POLYMERIC MATERIALS IN GLUING TECHNIQUES

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ABSTRACT

Polymeric materials have an important role in gluing technology due to their broad application in the wood industry, metal industry, glass, and ceramics industry as well as medicine. This article discusses the basic physicochemical aspects of bonding with adhesives and also, the mechanisms of action of the adhesive materials during bonding based on polymerization processes and different types of polymerization. It was emphasized that depending on the material used in gluing, various adhesives with different physicochemical characteristics facilitate and contribute to the quality of the bonded joints. In this way, it is an insured procedure that is suitable for materials that are sensitive to the effects of heat, because welding and soldering would deform the base material and often the total degradation of its mechanical properties.

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1. INTRODUCTION

From time immemorial, the gluing technique has been used to make many products from different materials. Particularly successful development of bonding materials has occurred in the last two or three decades. Today, the board of gluing techniques is experiencing constant expansion due to the development of quality adhesive materials, appropriate equipment, and technological processes.

The technology of gluing is extremely important and for a long time is the dominant binding process, for example, in the wood industry, while today it is used on other basic materials such as metals, ceramics, plastics, glass, etc. Using gluing technology, especially wood as a basic material is of great use-value, and the development of new adhesives has significantly ensured the quality of the bonded joints. The application of adhesive technology on metallic materials is currently relevant for purposes of a lower degree of responsibility (medicine applications), although at the global level, more and more often it is used on structures of greater responsibility, for example in aviation.

The application of gluing technology is especially suitable for thin metal parts of different shapes and sizes, and the construction of complex shapes of different materials. The stress concentrations in the metal are minimal, there is no twisting and creasing. The adhesive technology is especially suitable for materials that are sensitive to the effects of heat because welding and soldering would deform the base metal and often the total degradation of its mechanical properties [1-5].

2. COUPLING MECHANISM USING ADHESIVES

Bonding materials are most often achieved by an adhesive-cohesive mechanism that is evident in several basic materials such as wood, metals, heat-resistant plastics, ceramics, etc. Adhesion is the force of attraction between surfaces of two or more of the same or different materials brought into direct contact. Adhesion forces lead to the formation of an adhesion bond which is a consequence of the migration of molecules of the base material into the adhesive and vice versa, where the bond is achieved by chemical bonding, and physical and mechanical bonding.

Chemical bonding implies the realization of one and covalent bonds between the base material and the adhesive.

Physical bonding is realized by dipole-dipole intermolecular forces, and mechanical is conditioned by mechanical contact of contact surfaces. The formation of chemical bonds is especially realized in the contact of metals, metal oxides, and hydroxides with adhesives, while intermolecular Van der Waals bonds are realized in the use of synthetic highly polymerized substances and in bonding polar materials such as wood (cellulose). Also, mechanical bonding is important in porous materials such as wood, while metal damage has almost no role. Cohesion forces are those that hold matter together, with the molecules of polar and non-polar compounds being interconnected by intermolecular and chemical bonds. The mechanical strength of the bonded joint is the total strength and consists of adhesion and cohesion strength and is influenced by a large number of influencing factors, the most important of which are the chemistry and structure of the adhesive macromolecules.

It is known that polar compounds and heterochain polymers with equal macromolecular chain lengths and chain parallelism have significantly greater cohesion than non-polar compounds in wood gluing. Cohesive bonding is realized by the action of Van der Waals forces, a typical chemical covalent bond, and often hydrogen bonds. The adhesives used for bonding are in the liquid state, and curing is a chemical process in which adhesive monomers polymerize by polymerization and polycondensation mechanisms, which are explained in more detail in the next section [6, 7].

3. PHYSICO-CHEMICAL ASPECTS OF ADHESIVE BONDING

The mechanism of action of the adhesive during bonding is based on polymerization processes. A polymer is a compound of high molecular weight, and the structure is such that it can be considered to be composed of many small equal parts (Greek *Polys* = many, and *meros* = part). The process by which polymers are formed is called polymerization.

3.1 Polymerization mechanisms

Polymers are defined by their mechanism, which can take place as in the following:

- chain-reaction,
- step-reaction,

Coordination polymerization is a special type of chain-reaction polymerization

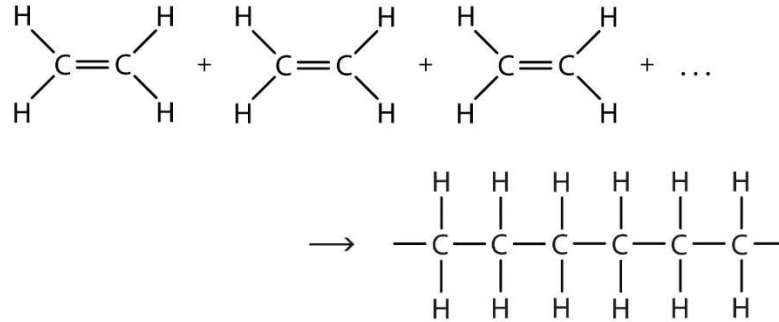### 3.1.1 Chain-reaction (Addition) polymerization mechanism

Polymerization by the chain reaction mechanism is reduced to free radical reactions or reactions in which ions participate as reactive particles. Depending on the type of initiator used, cations and anions can take over this function. The mechanism of the free radical polymerization chain reaction begins with the polymer chain growing by creating free radicals from unsaturated monomers that are added to the growing polymer chain to be obtained.

The presence of small amounts of initiators is required for polymerization. The most commonly used initiators are peroxides. These compounds cause the formation of free radicals by binding an oxygen molecule from peroxide to one C atom of an unsaturated compound, forming an even larger radical that further adheres to the next molecule and thus advances the chain reaction. The end of the chain reaction occurs by merging two radicals, whereby the radicals are consumed and new ones are not

formed. For example, the mechanism of obtaining poly(ethene) - commonly called polythene by chain polymerization of free radicals (shown in Figure 1).

Initiation or creation of free radicals begins with the use of the molecule-initiator R = R1

which is thermally unstable and by breaking into free radicals R and R1 (where R and R1 may or may not be the same) during heating; (Reactions 1-6 and Figure 2). These created radicals then react with the monomeric unit M:

Figure 1. Chain-reaction polymerization: the reaction of a few monomer units

$$R \cdot + M \rightarrow RM \tag{1}$$

$$RM_n \cdot + RM_n \cdot \rightarrow RM_{2n}R \tag{2}$$
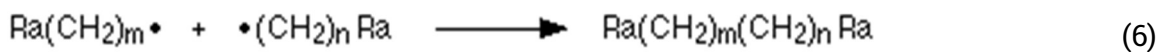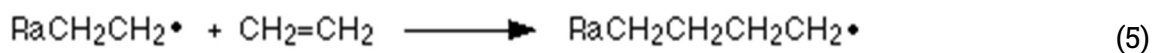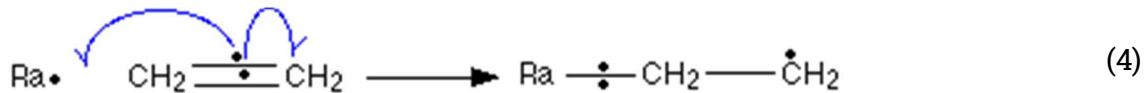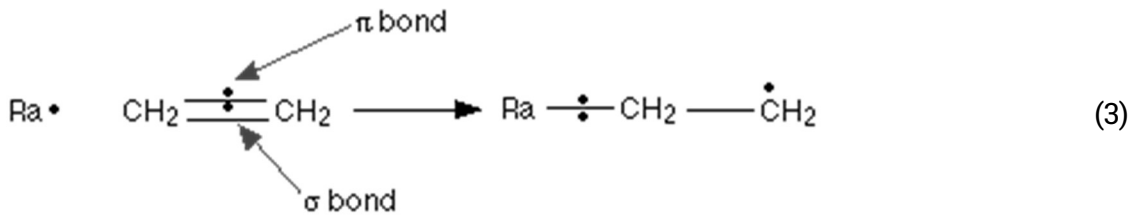
**Figure 2**. The reactions step of polymerization involves: (1)-initiation; (2)-propagation; (3)-termination

In the same way, the RM radical will react with the next monomer unit to form a growing polymer chain. The end of the chain and thus the reaction is formed by a combination of two radical chains that occurs at temperatures below 60 °C. The mechanism of the ionic polymerization chain reaction takes place depending on the type of compound used, so it can be cationic polymerization or anionic chain-reaction polymerization [8-12].

Cationic polymerization
Cationic polymerization takes place by a mechanism characteristic of chain reactions with the difference that the acid used here is the initiator. Different acids can be used as initiators: H_2SO_4, $AlCl_3$, and BF_3 with the addition of small amounts of water. The reaction mechanism goes through the intermediate state, which leads to the formation of carbocations (carbon ions). The formed carbocation adheres to the terminal

C-atom of the double bond and thus forms a new carbocation. This process is repeated until the chain is complete. Any of the carbon ions can be stabilized and the chain terminated by proton loss from any carbon atom located adjacent to the carbon ion.

Therefore, the product always contains a double bond per polymer molecule and consists of a mixture of isomers in which, preventing further isomerization, the double bond is in positions 1, 2, or 2, 3, which can be shown as follows (Figure 3).
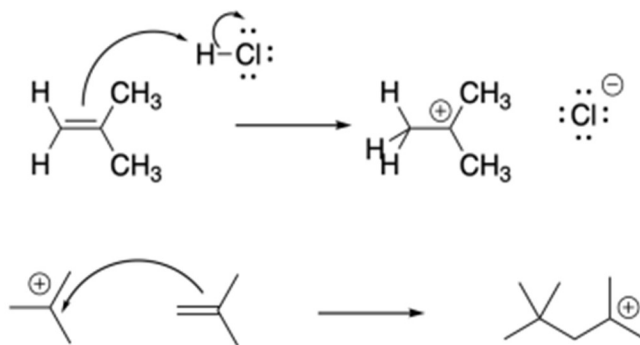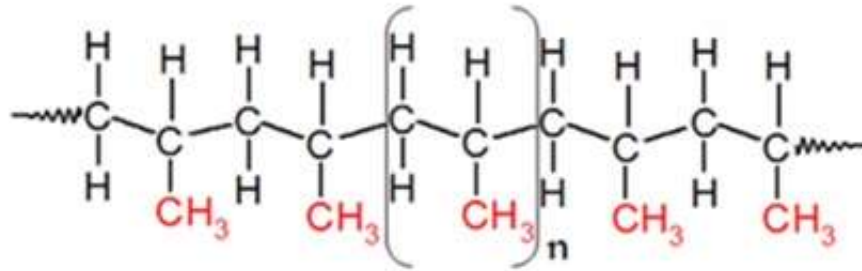

Figure 3. The cationic polymerization

An example of cationic polymerization is given for the formation of polyisobutylene and polypropylene is shown in Figure 4.

Polypropylene is produced by the chain-growth polymerization of propene (Figure 5).
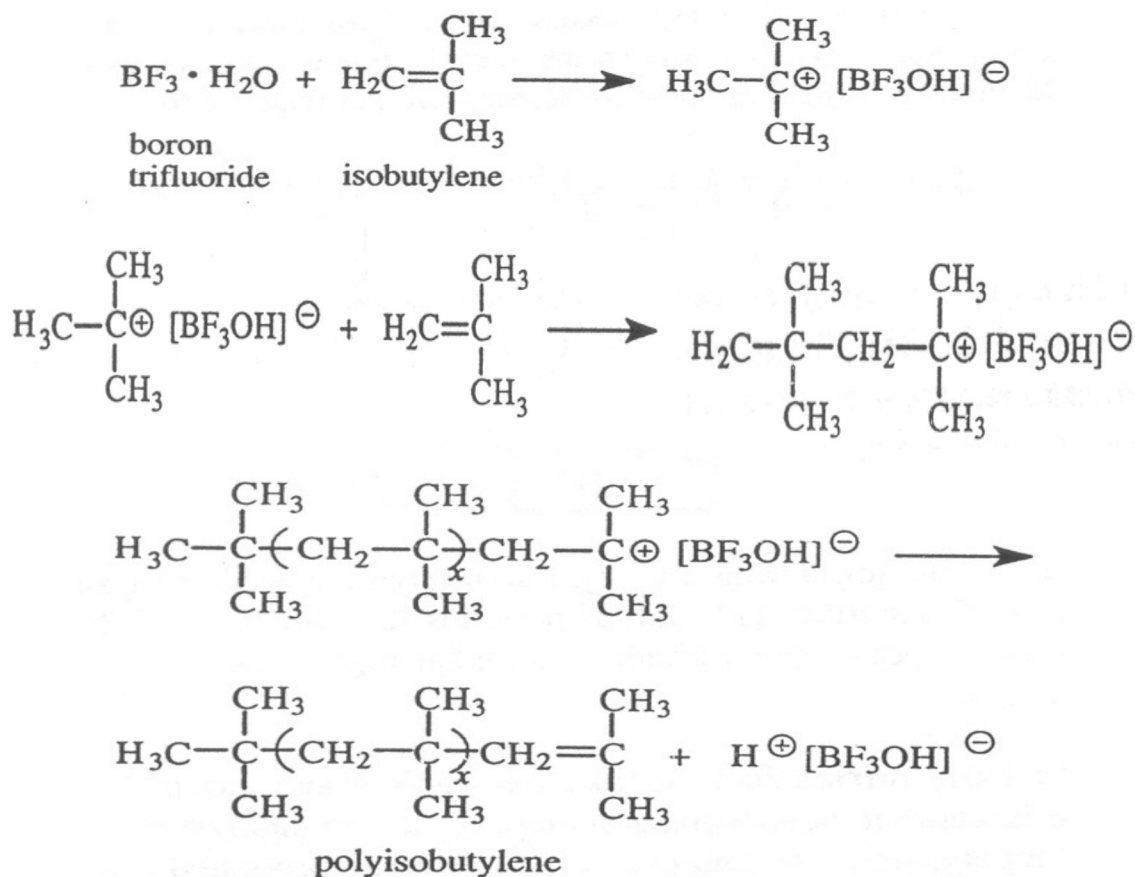
Figure 4. The formation of polyisobutylene

Figure 5. The molecular structure of polypropylene (PP)

Polypropylene is made from the polymerization of propene monomer (an unsaturated organic compound - chemical formula C_3H_6) by Ziegler-Natta polymerization or Metallocene catalysis polymerization (Figure 6).
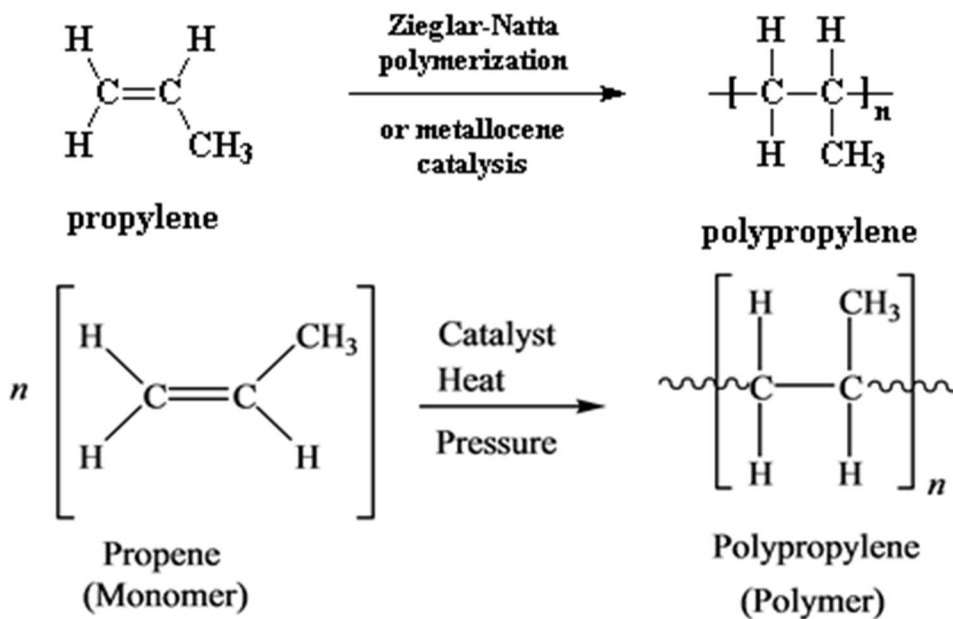
Figure 6. The formation of Polypropylene (PP)

Upon polymerization, PP can form three basic chain structures depending on the position of the methyl groups (Figure 7).
- Atactic (aPP) – Irregular methyl group (−CH₃) arrangement,
- Isotactic (iPP) – Methyl groups (−CH₃) arranged on one side of the carbon chain,
- Syndiotactic (sPP) – Alternating methyl group (−CH₃) arrangement

According to the used (co)polymerization or mixing process and formulation, polypropylenes can be hard or soft, opaque or transparent, light or heavy, insulating or conductive, neat or reinforced with cheap mineral fillers, short or long glass fibers, natural fibers or even self-reinforced [13-17].
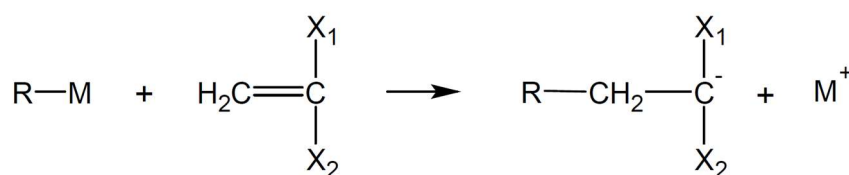
Anionic polymerization
Anionic polymerization takes place by a mechanism that takes place under the influence of the anion as the initiator, i.e under the influence of a base. LiNH₂ in-butyl lithium is most often used as the bases that activate the molecule of the polymerizable compound, i.e. organometallic lithium compounds or some other organometallic compounds are used. A general overview of anionic polymerization is given as follows (Fig.8):
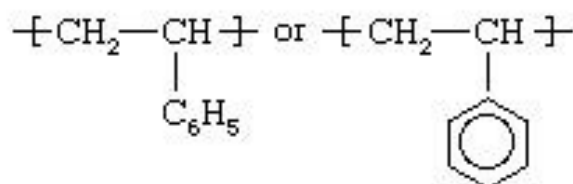An example of this polymerization method is given for the case of polystyrene formation in Figure 9.
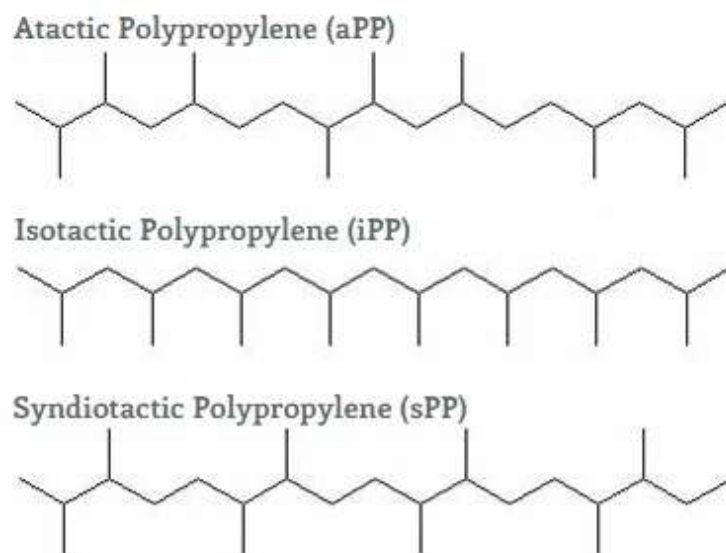
Figure 7. Basic chain structures of PP

Figure 8. The anionic polymerization

Figure 9. Basic chain structures of polystyrene

Anionic polymerization can be enhanced by the use of the metals Li and Na. For example, in the polymerization of styrene by the action of metallic Na on naphthalene, the Na atom transfers one electron (1) to naphthalene, so that the resulting radical anion gives the electron styrene (2) with the formation of styrene radical anion. Like other free radicals, the styrene radical-anion dimerizes into one dianion, which is the real initiator of this polymerization, and it begins to grow at both ends of the dianion (Figure 10).

Anionic polymerization is not limited to vinyl compounds, which react by binding to carbon-carbon double bonds. For example, the addition of a small amount of base to ethylene oxide converted into a high molecular weight polyether (Figure 11).

In anionic polymerization, the growth of the reaction chain is stopped due to contamination or the presence of a molecule that is not an integral part of the polymerization mechanism [18].

3.1.2 Coordination polymerization
In addition to the shown cationic and anionic polymerization, chain polymerization, according to the latest literature references, can also take place by a coordination mechanism. Coordinative polymerization is based on the use of metal cations and the creation of a coordination bond with organic ions [9].

industries
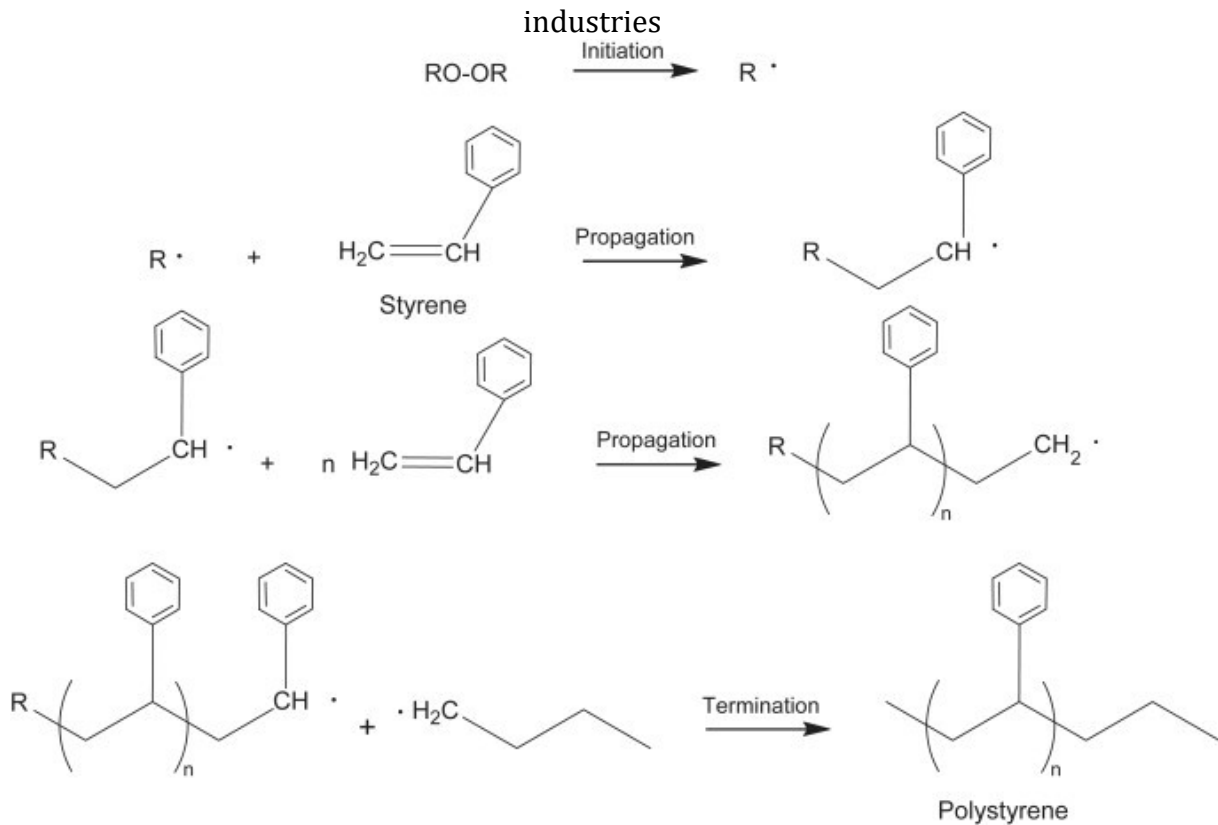
Figure 10. Polymerization of styrene
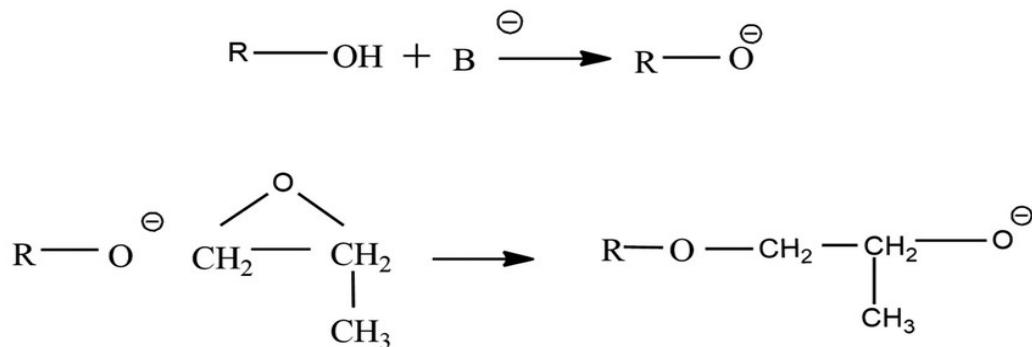
Figure 11. Basic chain structures of polyether

The introduction of ionic polymerization, and especially coordinate polymerization, has improved this area of chemistry. Particularly important here are the researches of Karl Ziegler and Giulio Natta (Nobel Prize in 1963 for work on catalysts by which the polymerization process could be controlled to such an extent as never before). These Ziegler-Natta catalysts are complexes of transition metal halides and organometallic compounds, such as triethylaluminum titanium trichloride. The reaction proceeds via nucleophilic addition to the carbon-carbon monomer double bond, with one organic group of the carbanion-like organometallic compound taking on the role of the nucleophile. The transition metal may additionally form a complex with the π-electrons of the monomer, the monomer being tightly bound at the reaction site; polymerization occurs by incorporating an alkene molecule into the bond between the metal and the growing alkyl group [10, 11].

Organic ions as chain carriers have a charge that is equal to the ion of the opposite charge or counters ion. Thus, the metal cation Li+ or Na+ is tightly bound to

the growing anion. Ionic pairs as well as larger groups can play a major role in polymerases. When the bond between the reaction center and the metal is predominantly covalent, we call this reaction "coordinate polymerization." The growing organic chain is not a pronounced anion but its reactivity is based on an anion-like character. An example is the formation of polyethylene by the coordination mechanism (Fig. 12).
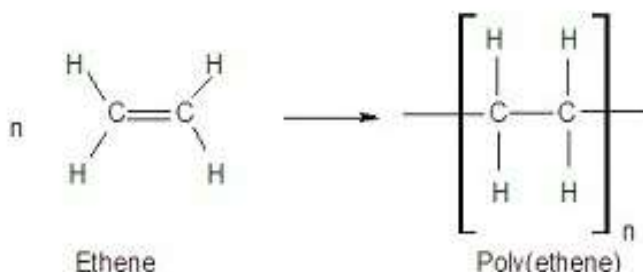
Figure 12. Polymerization of ethene

Polymerization with Ziegler-Natta catalysts has two advantages over free radical polymerization: 1) linear polymers are obtained, and 2) stereochemical control of the reaction is enabled.

For example, polyethylene, formed by free radical polymerization, has a highly branched structure, which is attributed to a special mode of chain transfer. Polyethylene, formed by coordinate polymerization (coordination process), is mostly unbranched. Unbranched molecules can easily bind to each other and then it is a polymer with a high degree of crystallinity. The exact mechanism of coordination polymerization is still unclear. However, it is believed that the transition metal is the active site. The ethylene is coordinated to the free site at the transition metal and inserted between the metal and the alkyl group R. The coordination process results in the stereospecificity of the polymerization. The rate of the reaction can be influenced by the nature of the other ligands present [13-15].

3.1.3 Step-reaction (condensation) polymerization

Polymerization by the mechanism of the stepwise reaction, i.e. polycondensation, takes place as a series of reactions that are mutually independent of each other. The polymer is formed by combining two monomer molecules into a dimer representing two molecules joined together, which can then again react with the other monomer and dimer, etc. until a long polymer is formed.

Two different functional groups are involved in the condensation polymerization reaction. These can be two different monomer particles (AA and BB) or the same monomer (AB). The reactions that take place can be illustrated by the example of the reactions that occur in the production of PET (polyethylene terephthalate) and are presented as follows:
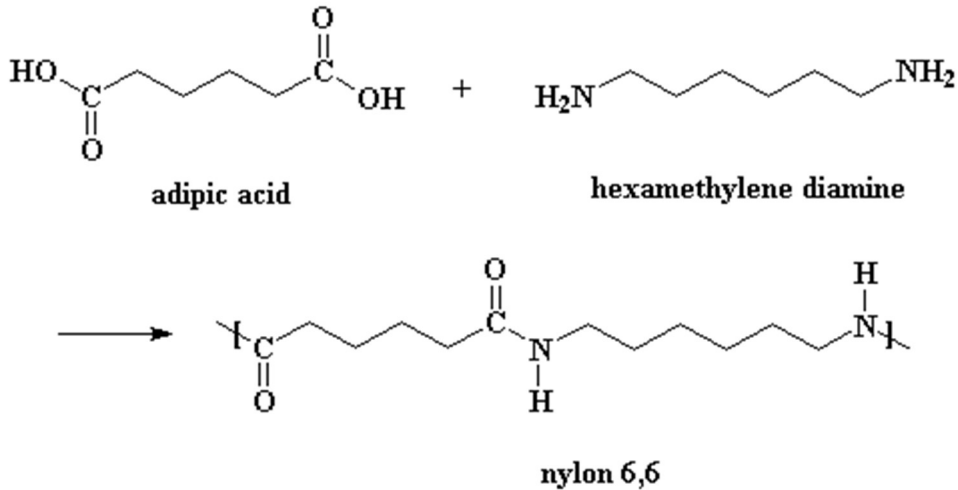
During condensation polymerization, a water molecule or some other simple molecule or compound is separated from each newly formed bond. In the PET synthesis reaction given above (Figure 12), the alcohol combines with the carboxylic acid group to give an ester bond and water. Another example of a condensation polymerization reaction is the synthesis and preparation of Nylon-6,6 in which a peptide bond is formed (Figure 13).

The reaction does not depend on a chain carrying free radicals or ions as in chain polymerization but the individual steps are independent of each other. If each monomer molecule contains only two functional groups, growth can only go in two directions, and a linear polymer (e.g. Nylon-6,6 or Dacron) is obtained. If the reaction can occur in more than two places on the monomer, then a highly intertwined polymer (e.g. Glyptal, alkyd resin) is formed. In condensation polymerization, the

reactive groups at both ends of each monomer react with each other. As the chain grows, it also has reactive groups at each end so that its length can become significantly longer if the two chains join together. Condensation polymerization is used in the preparation and production of polyester, nylon, and polyurethane [19].

Figure 13. The condensation polymerization
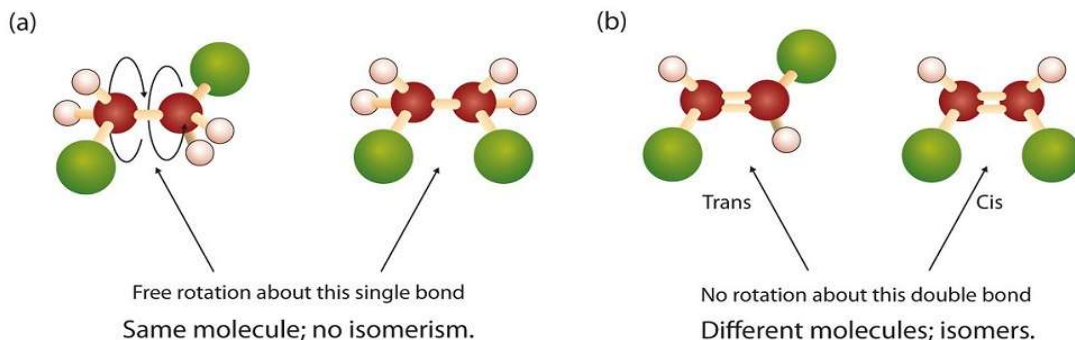
4. STRUCTURE OF POLYMER/ POLYMER STRUCTURE

4.1 Microstructure

Although the fundamental property of most polymers is the degree of polymerization, the structure of the chain is a significant factor that determines the macroscopic properties of the polymer. In this sense, the terms configuration and conformation are used to describe the geometric structure of polymers. The configuration is an arrangement determined by chemical bonding. The polymer configuration cannot be changed (rearranged) until the chemical bonds are broken (broken) and rearranged. Conformation is an order that is created by rotating a molecule around a single bond. These two structures are studied further in the text [20, 21].

Configuration

There are two types of polymer configuration: *cis-* and *trans-*. These structures cannot be changed in the physical sense or by rotation. The cis configuration predominates in the molecule when substituted groups on the same side of the C = C bond (Figure 14).
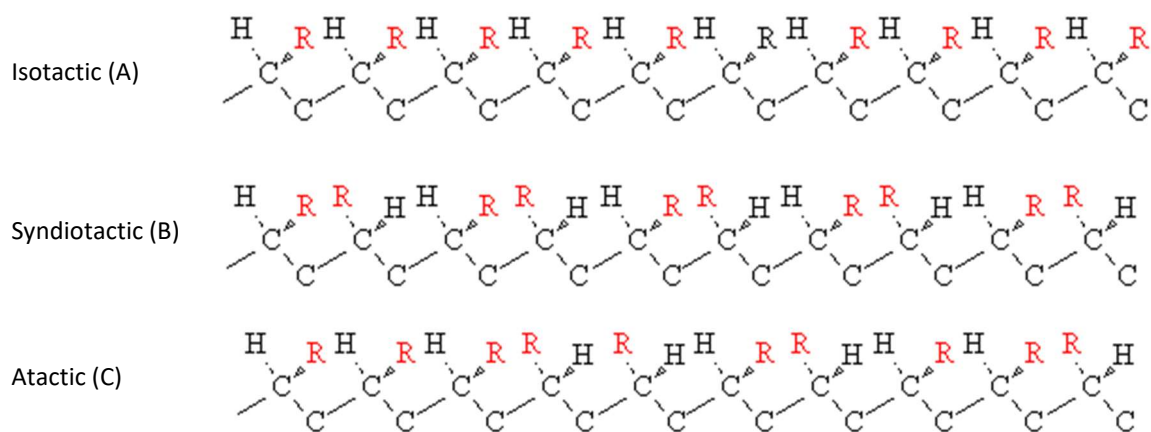
Figure 14. The configuration of polymer

Stereochemistry (spatial arrangement) is a term used to describe the configuration of polymer chains. The three clear and distinctive structures that are obtained are called: isotactic (A), where the arrangement of all substituents is on the same side of the polymer chain; syndiotactic (B) where the polymer chain is composed of

interchangeable (variable) groups and atactic (C), where the arrangement of substituents is a random or random combination of groups. The following structures show two of the three stereoisomers of the tidal chain (Figure 15). Conformation is the rotation of a part of a molecule around single bonds. If two atoms

are bound by a single bond, then rotation around this bond is possible, unlike a double bond, and this does not require breaking the bond itself and results in the formation of a more energetically favorable structure.

Isotactic (A)

Syndiotactic (B)

Atactic (C)

Figure 15. The configuration of polymer chains

The geometric arrangement of the bonds as a way of representing the polymer structure may vary. A branched polymer is formed when the "sides of the chain" are attached to the main chain [20, 21]. A simple example of a branched polymer is shown in Figure 16.
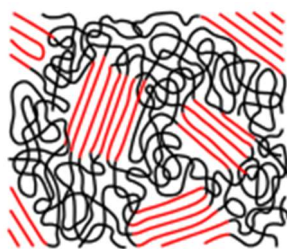
**Figure 16**. The configuration of a branched molecule of polymer

There are several ways to display the arrangement of branched polymers. One of these types is called "star branching". Star-shaped branching occurs when polymerization begins with only one monomer and has branches radially oriented outwards, i.e. outwards from this point. Polymers with a high degree of branching are called dendrites. Often in these molecules, the branches have their

own branching. In this way, the molecules get a spherical shape in three dimensions.

4.2 Macrostructure
The shape of the molecules and how the molecules are distributed in the solid state are important factors in determining the properties of polymers. Polymers can be crystalline and amorphous. To explain the difference between crystalline and amorphous materials as well as semicrystalline, the example of glass, as an amorphous material and crystalline ice was taken. Crystalline polymeric materials show a high degree of order that is formed by assembling and accumulating polymer chains. Amorphous materials or glass-like structures show a very low degree of order and the chains are intricate, as shown in Figure 17.
In the solid-state, amorphous and crystalline materials have different heating behavior. By applying heat, the glass changes from a solid, brittle material at room temperature, to a viscous liquid in contrast, by heating, ice changes from a solid to a liquid state.
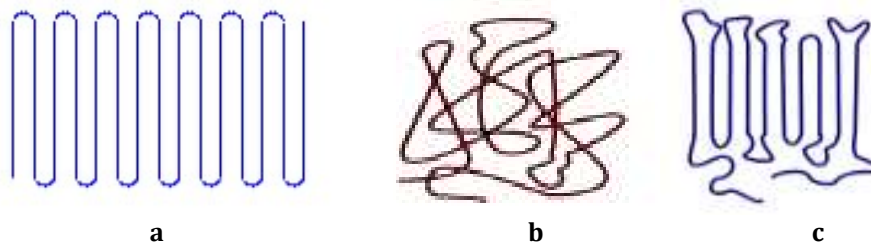
Figure 17. The arrangement of molecular chains in crystalline-**a**, amorphous-**b,** and semicrystalline-**c** polymers

The melting of the crystal leads to marked changes in the optical properties of the crystal itself. Crystalline materials have molecules arranged in repeating patterns or patterns. Salt is one of the simplest atomic structures with its components, Na and Cl ions, arranged in interchangeable arrays and the structure is cubic (cube). Salt, sugar, ice, and most metals are crystalline materials. As such, they tend to have a highly ordered and regular (symmetrical) structure [20, 21].

In contrast, amorphous materials have molecules arranged randomly in long chains that are curved and curved lines, which surround each other, thus making structures that are very different from each other. The morphology of most plumbers is a structure that is very different from each other. The morphology of most polymers is semi-crystalline, i.e. they form mixtures of small crystals and amorphous material. Some polymers are completely amorphous but most combinations with intricate and unoriented regions, surrounded by crystalline surfaces one of such combination is shown in the following Figure 18.
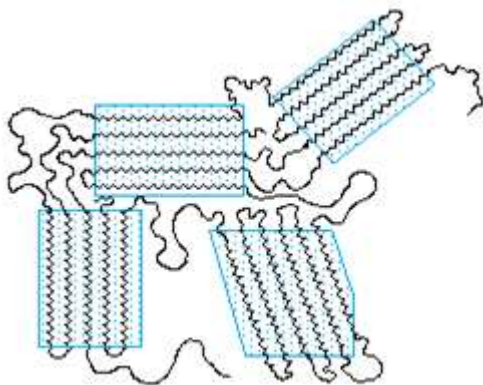
Figure 18. The morphology of plumbers

It was found that the degree of polymerization is a significant factor in determining the crystallinity of the polymer, as well as its macro mechanical properties. Polymers of lower molecular weights (short chains) are mostly crystals and generally lower mechanical strength is the reason that these are crystals and only weak Van der Waals forces act within the lattice. This allows the layers of crystals to slide slowly next to each other under tensile loads, causing the material to tear. The high degree of polymerization (amorphous polymers), on the other hand, are stronger because the molecules are in intertwined layers that are additionally connected by hydrogen bonds. In most polymers, a combination of crystalline and amorphous structures forms a material with more favorable properties in strength, i.e. in hardness and hardness. Also, the morphology of the polymer depends on the size and shape of the monomer-substituted groups. If the monomers are large and irregular, it is very difficult and complex to redistribute the polymer chain in a more orderly manner, which in turn results in an amorphous solid state. Smaller monomers and monomers that have very regular structures (like rods or rods) will form more crystalline polymers. The cooling method significantly affects the level of crystallinity. Slow cooling provides the time required for a higher level of crystallinity. Faster cooling or shorter crystallization time, on the other hand, leads to the separation of amorphous materials. Gradual curing (heating and holding at certain temperatures below the melting point of the crystal, followed by slow cooling) will lead to a significant increase in crystallinity in most polymers.

Synthetic polymers used as adhesives have different properties and they are conditioned by the chemical composition and structure of the material [22].

It has been shown that, with increasing molecular weight, the melting temperature of the polymer increases, reduces solubility, increases viscosity, and, to a certain degree, adhesion ability. Polymers that contain low molecular weight fractions to a certain extent have higher plasticity while increasing high molecular weight fractions increases strength, hardness as well as brittleness.

In the case of synthetic polymers formed by the condensation mechanism, it can generally be said that they are solid and hard. Those adhesives formed by the chain reaction mechanism melt relatively well and soften at lower temperatures.

5. CONCLUSION

The article presents the basic physicochemical aspects of bonding with adhesives. As shown, the mechanism of action of the adhesive is based on polymerization processes. In addition, the basics of adhesive polymerization by chain-reaction mechanism and step-reaction mechanism are given. Also, the mechanism of coordination polymerization, which is a special form of chain polymerization, is emphasized. This type of polymerization is important today because by using special catalysts, the polymerization process can be controlled extremely well.

Ziegler-Natta catalysts are organometallic compounds wherein the polymerization reaction takes place via nucleophilic addition to the carbon-carbon monomer double bond. By catalyzing the polymerization process, macrostructures can be achieved that provide the appropriate mechanical properties of the adhesive, i.e. the compounds achieved by their application, especially in biomedicine.

Conflicts of Interest

The authors declare no conflict of interest.

6. References

[1] N. Moszner, U. Salz, J. Zimmermann, Chemical aspects of self-etching enamel-dentin adhesives: a systematic review, *Dent Mater.*, 21(2005), p. 895-910

[2] A. Šapčanin, *Drvo-hemijski aspekt*, 1st ed., Coron's d.o.o. Sarajevo, Bosna i Hercegovina, 2019, pp. 82-100

[3] J. A. Manson and L. H. Sperling, *Polymer Blends and Composites*, New York: Plenum Press, 1976, pp. 378.

[4] L. Bateman, ed., *The Chemistry and Physics of Rubber-Like Substances*, New York: John Wiley and Sons, 1963, pp. 311.

[5] L. Pauling, R. B. Corey, H. R. Branson, The structure of proteins: two hydrogen-bonded helical configurations of the polypeptide chain, *Proceedings of the National Academy of Sciences of the United States of America 37*, 4 (1951), p. 205-11

[6] A. Pizz, and K. L. Mittal, *Handbook of Adhesive Technology*, 3rd ed., 2012, New York, NY 10016, U.S.A.

[7] C.E. Carraher, *Seymour/Carraher's Polymer Chemistry*, 7th Ed., CRC Press, Boca Raton 2008

[8] A. Ravve, *Principles of Polymer Chemistry*, 2nd ed., Kluwer Academic, New York 2012

[9] N. F. Sunday, Emerging Trends in Coordination Polymers and Metal-Organic Frameworks: Perspectives, Synthesis, Properties and Applications, *Arc Org Inorg Chem Sci.*, 1(2018), p. 39-51

[10] Giulio Natta, *J. of Poly. Sci.*, 34(1959), p. 531-549

[11] K. Ziegler, *Angew. Chem.*, 76(1964), p. 545-553

[12] W. Kaminsky, Highly active metallocene catalysts for olefin polymerization, *Journal of the Chemical Society, Dalton Transactions*, 9(1998), p. 1413-1418

[13] V. St-Onge, M. Cui, S. Rochon, J.-C. Daigle, J. P. Claverie, Reducing crystallinity in solid polymer electrolytes for lithium-metal batteries via statistical copolymerization, *Communications Materials*, 83(2021), p. 1-11

[14] F. Auriemma, C. De Rosa, A. Malafronte, M. Scoti, R. Di Girolamo, Solid-state polymorphism of isotactic and syndiotactic polypropylene, *Polypropylene Handbook*, 1(2019), p. 37-119

[15] M. D. Onofrei, A. M. Dobos, S. Ioan, Processes in cellulose derivative structures, *Nanocellulose Polymer Nanocomposites*, 1(2014), p. 355-391

[16] A. Zhugayevych, O. Mazaleva, A. Naumov, S. Tretiak, Lowest-energy crystalline polymorphs of P3HT, *The Journal of Physical Chemistry C*, 122(2018), p. 9141-9151

[17] V. Kottisch, J. O'Leary, Q. Michaudel, E. E. Stache, T. H. Lambert, B. P. Fors, Controlled cationic polymerization: single-component

initiation under ambient conditions, *J. Am. Chem. Soc.*, 141(2019), p. 10605−10609

[18] K. Ntetsikas, Y. Alzahrany, G. Polymeropoulos, P. Bilalis, Y. Gnanou, N. Hadjichristidis, Anionic polymerization of styrene and 1,3-butadiene in the presence of phosphazene superbases, *Polymers*, 9(2017), p. 1-14

[19] Naoya Ogata, Novel synthetic methods of condensation polymers and their applications as new composite and optoelectronic materials, *Pure &Appl. Chem.*, 63(1991), p. 951-960

[20] C. Hall, Polymers: molecular structure, In: *Polymer Materials*, Palgrave, London, 1981, https://doi.org/10.1007/978-1-349-10187-0_1

[21] C. De Rosa, F. Auriemma, A.Malafronte, M. Scoti, Crystal structures and polymorphism of polymers: Influence of defects and disorder, *Polymer Crystallization*, 1(2018), e10015

[22] W. F. Su, Structure morphology flow of polymer, *Principles of Polymer Design and Synthesis. Lecture Notes in Chemistry*, 82(2013), Springer, Berlin, Heidelberg. https://doi.org/10.1007/978-3-642-38730-2_3