

The effects of piezoelectric particles on the efficiency of mechanoATRP

Dominik Skopal

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Zásady pro vypracování

Anotace

Objev řízené radikálové polymerace, jako je radikálová polymerizace s přenosem atomu (ATRP), umožnil přípravu přesně definovaných polymerů s nízkou polydisperzitou, které jsou vysoce žádoucí pro environmentální, lékařské, energetické a další aplikace. Proces ATRP je zprostředkován Cu(I) komplexy generovanými z Cu(II) deaktivátorů za použití různých redukčních činidel. Kromě chemických činidel lze redukcí provádět pomocí vnějších stimulů, jako je mechanická energie. V takovém případě jsou elektrony redukující Cu(II) generovány piezoelektrickými částicemi působením ultrazvuku. Kvalifikační práce bude zaměřena na implementaci různých piezoelektrických částic do procesu ATRP a zkoumání jejich polymerační účinnosti. Generování elektronů bude řízeno koncentrací piezoelektrických částic a bude zkoumán výtěžek polymerace a molekulární struktura polymeru.

Student připraví literární rešerši na dané téma. Na základě rešerše budou zvoleny slibné systémy polymerů a piezoelektrických částic, kterým bude věnována pozornost. V praktické části student bude instruován, jak připravit ATRP roztoky, jak provádět reakce a analyzovat produkt. Dále bude studovat vliv koncentrace částic, případně katalytického systému a teploty. Na závěr dojde k vyhodnocení účinnosti a porovnání s doposud publikovanými systémy. Pro práci na nezbytných přístrojích bude instruován a zaškolen.

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L.S.

prof. Ing. Roman Čermák, Ph.D.
děkan

doc. Ing. Petr Smolka, Ph.D.
ředitel ústavu

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ABSTRAKT

Tato bakalářská práce se zaměřuje na optimalizaci piezoelektrických činidel v kontrolované radikálové polymerizaci s přenosem atomu řízené mechanickými silami (zkráceně mechanoATRP). Tato metoda umožňuje syntézu polymerů s přesně definovanou molekulovou hmotností a nízkým indexem disperzity, přičemž reakce probíhá pod externí kontrolou. Pro dosažení co nejvyšší efektivity z hlediska výtěžnosti a rychlosti reakce je nezbytná pečlivá optimalizace piezoelektrického činidla. Z různých piezoelektrických činidel dostupných v literatuře se oxid zinečnatý (ZnO) jeví jako velmi efektivní varianta. Tato práce zkoumá potenciál laboratorně syntetizovaného ZnO a optimalizaci jeho koncentrace. Výsledky ukazují, že ZnO bylo efektivní už v nízkých koncentracích (0,25 hm. %); v optimalizované koncentraci (1 hm. %) bylo dosaženo 87% konverze methyl akrylátu (MA) po 6 hodinách s pozoruhodně nízkou disperzitou, $D = 1,09$. Z celkového hlediska laboratorně syntetizovaný ZnO prokázal výjimečnou účinnost v mechanoATRP, což poukazuje na jeho potenciál pro použití v širším měřítku.

Klíčová slova: externě řízená ATRP, mechanoATRP, oxid zinečnatý, piezoelektrické nanočástice, methyl akrylát

ABSTRACT

This bachelor's thesis focuses on the optimization of piezoelectric agents in the atom transfer radical polymerization (ATRP) mediated by mechanical forces (in short, mechanoATRP). The mechanoATRP enables the synthesis of polymers with the desired molecular weight and a low dispersity index, while having external control over the reaction. To ensure the effectiveness of mechanoATRP in terms of high yields and fast reaction rates, the loading of the piezoelectric agents must be carefully optimized. Among various piezoelectric agents reported in the literature, zinc oxide (ZnO) appears to be effective. This thesis explores the potential of the custom-synthesized ZnO in mediating mechanoATRP, together with the optimization of its loading. The achieved results show that ZnO was effective in low loadings (0.25 wt%), and under optimum loading (1 wt%), it enabled 87% monomer conversion of methyl acrylate (MA) after 6 hours with remarkably low dispersity, $\bar{D}$ of 1.09. Overall, the custom-synthesized ZnO demonstrated the exceptional effectiveness in mediating mechanoATRP, which suggests its potential for larger-scale applicability.

Keywords: externally controlled ATRP, mechanoATRP, zinc oxide, piezoelectric nanoparticles, methyl acrylate

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I THEORETICAL PART

1 INTRODUCTION

This chapter summarizes the fundamental information closely related to the subject of the thesis. The term “polymer” is explained, including a brief historical background of polymer science and the importance of polymers in daily life. The classification of polymers is then given with the emphasis on the radical polymerizations and their mechanism. Then, the principles and types of controlled radical polymerizations (CRPs) are introduced. Special attention is given to the atom transfer radical polymerization (ATRP), one of the most useful techniques to prepare well-defined polymers. The advantages and recent developments of the ATRP are demonstrated in the most prominent examples in polymer chemistry. In the next section, the possibilities of the ATRP activation, including the activation via external stimuli, are briefly summarized. Considering the scope of this thesis, the most attention is paid to the ATRP mediated by mechanochemical forces, i.e., mechanoATRP.

1.1 Definition of a polymer

Polymers are large macromolecules composed of repeating multiple structural units called monomers. The term originates from two Greek words: *πολύς* (*poulús*) means “many”, and *μέρος* (*méros*) means “part”. This expression reflects the composition of these materials as chains of high-quantity repeating units [1]. The first theories about something as polymers can be traced back to 1832, when Swedish chemist Jöns Jacob Berzelius (Uppsala University) examined particles such as inorganic oxides and hydrocarbons and found out that there are compounds with the same proportionate composition but the number of constituent atoms is different. He called this polymeric, and later on, the term became generally used, and in the 1860s chemical dictionary, this term was included and defined [2].

1.2 Classification of polymers

Polymers are usually classified based on their origin into two main categories, natural and synthetic. Natural polymers are found in nature, in plants, animals, and microorganisms. They are crucial for living organisms. They include, for example, proteins (collagen, keratin, etc.), polysaccharides (cellulose, glycogen, etc.). There are, however, several limitations of the natural polymers, such as lower mechanical strength and predisposition to microbial degradation [3]. On the other hand, synthetic polymers are man-made, and include a huge variety of subclasses, such as polyolefins, polyacrylates, polyesters, polyamides, among others. They are engineered to have specific properties, which makes them usable in a wide

range of applications. These synthetic polymers are used in more industrial zones and offer numerous benefits such as durability, lightweight; they are usually also cost-effective, easy to process and shape, offer good chemical resistance, etc. Limitations of synthetic polymers can be environmental concerns (some synthetic polymers can be toxic or harmful to the environment when being synthesized, and also, their recycling can be challenging [3]). Considering the aims of this thesis, the following paragraphs will be primarily devoted to the synthetic polymers.

1.3 Importance of polymers in daily life

Polymers play a crucial role in our daily lives. Thanks to their versatility, cost-effectiveness, customizable properties, and other properties specified above, they represent an indispensable part of most of the products that we use and make our lives easier. The most important realms where we use polymers are electronics, healthcare, or even all sorts of consumer goods. Specifically, the typical example is polyethylene (PE), which is a common polymer highly used in packaging, household items such as containers or bags, footwear, or even automotive applications. Without polymers, most of the products that we use daily would be much more expensive and harder to obtain [4].

2 RADICAL POLYMERIZATIONS (CONVENTIONAL)

The term conventional radical polymerization usually refers to free radical polymerization (FRP). Since the 1980s, about 50% of the total worldwide production of synthetic polymers has been obtained by radical polymerization processes. To this day, the percentage of production of synthetic polymers obtained by radical polymerization has decreased, but it is still a major part of it [2].

2.1 History of polymerization

The process of polymerization was first mentioned in Paris in 1863, when J. J. Berthelot (Sorbonne University) was describing conversion reactions of certain compounds, such as styrene, to their “polymerides”. He called such a reaction a “polymeric transformation”. Later, this process was commonly referred to as polymerization. Berthelot also came up with the theory that all substances that can add water, chlorine, or hydrogen can be polymerized, and also predicted that structures that are not complete can also be polymerizable. According to him, there were three possibilities to initiate such a process. By direct application of heat, by simultaneous reaction, and due to the influence of a “nascent” state. Thanks to all of this, Berthelot can be considered the first polymer chemist [2].

2.2 Definition of radicals

The easiest definition of the radical is an atom, ion, or molecule with an unpaired valence electron. Electrons usually prefer to stay in pairs due to stability, but when there is an unpaired electron, we call it a radical. Since the radicals are unstable and reactive, they are known for their drive to interact with other molecules to stabilize themselves. This reaction often sets off chain reactions and is the key factor for all the radical polymerizations.

2.3 History of radicals

The first mentions of the term “radical” are traced back to the 19th century. The first reported stable radical was triphenylmethyl in 1900 by Moses Gomberg, (University of Michigan) He was often referred to as the father of radical chemistry. After this discovery, radicals have become an important part of organic chemistry. The topic called radical polymerization was brought up in 1920 by Herman Straudinger (Swiss Federal Institute of Technology in Zurich) in the publication “Über Polymerisation” [2]. Thanks to his discoveries, he is widely recognized as the father of polymer science.

2.4 The mechanism of free radical polymerization

FRP follows the reaction mechanism that is completed by three steps. Each of the steps plays a crucial role in the formation of the final polymer. The first step is initiation, where radicals are generated. After initiation, propagation begins, where the growth of the polymer chain occurs. And the next and final step is termination, where the reactive chain ends [5].

2.4.1 Initiation

In initiation, there is a radical being created from nonradical species. As initiators, substances such as benzoyl peroxide (BPO), azobisisobutyronitrile (AIBN), or other peroxides or azo compounds are often used. Purposely, initiators are compounds that decompose upon heating or other conditions [5].

2.4.2 Propagation

In the second step, called propagation, the free radicals generated in the first phase (initiation) react with monomer molecules to form new radical species. This step involves the addition of monomer units to the growing polymer chain until the radical site is terminated. This phase is characterized by rapid growth of the chain length, which is influenced by factors such as monomer concentration and the nature of the radical species etc. [6].

2.4.3 Termination

This is the final phase of the conventional radical polymerization. In this step, the active radical chains are being deactivated. The deactivation means ending the process. Termination can occur through various mechanisms. Examples of these mechanisms are combination, where two radical chains join to form a stable bond, or disproportionation, where one radical transfer a hydrogen atom to another, resulting in two stable products. The termination step is critical as it affects the molecular weight distribution and overall yield of the polymer. The efficiency of termination can be influenced by the concentration of radicals and the presence of chain transfer agents, which can lead to a reduction in the average molecular weight of the polymer [7].

3 CONTROLLED (LIVING) RADICAL POLYMERIZATION

Conventional radical polymerization has a limited ability to provide materials with highly specific and uniform characteristics, and therefore, it has evolved into several advanced techniques. These techniques enable control of the polymer structure and its properties at the molecular level. A variety of techniques have been developed, but some of them, such as atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT) polymerization, and nitroxide-mediated polymerization (NMP), stand out due to their unique mechanisms and broad applicability.

3.1 Atom Transfer Radical Polymerization (ATRP)

Atom Transfer Radical Polymerization (ATRP) is a type of controlled radical polymerization discovered by Prof. Krzysztof Matyjaszewski (1950–today) at Carnegie Mellon University in 1995. ATRP offered precise control over properties such as molecular weight or topology, possibility to prepare new materials/hybrids with complex architectures [8].

3.2 Reversible Addition-Fragmentation Chain Transfer (RAFT)

Reversible addition-fragmentation chain transfer (RAFT) is another CRP technique that employs a RAFT agent to mediate the polymerization process. The RAFT agent contains a thiocarbonylthio group, which can reversibly react with growing polymer radicals, allowing for the formation of a stable intermediate. This method allows for precise control over molecular weight and polydispersity, making it suitable for synthesizing complex polymer architectures, including block copolymers and polymer brushes [9].

3.3 Nitroxide-Mediated Polymerization (NMP)

Nitroxide-mediated polymerization (NMP) does not need a metal catalyst because it uses nitroxide radicals to mediate the polymerization. This can be effective for some of the monomers that are more sensitive than the others, and it can produce well-defined polymers with controlled molecular weights [10].

4 ATOM TRANSFER RADICAL POLYMERIZATION (ATRP)

The beginnings of ATRP are being traced back to 1995, and due to its popularity and high usage, ATRP has led to significant discoveries in new materials and is commonly used for composite/hybrid systems, surface modifications, in pharmaceuticals, medicine, energetic materials, etc. The process also made significant progress in time.

4.1 Principle

ATRP is a controlled radical polymerization technique that utilizes a transition metal catalyst, typically copper, to mediate the polymerization process. The polymerization is initiated by reversible activation of a dormant species (macroinitiator) through the transfer of a halogen atom from the growing polymer chain to the metal complex, generating a radical that can propagate the polymer chain [8]. The fundamental principle of the ATRP is displayed in Figure 1.

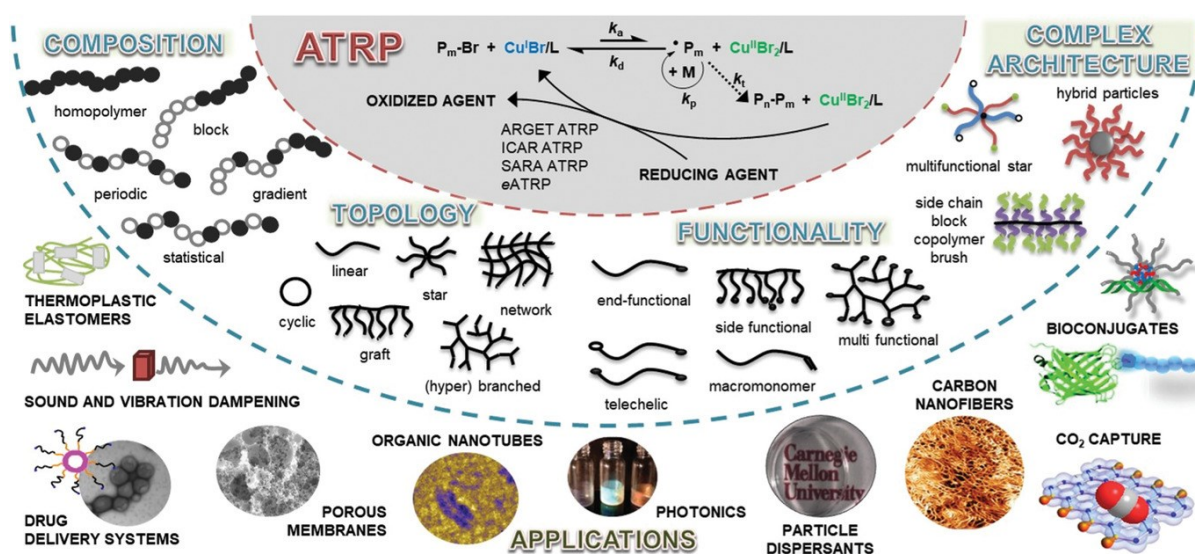


Figure 1: A brief ATRP scheme, an overview of possibilities in composition, topology, functionality and creating complex architectures, and a demonstration of multiple applications used in the various industries. The figure was reprinted from: [11].

4.2 Advantages of ATRP

The ATRP offers several significant advantages that make it a preferred method for controlled radical polymerization. These advantages make the ATRP a powerful tool in modern chemistry.

4.2.1 Control over molecular weight and dispersity

ATRP allows excellent control over the molecular weight of the resulting polymers and their polydispersity index ($\bar{D}$). This control is achieved due to a specific mechanism of the ATRP that is based on the reversible activation and deactivation of the growing polymer chains, enabling the synthesis of polymers with narrow molecular weight distributions ($\bar{D} < 1.2$), which is not possible to achieve by the standard CRP methods [12].

4.2.2 Versatility in polymer architecture

Using the ATRP, a wide variety of polymer architectures, including block copolymers, star-shaped or comb-like polymers, and polymers with specific functionalities, can be efficiently prepared. This is achieved by the use of different monomers and initiators and gives access to the design of complex materials that can be used for specific applications. By carefully selecting the monomers, initiators, and conditions of the reaction, it is possible to prepare complex macromolecular structures such as block copolymers, star-shaped, comb-like, brush-like, or hyperbranched polymers. It also allows control over architectural features like composition, topology, and functionality. This control is essential for designing polymers for advanced applications in for example biomedicine or nanotechnology [12–14].

4.2.3 Oxygen tolerance

Earlier, the reactions were really sensitive to oxygen. Thanks to recent discoveries in ATRP, it is possible to perform polymerizations in open-air environments. This is allowed by the use of dual photo redox/copper catalysis, and yields a significant simplification of the workflow [15].

4.2.4 Compatibility with various reaction conditions

ATRP is compatible with a wide range of solvents and can be conducted under diverse conditions, including aqueous and organic media. This flexibility allows for the synthesis of polymers that may be sensitive to other polymerization methods [16].

4.2.5 Functionality

ATRP offers several methods to incorporate functionality into polymer chains. The main approaches that allow controlling the functionality include monomer selection, which is the most straightforward method. The preferred monomers contain functional groups and must be tolerant of ATRP conditions. The functional groups that can be incorporated into the

polymer chain are, for example, amino, hydroxy, etc. An alternative approach is based on the usage of monomers with protected functional groups, such as t-butyl acrylate (t-BA). These were methods utilizing only specific monomers, but functionality can be tailored by specific positioning of the functional groups or by post-polymerization modification. Such modifications are, for example, connecting polymer chain ends to create a block copolymer [13].

4.3 Ligands

4.3.1 Ligands in the conventional ATRP

In the ATRP, ligands are fundamentally important. They play a key role by tuning the redox potential of the metal catalyst, which leads to stabilization of both the activator, Cu(I), and the deactivator, Cu(II), enabling the control of activation or deactivation, which defines the ATRP. Without a proper ligand, the activation of dormant chains into radicals would be inefficient, and it would lead to slow polymerization rates. Something similar would happen with deactivation, where the radical concentration is allowed to rise, increasing the termination event, and that would affect molecular weight distribution. Also, without the ligand, the catalyst complex might start to degrade [17].

4.3.2 Ligands in the externally controlled ATRP

In externally controlled ATRP, ligands play an even more crucial role, especially in mechanoATRP, electrochemically mediated ATRP (eATRP), or photoinduced ATRP (photoATRP), due to the dynamic nature of these techniques. The ligand does all of mentioned above, but also must be externally controllable. In each method, the mechanism is similar; the Cu(II) deactivator is always reduced back to the Cu(I) activator, but the execution is different. In the photoATRP, an external light source is used to photoreduce the deactivator, in the eATRP, applied voltage at the electrode is used to reduce the deactivator and in the mechanoATRP, the ultrasound generates the radicals in the solvent, which chemically reduce the Cu(II) ligand to the Cu(I). This makes the ligand not only the passive coordinator but also an active enabler of catalyst switching, which is dynamic, fast, and reversible [18].

4.3.3 Specific examples of ligands

There is not a single specific ligand that is used for all the ATRP methods, it is the complete opposite. One of the ligands worth mentioning is tris(2-pyridylmethyl)amine (TPMA). TPMA is widely used not only in the mechanoATRP, but also in the conventional ATRP and photoATRP. Next ligand, which can also be used in photoATRP and mechanoATRP cases, is pentamethyldiethylenetriamine (PMDETA), but it faces key limitations, such as lower stability under high-intensity external stimuli. For eATRP, the typical ligand used is tris[2-(dimethylamino)ethyl]amine (Me₆TREN), due its outstanding electrochemical response [17]. The overview of ligands and their activities is presented in Figure 2.

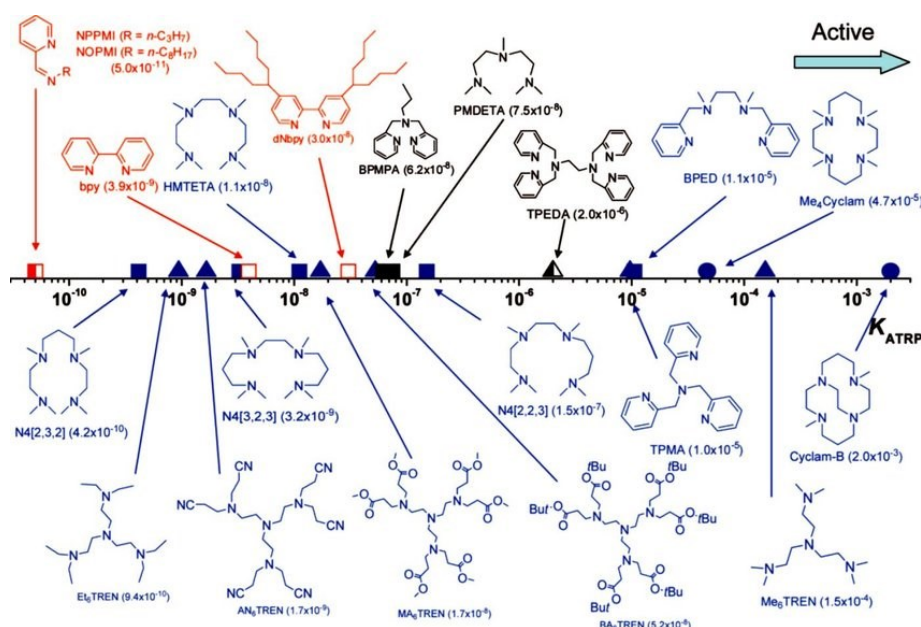


Figure 2: Activity diagram of commonly used ligands in various ATRP reactions displayed on a logarithmic scale. The figure was reprinted from: [19].

4.4 Challenges of the ATRP

Over the past years, ATRP has gained great success. Despite that, ATRP faces several challenges. One of the biggest challenges is relatively high catalyst concentrations. Traditional ATRP uses a high amount of copper catalyst (often thousands of ppm) to maintain the equilibrium [20], which often leads to difficulties in product purifying. Although ATRP is considered controlled, there are still uncontrolled reactions happening, especially at higher monomer conversions, compromising the shape of the polymer chains. Although the ATRP is considered a living process, its temporal control was facilitated just recently by developing the “externally controlled” ATRP.

5 EXTERNALLY CONTROLLED ATRP

The 1956 landmark work on ionic polymerization started the development of other controlled/living polymerization procedures. In an optimal controlled polymerization process, polymer chains increase in length uniformly, avoiding permanent chain transfer or termination reactions. The pure living process is impossible to achieve due to unavoidable radical–radical termination, and it is also diffusion-controlled. In recent years, significant development of the externally controlled ATRP methods has been achieved. These achievements allowed spatial and temporal regulation of the polymerization process through the application of external stimuli [18].

The key feature of the externally controlled ATRP is the ability to adjust the activation-deactivation equilibrium using non-chemical methods. The techniques that will be mentioned in this chapter are eATRP, photoATRP, and mechanoATRP. Using these methods offers several benefits over traditional ATRP. Benefits worth mentioning are precise control over polymerization kinetics, the ability to start, stop, and restart polymerization on demand, and reduced catalyst loadings or simplified purification procedures [18].

5.1 MechanoATRP

Mechanochemically-mediated ATRP is a form of externally controlled ATRP that allows regulation of the polymerization process by using mechanical forces (ultrasound in the presence of piezoelectric nanoparticles). There are several factors that regulate the kinetics of the mechanoATRP process. The first one was the dielectric constants (ϵ) of the piezoelectric transducers. A higher dielectric constant facilitated more efficient electron transfer to the Cu catalysts. The second factor is the crystal structure and particle size of the piezo-transducers. For example, cubic barium titanate (BaTiO_3) does not show as strong a piezoelectric effect as tetragonal BaTiO_3 nanoparticles, whose crystals are highly distorted. Smaller nanoparticles achieved greater mechanoelectric conversion due to their larger surface-to-interface effect and higher specific surface area. The next factor was the amount of transducer particles used. Increasing their loading generally leads to a faster polymerization rate, suggesting a higher concentration of the radical. The last factor is the addition of a surface modifier. To enhance electron transfer efficiency between transducers and electron acceptors in this heterogeneous system, various solubilizers and surface modifiers can be employed to stabilize the transducer nanoparticles and maintain their

uniform dispersion. The more effective reducing agent under ultrasonication was shown to be zinc oxide (ZnO) nanocrystals, despite a higher piezoelectric constant of BaTiO₃. The reasons are the smaller size of particles of ZnO and the strong interaction with Cu(II) complexes that increased the localized concentration of the catalyst on the particle surface [18].

MechanoATRP can also be used as a switchable CRP where the electron transfer is mediated by an external stimulus. Due to this strategy, mechanoATRP offers spatial and temporal control over the kinetics of the reaction, architecture, composition, and functionality by pausing and restarting the driving force. In other words, the conversion of the monomer using this technique was negligible in the absence of sonication; meanwhile, the polymer chain was still growing after re-exposure to the mechanical force. Also, the polymers prepared by this technique retained all the features of materials made by conventional ATRP, such as the fidelity of the chain ends [18].

5.1.1 Mechanism of the mechanoATRP

The first step is the sonication-induced radical generation. When the radicals are generated, they react with Cu(II) species, reducing them to Cu(I) activators. The newly formed Cu(I)/ligand complexes abstract a halogen atom from the dormant initiator (R-X), generating a propagating radical and regenerating the Cu(II) ligand. Then, the radical adds to monomer units, creating the polymer chain. The last step is the deactivation, when the growing radical reacts with the Cu(II)/ligand to reform the dormant R-X species, which closes the controlled cycle [18].

5.1.2 MechanoATRP and SonoATRP comparison

MechanoATRP utilizes mechanical forces to modulate the activation-deactivation equilibrium between Cu(I) and Cu(II) complexes. The mechanical stimulus can be applied using various methods, including shear forces (triboATRP) [21]. These mechanical forces cause the reduction of Cu(II) to Cu(I), which activates the dormant polymer chains and initiates polymerization. In the sonoATRP technique, ultrasound waves create cavitation bubbles in the reaction medium, which then collapse. This generates localized areas of extreme temperature and pressure, leading to the formation of highly reactive species. The reduction of Cu occurs in these areas, and by that, ATRP is driven towards an active state. This approach differs from traditional ultrasound-driven radical polymerizations that rely on breaking weak bonds through force. Instead, it employs a piezochemically initiated CRP,

which transforms mechanical energy into electrons at the piezoelectric material's interface through charge separation. MechanoATRP involves a mechano-induced electron transfer (MET) process, causing a mechanical stimulus to be transduced to an electrical signal. Transducers used are BaTiO₃ and ZnO nanoparticles, while Cu(II) complexes are used as catalysts. When subjected to ultrasonic agitation as a mechanical stimulus, piezoelectric particles transfer electrons to the Cu(II) precursor, generating Cu(I)-based species that activate the alkyl halide [18].

5.1.3 Advantages and challenges

The biggest advantage might be the ability to use lower catalyst concentrations compared to traditional ATRP. Next mentionable advantages are precise control over the polymerization, allowing us to create well-defined polymers with customized molecular weight and dispersity. Using mechanoATRP we are able to prepare block copolymers and make polymerization using challenging monomers that are difficult to control using conventional ATRP. Really important is that mechanoATRP polymerization processes are more eco-friendly than the rest, because the reaction proceeds at laboratory temperature, which lowers the energy requirements and saves the electricity. One of special advantages is that mechanical energy can penetrate through the obstacles, so it is possible to initiate the reaction “remotely“. MechanoATRP also has some challenges compared to conventional ATRP. Mechanical forces applied can cause polymer degradation in the process. Also, because the mechanoATRP technique is still under development, there is still limited understanding of the exact mechanisms of mechanoATRP [18].

5.2 eATRP

Electrochemically mediated ATRP is an externally controlled variant of ATRP, where an applied electrical potential regulates the oxidation state of the catalyst (typically a copper complex). This enables the deactivation and reactivation of the polymerization process. The concentrations of the catalyst are extremely low (ppm levels), and this reaction is oxygen tolerant under optimized conditions [22].

II PRACTICAL PART

6 MATERIALS AND METHODOLOGY

All chemicals and reagents were obtained from commercial suppliers and used without further purification unless otherwise specified. Zinc acetate dihydrate (ZAD, p.a.), diethylene glycol (DEG, $\geq 99.0\%$), oleic acid (OA, $\geq 99.0\%$), and methanol ($\geq 99.6\%$) were used for the synthesis of the ZnO nanoparticles (NPs). Chemicals for mechanoATRP included methyl acrylate (MA, 99%), ethyl- α -bromoisobutyrate (EBiB, 98%), tris(2-pyridylmethyl)amine (TPMA, 98%), copper(II) bromide (CuBr_2 , 99%), as well as barium titanate (BaTiO_3 , powder), which were all purchased from Sigma-Aldrich (USA). Before its use, MA was purified by passing through a column of aluminum oxide (activated, Brockmann I) to remove inhibitors. Solvents dimethyl sulfoxide (DMSO, $\geq 99.7\%$), tetrahydrofuran (THF, anhydrous $\geq 99.9\%$), and deuterated chloroform (CDCl_3 , 99.8%) were also purchased from Sigma-Aldrich (USA).

6.1 Synthesis of stabilized ZnO nanocrystals

The ZnO nanocrystals were synthesized via a facile microwave (MW)-assisted polyol technique. In a typical procedure, 32 mmol (7.02 g) of ZAD, serving as the precursor, was dispersed in 50 mL of DEG, which represented a medium. Afterwards, the OA (2.3 mmol, 0.660 g) was added as a capping agent, controlling the growth of ZnO nanocrystals and preventing their agglomeration. The mixture was then stirred for 10 minutes, ensuring homogeneous distribution of the reactants. The mixture in the Teflon vessel was sealed and placed into the MW reactor (Magnum II, Ertec, Poland), set to 100% intensity with the reaction time of 15 minutes. The temperature and pressure steeply increased, reaching 245–250°C and 45–50 bar, which promoted the nucleation and growth of the ZnO nanocrystals. After completing the reaction, the reactor was cooled to 45°C using the water circuit, and the ZnO product was separated using centrifugation (EBA 21 Hettich, Germany) for 5 minutes at 6000 rpm. To remove any residual impurities or unreacted species, the nanocrystals were washed multiple times with methanol. The purified ZnO nanocrystals were dried under reduced pressure (150 mbar) at 65°C overnight.

6.2 General procedure for the ZnO mediated ATRP

In a standard procedure [23], the ATRP reactants, methyl acrylate (MA, 1.92 mL, 21.2 mmol, 100 eq.), ethyl- α -bromoisobutyrate (EBiB, 31.1 μ L, 0.21 mmol, 1 eq.), tris(2-pyridylmethyl)amine (TPMA 0.16 eq., 33.9 μ mol), CuBr₂ (1.9 mg, 8.5 μ mol, 0.04 eq.) and dimethyl sulfoxide (DMSO, 50 vol.%) were sequentially added into the reaction flask. The amount of ZnO loading was calculated following the formula: $0.25 \times X$ wt% (where $X = 0, 1, 2, 3, 4$, or 8), relative to the weight of the monomer (MA) and the solvent (DMSO). The mixture was then placed in the vortex mixer (TX4, Velp Scientifica, Italy) and carefully purged with argon (5 minutes), using the needle inserted through a rubber septum. The other needle was used to equilibrate the pressure in the vial. Then, the vial with the ATRP mixture was exposed to the shock waves in an ultrasonic bath (T490 DH, Elma Transsonic Digital, Germany), operating at 40 kHz. A constant temperature of around 35°C was maintained using the heat controller (CC-K6, Huber Pilot One, Germany) coupled with the bath in the custom-built setup (Figure 3). The reaction vial was placed in the polystyrene-based holder with a fixed location in the bath to ensure reproducibility of the experiments. Each mechanoATRP reaction proceeded for 6 hours, and the aliquots (of 100 μ L) were withdrawn after 2, 4, and 6 hours. To optimize the efficiency of the mechanoATRP process, a series of reactions with different ZnO loadings was performed, and their performance was compared with the commercial BaTiO₃ nanocrystals. The reference reaction was executed without using any piezoelectric agents.

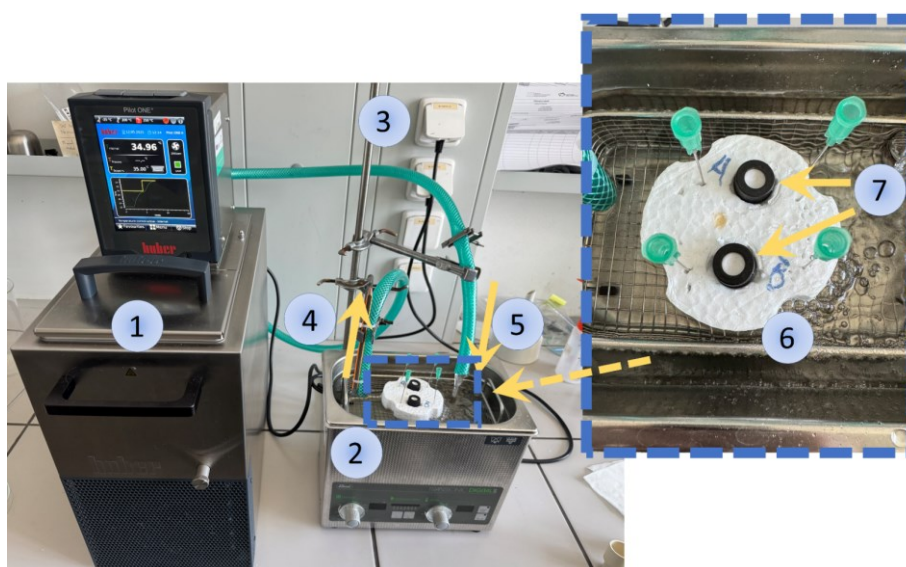


Figure 3: The experimental apparatus. Thermostatic device (1), ultrasonic bath (2), powered supply (3), water inlet/outlet (4, 5), polystyrene holder (6), and reaction vials (7).
(Source: own elaboration)

6.3 Characterizations of the ZnO nanocrystals

6.3.1 Transmission electron microscopy (TEM)

The dimensions and morphology of ZnO nanocrystals were inspected using the TEM on the JEM2100Plus (JEOL, Japan), equipped with the LaB₆ emission source, operating at an accelerating voltage of 200 kV.

6.3.2 X-ray diffraction (XRD) analysis

The crystallography study was performed on a Miniflex 600 (Rigaku, Japan) scanning at a speed of 3°/min and using a Co-K α radiation source ($\lambda = 1.789 \text{ \AA}$), within the range 2θ from 10° to 90°.

6.4 Characterizations of mechanoATRP product

6.4.1 Nuclear magnetic resonance (NMR) spectroscopy

The aliquots (50 μL) were dissolved in 1 mL of deuterated chloroform (CDCl_3) at laboratory temperature and passed through the column of alumina to remove the catalytic system and ZnO nanocrystals. The NMR spectra were recorded on a JEOL 400 MHz spectrometer (Japan) and processed using the MNova 6 (Mestrelab Resources).

6.4.2 Gel permeation chromatography (GPC)

The GPC traces were collected on a Waters HPLC system equipped with a Waters model e2695 and Waters model 2414 differential refractometer (Waters Corporation, USA). The aliquots (50 μL) were dissolved in THF (2–3 mg/mL) stabilized with BHT (240 mg/L), and filtered using a syringe PTFE filter (pore size of 0.45 μm). The separation was carried out on a series of gel-mixed bed columns (Polymer Laboratories, UK) as follows: 1 $\times$ PLgel-Mixed-A bed column (300 $\times$ 7.5 mm, 20 μm), 1 $\times$ PLgel-Mixed-B bed column (300 $\times$ 7.5 mm, 10 μm), and 1 $\times$ PLgel-Mixed-D bed column (300 $\times$ 7.5 mm, 5 μm); the temperature of the mobile phase was 40°C, its flow rate was set to 1.0 mL/min, and the injected volume equalled 100 μL . The GPC traces were processed using Empower 3 software to extract the mass average molar mass (M_w), number average molar mass (M_n), and polydispersity index ($D = M_w/M_n$) of the tested samples.

7 RESULTS AND DISCUSSION

The ZnO nanocrystals with the OA capping agent were synthesized using the MW-assisted method. Figure 4A shows the morphology of the ZnO in the representative TEM micrograph. As seen, the individual particles generally had a uniform oblate shape with a diameter of around 15–20 nm. The corresponding XRD spectrum, displayed in Figure 4B, contained a set of sharp peaks, suggesting a high crystallinity of the ZnO. Therefore, the synthesized ZnO nanocrystals were assumed to be highly efficient in the mechanoATRP. The diffraction peaks were centred at 2θ of 37.1° , 40.1° , 42.3° , 55.8° , 66.9° , 74.5° , 78.9° , 80.9° , and 82.4° , which are related to (100), (002), (101), (102), (110), (103), (200), (112), and (201) crystallographic planes typical for the hexagonal wurtzite structure [23].

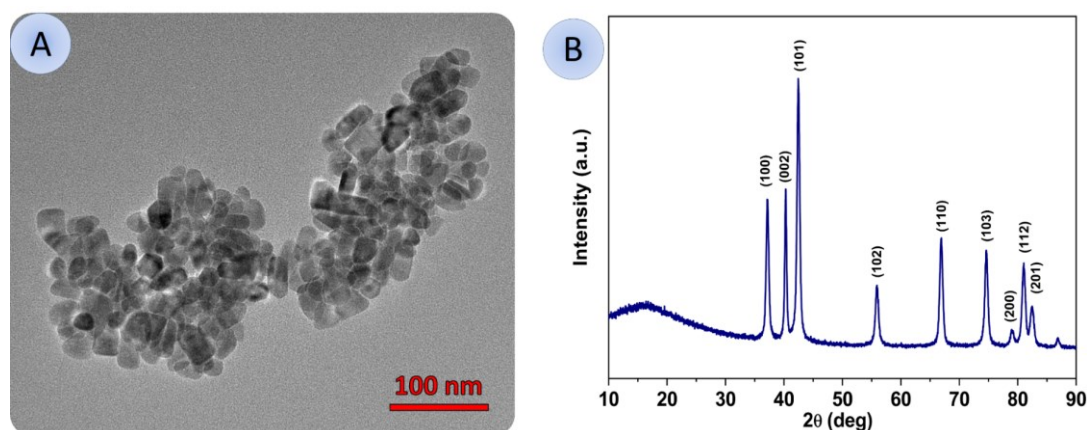


Figure 4: TEM image (A), XRD spectrum (B) of the ZnO synthesized via the MW-assisted approach.
(Source: own elaboration)

The custom-synthesized ZnO nanocrystals were applied in the mechanoATRP of MA. As reported earlier [23], the formulation for this reaction requires an excess of ligand (e.g., CuBr_2/L ratio of 1/4) as it relies on the catalyst regeneration by amines. The efficiency of the reaction was optimized by varying the ZnO loading from 0.25 to 2 wt%, and the NMR and GPC results are summarized in Table 1. In the reference reaction (Table 1, Entry 1), in the absence of the ZnO nanocrystals, no monomer conversion was observed, indicating the lack of thermally induced polymerization. After using as low as 0.25 wt% of the ZnO (Table 1, Entry 2), the mechanoATRP did not proceed for at least 2 hours, showcasing a long induction period. However, after 4 hours, a small conversion was detected, and increased up to 28%, after 6 hours. Such a result demonstrates a high efficiency of the synthesized ZnO nanocrystals in mediating mechanoATRP, compared to other particles, such as $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ [24].

Table 1: Effect of the ZnO loading on the efficiency of the mechanoATRP of MA.

Entry ^a	ZnO loading (wt%)	Time (h)	M_n^b	M_w^b	$\bar{D}^b$ (–)	conv. ^c (%)
1	0	2	–	–	–	–
		4	–	–	–	–
		6	–	–	–	–
2	0.25	2	–	–	–	–
		4	726	1072	1.41	8
		6	2636	3044	1.16	28
3	0.50	2	2059	2428	1.18	22
		4	5131	5666	1.10	54
		6	6277	6855	1.09	67
4	0.75	2	3525	4323	1.23	37
		4	5802	6623	1.14	79
		6	7046	7931	1.13	85
5	1	2	3880	4479	1.15	43
		4	6859	7509	1.09	72
		6	7843	8534	1.09	87
6	2	2	4058	5085	1.25	44
		4	6064	7200	1.19	68
		6	7141	8310	1.16	78

^aReaction conditions: [MA]₀/[EBiB]₀/[CuBr₂]₀/[TPMA]₀ = 100/1/0.04/0.16 in 50% (v/v) DMSO argon-purged, closed-cap reactor bearing 20% (v/v) of aerated headspace, at 35 °C.

^bDetermined by GPC analysis (THF as eluent), calibrated to a linear PMMA standard.

^cDetermined from ¹H NMR spectra (CDCl₃ as solvent).

(Source: own elaboration)

As the ZnO loading increased (Table 1, Entries 3–6), the monomer conversion generally increased as well for the corresponding withdrawal times, which indicated the formation of longer polymer chains. The GPC traces, shown in Figure 5, were shifted toward shorter retention times, confirming a higher molecular weight of the synthesized poly(methylacrylate) (PMA). In all the cases, the GPC peaks were monomodal and uniform, demonstrating the well-controlled mechanoATRP process.

However, after closer inspection, a non-trivial dependence of the conversion on the ZnO loading was observed. The efficiency of the mechanoATRP significantly increased when using 0.5 and 0.75 wt% loading of the ZnO nanocrystals (Table 1, Entries 3, 4) because of more intense regeneration of Cu(I)/L activators. When using ZnO loading of 1 wt%

(Table 1, Entry 5), the polymerization was considered the most effective. It achieved 43% conversion after 2 hours and 87% conversion after 6 hours, together with exceptionally low $\bar{D}$ (~ 1.09). Interestingly, after increasing the ZnO loading to 2 wt%, the conversion at short reaction time was almost identical, but after longer polymerization times (6 hours), its efficiency notably decreased (Table 1, cf. Entries 5 and 6) while $\bar{D}$ values slightly increased. It is assumed that these negative phenomena were caused by the sedimentation of the ZnO nanocrystals, which resulted in a nonhomogeneous environment. It should be noted, however, that future experiments are needed to confirm this hypothesis. Overall, the 1 wt% loading of the ZnO nanocrystals was deemed optimal for the given experimental conditions.

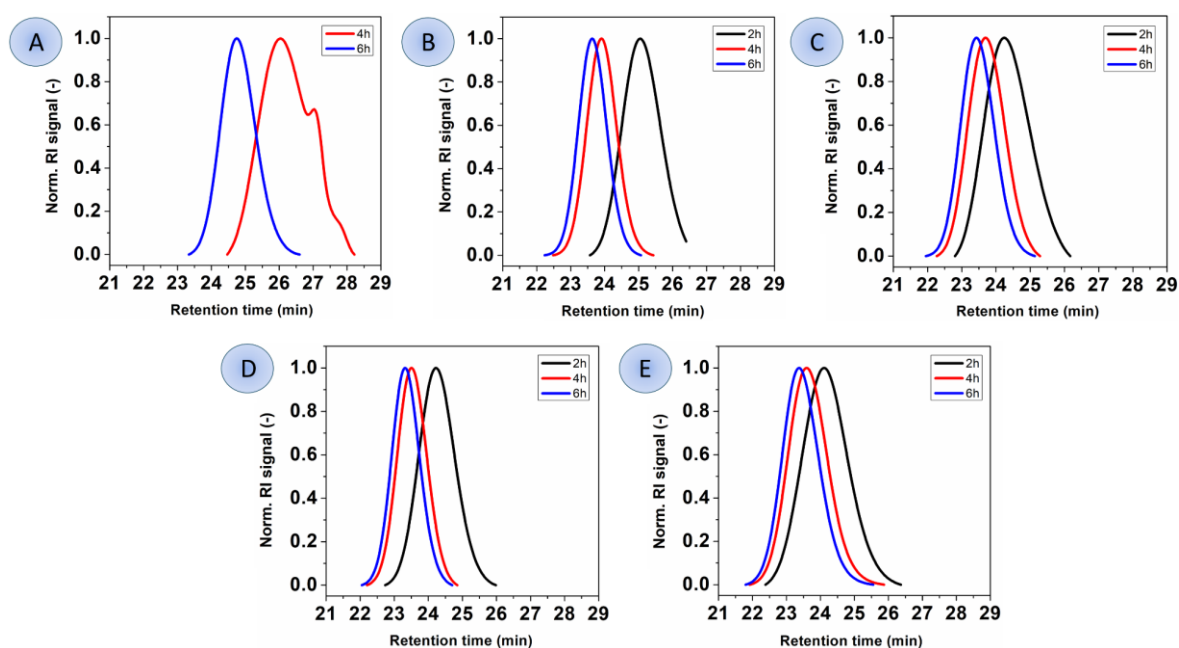


Figure 5: GPC traces at different reaction times for the mechanoATRP with different ZnO loadings (A, B, C, D, and E) loading of the ZnO nanocrystals ($0.25 \times X$ wt% (where $X = 0, 1, 2, 3, 4$, or 8)). Reaction conditions: $[MA]_0/[EBiB]_0/[CuBr_2]_0/[TPMA]_0 = 100/1/0.04/0.16$ in 50% (v/v) DMSO argon-purged, closed-cap reactor bearing 20% (v/v) of aerated headspace, at 35 °C.

(Source: own elaboration)

When comparing the achieved results to recent literature, e.g., Liu et al. [25], who involved the ZnO nanorods prepared by chemical bath deposition, our obtained result (Table 1, Entry 5) was superior in terms of efficiency and conversion. The highest conversion in the preceding study was 70% after 4 hours, when employing ZnO loading of 1.2 wt%. Their reaction also yielded higher $\bar{D} > 1.3$, indicating worse control over the mechanoATRP process. However, it should be noted that there were several differences in

the formulation and methodology. For instance, the authors [25] used a higher Cu(II)/L ratio, which should promote the reaction, but a lower temperature (ranging from 20 to 30°C) that potentially decreased the polymerization rate, etc. For these reasons, the direct comparison of the achieved results is not entirely possible.

Finally, for demonstration purposes, the custom-synthesized ZnO nanocrystals in the formulation $[MA]_0/[EBiB]_0/[CuBr_2]_0/[TPMA]_0 = 100/1/0.04/0.16$ were replaced with the commercial BaTiO₃ particles (loading of 5 wt%), which recently showed potential in mediating ATRP [26]. In our case, however, the reaction with BaTiO₃ did not proceed even after 6 hours, despite a higher loading, demonstrating the superior efficiency of the applied ZnO nanocrystals. The other publication reported moderate conversion of 58% after 8 hours when using BaTiO₃ at comparable loadings (4.5 wt%), but their mechanoATRP reaction was executed at a higher Cu(II)/L ratio (of 1/6) and higher temperatures (< 45°C), suggesting that thermally-activated ATRP could not be ruled out [27]. Similarly, Zhou et al. [28] reported a conversion over 90% (after 4 hours) when using BaTiO₃ and performing mechanoATRP at unusually high temperatures (of 50 °C), while using a more active ligand (Me₆TREN). To conclude, our result showcase the superior performance of the synthesized ZnO nanocrystals in mediating mechanoATRP, which yielded high conversions (87%) at remarkably low loadings (1 wt%) and temperature (35°C), and at the same time, relatively low (1/4) Cu(II)/L ratio.

CONCLUSION

In the theoretical part, the conventional free radical polymerization (FRP) was described, followed by a brief overview of advanced controlled radical polymerization (CRP) methods, especially, atom transfer radical polymerization (ATRP). This method offers significant advantages compared to conventional FRP, such as control over molecular weight and dispersity or the ability to synthesize complex polymer structures, which can be used in numerous applications. The limitations of the ATRP are briefly mentioned, including the necessity of high catalyst loading and challenging temporal control. These limitations can be addressed by externally controlled ATRP methods, where the external stimulus is used to regulate and control the reaction. Such techniques enable excellent on-demand control and even reduce the required catalyst loading. The externally controlled ATRP methods that are briefly presented include sonoATRP, eATRP, and photoATRP, while special attention is devoted to mechanoATRP. MechanoATRP utilizes ultrasound and piezoelectric particles to mediate the polymerization process, bringing several benefits that were elaborated in detail. In the experimental part, the mechanoATRP reaction was tested using zinc oxide (ZnO) particles as piezoelectric agents, which were custom-synthesized via a facile microwave (MW)-assisted technique. The ZnO nanocrystals possessed a uniform oblate shape with a diameter of around 15–20 nm, as revealed by transmission electron microscopy (TEM). High crystallinity of the ZnO product was confirmed using the X-ray diffraction (XRD) analysis. The loading of the ZnO was systematically optimized for the mechanoATRP of methyl acrylate (MA). Synthesized ZnO nanocrystals showed promising performance in mediating mechanoATRP, even at very low loadings (0.25 wt%). Under the optimized conditions, when using 1 wt% of ZnO, polymerization reached 87% monomer conversion within 6 hours, with narrow dispersity $D = 1.09$. However, using even higher ZnO loading (2 wt%) was less effective, most likely due to more pronounced sedimentation effects. Although some previous articles reported even higher conversions, such results were achieved by using significantly higher loading of piezoelectric agents, higher temperatures (around 50 °C), and higher catalyst concentrations.

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LIST OF ABBREVIATIONS

ATRP	Atom Transfer Radical Polymerization
mechanoATRP	ATRP mediated by mechanochemical forces
ZnO	Zinc Oxide
MA	Methyl Acrylate
CRP	Controlled Radical Polymerization
PE	Polyethylene
FRP	Free Radical Polymerization
BPO	Benzoyl Peroxide
AIBN	Azobisisobutyronitrile
RAFT	Reversible Addition–Fragmentation Chain Transfer
NMP	Nitroxide-Mediated Polymerization
t-BA	tert-Butyl Acrylate
eATRP	Electrochemically Mediated ATRP
photoATRP	Photoinduced ATRP
TPMA	Tris(2-pyridylmethyl)amine
PMDETA	Pentamethyldiethylenetriamine
Me ₆ TREN	Tris[2-(dimethylamino)ethyl]amine
BaTiO ₃	Barium Titanate
MET	Mechano-induced Electron Transfer
ZAD	Zinc Acetate Dihydrate
DEG	Diethylene Glycol
OA	Oleic Acid
NPs	Nanoparticles
EBiB	Ethyl- α -bromoisobutyrate
CuBr ₂	Copper(II) Bromide

DMSO	Dimethyl Sulfoxide
THF	Tetrahydrofuran
CDCl ₃	Deuterated Chloroform
MW	Molecular Weight
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction
NMR	Nuclear Magnetic Resonance
GPC	Gel Permeation Chromatography