



Review Article

Cyanoacrylate Chemistry and Polymerization Mechanisms

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ABSTRACT

Cyanoacrylates have gained widespread attention and found applications across various industries due to their exceptional bonding capabilities. This study delves into the fundamental aspects of cyanoacrylate chemistry and polymerization mechanisms to address the challenges associated with premature curing and enhance the understanding of the underlying processes. Cyanoacrylates, recognized for their exceptional adhesive properties, undergo rapid polymerization catalyzed by minute amounts of moisture. The essence of the problem lies in the need to optimize the polymerization process to prevent premature bonding and ensure controlled curing. The investigation involves a comprehensive analysis of cyanoacrylate's chemical makeup, and its adhesive potency. Notably, the study explores the inadvertent discovery of cyanoacrylates during World War II, underscoring their versatile applications and the need for a nuanced understanding of their reactivity. Findings reveal the intricacies of cyanoacrylate polymerization, shedding light on the factors influencing the process, including temperature, humidity, and substrate composition.

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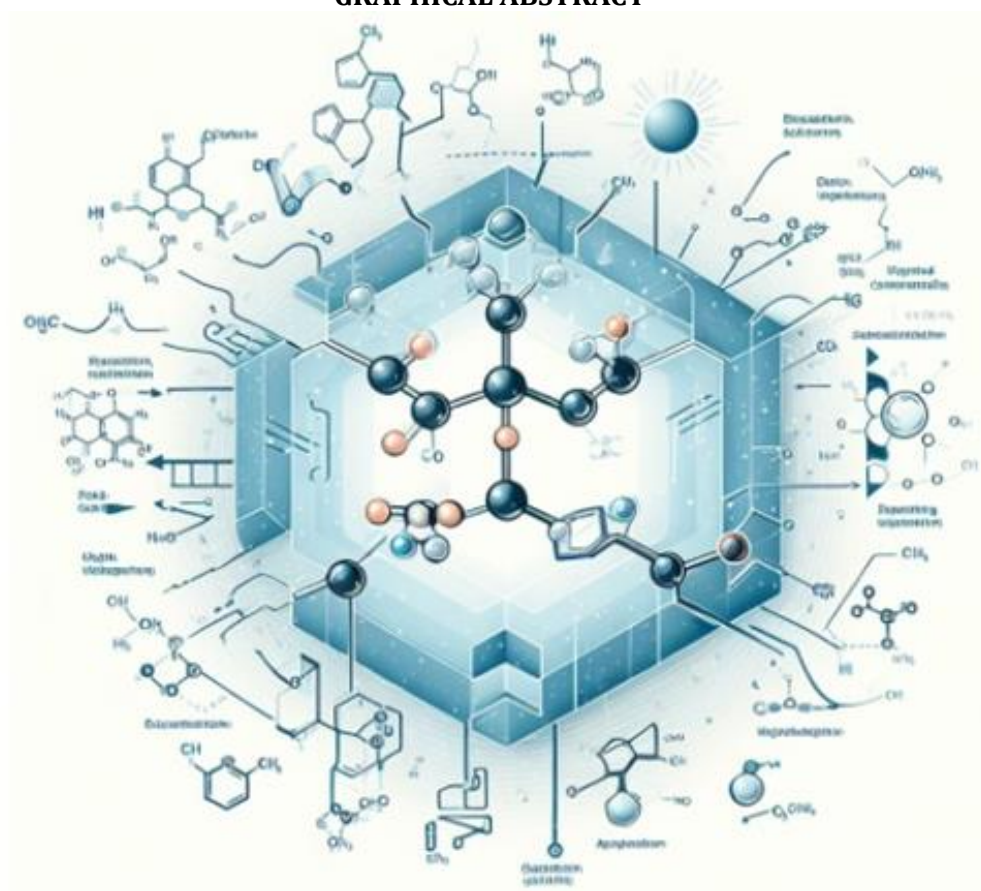
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GRAPHICAL ABSTRACT



Introduction

The amazing adhesive characteristics of this diverse family of chemicals are supported by the chemistry of cyanoacrylate, which is both fascinating and extremely useful in science. Because they can quickly and effectively link various materials together, cyanoacrylates, also referred to as "super glues" or "instant adhesives," have become a commonplace in our daily life [1]. Cyanoacrylate is a family of strong, fast-acting adhesives with industrial, medical, and household uses. They are derived from ethyl cyanoacrylate and related esters. The cyanoacrylate group in the monomer rapidly polymerizes in the presence of water to form long, strong chains. Cyanoacrylate esters are colourless, monomeric liquids sold commercially as quick-setting, high-strength adhesives. They polymerize rapidly at ambient temperature via

an anionic mechanism in the presence of weak bases such as alcohol and water. Cyanoacrylates can be further used in dentistry, to create some types of fillings [2]. Ethyl 2-cyanoacrylate is the primary active ingredient in most superglue, as displayed in Fig 1. Polymerization mechanism is the process of how monomers react to form polymers. There are two main types of polymerization mechanisms: step-growth and chain-growth. Step-growth polymerization involves the repeated condensation of monomers with functional groups, such as carboxylic acids, alcohols, amines, etc. The monomers lose small molecules, such as water or ammonia, as by-products. The polymer chains grow gradually until they reach high molecular weights. Examples of step-growth polymers are polyesters, polyamides, and polyurethanes. In

contrast, chain-growth polymerization involves the initiation, propagation, and termination of a chain reaction that adds monomers with double bonds, such as alkenes, to the growing polymer chain. The polymer chains grow rapidly and reach high molecular weights in a short time. Examples of chain-growth polymers are polyethylene, polypropylene, and polystyrene. Polymerization mechanisms determine the structure, properties, and applications of polymers. Likewise, they affect the kinetics, thermodynamics, and control of the polymerization reactions [3]. Cyanoacrylate chemistry involves the polymerization of cyanoacrylate monomers, which are strong, fast-acting adhesives used in various industries, medicine, and dentistry. Cyanoacrylate monomers polymerize anionically, typically in the presence of weak bases such as water or alcohol. The polymerization is initiated by anionic species, which can be hydroxyl ions, bromide ions, or bases like amines and phosphines.

The polymerization process involves the conjugate addition of anionic nucleophiles or bases to the cyanoacrylate monomer. This addition results in the formation of a propagating carbanion on the α -carbon, which is resonance-stabilized through the CN and CO₂R groups. The polymerization mechanism of cyanoacrylates involves rapid anionic polymerization in the presence of weak bases, resulting in the formation of long, strong chains and the unique adhesive properties of cyanoacrylate adhesives [4].

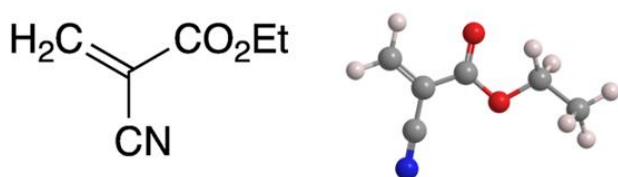


Fig 1.Structure of Ethyl 2-cyanoacrylate [1]

A historical perspective adds depth to the novelty of cyanoacrylate chemistry. Originally sought for clear plastics during World War II, scientists stumbled upon these adhesives serendipitously. This accidental discovery not only showcases the historical significance of cyanoacrylates but also underscores their uniqueness as a product of unintended experimentation. The versatility of cyanoacrylate adhesives extends beyond their rapid curing capabilities. As this exploration unfolds, it becomes evident that the chemistry and polymerization mechanisms of cyanoacrylates are not only scientifically intriguing, but also practically revolutionary. The novelty lies not only in their unique chemical structure and rapid bonding, but also in their historical roots and the unintended yet impactful discovery during a critical period in history. This study delves into the intricacies of cyanoacrylate chemistry, aiming to unravel the secrets behind their exceptional adhesive properties and broaden our understanding of their diverse applications [5].

Cyanoacrylates are used to construct electronic prototypes, fly model airplanes, coat nuts, and bolts for retention. Their ability to bond metal and general adaptability has made them well-liked among modellers and tiny enthusiasts. They are further employed in medicine as tissue sealants. The molecular structure of cyanoacrylate and the distinct polymerization mechanism, as depicted in Fig 2, set apart from other adhesives serve as the fundamental building blocks of its chemistry. A cyano (CN) moiety is present in the acrylate group of cyanoacrylate molecules [6].

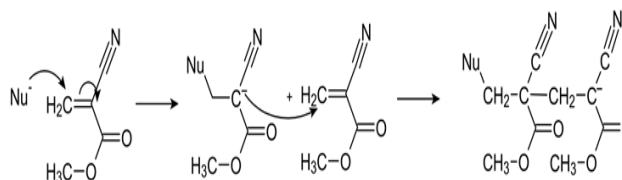


Fig 2.Polymerization of methyl-2-cyanoacrylate [3]

They are adept at adhering because of this structural characteristic, despite its seeming subtlety. A series of chemical reactions are started when these molecules come into touch with moisture, even in minute amounts, and they quickly create a robust and long-lasting polymeric network [7]. The exothermic and relatively instantaneous nature of this reaction allows cyanoacrylates to connect materials in a matter of seconds. Since few traditional adhesives can match their speed and effectiveness, cyanoacrylates have become widely used in a variety of industries [8]. This overview lays the groundwork for a more in-depth investigation of the chemistry of cyanoacrylate, focusing on the intricate molecular and chemical interactions that underpin its adhesive properties. In addition, it emphasizes the long-lasting impact of this amazing class of chemicals by implying the wider applications and relevance of cyanoacrylates in various industries, including industrial manufacturing, medical, and common household maintenance. The cyanoacrylate chemistry will be more thoroughly explained in the following sections of this study, giving light on its molecular characteristics, polymerization processes, and the wide range of applications it serves. The aim of the article is to explore the chemistry of cyanoacrylate.

Molecular structure of cyanoacrylate

The family of cyanoacrylate adhesives, which includes ethyl cyanoacrylate and related esters, is known for their strength and speed of action. Ethyl cyanoacrylate, which is the active component in the majority of commercial superglues, is the most prevalent monomer. In the presence of water, specifically hydroxide ions, the molecule's cyanoacrylate group quickly polymerizes to create molecules that resemble chains, creating extensive, durable chains that connect the bonded surfaces [9]. The strong, glassy resins made of polymer chains are

excellent for joining surfaces that are close together. The cyanoacrylate molecule reacts with any basic surface quickly due to the nitrile (CN) and ester (RCOOR) groups' extremely polar makeup, especially when moisture is present. The molecules quickly polymerize to produce cyanoacrylate repeating units with a polar character that resemble chains of molecules. The molecular structure of cyanoacrylate is characterized by the presence of a cyanoacrylate group, which are a functional group composed of a nitrile group and an ester group. The chemical formula for ethyl cyanoacrylate is $C_6H_7NO_2$, and its empirical formula is $C_4H_5NO_2$ [10]. These molecules' essential elements:

Cyanoacrylate group ($CH_2=C(CN)COO-$)

Alpha-cyanoacrylate is the primary component of the cyanoacrylate molecule. The cyanoacrylate's nitrile group (CN) and carbon-carbon double bond (C=C) are both present in this group, which also provides the substance its adhesive power. Since it reacts with minute amounts of moisture to start the polymerization process, the nitrile group's (CN) presence is a key component [11].

Ester group (COOR)

The ester group, denoted as COOR, to which the alpha-cyanoacrylate group is joined is attached contains a number of organic substituents. Different forms of cyanoacrylate compounds might result from variations in the specific R-group [12].

The alkyl group (R)

The R-group in the ester part of the cyanoacrylate molecule might differ amongst different cyanoacrylate compounds. Methyl, ethyl, and isobutyl are frequently used R-groups [13].

Cyanoacrylate synthesis

The Knoevenagel Reaction is the key component in the production of cyanoacrylate [14]. An alkyl cyanoacetate and formaldehyde (methanal) have

condensed to create this. Alkyl cyanide is converted into an enolate in the first phase. The electrophilic carbon on the formaldehyde is attacked by the produced enolate anion because it functions as a nucleophile. Next, the -OH group is released during the condensation step, resulting in the formation of methyl-2-cyanoacrylate. Because the monomer is incredibly reactive in the presence of base, it

polymerises after the condensation process when produced on an industrial scale [15].

As a result, the polymer should be cracked, resulting in a sloppy combination of the monomer and fragments of the broken-down polymer, as demonstrated in Fig 3. A distillation process is used to separate the pure monomer from the impure mixture. Until all of the pure monomer is extracted, the remaining mixture is recycled and cracked once more [16].

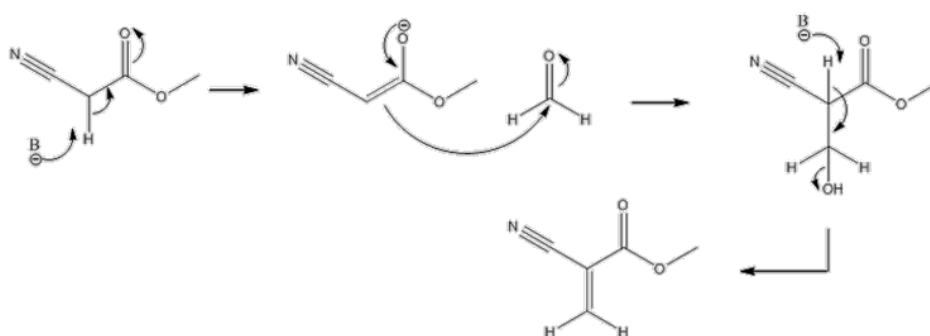


Fig 3. Cyanoacrylate synthesis [14]

Bond strength and durability of cyanoacrylate

The high-strength bonding that cyanoacrylate adhesives are known for can reach over 20 MPa. A wide range of substances, including metals, polymers, rubber, ceramics, and even some porous substrates like textiles, can create strong connections with them. The weak chemical and physical resistance of cyanoacrylate adhesives, however, reduces their endurance. How long an adhesive can sustain the strength claimed is referred to as its durability [17]. The strength of cyanoacrylate adhesives may be reduced to the point of bond failure when exposed to chemicals or impact. Because cyanoacrylates create a brittle, high-strength bond, they will struggle to survive light impact from movement or vibration. In the presence of water, the C=C groups in cyanoacrylate adhesives quickly go through chain-growth polymerization to generate long, sturdy chains that bind the bonded surfaces together [18]. If left unopened, cyanoacrylate adhesives have a shelf-life of

around one year from production and one month if used. The majority of their applications are as adhesives, joining a variety of materials, such as human skin and tissues, natural fibres, cotton, wool, and leather. Cyanoacrylates are used to construct electronic prototypes, fly model airplanes, and coat nuts and bolts for retention. Rubber or anhydride, toughening compounds with elastic qualities, can be added to cyanoacrylate adhesives to increase their shear strength. These substances aid in toughening basic cyanoacrylate formulations for applications requiring higher strengths, especially for improved shear strength. The product cyanoacrylate gel has a very high viscosity and sticks nicely to porous surfaces, whereas most basic cyanoacrylates have a relatively low viscosity and can be tricky to handle. Prior to use, it is crucial to test the accelerator on all bonding surfaces when using cyanoacrylate adhesives to guarantee compatibility [19].

To encourage adhesive bond growth, the bonding surface should be well-cleansed before applying the accelerator and adhesive. It is important to wear the appropriate safety equipment to prevent accidental contact with the accelerator and glue, and the application area should have adequate ventilation to prevent breathing considerable amounts of the evaporating solvent. Bond strength-related variables include:

(1) For cyanoacrylate adhesives to form strong connections, a smooth surface is essential. Surfaces need to be spotless, dry, and devoid of impurities like grease, oil, or grime. By expanding the surface area for adhesive contact, roughening or etching the surfaces can also strengthen the connection [20].

(2) Metals, plastics, rubber, and ceramics are just a few of the materials that cyanoacrylate adhesives are compatible with. Bond strength, however, can be impacted by the adhesive's compatibility with the materials being joined. For the particular materials involved, selecting the appropriate cyanoacrylate formulation is crucial.

(3) The bond strength of the bonded joint is significantly influenced by the joint's design. Both the adhesive and the joint should be used uniformly to disperse tension across the bonded area. The connection can be weakened by stress concentrations, acute angles, or poor joint fit [21].

(4) Cyanoacrylate adhesives cure quickly, although the bond strength might continue to increase over time depending on the temperature and curing period. In general, faster healing is achieved at higher temperatures, which may also strengthen bonds. However, in some formulations, too much heat might lead to brittleness.

(5) Cyanoacrylates are renowned for having poor gap-filling properties. Bond strength can be increased using thin bond lines. Special formulations with additional fillers or

thixotropic qualities may be required if gap-filling is required [22].

Polymerization mechanism

When water or weak basic conditions are present, the cyanoacrylate polymerization mechanism involves the quick production of lengthy, powerful chains. The cyanoacrylate polymerization mechanism is as follow:

Initiation

When the adhesive comes into touch with minute amounts of moisture, cyanoacrylate begins to polymerize. The air's humidity alone may be enough to start the response. The electrophilic carbon ($C=C$) in the cyanoacrylate molecule is attacked by moisture, acting as a weak nucleophile and rupturing the carbon-carbon double bond. As a result, the molecule develops an anion ($C=C^-$) at one end and a cation (H_3O^+) at the other. The highly reactive anion that is produced acts as the catalyst for the chain reaction that causes polymerization [23].

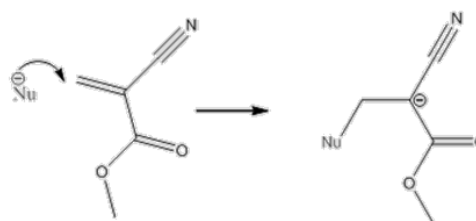


Fig 4. Initiation reaction of cyanoacrylate [23]

Chain propagation

An additional cyanoacrylate molecule is attacked by the anion created in the initiation stage, which acts as a nucleophile. As a result of this nucleophilic attack, a series of cyanoacrylate molecules begin to join one another. The cyanoacrylate anion attacks the electrophilic carbon atom in a different cyanoacrylate molecule to carry out the reaction through nucleophilic addition. As a result, a developing polymer chain made up of repeated

cyanoacrylate units is created. Cyanoacrylate polymerization is highly exothermic, which means a lot of heat is released. One remarkable quality of cyanoacrylate adhesives is the heat creation. The exothermic nature of the reaction aids in the adhesive's quick curing, which enables it to quickly set and attach materials [24].

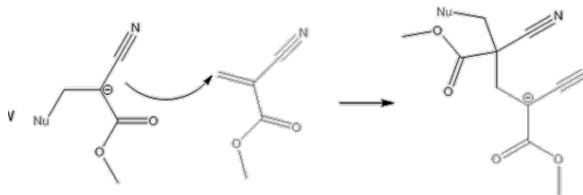


Fig 5. Propagation reaction of cyanoacrylate [24]

Termination step

The presence of water, air, and acidic protons causes the reaction to end because they react with the nucleophile, effectively quenching the reaction [25]. The type of acid has an impact on cyanoacrylates as well; weak acids prevent or slow down polymerization, whereas strong acids entirely halt it. The anion exists as a "living" polymer if the reaction is not stopped. Should another monomer be added to the process, the living polymer might spread further, attack the monomer, and prolong the carbon chain [26].

Factors influencing cyanoacrylate

Substrate compatibility

Although cyanoacrylate adhesives are well-renowned for their adaptability, not all substances can be used with them. They stick nicely to a variety of materials, such as metals, plastics, rubber, wood, ceramics, and even some fabrics. The type of substrate and the precise formulation of the adhesive can have an impact on compatibility, though [27]. The cyanoacrylate's chemical compatibility with the materials being bonded must be taken into account. It may be more difficult to adhere to

some substrates because they are chemically inert or have low surface energy. Materials with a high surface energy, such as metals and glass, tend to encourage better cyanoacrylate adhesive wetting and adherence [28].

Contrarily, bonding to low-energy surfaces like polyethylene and polypropylene can be more difficult. To improve adhesion in these circumstances, surface preparation or unique cyanoacrylate formulations may be necessary. The surface porosity and roughness of the substrate might affect how well the adhesive bonds. Surfaces that are smooth and without pores typically offer better contact for adhesive bonding. Cyanoacrylate may permeate the pores of porous surfaces, which may have an impact on the binding strength and cure time [29].

Surface preparation and cleaning

The cleanliness of the surfaces to be bonded is one of the most important variables in generating strong cyanoacrylate bindings. Contaminants that establish a barrier between the adhesive and the substrate, such as oils, greases, dust, or residues, can impede bonding [30]. Cleaning with abrasion or solvents can help get rid of these impurities and strengthen bonding. To improve adhesion, some substrates may benefit from surface activation treatments like plasma treatment or corona treatment. By changing the surface chemistry and raising the substrate's surface energy, these techniques enhance the wetting and bonding properties of cyanoacrylate adhesives [31].

Humidity and temperature

The temperature has an impact on how quickly cyanoacrylate adhesives cure. Lower temperatures could slow the drying process down, while higher temperatures typically speed it up. It's crucial to take into account the optimal operating temperature range of cyanoacrylate formulation and modify working circumstances accordingly [32]. Cyanoacrylates

need moisture to start the polymerization process that leads to the formation of their molecules. The bond may not form properly or the curing process may take longer in low-humidity situations. On the other hand, high humidity may promote a more rapid and exothermic curing process. For consistent and reliable results, proper moisture management is essential [33].

Chemical accelerators and inhibitors

Some situations or substances can hinder the curing of cyanoacrylate adhesives, slowing down or halting it. Amines, sulfur compounds, and certain metals (such as copper and brass) can all act as inhibitors. Bonding problems can be avoided by identifying potential inhibitors and avoiding their interaction with the glue. On the other hand, when a faster bonding process is necessary, accelerators or activators can be utilized to quicken the curing process [34]. These are frequently employed in conditions where delayed curing may otherwise be caused by low humidity or particular material combinations. To achieve dependable and efficient cyanoacrylate bonding, it is crucial to comprehend these components and how they interact. Successful bonding applications in an environment require careful substrate selection, surface preparation, environmental control, and understanding of the chemistry involved [35].

Specialized formulations and applications

Cyanoacrylate adhesives have a wide range of specialized formulations and applications. Some of these applications are mentioned as follow:

Cyanoacrylate variants for specific purposes

From water-thin liquids to thixotropic no-run gels, cyanoacrylate adhesives come in various viscosities. To increase the shear strength of cyanoacrylate adhesives, toughening chemicals having elastic qualities, such as rubber or anhydride, can be used. Special cyanoacrylate glue compositions have undergone testing and

been approved for use in medical applications [36]. These variations contain unique ingredients that, after curing, increase their flexibility and decrease their brittleness.

They are appropriate for tasks like rubber bonding and flexible plastic repairs where the bonded components may suffer minute movements. These cyanoacrylate adhesives are thicker and suited for vertical applications and gap filling. They are perfect for tasks that call for a more viscous adhesive, such as connecting porous materials and rough surfaces. Some cyanoacrylates are designed to have less of a smell, making them better suited for use in small spaces or around people who are sensitive to strong aromas. They provide comparable bonding power and longevity [37].

Industrial applications

In locations where products are assembled, cyanoacrylate adhesives are employed to create hard thermoplastics with great adherence to numerous surfaces. Cyanoacrylate chemistry, specifically the anionic polymerization mechanism, finds various industrial applications, primarily in the adhesive field. The rapid anionic polymerization of cyanoacrylate monomers in the presence of weak bases such as water or alcohol is responsible for their quick-setting, high-strength adhesive properties. Industrial cyanoacrylates, also known as super glues or instant adhesives, are used in manufacturing for their quick bonding, high bond strengths, and easy application with automated or semi-automated equipment. They offer advantages over mechanical fasteners, such as speed, cost reduction, and improved appearance. In addition, cyanoacrylates have found applications in various other industrial and niche fields, including cosmetology, beauty, electronics, woodworking, and as retention dressings for nuts and bolts. Furthermore, cyanoacrylate chemistry is utilized in the forensics field through the cyanoacrylate fuming

method, which is used to make latent prints visible for detection, acquisition, and analysis [38].

Cyanoacrylate adhesives are used in manufacturing and assembly processes to quickly connect components in various industries, including electronics, automotive, aerospace, and so forth. Their quick cure time is advantageous in quick assembling procedures. Specific industrial formulas with high bond strength and durability are created for use in structural bonding applications. In load-bearing applications, these adhesives are utilized to join metals, composites, and other materials. Cyanoacrylates are used as threadlockers to hold nuts, bolts, and screws firmly in place and stop them from coming undone as a result of vibration and temperature cycling [39].

Medical and healthcare applications

Wound closure

In place of sutures or staples, medical-grade cyanoacrylate adhesives are used to close wounds. They are useful in emergency treatment and operations because they heal quickly and leave little scarring.

Applications in dentistry

They include bonding orthodontic brackets, bridges, and crowns. Dental cyanoacrylates are utilized for this purpose. In a dental environment, they provide dependable, firm adherence [40].

Orthopedic devices

Cyanoacrylate adhesives are used in orthopedics to attach implants, reinforce bone structure, and connect prosthetic components together. In both human and veterinary medicine, cyanoacrylate adhesives are used as a liquid bandage, for orthopedic and dental purposes, and to close wounds. Since cyanoacrylate adhesives are not particularly hazardous, major harm or impairment is uncommon. To efficiently close wounds, topical

cyanoacrylate adhesive of medical grade is employed [41].

Household and DIY applications

General Repairs: Cyanoacrylate adhesives are frequently used for last-minute home repairs such fixing broken toys, furniture, and plastic or metal objects.

Crafts and Hobbies: Cyanoacrylate adhesives are used in different projects by crafters and hobbyists that involve the use of wood, plastic, and other materials. For crafting, the availability of colourful variations is especially helpful [42].

Cyanoacrylate adhesives: They are frequently used to fix shoes, particularly to reattach soles, heels, or other component parts. Uses for cyanoacrylate adhesives include gluing fake nails, nail tips, and nail wraps in domestic and independent projects. Eyelash extension glue made of cyanoacrylate is utilized in the cosmetology and beauty sectors. Repairing broken things, such as toys, spectacles, and jewellery, uses cyanoacrylate glue [43-45].

Recent advances and future prospects of cyanoacrylate chemistry

The Knoevenagel condensation has been used to make cyanoacrylates, but the process results in a prepolymer that must be broken down to a monomer at a high temperature, which is expensive and prevents the production of some temperature-sensitive monomers. An "crackless" technique of producing cyanoacrylates and other 1,1-disubstituted ethylene monomers employing an ammonium or iminium salt as a catalyst was patented by Afinitica [46]. The new method skips the depolymerization stage and avoids the high-pH conditions of the Knoevenagel condensation by stopping at the monomer. Separately, Afinitica created a device that accelerates the curing of cyanoacrylate using UV light and a photoinitiator. A recent study examined the

characteristics of novel cyanoacrylate adhesives for use in self-healing concrete systems [47-49]. Since cyanoacrylate adhesives dry quickly and provide hard thermoplastics with superior substrate adhesion, they are frequently employed in structural and industrial applications. Plastics made of poly (ethyl cyanoacrylate) have been created that can be recycled in a closed-loop system. Interventional radiologists are very interested in N-butyl cyanoacrylate (NBCA) because of its good biological characteristics and efficacy [50-53].

Conclusion

The exploration of Cyanoacrylate Chemistry and Polymerization Mechanisms reveals a fascinating interplay of unique properties that contribute to the rapid, moisture-catalysed polymerization process, and exceptional adhesive strength characteristic of cyanoacrylate adhesives. From their historical roots as an accidental discovery during World War II to their widespread applications in industrial, medical, and domestic settings, cyanoacrylates have proven to be a remarkable class of adhesives with versatile utility. The significance of understanding the chemistry behind cyanoacrylates lies in the ability to harness their full potential and address challenges associated with premature curing. The exothermic and rapid nature of polymerization, catalysed by trace amounts of moisture, presents both opportunities and challenges. While this rapid curing is advantageous in many applications, it can be a limitation when precise control over the bonding process is required. Looking ahead, future prospects of cyanoacrylate chemistry are marked by emerging applications and research goals. Recent studies have delved into the characteristics of novel cyanoacrylate adhesives for self-healing concrete systems, showcasing the potential for these adhesives to contribute to innovative construction materials. The quick-

drying nature and superior substrate adhesion of cyanoacrylate adhesives make them valuable in structural and industrial applications. A notable advancement includes the development of recyclable plastics made from poly(ethyl cyanoacrylate), offering a sustainable solution in closed-loop systems. This development aligns with the growing emphasis on eco-friendly materials and waste reduction in various industries.

As we contemplate the future trajectory of cyanoacrylate chemistry, it becomes evident that ongoing research and innovation will be pivotal in addressing existing challenges and unlocking new potentials. To exhibit even better performance, future research efforts may focus on refining catalyst systems, optimizing curing processes, and exploring additional applications in response to evolving industrial, environmental, and medical needs. The continuous evolution of cyanoacrylate chemistry holds the promise of contributing to sustainable, efficient, and innovative solutions in a variety of fields. The industry's dedication to responsible chemistry is demonstrated by the creation of eco-friendly and biodegradable cyanoacrylate glue formulations as sustainability becomes an increasingly important issue. Nevertheless, there are still difficulties as the field develops. Researchers must continue to address problems like brittleness and tensile strength while attempting to strike a balance between rapid cure and dependable performance. Considerations for safety, regulation, and ethics must come first, especially in industries where people's well-being is at stake.

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