la sensibilidad de ANAIS-112 usando aprendizaje automático y una nueva aproximación experimental). Convenio de Colaboración entre el Gobierno de Aragón, la Fundación Centro de Estudios de Físicas del Cosmos de Aragón, la Universidad de Zaragoza y el Instituto Tecnológico de Aragón para la ejecución de líneas de actuación de I+D+i en el marco de los planes complementarios previstos en el Plan de Recuperación, transformación y Resiliencia-MRR, financiado por Ministerio de Ciencia e Innovación (65 %) y Gobierno de Aragón (35 %). Duración desde el 7 de octubre de 2022 hasta el 29 de septiembre de 2025. IP: María Martínez Pérez.
- Miembro del equipo colaborador en el proyecto de divulgación "Artículos científicos para todos", financiado por FECYT. Ref.: FCT-23-19323 (Programa de Cultura Científica y de la Innovación). Duración desde el 1 de octubre de 2024 hasta el 30 de septiembre de 2025. IP: María Eugenia Dies Álvarez.
- Embajadora del Grupo Especializado de Mujeres en Física (GEMF) de la Real Sociedad Española de Física en la Universidad de Zaragoza desde 2023.
- Miembro del comité evaluador del premio RSEF-EPJ+ a las mejores tesis doctorales

de las divisiones y grupos especializados de la RSEF, correspondiente al año 2024.
- Miembro del jurado evaluador del Physicathon Universitario "Physics Around the Clock", 5ª edición, 24-25 febrero.
- Miembro del comité editorial de la revista conCiencias.digital, revista de la Facultad de Ciencias de la Universidad de Zaragoza.

Composición de la Academia a 31 de diciembre de 2024

Junta de Gobierno

Presidente:	D. Antonio Elipe Sánchez
Vicepresidente:	D. Fernando José Lahoz Díaz
Académico Editor:	D. Enrique Artal Bartolo
Académico Bibliotecario:	D. Andrés Pocoví Juan
Académico Web:	D. Pablo Alonso Gascón
Académico Tesorero:	D. Miguel Ángel Rebolledo Sanz
Académico Secretario:	D. Alberto Elduque Palomo

Académicos Numerarios y de Honor

A fecha 31 de diciembre de 2024 hay 35 académicos de número, 3 académicos de honor y cuatro académicos nombrados que no han leído todavía su discurso. Se listan a continuación, por secciones, citando número de medalla y fecha de ingreso o de nombramiento.

Sección de Exactas

Presidente:	Dña. María Teresa Lozano Imízcoz	(medalla 22)	*22 enero 1998*
Académicos:	D. Mariano Gasca González	(medalla 1)	*1 diciembre 1988*
	D. Manuel Calvo Pinilla	(medalla 25)	*10 marzo 1998*
	D. Eladio Domínguez Murillo	(medalla 27)	*25 marzo 1999*
	D. Antonio Elipe Sánchez	(medalla 16)	*30 marzo 2000*
	D. Jesús Bastero Eleizalde	(medalla 17)	*9 noviembre 2000*
	D. Manuel Doblaré Castellano	(medalla 19)	*3 noviembre 2005*
	D. Alberto Elduque Palomo	(medalla 29)	*23 febrero 2006*
	D. Enrique Artal Bartolo	(medalla 4)	*24 noviembre 2009*
	D. José Esteban Galé Gimeno	(medalla 10)	*31 enero 2018*

Sección de Físicas

Presidente:	D. Pablo Javier Alonso Gascón	(medalla 35)	*16 mayo 2002*
Académicos:	D. Miguel Ángel Rebolledo Sanz	(medalla 14)	*11 mayo 2000*
	D. José Fernando Cariñena Marzo	(medalla 33)	*6 noviembre 2001*
	D. Juan Bartolomé Sanjoaquín	(medalla 3)	*27 octubre 2016*
	D. Ricardo Ibarra García	(medalla 20)	*19 diciembre 2016*
	D. Manuel Asorey Carballeira	(medalla 18)	*27 mayo 2021*
	D. Luis Martín Moreno	(medalla 7)	*25 mayo 2022*
	D. Fernando María Luis Vitalla	(medalla 39)	*25 enero 2023*
	Dña. María Luisa Sarsa Sarsa	(medalla 40)	*18 septiembre 2024*
	D. Conrado Rillo Millán	*Electo el 3 de julio de 2024*	

Sección de Químicas

Presidente:	D. Luis Antonio Oro Giral	(medalla 11)	*4 junio 1981*
Académicos:	D. José Santiago Urieta Navarro	(medalla 5)	*2 diciembre 1997*
	D. Carlos Gómez-Moreno Calera	(medalla 6)	*21 octubre 1999*
	D. Juan Forniés Gracia	(medalla 24)	*26 junio 2000*
	D. Ángel García de Jalón Comet	(medalla 30)	*29 noviembre 2001*
	D. Juan Francisco Cacho Palomar	(medalla 13)	*2 diciembre 2003*
	D. Miguel Pocoví Mieras	(medalla 32)	*20 mayo 2004*
	D. José Luis Marqués Insa	(medalla 37)	*24 noviembre 2005*
	D. José Luis Serrano Ostáriz	(medalla 26)	*12 diciembre 2006*
	D. Fernando Lahoz Díaz	(medalla 2)	*3 mayo 2017*

Sección de Naturales*

Presidenta:	Dña. María Caridad Sánchez Acedo	(medalla 9)	*12 diciembre 2000*
Académicos:	D. Andrés Pocoví Juan	(medalla 28)	*4 abril 2019*
	D. José Luis Simón Gómez	(medalla 12)	*13 julio 2020*
	D. Ignacio Pérez-Soba Diez del Corral	(medalla 31)	*28 marzo 2023*
	Dña. Blanca Bauluz Lázaro	(medalla 38)	*28 junio 2023*
	D. Javier San Román Saldaña	(medalla 8)	*20 septiembre 2023*
	Dña. Berta Sáez Gutiérrez	*Electa el 17 de abril de 2024*	
	D. José Luis Peña Monné	*Electo el 17 de abril de 2024*	
	D. José Manuel Nicolau Ibarra	*Electo el 17 de abril de 2024*	

*En esta sección hay una vacante.

Académicos de Honor

D. Luis Joaquín Boya Balet	*16 mayo 2019*
D. Rafael Núñez-Lagos Roglá	*9 octubre 2019*
D. Juan Pablo Martínez Rica	*14 diciembre 2022*

Académicos Correspondientes

A fecha de 31 de diciembre hay 49 académicos correspondientes que se han distribuido por secciones y ordenados por fechas de nombramiento

Sección de Exactas

D. José M. Montesinos Amilibia	(7 abril 1992)
D. Claude Brezinski	(9 mayo 2002)
D. Charles A. Micchelli	(9 mayo 2002)
D. José Luis Fernández Pérez	(24 septiembre 2002)
D. Gilles Pisier	(24 septiembre 2002)
D. José Ángel Docobo Durántez	(21 abril 2005)
D. Sylvio Ferraz Mello	(21 abril 2005)
D. Francisco Marcellán Español	(4 noviembre 2004)
D. Santos González Jiménez	(27 abril 2006)
D. Efim Zelmanov	(5 octubre 2011)
D. Jesús Carlos Fernández Asensio	(7 junio 2013)
D. José Garay Pablo	(3 junio 2015)
D. Juan Luis Vázquez Suárez	(3 junio 2015)
D. Jesús Sanz Serna	(24 octubre 2018)
D. Ernesto Estrada	(17 diciembre 2024)

Sección de Físicas

D. Alberto Galindo Tisaire	(1 octubre 1967)
D. Eusebio Bernabeu Martínez	(1982)
D. Giuseppe Marmo	(9 mayo 2002)
Dña. María Josefa Yzuel Giménez	(9 mayo 2002)
D. José Adolfo de Azcárraga	(25 septiembre 2008)
D. Albert Figueras Dagá	(25 septiembre 2008)
D. Fernando María Legarda Ibáñez	(25 septiembre 2008)
D. Javier Llorca Martínez	(25 septiembre 2008)
D. Miguel V. Andrés Bou	(23 marzo 2009)
D. Javier Sesma Bienzobas	(7 mayo 2014)
D. Juan Ignacio Cirac Sasturaín	(3 junio 2015))
D. Antonio Hernando Grandes	(16 Febrero 2017))
D. Francisco Javier Solís Céspedes	(4 Octubre 2017)

Sección de Químicas

D. Ekkehardt Hahn	(13 junio 2002)
D. Pierre Braunstein	(13 junio 2002)
D. José María Ordovás Muñoz	(13 febrero 2008)
Dña. Mª Carmen Orosia Claver Cabrero	(13 febrero 2008)
D. Avelino Corma Canós	(15 octubre 2015)
D. Fernando Cossío Mora	(15 octubre 2015)
D. Carlos Genzor Asín	(17 de abril de 2024)

Sección de Naturales

D. Leandro Sequeiros Sanromán	(9 mayo 2002)
D. Luis Villar Pérez	(9 mayo 2002)
D. Adrian Michael Harvey	(13 junio 2002)
D. Mario Panizza	(13 junio 2002)
D. Carlos López Otín	(19 diciembre 2006)
D. Miguel Delibes de Castro	(23 febrero 2011)
D. Eladio Liñán Guijarro	(3 junio 2015)
D. Francisco García Novo	(15 octubre 2015)
Dña. Gloria Cuenca Bescós	(4 julio 2022)
D. Juan Marín Velázquez	(24 noviembre 2022)
Dña. María Luisa Peleato Sánchez	(13 diciembre 2022)
D. Eduardo Martínez de Pisón Stampa	(3 julio 2024)
D. Gregorio Montero González	(3 julio 2024)
Dña. María Patrocinio Morrondo Pelayo	(3 julio 2024)

Zaragoza, diciembre de 2024

INSTRUCCIONES PARA LOS AUTORES

Abstract

The *Revista de la Real Academia de Ciencias* publishes original research contributions in the fields of Mathematics, Physics, Chemistry and Natural Sciences. All the manuscripts are peer reviewed in order to assess the quality of the work. On the basis of the referee's report, the Editors will take the decision either to publish the work (directly or with modifications), or to reject the manuscript.

1 Normas generales de publicación

1.1 Envío de los manuscritos.

Para su publicación en esta Revista, los trabajos deberán remitirse a

Académico Editor
Revista de la Academia de Ciencias
Universidad de Zaragoza
50009 Zaragoza

o bien electrónicamente a la cuenta `artal@unizar.es`.

La Revista utiliza el sistema de *offset* de edición, empleando el texto electrónico facilitado por los autores, que deberán cuidar al máximo su confección, siguiendo las normas que aquí aparecen.

Los autores emplearán un procesador de texto. Se recomienda el uso de LaTeX, para el que se han diseñado los estilos `academia.sty` y `academia.cls` que pueden obtenerse directamente por internet en `http://www.raczar.es` o por petición a la cuenta de correo electrónico: `artal@unizar.es`.

1.2 Dimensiones

Se recomienda que el texto de los trabajos, redactados en español, inglés o francés, no exceda de 25 páginas, siendo preferible una extensión de 6 a 20 páginas como promedio. El texto de cada página ocupará una caja de 16×25 cm, con espacio y medio entre líneas.

2 Presentación del trabajo.

Los trabajos se presentarán con arreglo al siguiente orden: En la primera página se incluirán los siguientes datos:

a) *Título del trabajo:* Conciso, pero ilustrativo, con mayúsculas.
b) *Autor:* Nombre y apellidos del autor o autores, con minúscula.
c) *Centro:* Centro donde se ha realizado, con su dirección postal.
d) *Abstract:* En inglés y con una extensión máxima de 200 palabras.
e) *Texto*

A) Los encabezamientos de cada sección, numerados correlativamente, serán escritos con letras **minúsculas** en negrita. Los encabezamientos de subsecciones, numerados en la forma 1.1, 1.2, ..., 2.1, 2.2, ..., se escribirán en *cursiva*.

B) Las fórmulas estarán centradas y numeradas correlativamente.

C) Las referencias bibliogáficas intercaladas en el texto, deben ser fácilmente identificables en la lista de referencias que aparecerá al final del artículo, bien mediante un número, bien mediante el nombre del autor y año de publicación.

D) Las figuras y tablas, numeradas correlativamente, se intercalarán en el texto. Las figuras se enviarán en formatos `EPS, PDF, PNG, JPG`. Los apéndices, si los hay, se incluirán al final del texto, después de la bibliografía.

E) Para las referencias bibliográficas se recomienda el uso de BibTeXcon los estilos `amsplain` o `amsalpha`.

3 Notas finales

La Revista permite la inclusión de fotografías o figuras en color, con un coste adicional que correrá a cargo de los autores.

Enrique Artal
Académico Editor

Intercambio de Publicaciones

Relación de revistas nacionales que recibe en intercambio la Biblioteca de la Academia de Ciencias

1. *A Ciencia Cierta* – Academia Malagueña de Ciencias.
2. *Acta Botanica Barcinonensia* – Dep Biología Vegetal. Univ. Barcelona.
3. *Anales del Jardín Botánico de Madrid*
4. *Anales UNED Calatayud*
5. *Animal Biodiversity and Conservation* – Museu de Zoologia
6. *Anuari de la Reial Acadèmia de Ciencies i Arts de Barcelona*
7. *Boletín de la Academia Malagueña de Ciencias*
8. *Boletín Geológico y Minero* – Instituto Geológico y Minero de España
9. *Collectanea Botanica* – Institut Botànic (Barcelona)
10. *Collectanea Mathematica* – Universitat de Barcelona
11. *Extracta Mathematicæ* - Universidad de Extremadura
12. *Gaceta de la Real Sociedad Matemática Española*
13. *Lucas Mallada: Revista de Ciencias* – Inst. Est. Altoaragoneses.
14. *Manuals del Museu* – Museu de Ciències Naturals de Barcelona
15. *Memòries de la Reial Acadèmia de Ciencies i Arts De Barcelona*
16. *Naturaleza Aragonesa* – Sociedad de Amigos del Museo Paleontológico de la Universidad de Zaragoza.
17. *Trabajos de Geología* – Universidad de Oviedo
18. *Zoologia Bætica*. UNIVERSIDAD DE GRANADA.

Relación de revistas internacionales que recibe en intercambio la Biblioteca de la Academia de Ciencias

1. *Abhandlungen der Senckenberg für Naturforschung* – Senckenberg Research Institute
2. *Acta Entomologica Musei Nationalis Pragœ*
3. *Acta Geologica Polonica* - Warszawa
4. *Acta Mathematica Hungarica*
5. *Acta Matematica Sinica* - New Series China
6. *Anales de la Academia Nacional de Ciencias Exactas, Físicas y Naturales de Buenos Aires*
7. *Annalen des Naturhistorischen Museums in Wien. Serie A*
8. *Annalen des Naturhistorischen Museums in Wien. Serie B*
9. *Annales Fennici Mathematici*
10. *Annales Academiæ Scientiarum Fennicæ. Mathematica Dissertationes* – Helsinki, Suomalainen Tiedeakatemia
11. *Annali del Museo Civico di Storia Naturale "Giacomo Doria"*
12. *Arkiv För Matematik*
13. *Atti della Accademia Ligure di Scienze e Lettere. Serie VII*
14. *Boletín de la Sociedad Matemática Mexicana. Tercera Serie.*
15. *Brenesia: Revista de Biodiversidad y Conservación* – Museo Nacional de Costa Rica
16. *Bulletin de la Classe de Sciences* – Academie Royale de Belgique – Bruxelles
17. *Bulletin of the American Mathematical Society. New Series*
18. *Bulletin of the London Mathematical Society*
19. *Bulletin of the Polish Academy of Sciences*
20. *California Agriculture* – University of California
21. *Commentationes Mathematicæ : Annals of the Polish Mathematical Society, Series I*
22. *Dædalus - Journal of the American Academy of Arts and Sciences*
23. *Doriana - Supplementa agli Annali del Museo Civico di Storia Naturale "G. Doria"*
24. *Facta Universitatis - Series: Mathematics And Informatic* – University of Nis, Serbia
25. *Filomat* – University of Nis, Serbia
26. *Folia Zoologica* – Czechoslovak Academy of Sciences
27. *Functiones et Approximatio Commentarii Mathematici* - Poznań
28. *Glasnik Matematički Serija III* - Zagreb

29. *Hiroshima Mathematical Journal*
30. *Hokkaido Mathematical Journal*
31. *Jahrbuch Bayerische* – Akademie der Wissenschaften
32. *Jahrbuch der Akademie der Wissenschaften in Göttingen*
33. *Journal of the London Mathematical Society*
34. *Klapalekiana* – Czech Entomological Society
35. *Lecturas Matemáticas* - Colombia
36. *Mathematical Reports* – Romanian Academy
37. *Palæobiodiversity and Palæoenvironments* – Senckenberg Research Institute
38. *Proceedings of the London Mathematical Society*
39. *São Paulo Journal of Mathematical Sciences*
40. *SUT Journal of Mathematics* - Science University of Tokio

Colabora: