

# Advancements in Polymer Science: Synthesis, Characterization, and Biomedical Applications of Homopolymers and Copolymers

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## Abstract

Polymer science encompasses a different range of materials critical to industries spanning from packaging to biomedicine. Understanding the synthesis, characterization, and applications of common homopolymers and copolymers is fundamental to advancing polymer research and development. In this comprehensive review, we explore various preparation methods, including free radical, anionic, and cationic polymerization, utilized for synthesizing homopolymers and copolymers. Furthermore, we investigate solvent choices commonly employed for polymer characterization, ranging from neat conditions, polar protic and polar aprotic solvents. We also explored characterization techniques, including Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance (NMR), Atomic Force Microscopy (AFM), Differential Scanning Calorimetry (DSC), and Thermogravimetric Analysis (TGA). In addition to industrial applications, we highlight the diverse biological applications of homopolymers, poly (2-hydroxyethyl methacrylate) (pHEMA) and polystyrene, which find its extensive use in biomedicine. By synthesizing and analyzing this wealth of information, this review aims to provide a comprehensive understanding of the synthesis, characterization, and applications of homopolymers and copolymers, with a particular focus on their biological applications. This holistic approach not only contributes to advancements in polymer science and technology but also fosters innovation in biomedicine, ultimately benefiting human health and well-being.

## Keywords

Homopolymer, Copolymer, Poly(2-hydroxyethyl methacrylate) (pHEMA) Polystyrene, Free Radical Polymerization, Atomic Force Microscopy, Solvent Polarity

## 1. Introduction: Common Homopolymers and Copolymers

Polymers made up of at least two chemically distinct monomers are known as copolymers. In principle, copolymerization of multiple monomers in varied amounts can be used to create an unlimited number of distinct macromolecules. There are many ways for inserting monomers into polymer chain, as well as their sequencing, which results in various chemical diversity. [1] Copolymers can be classified depending on how the constituent units (also known as structural units) are organized along the chain. [2] Alternating copolymers, statistical copolymers, and block copolymers are all examples of linear copolymers, which have a single main chain. Branched copolymers are made up of a single main chain with one or more polymeric side chains. They can be grafted, star-shaped, or have various structures. **Figure 1** shows different types of polymers: 1) homopolymer; 2) alternating copolymer; 3) random copolymer; 4) block copolymer; 5) graft copolymer.



**Figure 1.** Different types of polymers: 1) homopolymer 2) alternating copolymer 3) random copolymer 4) block copolymer 5) graft copolymer.

Acrylonitrile butadiene styrene (ABS), styrene/butadiene co-polymer (SBR), nitrile rubber, styrene-acrylonitrile, styrene-isoprene-styrene (SIS), and ethylene-vinyl acetate are examples of commercial copolymers created through chain-growth polymerization. Step-growth polymerization, which is used to make the nylon-12/6/66 copolymer of nylon 12, nylon 6, and nylon 66, as well as the copolyester family, is another method of manufacturing.

A copolymer is a polymer with at least two different monomers chemically. An infinite range of various macromolecules can be synthesized in variable amounts in principles because of copolymerization of various monomers. [3] These chemical diversities are improved by the various approaches available for integrating the co-monomers into their sequences and chains.

These possibilities are defined and explained below. Copolymers can be categorized into 1) Statistical Copolymers: These copolymers have randomly distributed monomer units along the polymer chain. Each chain may have a different sequence of monomers, leading to statistical variations in the composition. [4] These are useful for applications where a random distribution of monomers is desired. 2) Alternating Copolymers: In alternating copolymers, the monomers

M1 and M2 are arranged in a regular pattern along the polymer chain. Each monomer alternates with the other, leading to a well-defined sequence. This type of copolymerization is often used when precise control over the chemical structure is required. 3) Block Copolymers: Block copolymers consist of two or more chemically distinct blocks or segments linked together in a linear fashion. These blocks can vary in size and chemical composition. Block copolymers often undergo phase separation, forming distinct domains of each block. This phase separation can lead to the formation of various nanostructures, making block copolymers valuable in a wide range of applications such as in materials science and drug delivery. [5] 4) Graft Copolymers: Graft copolymers consist of one type of polymer chain (M2) grafted onto the backbone of another polymer (M1). This results in a branched structure where the side chains (M2) are attached to the main polymer chain (M1). Graft copolymers combine the properties of both the backbone and the side chains, offering unique material properties and applications. Each type of copolymer offers distinct advantages and can be tailored to specific applications based on their structural characteristics and properties.

Homo and copolymers of poly(2-hydroxyethyl methacrylate) (PHEMA) and polystyrene (PS) offer unique advantages in various applications within polymer science. The synthesis of block copolymers such as PS-*b*-PHEMA has been explored for the preparation of smart porous membranes, showcasing molar masses in the range of 91 to 124 kg·mol<sup>-1</sup> with a pHEMA content of 13 to 21 mol%. [6] These block copolymers have been utilized for high water flux membranes and ceramic templates, highlighting their potential in membrane applications. [7] Moreover, the construction of amphiphilic graft copolymers incorporating pHEMA backbone and various grafts has been investigated, demonstrating the versatility of these copolymers in aqueous lubricating properties. [8] Additionally, the synthesis of graft copolymers like pHEMA-*g*-PS, where pHEMA serves as the trunk and PS as the branch, has been reported, showcasing the potential of these copolymers in interfacial applications. [9] Furthermore, the preparation of functional graft copolymers by solution copolymerization, such as poly(HEMA-*co*-MMA-*g*-PMMA), has been explored, indicating the potential application of these copolymers as dispersants in nonaqueous phase dispersion polymerization. [10] The utilization of PS-*b*-PHEMA block copolymers has been highlighted for the bottom-up preparation of functional porous membranes, emphasizing their role in membrane engineering. [11]

In addition, homo-polymerization of enediynes through the Bergman cyclization presents a fascinating strategy due to its benefits of facial operation, high efficiency, tailored structure, and catalyst-free operation. [12] On the other hand, co-polymers like (F-S N) *n* exhibit a higher HOMO compared to polyfluorene homo-polymers, showcasing advantages in electronic properties. [13] Additionally, the use of donor and acceptor monomers with regular arrangements in co-polymers allows for controlled phase separation and energy levels, influencing doping properties and HOMO-LUMO band gap. [14] Moreover, the development of homo-polymers like 2,2'-Bithiazolothienyl-4,4',10,10'-tetracarboxydiimide (DTzTI),

a novel imide-functionalized thiazole (PDTzTI ) has shown advantages in achieving high electron mobility, low off-current, and high on-current/off-current ratio, particularly beneficial for n-type polymer semiconductors. [15] Furthermore, the deep-lying HOMO levels in certain homo-polymers contribute to enhanced chemical stability in oxygen. [16] Co-polymers can also benefit from precise side-chain engineering to optimize fibril network morphology, leading to high-performance bulk-heterojunction organic solar cells. [17] In the context of materials science, the incorporation of CO<sub>2</sub>-responsive polymers into various structures has shown promise in creating switchable materials with diverse applications. [18] Additionally, porous polymers have emerged as advanced functional materials in catalysis, offering abundant coordination sites for single-site metals. [19] The rational design of conjugated polymers has significantly contributed to the efficiency of bulk heterojunction solar cells, emphasizing the importance of polymer selection in achieving high power conversion efficiency. [20]

Factors influencing the molecular weight of polymers are crucial in determining their properties and applications. The molecular weight of polymers can be influenced by various factors as evidenced in the literature. The molecular weight of supramolecular polymers, for instance, plays a critical role in their applicability and properties. [21] Studies have shown that the molecular weight of polymers affects their structure-function properties, and traditional techniques for determining molecular weight may have limitations. [22] Additionally, the crystallization behavior of polymers can be impacted by changes in molecular weight, affecting molecular mobility and relaxation times. [23] The molecular weight of polymer additives, along with temperature, can influence crystallization kinetics. [24] Moreover, the molecular weight of polymers is essential for understanding their properties, as it is a key factor in determining their viscoelasticity. [25] The performance of grafted polymers on solid surfaces can be affected by the molecular weight, influencing factors such as grafting thickness and surface roughness. [26] Furthermore, the efficiency of processes like polymer flooding is closely tied to the molecular weight of the polymer used. [27] The matching relationship between polymer molecular weight and reservoir permeability in processes like ASP flooding has been investigated to optimize performance. [28] The molecular weight of polymers is a critical parameter that influences various aspects of their behavior, properties, and applications. Understanding and controlling the molecular weight of polymers is essential for tailoring their properties to specific needs and optimizing their performance in different applications.

## 2. Methods of Preparation

### 2.1. Free Radical Polymerization

Free-radical polymerizations (FRPs) are processes wherein polymers are synthesized through the successive addition of free-radical building blocks. [29] Vari-

ous mechanisms can generate free radicals, often involving initiator molecules. These initiating free radicals then add non-radical monomer units, leading to the growth of polymer chains. FRPs serve as primary synthesis routes for a wide range of material composites and polymers due to the relatively nonspecific nature of chemical interactions involved, allowing for versatile polymerization reactions. [29]

FRPs belong to the category of chain-growth polymerizations, alongside coordination, anionic, and cationic polymerizations. [30] The progress of the reaction in FRPs is quantified by measuring the conversion of monomers into polymers. The random nature of events governing the length of each polymer chain results in molecular weight distributions (MWDs) rather than specific molecular weights typical of smaller molecules. Obtaining full MWDs can be achieved through kinetic methods or probabilistic arguments. [31]

Various techniques such as reversible addition-fragmentation transfer (RAFT) polymerizations, atom transfer radical polymerizations (ATRP), nitroxide-mediated radical polymerizations (NMRPs), and stable free radicals (SFRs) are employed in radical polymerizations. These methods are reliable for generating polymers with high molecular weights. [32]-[43] The process of radical polymerization (FRP) involves several key steps, as observed by the formation of polystyrene under the influence of initiators like azoisobutyronitrile (AIBN) or benzoyl peroxide (BPO). [10] Initiation begins with the decomposition of these compounds, yielding stable radicals such as isobutyronitrile and phenyl radicals. While both are capable of initiating styrene polymerization, oxygen-based radicals from peroxides are less effective due to their propensity to abstract hydrogen atoms rather than directly add to double bonds. Propagation proceeds as initiated radicals induce pi bond cleavage in styrene, generating benzylic radicals which continue to add more styrene molecules, forming new benzylic radicals at each step. [44] Notably, region-selectivity occurs during propagation, favoring the formation of stable radicals due to delocalization, particularly through the benzene ring. [44] Termination marks the end of radical reactions, where two radicals combine to eliminate their radical nature, commonly through head-to-head bonding of benzylic radicals. Additionally, termination events may involve one radical abstracting a hydrogen atom from another chain head. [44] Together, these steps explain the elaborate mechanisms governing radical polymerization and the synthesis of polymers like polystyrene.

## 2.2. Kinetics of Radical Polymerization

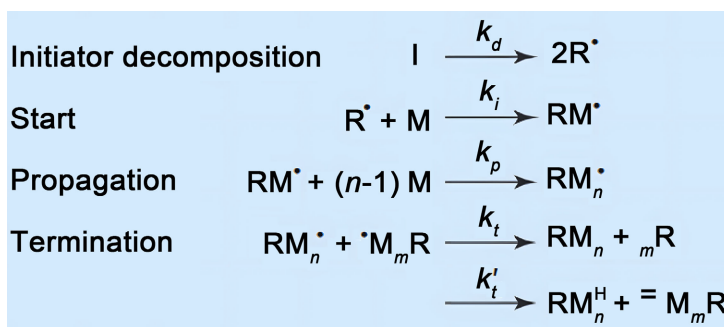
Based on the most precise mechanism, a radical polymerization can be divided into several individual reaction steps. The kinetics of these processes can be described by kinetic equations for each step, and from these equations, the overall kinetics of the polymerization reaction can be derived.

**1) Initiation:** This step involves the initiator molecule breaking down into two radicals, typically through a process known as dissociation, with a rate constant

represented. These radicals are reactive and can initiate the polymerization process by adding monomers. [1]

**2) Growth:** The radical formed in the initiation step adds to monomers, initiating the growth of the polymer chain. This step is characterized by a rate constant.

**3) Termination:** Termination occurs when polymer chains stop growing. It can happen through radical combination or disproportionation. Radical combination involves two radicals coming together to form a stable product (with  $k_t$ ), while disproportionation involves a radical reacting with a growing chain to produce a saturated chain and an unsaturated chain ( $k'_t$ ) as depicted in **Scheme 1**. [1]



**Scheme 1.** Formal scheme for radical polymerization. I initiator,  $R^\bullet$  initiator radical, M monomer,  $RM^\bullet$  initiator radical extended by a single monomer unit,  $RM_n^\bullet$  initiator radical extended by n monomer units,  $RM_n^H$  polymer with a saturated chain end,  $RM_m$  polymer with an unsaturated chain end.

The change in monomer concentration with time at a given temperature is a key aspect studied in radical polymerization kinetics. Temperature plays a significant role in determining the dominance of termination pathways. With an increase in temperature, termination by disproportionation typically becomes more important because  $E_{A,disp.} > E_{A,comb.}$  [1] The example of AIBN-initiated polymerization of the monomer  $CH_2 = CHR'$  is used to illustrate the individual steps of initiator decomposition, initiation, growth, and termination. AIBN (azo-bis-isobutyro-nitrile) is mentioned as an example of an initiator molecule, which dissociates into radicals that can initiate the polymerization process. [1]

## 2.3. Ionic Polymerization

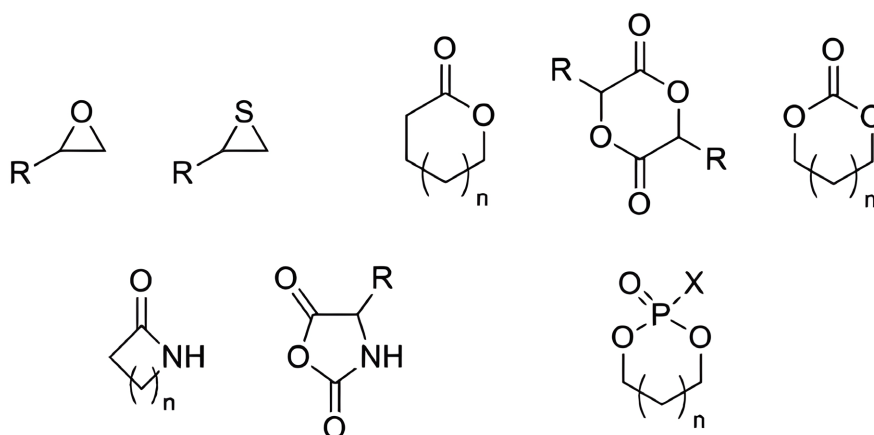
Ionic polymerization, like radical polymerization, is based on a chain mechanism in which the active centers are either cations (cationic polymerization) or anions (anionic polymerization).

### 2.3.1. Anionic Polymerization

Anionic polymerization is a chain reaction that, under the right conditions, runs without chain termination or transfer reactions, earning it the moniker “living polymerization.” [45] After complete polymerization, the phrase “living polymer-

ization” is used to characterize systems in which active centers remain at the end of each chain. If more monomers are introduced, the active centers’ chains continue to develop, and their degree of polymerization increases. [46] Anionic polymerization, like cationic polymerization, has a high selectivity for monomers, albeit it works best with monomers that have acceptor groups next to their double bonds.

Anionic ring-opening polymerization is a type of polymerization process characterized by chain growth, where the initiation and propagation stages involve the opening of cyclic monomers induced by the addition of anionic initiators and anionic chain ends, respectively. [47] Monomers suitable for anionic ring-opening polymerization (anionic ROP) are cyclic molecules with high electrophilicity. Examples of such cyclic monomers include epoxides and episulfides, which contain three-membered rings and exhibit ring strain, making them prone to undergoing anionic ROP. [47] Additionally, cyclic compounds containing carbonyl groups, such as lactones, cyclic carbonates, and lactams, can undergo anionic ROP through nucleophilic attack by nucleophiles, although the efficiency of this process may vary depending on the size of the ring as shown in **Figure 2**. Analogues of these compounds containing thiocarbonyl and phosphorus groups are also suitable as monomers for anionic ROP. [47]



**Figure 2.** Cyclic monomers for anionic ring opening polymerization.

### 2.3.2. Cationic Polymerization

Cationic polymerization is a highly effective method for producing precise polymers and advanced materials. The advent of living cationic polymerization has opened up new pathways to creating complex polymer architectures that were previously difficult to achieve. Another notable advancement in this field is the use of external stimuli such as light and electricity to control cationic polymerization, which finds applications in surface fabrication, patterning, additive manufacturing, and other areas of advanced material engineering. [48] The field has seen rapid progress, with several reviews focusing on key aspects of living cationic polymerization. These include controlled cationic polymerization catalyzed by Lewis acids, [49] living cationic polymerization mediated by the reversible

addition-fragmentation chain transfer (RAFT) mechanism, [50] and photoinitiated and photocontrolled cationic polymerization. [51]

### 3. Effect of Solvents on Polymerization Process

On copolymerization of solutions, various studies have established that solvents do not affect the comparative consumptions of the two monomers, and therefore do not affect compositions of copolymers. Nevertheless, as the solvent and monomer polarity increases, these generalities start to break down.

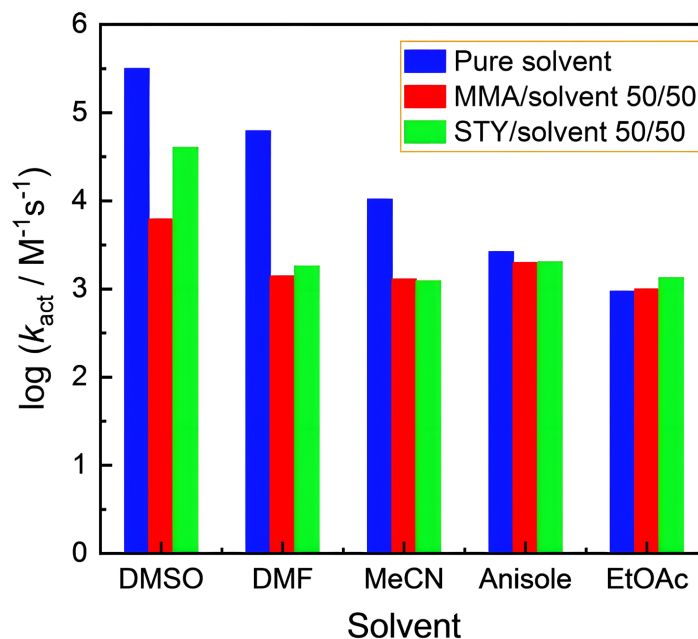
Research on how different solvents affect the chemical composition and speed of copolymerization involving styrene (ST) and three methacrylates have been studied by many scientists. Typical example, by employing advanced techniques like pulsed-laser polymerization, scientists by varying the polarity of solvents, have examined the influence of solvents like n-butanol, toluene, and DMF, on the structure and reactivity of (ST) and MA. [52] The results showed that solvents altered the composition of certain copolymers compared to standard methods. Specifically, n-butanol impacted the composition of one copolymer while DMF affected all three systems. [52] Additionally, solvents affected the rate at which copolymerization occurred, with n-butanol speeding up one system and DMF slowing down all systems. These findings challenged existing models of copolymerization, suggesting that hydrogen bonding interactions play a crucial role and need to be explicitly considered in future studies. [52]

In another work, different research groups also investigated how methyl methacrylate (MMA) polymerizes in different aromatic solvents. [53] They determined both the speed at which the polymerization progresses (propagation-rate constants,  $k_p$ ) and the rate at which it terminates (termination-rate constants,  $k_t$ ) through intermittent illumination techniques. [53] They found that changes in  $k_p$  values for MMA with aromatic solvents followed a similar pattern to those observed with phenyl methacrylate (PMA), although the effect of the solvent on MMA was slightly less pronounced. [53] This can be explained by the formation of a complex between the solvent and the reacting molecules, which affects the stability of the reaction. The dependence of  $k_p$  values on the concentration of the monomer suggests that when a solvent interacts with the reacting radicals, they become temporarily inactive. [53] Computational studies have also been done to investigate how styrene (ST) and 2-hydroxyethyl methacrylate (HEMA) react in different solvents-bulk, DMF, and toluene. Aviyente *et al.* used computational methods to calculate the speed of polymerization and predict how the monomers (ST and HEMA) interact and form copolymers. [54] Their findings showed that in bulk and toluene, the reactions followed similar patterns, while in DMF, HEMA tended to interact differently due to hydrogen bonding, affecting its reactivity during polymerization. Consequently, the composition of copolymers changed in DMF, with less HEMA incorporated. Additionally, their calculations of radical species supported their experimental observations, confirming that the rate of copolymerization in the ST-HEMA system was highest in bulk and tolu-

ene, and lowest in DMF. [54]

Durante *et al.* contrast with traditional radical polymerization, performed atom transfer radical polymerization (ATRP) and noticed that such studies are significantly influenced by the choice of solvent, likely due to its impact on the activation step. [55] In their work, they conducted a study to understand how the initiator ethyl  $\alpha$ -bromoisobutyrate is activated by  $[\text{Cu}^{\text{I}}\text{TPMA}]^+$  (TPMA = tris(2-pyridylmethyl)amine), a commonly used initiator/catalyst pair in ATRP. They investigated this process in various solvents, including DMSO, DMF, MeCN, anisole, ethyl acetate, and mixtures of these with 50% styrene (STY) and methyl methacrylate (MMA). [55]

The study found that the rate of activation ( $k_{\text{act}}$ ) varied significantly across solvents, with values differing by orders of magnitude. For instance,  $k_{\text{act}}$  ranged from  $3.14 \times 10^5 \text{ mol}^{-1}\cdot\text{dm}^3\cdot\text{s}^{-1}$  in DMSO to  $9.41 \times 10^2 \text{ mol}^{-1}\cdot\text{dm}^3\cdot\text{s}^{-1}$  in ethyl acetate. Interestingly, these differences correlated strongly with the solvent's polarity/polarizability parameter,  $\pi^*$ . Moreover, the effect of MMA or STY on activation depended on the compatibility of their polarities with the solvent: in polar solvents, the addition of monomer led to a substantial decrease in  $k_{\text{act}}$ , while in nonpolar solvents, it remained largely unaffected as depicted in **Figure 3**. [55]



**Figure 3.** Comparison of  $k_{\text{act}}$  values obtained in different solvents and solvent/monomer mixtures at 25°C. [55]

Barb *et al.* for instance first argued that maleic anhydrides and styrene propagation mechanisms were influenced in solvents by complexation of co-monomers. Copolymerization of styrene with maleic anhydride has been reported to differ significantly compared to reactivity of styrene with acrylonitrile. [56] This supports the underlying reasons that slight variation of solvent polarity has greater impact on polymer design.

Loretta and Robin employed pulsed laser polymerization (PLP) along with size exclusion chromatography (SEC) and nuclear magnetic resonance (NMR) to determine kinetic coefficients for 2-hydroxyethyl methacrylate (HEMA) copolymerization with butyl methacrylate (BMA) in different solvents. [57] The choice of solvent significantly influenced both the copolymer's composition and the composition-averaged propagation rate coefficient ( $k_{p, \text{cop}}$ ). When compared to the bulk system, n-butanol and dimethylformamide decreased HEMA's reactivity during copolymerization, while xylene enhanced it. [57] The impact of the solvent varied depending on the concentration of the monomers, as demonstrated by systematic studies of monomer/solvent mixtures with 50 vol%, 20 vol%, and 10 vol% monomer. This observed behavior was attributed to the influence of hydrogen bonding on monomer reactivity. The experimental data was fitted using the terminal model of radical copolymerization to estimate reactivity ratios and  $k_p$ , HEMA. [57]

In another work, Furuncuoğlu *et al.* used density functional theory (DFT) calculations along with other models to study the kinetics of free-radical homopolymerization and copolymerization of styrene (ST) and 2-hydroxyethyl methacrylate (HEMA) in three different environments-bulk, DMF, toluene. [58] By applying conventional Transition State Theory (TST), they calculated the rate parameters for polymerization. The calculated propagation rate constants were then utilized to predict the reactivity ratios of the monomers, which were in turn used to evaluate the copolymer composition using the Mayo-Lewis equation. [58] It was observed that copolymerization reactions in bulk and toluene exhibited similar transition geometries, while DMF tended to interact with HEMA molecules through hydrogen bonding, thereby reducing the reactivity of HEMA during homopolymerization and towards ST during copolymerization. Furthermore, calculations of copolymer composition indicated a decrease in the amount of HEMA monomer in the ST-HEMA copolymer system in the polar DMF solution. [58] The calculated spin densities of the radical species aligned with the rate parameters and confirmed that the copolymerization propagation rate of the ST-HEMA system followed the order:  $k_p$  (bulk)  $\approx$   $k_p$  (toluene)  $>$   $k_p$  (DMF).

2-Hydroxyethyl acrylate (HEA) is often used to adjust the properties of resins and introduce crosslinking sites. Its role in radical copolymerization kinetics is influenced by hydrogen bonding, which varies depending on the solvent used. [59] Robin and Schier used pulsed-laser polymerization to systematically study how different solvents affect the rate at which HEA is incorporated into copolymers with butyl methacrylate (BMA). They examined various solvents such as xylenes, dimethyl formamide (DMF), n-butanol (BuOH), methyl isobutyl ketone (MIBK), and butyl propionate. Their findings revealed that the choice of solvent has a greater impact on the composition of the copolymer than on the rate of propagation. [59] In bulk, HEA is incorporated into the copolymer with BMA at higher rates compared to butyl acrylate (BA). However, the presence of DMF and BuOH reduces the rate of HEA incorporation. On the other hand, other solvents increase HEA's reactivity. [59] For instance, in xylenes, the reactivity

ratios for BMA/HEA copolymerization indicate high HEA incorporation rates. Interestingly, the propagation rate coefficients could be described by the terminal model for polymerization in certain solvents like xylenes, MIBK, and butyl propionate, but not in the bulk system. [59]

In general, the impact of solvents on reactivity ratios ( $r_i$ ) and overall composition-averaged copolymer propagation rate coefficients ( $k_{p,\text{cop}}$ ) isn't typically noticeable in methacrylic ester radical copolymerization. However, when hydroxyl-bearing comonomers like 2-hydroxyethyl methacrylate (HEMA) are involved, significant deviations from this norm occur in both  $r_i$  and  $k_{p,\text{cop}}$ . This deviation is heavily influenced by the choice of solvent and is rooted in hydrogen bond interactions. To better understand this phenomenon, Rooney and Robin investigated how hydrogen bonding affects the kinetics of organic solution (meth)acrylic ester radical (co)polymerization by examining trends in structure/reactivity for methacrylate homopropagation rate coefficients ( $k_p$ ) and the relative reactivity of methacrylate macromonomers during copolymerization. [26] Additionally, the investigators outlined the peculiarities that characterize the apparent heightened reactivity of hydroxyl-bearing monomers during copolymerization. Finally, Rooney and Robin also presented a modeling framework aimed at systematically capturing the impact of solvent and hydrogen bonding on copolymer composition. The model included specific intramolecular hydrogen bond associations between monomer and growing chain and was applied to several methacrylate, acrylate, and styrene copolymerizations. [60]

In a separate work, Robin *et al.*, used a combination of pulsed-laser polymerization, size exclusion chromatography, and nuclear magnetic resonance to investigate how the choice of solvent and the structure of monomers influence the copolymerization propagation kinetics of 2-hydroxyethyl acrylate (HEA) and 2-methoxyethyl acrylate (MEA). [61] The similar structures of these monomers allowed the researchers to specifically examine the impact of hydrogen bonding, which enhanced the incorporation of HEA into copolymers compared to butyl acrylate (BA), depending on the solvent used. The copolymer-averaged propagation rate coefficient,  $k_{\text{copp}}$ , for HEA/BA is also higher than that of BA homopropagation and was significantly affected by the choice of solvent. [61] On the other hand, copolymerization of MEA with BA and butyl methacrylate (BMA) in various solvents displayed typical behavior, with no significant solvent effects observed on  $k_{\text{copp}}$  or reactivity ratios, except for an increased in  $k_{\text{copp}}$  in n-butanol (BuOH). The value of  $k_{\text{MEAp}}$  was determined to be  $35,000 \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$  at  $50^\circ\text{C}$ , which is 30% higher than the value for BA. In a simplified modeling approach, penultimate-unit parameters for BMA/BA were utilized to describe the evolution of  $k_{\text{copp}}$  for BMA/MEA in bulk. [61]

## 4. Selected Polymers

### 4.1. Selected Polymers and Their Methods of Preparations

#### Poly(2-hydroxyethyl methacrylate)

Poly(2-hydroxyethyl methacrylate), known as pHEMA, is a polymer highly valued for its biocompatibility, clarity, hydrophilicity, and remarkable durability, resisting crack propagation and bearing heavy loads effectively. [62] Originating from the toxic monomer HEMA, pHEMA undergoes a non-toxic transformation during polymerization. Its pivotal role in the development of modern soft hydrogel contact lenses traces back to the groundbreaking work of Otto Wichterle and Drahoslav Lim in the 1960s. [63] Initially utilized as an orbital implant, the favorable biological and mechanical properties of pHEMA prompted its exploration for contact lens applications. [64]

Since then, pHEMA has found versatile applications across biomedical fields, including soft contact lenses, bone tissue regeneration, drug delivery systems, artificial corneas, wound dressings, and prostheses. Soft contact lenses made from pHEMA offer flexibility and oxygen permeability crucial for eye health, in contrast to rigid gas-permeable materials like PMMA used in hard contact lenses. [62]

To bolster the mechanical strength of PHEMA-based hydrogels, a uniform network with robust ionic coordination interactions has been devised by Wang *et al.* [65] Leveraging the biocompatible monomer maleic acid, MA, which contains two carboxyl groups capable of forming numerous coordination bonds with  $\text{Fe}^{3+}$ , facilitates the creation of binding sites evenly distributed along the backbone chains. [65] The pronounced polarity and cis replacement structure of MA ensure this distribution, effectively impeding the separation of PHEMA chains and yielding a homogeneous network. Thus, the pairing of MA and  $\text{Fe}^{3+}$  was chosen by the investigators to synthesize an enduring PHEMA-based hydrogel network. [65] Central to this approach was the establishment of strong coordination interactions between the carboxylate groups of copolymerized maleic acid (MA) units and  $\text{Fe}^{3+}$ . This interaction prevented the phase separation of PHEMA chains in water, resulting in a uniform network structure. [65] This uniformity mitigated stress concentrations, while the dynamic coordination crosslinking mechanism efficiently dissipated energy, maintaining network elasticity. The culmination of these factors yielded hydrogels with exceptional tensile strength (3.44 MPa), elastic modulus (14.22 MPa), and toughness (4.17 MJ/m<sup>3</sup>). These values surpass those of pure PHEMA hydrogels by 22.7, 43.1, and 24.2 times, respectively. [65]

To synthesize low molecular weight PHEMA, controlled radical polymerization techniques are indispensable. Among the most successful methods are reversible addition fragmentation chain transfer (RAFT) and atom transfer radical polymerization (ATRP). Both have been effectively employed in HEMA polymerization, including the synthesis of HEMA-based block copolymers. [66] However, limitations exist that hinder their widespread use in biomedical applications.

In RAFT, a RAFT agent, often a thiocarbonyl-based compound, governs polymerization. [67] To achieve low molecular weight polymers, high concentrations of RAFT agents are necessary. If not removed post-polymerization,

these agents can impart coloration or toxicity to the polymers. [66] ATRP, on the other hand, utilizes a transition metal catalyst, typically a Cu(I)/(II) system, in relatively high concentrations. [35] The imbalance between Cu(I) and Cu(II) necessitates high catalytic concentrations. [68] [69] Removing the copper post-polymerization poses challenges despite advancements in catalyst removal techniques. [70]

Advancement in ATRP, known as “activators regenerated by electron transfer (ARGET) ATRP,” addresses these challenges. This method employs an excess reducing agent to regenerate Cu(I) from Cu(II), maintaining an appropriate Cu(I)/(II) balance. [71] ARGET ATRP reduces copper concentrations to parts per million (ppm) levels, simplifying catalyst removal by polymer precipitation. [72] Moreover, ARGET ATRP demonstrates tolerance to limited oxygen levels, eliminating the need for extensive deoxygenation steps. Various monomers and reducing agents have been successfully utilized in ARGET ATRP. [72]

Despite the advantages, using ATRP in polar solvents can compromise polymerization control, resulting in higher molar mass dispersity. [73] Nevertheless, PHEMA has been synthesized using ATRP in methanol or methanol/water solvent systems, albeit with slightly higher molar mass dispersities compared to nonpolar media. [73] Overcoming the challenge of synthesizing low molecular weight PHEMA with minimal catalyst levels, recent studies have employed ARGET ATRP at ambient temperatures. Optimization of ligand to copper ratios, reducing agent concentrations, and catalyst levels have enabled controlled polymerization, yielding water-soluble PHEMA with minimal catalyst content. [73]

### **Polystyrene**

Polystyrene (PS) is a polymer derived from the monomer styrene, a liquid hydrocarbon sourced from petroleum. [74] Typically solid at room temperature, PS can be melted at higher temperatures for molding or extrusion purposes, then cooled to regain its solid form. Styrene, being an aromatic monomer, imparts aromatic characteristics to PS. [74]

BASF pioneered the commercial production of PS in the 1930s, and since then, it has found extensive use across various plastic products. In geosynthetics, PS is predominantly employed in its expanded form, comprising approximately 5% PS and 95% air. [74] This expanded PS boasts low thermal conductivity due to the voids filled with trapped air, making it ideal for insulation in building structures. PS for architectural and engineering applications can also be extruded into standardized shapes or formed into sheets with diverse patterns. Previously, expanded PS contained chlorofluorocarbons, but with environmental concerns in mind, safer blowing agents are now utilized. [74]

Polystyrene is a versatile material widely used in medical applications due to its affordability, low density, clarity, and dimensional stability, along with its compatibility with radiation sterilization. It comes in two primary forms: crystal polystyrene and high impact polystyrene (HIPS). [75] Crystal polystyrene finds use in labware like petri dishes and tissue culture trays, while HIPS is utilized in thermoformed products such as catheter trays, heart pump trays, and epidural

trays. Both types are also employed in respiratory care equipment, syringe hubs, and suction canisters, competing favorably with PVC, polypropylene, and acrylics in labware and packaging for kits and trays. [75]

Crystal polystyrene resins, supplied typically as one-eighth-inch granules, are clear and glassy. When biaxially oriented, known as oriented polystyrene (OPS), they transition from brittle to flexible and durable. [75] OPS is formed by stretching the polystyrene sheet transversely, toughening what would otherwise be brittle. Injection-molded crystal grades serve various purposes, from cutlery and drink cups to medical labware and housewares. High-heat crystal grades are employed in applications like medical products and packaging. Extruded high-heat crystal grades are used in foam sheets for meat trays and foam board stock for insulation. [75]

High impact polystyrene grades are enhanced with polybutadiene elastomers, with high-impact grades containing around 6% - 12% elastomers and medium-impact grades about 2% - 5%. HIPS resins offer easy processing, good dimensional stability, impact strength, and rigidity. Some high-performance HIPS grades now rival more expensive engineering resins, finding applications in appliances and consumer electronics. Injection-molded HIPS resins are utilized in appliances, premium office accessories, and toys, while extruded HIPS resins are common in food packaging, dairy containers, and disposable tableware. [75] Polystyrene exists in three forms: atactic, isotactic, and syndiotactic. However, commercially available polystyrene mainly comprises atactic polystyrene. [75]

Another study explored the fabrication of a highly stable hyper cross-linked polystyrene (PS) organogel using  $\gamma$ -ray irradiation in tetrachloroethylene solvent, a novel eco-friendly synthesis method. [76] The degree of crosslinking, hydrophobicity, and swelling behavior of the PS organogel in various solvents was investigated. Additionally, the capacity of the PS organogel to selectively absorb chlorinated pollutants (CPs) from synthetic petroleum wastewater effluents was optimized using response surface methodologies (RSM), considering factors like pH, CP concentrations, temperature, PS amount, and absorption time. [76] Tests were conducted to assess the applicability and recyclability of the PS organogel for decontaminating real petroleum wastewater effluent, evaluating its economic viability in practical scenarios. Through in-situ cationic polymerization, a cross-linked PS organogel with 91% crosslinking was synthesized. The PS organogel exhibited high selectivity for chlorinated molecules over other organic molecules, with 80 - 184 times greater absorption capacity. [76] Response surface modeling confirmed the PS organogel's ability to absorb CPs effectively across a wide range of pH and temperature conditions. ANOVA analysis validated the developed CPs absorption model onto the PS organogel, highlighting its accuracy. [76]

At ambient temperature, anionic polymerization has been utilized to produce branched polystyrenes with diverse molecular weights and structures. This method involved incorporation of a distyryl branching comonomer into a conventional sec-butyllithium-initiated polymerization of styrene. [77] By control-

ling the length of the primary chains within the branched polymers and strategically placing the branching points along these chains, variations in glass transition temperature were achieved. [77] Interestingly, there was no direct correlation between the molecular weight of the branched polymer and its glass transition temperature. Instead, the length of the individual chains composing the branched macromolecules strongly influenced this property. [77]

## 4.2. Challenges in the Synthesis of Polymers

The synthesis of polymers poses various challenges that affect their production and properties. One significant challenge is achieving high molecular weight polyacrylate polymers using controlled/living radical polymerization techniques like RAFT, ATRP, and NMP, which have been successfully reported by only a limited number of specific methods. [78] [79] Redox polymerizations, initiated by a redox reaction between oxidizing and reducing agents, also present challenges in polymerization processes. [80] Additionally, the synthesis of heterocyclic polymers through triple-bond-based polymerizations faces technological significance along with synthesis challenges. [81]

Difficulties also arise in copolymerization processes involving nonconjugated  $\alpha,\omega$ -diolefin/propylene due to the low reactivity of high molar mass macromonomers, leading to low efficiency and process complexity. [82] The synthesis of unsubstituted polythiophene is challenging due to its insolubility despite promising properties, hindering its production. [83] Incorporating cellulose nanocrystals into polymer latex particles can lead to nanoparticle aggregation, processing difficulties, and weak mechanical properties. [84]

Furthermore, challenges in polymer synthesis extend to the production of polymeric thin films with high electrical conductivity, where processing difficulties and inhomogeneous distributions of components limit their utility. [85] The development of porous polymer-silica composites for thermal insulating materials faces challenges related to high production costs and extreme fragility, impacting their commercial applications. [86] Additionally, the synthesis of self-assembled graphene oxide microcapsules in Pickering emulsions for self-healing epoxy coatings may encounter difficulties in solidification and reaction maintenance within the microcapsules. [87] The challenges in polymer synthesis encompass various aspects such as achieving high molecular weight, coping with low reactivity of macromonomers, addressing insolubility issues, managing nanoparticle aggregation, ensuring homogeneous distributions, and overcoming production costs and fragility concerns. These challenges highlight the complexity and intricacies involved in synthesizing polymers with desired properties and functionalities.

## 5. Characterization

### 5.1. Method of Characterization

Polymer characterization allows scientists to unlock information about the prop-

erties of polymer materials. As polymer materials have innumerable applications, polymer characterization is hugely relevant to a wide range of sectors and industries. In attempt to identify a polymer we usually sought for the 1) chemical identity—this answers the question of what polymer is this? What additives are present? Is there any contamination? 2) morphology—that is amount of crystallinity and optical properties 3) molecular weight—molecular weight distribution 4) solution behavior—viscosity, flow, and gel 5) thermal behavior—glass transition, melt and decomposition temperature, melt viscosity and 6) mechanical properties—tensile strength, modulus, impact, creep and dimensional stability.

Scientists rely on a variety of techniques for polymer characterization as depicted in **Table 1**.

**Table 1.** Possible characterization techniques for polymers.

What do you need to know?	Possible Characterization Technique
Chemical Identity	FTIR, Raman, NMR GC-MS
Molecular Weight	Viscometer, Chromatography, MS
Solution Behavior	Viscometer Rheometer
Thermal Behavior	DSC TGA
Mechanical Properties	DMA
Morphology	Optical Microscopy, DSC

### 5.1.1. Chromatographic Polymer Characterization

Chromatography, an analytical technique used to separate mixtures into individual components, is one of the most useful tools for polymer characterization.

### 5.1.2. Thermal Polymer Characterization

A variety of thermal analysis techniques are used to characterize polymers and gain insight into structure and behavior. Differential Scanning Calorimetry (DSC) is one of the most common and measures how much heat is needed to increase the temperature of a polymer sample. Data helps manufacturers and product developers determine key thermal transition temperatures. These include glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ) and crystallisation temperature ( $T_c$ ). [88] Other useful thermal analysis techniques for polymer characterization include Thermogravimetric analysis (TGA), thermomechanical analysis (TMA) and Dynamic Mechanical Analysis (DMA). From widely used materials like nylon to complex polymeric nanocomposites, modern spectroscopy is redefining how polymer materials are characterized.

### 5.1.3. Spectroscopic Polymer Characterization

Of particular interest, the use of Near-Infrared (NIR) spectroscopy and NIR imaging for polymer characterization is now common. Near-Infrared (NIR) spectroscopy and imaging have become widely utilized for characterizing polymers.

This method involves examining electromagnetic spectra in the NIR range and finds broad application in industries like engineering and manufacturing. [89] NIR light can deeply penetrate polymeric substances, making this technique suitable for analyzing products of different sizes, from micrometers to centimeters. In industrial settings, NIR spectroscopic imaging is valuable for tasks like quality assurance, examining polymer films, and identifying specific components within numerous parts. [89]

#### **5.1.4. Microscopic Polymer Characterization**

Microscopic polymer characterization is a potent method for uncovering surface structures and patterns within polymer materials. By employing sophisticated instruments, researchers can look deeper than what's observable with the naked eye, examining individual atoms constituting polymers. In recent years, traditional optical microscopes have been supplanted by advanced techniques like Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). These electron microscopy methods offer superior resolution, enabling analysts to produce high-detail images of polymer samples.

#### **5.1.5. Rheometric Polymer Characterization**

Polymers have a higher molecular weight than other materials, which means they can exhibit unusual deformation behaviors. It's this characteristic that makes many polymers elastic and viscous. Rheometric polymer characterization allows researchers to analyze the viscoelastic properties of polymers, optimize manufacturing formulas and improve product performance. [90]

#### **5.1.6. Mechanical Polymer Characterization**

Strength, elasticity, viscoelasticity, and anisotropy stand among the crucial characteristics defining polymers, collectively termed mechanical properties. These properties are shaped by interactions among polymer chains, dictating how they respond to external forces. The capacity of chains to elongate and reorient under stress further influences mechanical behavior. [91] The occurrence of crazing, marked by whitening when a polymer undergoes stress, also plays a role in determining mechanical properties. Typically, polymers are classified as elastomers, plastics, or rigid polymers based on their mechanical attributes. [91]

### **5.2. Fourier Transform Infrared Spectrometry (FTIR)**

FTIR, or Fourier Transform Infrared Spectroscopy, serves as a powerful tool for answering the fundamental question, "What is this?" It offers a relatively user-friendly approach, allowing for the rapid analysis of a diverse range of materials. FTIR employs four primary sampling methods: Transmission, Attenuated Total Reflectance (ATR), Diffuse Reflectance, and Specular Reflectance. Regardless of the method used, the sample is exposed to an infrared energy beam. Through absorption and transmission of this energy, the sample reveals its unique chemical structure. Consequently, FTIR generates a distinctive spectrum for each compound, facilitating accurate identification and analysis. [92]

### 5.3. Nuclear Magnetic Resonance (NMR) Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is a highly versatile and powerful technique that has expanded into nearly all subdisciplines of chemistry and materials science. Commonly, an NMR spectrum presents peaks at different chemical shifts corresponding to nuclei of different chemical environments, allowing structural analysis and compositional characterization. More sophisticated and multidimensional NMR techniques connect NMR parameters such as chemical shift, line width, couplings, and relaxation rates to the structure and dynamics of the polymer chains at the atomic level. [93]

Common one-dimensional (1D) NMR techniques (e.g.,  $^1\text{H}$  and  $^{13}\text{C}$ ) are often used to provide information on reaction conversion, functionalization, product purity, and monomer content. 1D NMR is particularly useful in elucidating the composition of copolymers, where recent advances in quantitative NMR measurements coupled with high-resolution mass spectrometry have enabled sequence-level characterization. [94]

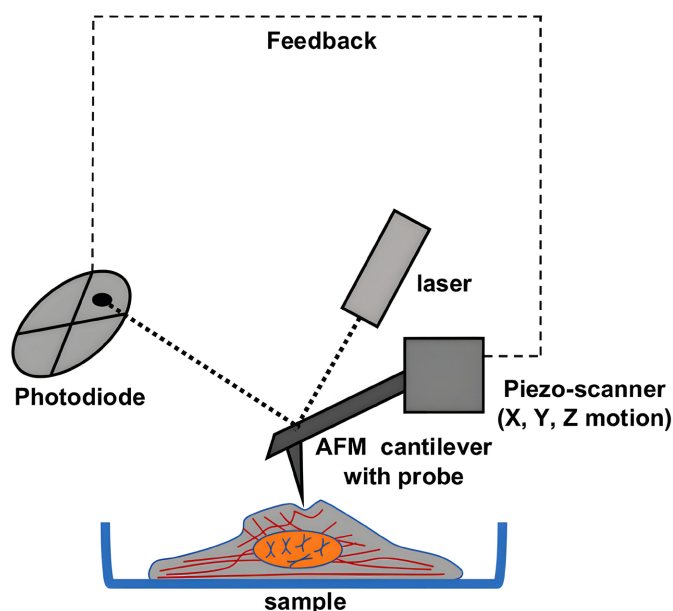
### 5.4. Atomic Force Microscopy

Atomic Force Microscopy (AFM) has become a crucial tool to examine the structure, mechanics, and activity of various molecules with high precision. [95] Since its invention, AFM has found widespread use not only in fields like materials science, engineering, and medical research. [96]

In AFM, a sharp tip attached to a flexible cantilever is used to scan the surface of non-conductive samples. This scanning process can be done in different modes: contact mode, where the tip maintains a set distance from the sample surface while scanning; semi-contact mode, where the tip briefly touches the sample surface at the bottom of each oscillation; and non-contact mode, where the tip hovers just above the sample surface without making direct contact. [97] By precisely controlling the interaction between the tip and the sample surface, AFM enables researchers to obtain detailed information about morphology, biomechanics, and contraction activity. This ability to characterize samples at such a fine scale has made AFM an indispensable tool for understanding the materials and for advancing research in various scientific disciplines. [97]

The Atomic Force Microscope (AFM) operates on the principle of measuring surface topography by scanning a sharp tip across a sample while maintaining a constant interaction force between the tip and the sample. [97] The system consists of a cantilever with a sharp tip attached to it. As the tip interacts with the sample surface, the cantilever deflects as shown in **Figure 4**. To measure these deflections, an optical amplification system is employed. A laser beam is directed onto the cantilever, and the reflected beam is detected by four photodiodes arranged in a cross configuration. [97] Any movement of the cantilever tip alters the angle of reflection, which is detected by the photodiodes. During scanning, as the tip moves across the sample surface, the interaction force between the tip and the sample is kept constant using a feedback mechanism. This ensures ac-

curate and consistent measurements of surface features. [97]



**Figure 4.** Schematic diagram of atomic force microscope. [97]

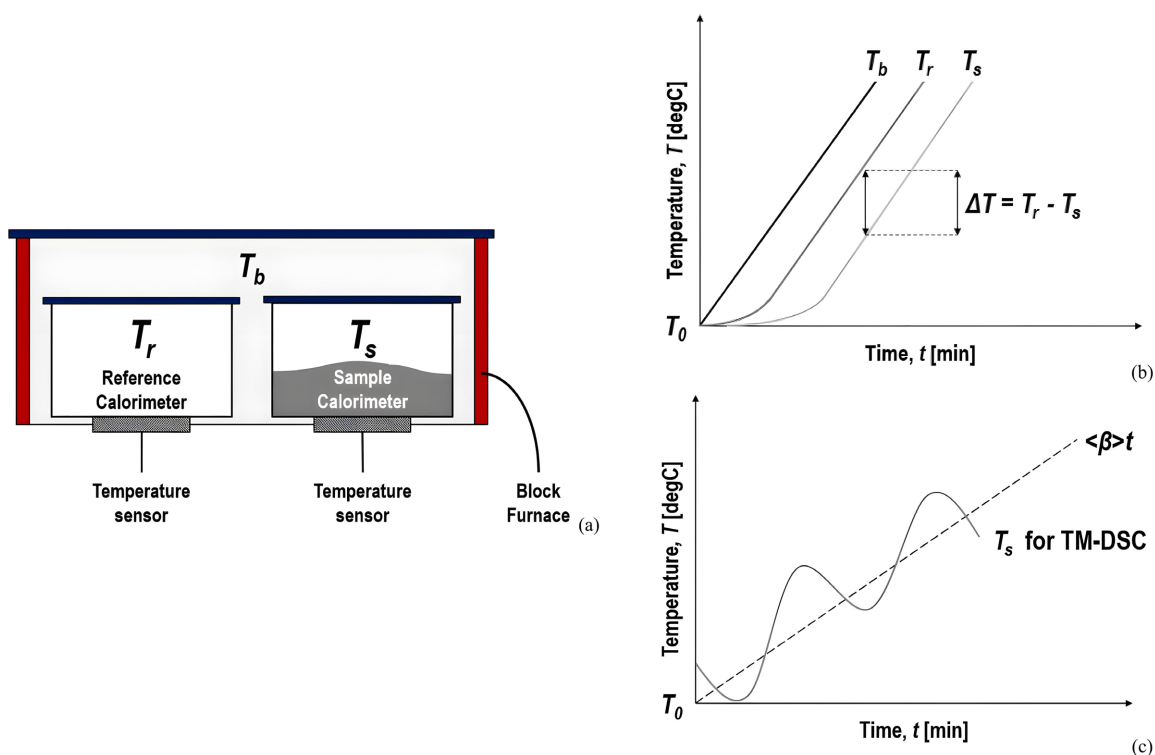
### 5.5. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) is frequently combined with other electro-analytical methods to analyze the thermal characteristics of polymers. DSC measures the heat flow produced when a sample undergoes various temperature changes, providing insights into important properties like glass transition temperature, crystallization behavior, and melting point. [98] The history of how a polymer is treated thermally significantly affects its glass transition temperature and crystallinity. Annealing, for example, involves heating a semi-crystalline polymer to a temperature higher than its glass transition but lower than its melting point. This process allows the polymer chains to move and crystals to form, which can greatly increase the material's crystallinity. Manufacturers who use injection molding capitalize on this understanding by controlling the temperature of the mold to influence the crystallinity of semi-crystalline thermoplastics. By carefully adjusting the mold temperature, they can ensure that the polymer fills the mold and cools in a way that achieves the desired level of crystallinity. This control over crystallinity is crucial for meeting the specific physical requirements of the molded parts. The thermogram obtained during the analysis provides material properties including temperatures at the glass transition ( $T_g$ ), onset of melting, peak of melting ( $T_m$ ), and enthalpy of fusion ( $\Delta H$ ) used to calculate crystallinity. These measurements can be specific to a particular polymer, confirming the polymer identity. [99]

In principle differential scanning calorimetry (DSC) is a method used to measure how much heat flows into or out of a material as its temperature changes continuously. [100] In a DSC unit, there are two calorimeters placed in

a furnace block to minimize heat loss. This setup allows for measurements in either temperature-linear (TL) or temperature-modulated (TM) scanning modes. Even when using the same technique, different glass transition temperature ( $T_g$ ) values can be obtained by employing various methods and protocols, such as heat flux and power compensation calorimeters, as well as different scanning programs. [101]

Each calorimeter typically consists of a small pan, often made of aluminum for good heat conduction, with a temperature sensor underneath to track temperature changes. The sample calorimeter holds the material being analyzed, while the reference calorimeter contains an identical pan without any material. [101] This configuration enables accurate measurement of heat flow in the sample compared to a baseline reference as depicted in **Figure 5**.



**Figure 5.** Differential scanning calorimetry: (a) schematic representation, and two heating scans (b) TL-DSC and (c) TM-DSC. [100]

## 5.6. Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) is another widely used thermal analysis technique. It works by measuring weight changes when the polymer is exposed to different temperatures. Increases or decreases in weight can be used to predict how a polymer will behave when exposed to harsh environments. Data can also be used to predict how polymeric materials will react to processes such as oxidation and decomposition. TGA is often carried out in a well-controlled atmosphere such as a vacuum or an inert gas filled environment to control the nature of the thermal decomposition by preventing oxidation. The measurements can

be presented in plots that are either temperature-dependent or time-dependent where changes in mass can usually be attributed to material volatility or degradation. [93]

## 6. Application of Some Selected Polymers

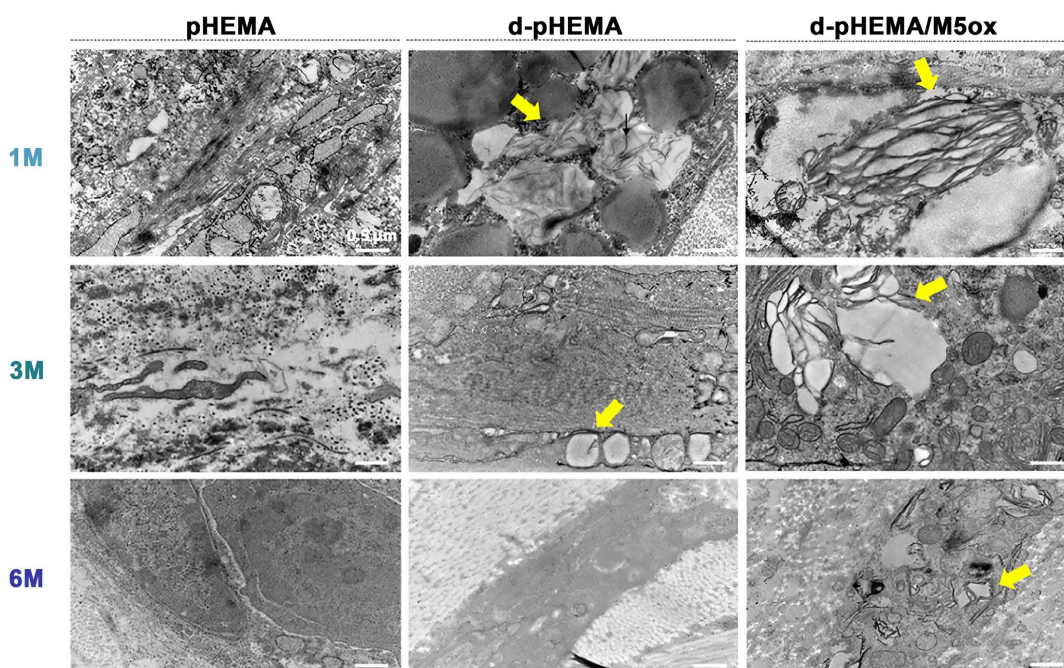
Poly(2-hydroxyethyl methacrylate) (PHEMA) and polystyrene are two versatile polymer materials that have found extensive use in various biological applications due to their unique properties and ease of fabrication. These polymers have been extensively studied and engineered to meet the diverse demands of biotechnology, biomedical engineering, and healthcare. In this introduction, we will provide an overview of the biological applications of PHEMA and polystyrene, highlighting their key characteristics and recent advancements in the field of therapeutic agents, making it ideal for localized drug delivery applications.

### **poly(2-hydroxyethyl methacrylate)-PHEMA**

Poly(2-hydroxyethyl methacrylate) (PHEMA) has been found to be used as hydrogel polymer due to its biocompatibility, water absorption capacity, and flexibility. These properties make PHEMA an attractive material for biomedical applications, including drug delivery systems, tissue engineering scaffolds, contact lenses, and wound dressings. PHEMA hydrogels can mimic the mechanical properties of natural tissues, providing a suitable environment for cell growth, proliferation, and tissue regeneration. Moreover, the hydrophilic nature of PHEMA allows for the controlled release.

Scientists have studied PHEMA with the purpose of addressing the challenge of developing biocompatible, non-fouling, and biodegradable hydrogels for blood-contacting devices. [102] Two types of hydrogels were evaluated by Durate *et al.*, degradable poly(2-hydroxyethyl methacrylate) (d-PHEMA) hydrogels and d-PHEMA hydrogels reinforced with oxidized few-layer graphene (d-PHEMA/M5ox). These hydrogels were implanted subcutaneously in rats for 6 months to assess their biocompatibility, biodegradation, and any potential side effects such as irritation, chronic toxicity, or immune response. [102] The results showed that both types of hydrogels degraded over the 6-month period, although degradation was slower for d-PHEMA/M5ox. Degradation products were found in intracellular vesicles, indicating the breakdown of the hydrogels within the body as observed in **Figure 6**. Importantly, no inflammation or infection was observed at the implantation sites, and histopathological examination of parenchymal organs revealed no abnormalities.

Immunohistochemistry confirmed that both d-PHEMA and d-PHEMA/M5ox hydrogels exhibited high anti-adhesiveness, meaning they were resistant to cellular adhesion. Gene expression analysis showed the presence of both M1 and M2 macrophages at all time points, with a balanced M1/M2 profile after 6 months suggesting an anti-inflammatory environment and no chronic inflammation. [102] This was further supported by cytokine analysis, which showed no significant changes in the levels of pro-inflammatory (IL- $\alpha$ , TNF- $\alpha$ ) and anti-inflammatory (IL-10) cytokines. [102]



**Figure 6.** Identification of the degradation products of pHEMA, d-pHEMA and d-pHEMA/M5ox implanted films. TEM micrographs of the explants with adhered tissue upon 1M, 3M and 6M implantation. Yellow arrows indicate degraded products present in vacuoles (scale bar = 0.5  $\mu\text{m}$ ). [102]

Overall, the study demonstrated that modifying pHEMA towards a degradable material did not compromise its inherent properties, particularly its anti-adhesiveness and biocompatibility. These findings suggest that these hydrogels have the potential to be used as a starting point for further modifications aimed at promoting cellular adhesion and proliferation for tissue engineering applications, including the design of blood-contacting devices with different load-bearing requirements.

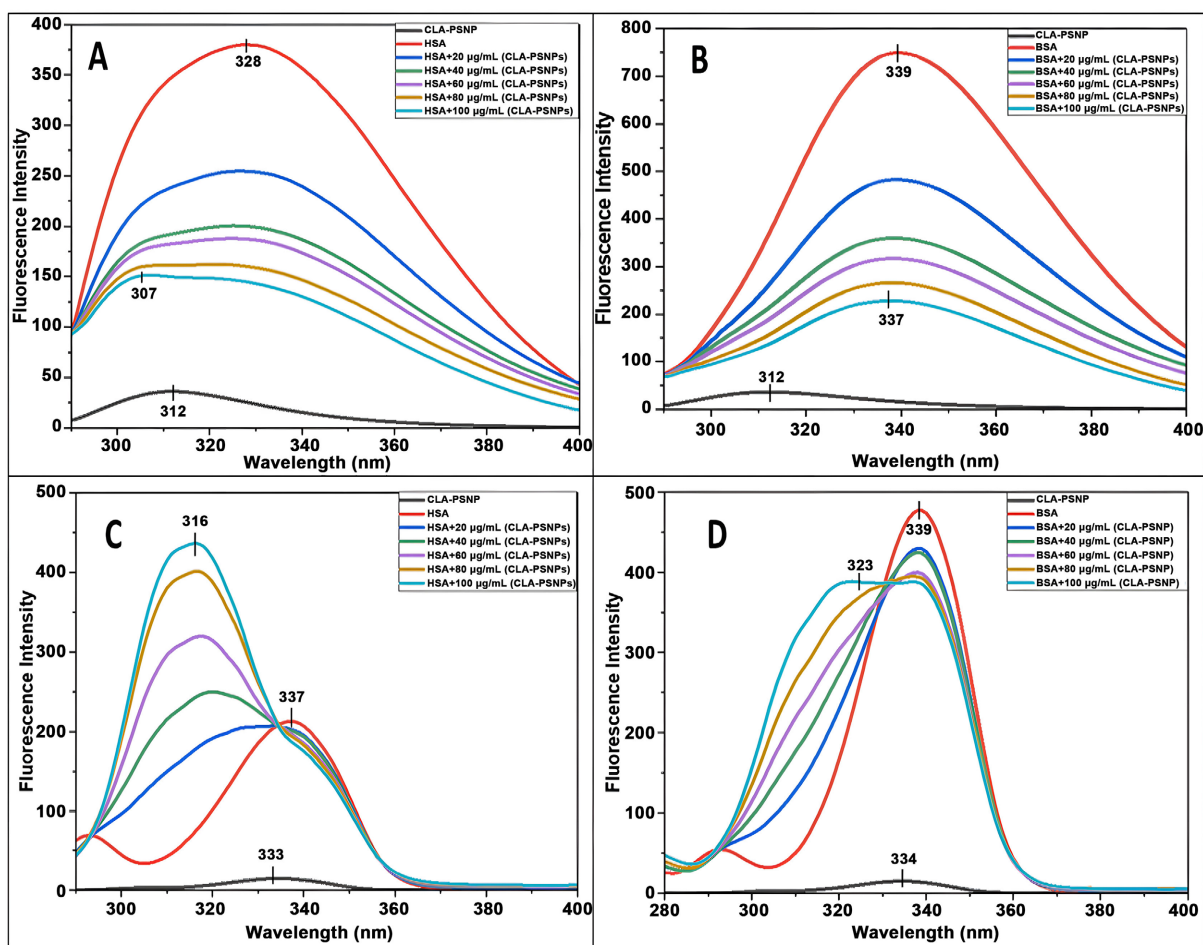
pHEMA structures are the basis for applications ranging from thermoplastic elastomers to information storage, drug delivery, and photonic materials. pHEMA copolymers are very attractive for use in the production of functional nanostructures. The most attractive quality is their length as well as spatial organization which can be controlled through block copolymer morphology. [62]

Biomedical applications of pHEMA include soft contact lenses, bone tissue regeneration, ocular drug delivery and controlled drug delivery systems, artificial corneas, artificial skin, wound dressings, breast augmentation, catheters, intrauterine inserts, and prosthesis. [62] pHEMA has excellent optical properties; hence it is primarily used in ophthalmic applications to manufacturing contact lenses. A reduction in cross-linking density produces a softer, more malleable hydrogel suitable for soft tissue regeneration. On the other hand, introducing mesoscopic porogens helps overcome limited permeability, thereby promoting vascular ingrowth and cellular attachment [62] pHEMA nanoparticles are used in magnetic drug targeting following the addition of iron oxide, which imparts superparamagnetism to the nanoparticles. [62]

## Polystyrene

Polystyrene is a thermoplastic polymer widely used in biological research and medical diagnostics. Its optical clarity, chemical inertness, and ease of surface modification make polystyrene a preferred material for cell culture dishes, microfluidic devices, and diagnostic assays. Polystyrene surfaces can be functionalized with bioactive molecules such as proteins, antibodies, or peptides to promote cell adhesion, proliferation, and differentiation. Additionally, the optical transparency of polystyrene enables real-time monitoring of cellular processes using microscopy techniques, making it invaluable for studying cell behavior and interactions *in vitro*.

The appearance of contaminants such as antibiotics and nanoplastics has sparked concern for their possible harm to ecosystems. One notable concern is how antibiotics stick to nanoplastic surfaces, potentially aiding their spread over long distances and enhancing their combined effects. Some researchers explored how clarithromycin, a common antibiotic, attaches to polystyrene nanoplastics and how this complex interacts with serum albumin, an important protein in biological systems. [103]



**Figure 7.** (A), (B) Fluorescence quenching spectra, and (C), (D) Synchronous fluorescence spectra ( $\Delta\lambda = 60$  nm) of HSA and BSA in the presence of varying concentrations of CLA-PSNP. [103]

Using various spectroscopic techniques, they investigated how clarithromycin interacts with nanoplastics under conditions mimicking those in the body. They found out that around 22.8% of the drug was attached to the surface of polystyrene nanoplastics after six hours. Additionally, fluorescence spectroscopy results showed that the presence of the clarithromycin-polystyrene nanoplastics complex reduced the fluorescence of serum albumin, indicating a quenching effect as depicted in **Figure 7**. [103]

To understand these interactions better, the researchers determined how many molecules of clarithromycin bind to each nanoplastic, along with the strength and spontaneity of the binding process. [103] They discovered that the binding occurs naturally and is influenced by hydrophobic interactions. Furthermore, the analysis of fluorescence and spectroscopic data revealed changes in the structure of serum albumin when it interacts with the clarithromycin-polystyrene nanoplastics complex, potentially affecting its function. [59] Overall, the study provides insights into how clarithromycin attaches to polystyrene nanoplastics and interacts with serum albumin, highlighting potential concerns for biological toxicity at the molecular level. Understanding these interactions can help develop strategies to mitigate the environmental and health impacts of emerging contaminants, safeguarding ecosystems and human well-being.

## 7. Conclusions

This review has provided an overview of the synthesis, characterization, and application of homopolymers. Through exploration of preparation methods such as free radical, anionic, and cationic polymerization, along with characterization techniques including FTIR, NMR, AFM, DSC, and TGA, we have gained insights into the fundamental aspects of polymer science. Additionally, the examination of solvent choices for polymer characterization has enhanced our understanding of how environmental factors can influence material properties. Furthermore, the focus on biological applications has highlighted the significant contributions of polymers such as poly(2-hydroxyethyl methacrylate) (pHEMA) and polystyrene to biomedicine. pHEMA hydrogels have demonstrated biocompatibility and are widely used in tissue engineering scaffolds and medical devices, while polystyrene finds applications in cell culture and diagnostic assays. These examples highlight the versatility and importance of polymers in addressing critical healthcare needs.

Moving forward, continued research and innovation in polymer science hold promise for further advancements in material design, characterization techniques, and biomedical applications. By leveraging interdisciplinary approaches and incorporating insights from fields such as chemistry, biology, and materials science, we can continue to push the boundaries of polymer technology. Ultimately, this ongoing exploration will lead to the development of novel materials and technologies that benefit society by improving human health, enhancing sustainability, and driving technological progress.

## Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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