

CHAPTER 12

Sonochemical protocol of polymer synthesis

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1. Emulsion polymerization

An individual method which applied for several radical chain polymerizations is called emulsion polymerization that monomers polymerize in the appearance of emulsions (i.e., colloidal dispersions). The method of emulsion polymerization has some advantages which can be listed as follow:

- The ease of process control resulting from the condition of the emulsion approach.
- As compared to bulk polymerization, the problems associated with temperature and viscosity are much less significant.
- *Latex* as the produce of an emulsion polymerization is applied in the absence of further treatments [1].

As of now, we can assume that the rate and speed of emulsion polymerizations can be accelerated by ultrasonic irradiation. This acceleration is the result of the following two properties of irradiation which are explained as follows:

- Degassing effect of ultrasonic cavitation;

Causes the oxygen to deploy efficiently from reactants causing the transfer reactions to be less possible, which shortens the induction period and thus leads to a higher polymerization rate.

- Ultrasound cavitation causes a localized heating of the reaction medium [2].

As explained for emulsion polymerization, ultrasonic-assisted emulsion polymerization comparing common emulsion polymerization has the following advantages as an example;

- Absence of chemical initiators
- Rapid polymerizations
- Production of nanosized latex particles
- Production of polymers with high molecular weights [3].

Ultrasound is an initiator which causes chemical linkages of molecules to be broken, and hence the rate of polymerization enhances, which can be used in extreme states created through acoustic cavitation in the area of polymer science [1]. Ostroski and Stambaugh explained the significant acceleration of a conventional emulsion polymerization using

the sonication method in the 1950s. It was concluded that ultrasonic induced agitation will result in a faster and improved emulsification stemming which was caused because of the increased decomposition of the chemical initiator in aqueous solutions.

Ultrasound as an initiator for the polymerization of acrylonitrile was first used in early 1951. To this day, researchers have been mostly concerned with the homopolymerization of a monomer in a good solvent, and pure monomer melt [3].

Kruus and Patraboy, with the help of intense ultrasound, have done the polymerization initiation of methyl methacrylate monomer in a solution of vinyl monomer [4].

The final latexes with diameters of 50 nm were produced under ultrasonic irradiation in the polymerization of styrene in aqueous medium emulsion, in the absence of an initiator, which was conducted at 30°C. The molecular weights of polystyrene were high ($>10^6$). Ultrasonic initiation is an alternative process for the synthesis of small latex particles. This process requires low levels of surfactants as stabilizers for emulsion polymerization [2].

Moreover, Cheung and Gaddam studied the effects of ultrasound on methyl methacrylate and styrene emulsion polymerization. At different temperatures, they used Azobisisobutyronitrile and Potassium persulfate as initiators. They reported a higher polymerization rate at low temperatures (50°C) under ultrasound treatment. They also reported that ultrasound at higher temperatures (70°C) does not affect the polymerization rate. Thus, reaction temperature is a key during the polymerization assisting with the ultrasound. High vapor pressure, which is the result of higher temperatures, guides to the formation of a fewer amount of radicals due to less intense cavity collapse. These radicals are required for polymerization to be initiated. Therefore, for energy saving, ultrasound is used in emulsion polymerization at lower temperatures [5]. As an example, *n*-butyl acrylate emulsion polymerization assisting with ultrasound initiation without using a chemical initiator has been investigated. The obtained results showed that high evaluation of *n*-butyl acrylate through a high ejection rate of N_2 can be achieved in a shorter time if the ultrasonic method is employed [6].

In another investigation, the factors deciding the rates of ultrasound-assisted initiated polymerization of various methylacrylate monomers were studied. The procedure of these chemical reactions was according to pseudo-first-order kinetics as indicated by the results. Pseudo-first-order kinetics confirms the utilization of a zero-one model such that pseudo-instantaneous termination occurs by entering a radical to a particle including a rising radical for polymerization. The polymerization rate of monomers, as indicated by the experimental results, is related to the variances in the monomers surface operations [7].

Fig. 1 shows the general process of the macromolecule latex's preparation, as proposed by Bradley and Grieser. In short, dispersion of monomer droplets in the aqueous phase is achieved *via* the efficacy of the cavitation process. The stabilization of these

droplets is done through the adsorption of surfactant molecules on the monomer droplet/water interface. The acoustic cavitation process generates primary radicals ($\text{H}\cdot$ and $\text{OH}\cdot$) which release a monomer droplet directly and cause the initiation of the polymerization reaction within a droplet. Or these radicals can interact with the monomer structures adsorbed to the interface of the cavitation bubble/solution and create monomeric radicals, which can cause the same direct diffusion to a monomer droplet and start the polymerization reaction. Therefore, the droplet of monomer is polymerized, and eventually a latex particle is formed [8, 9].

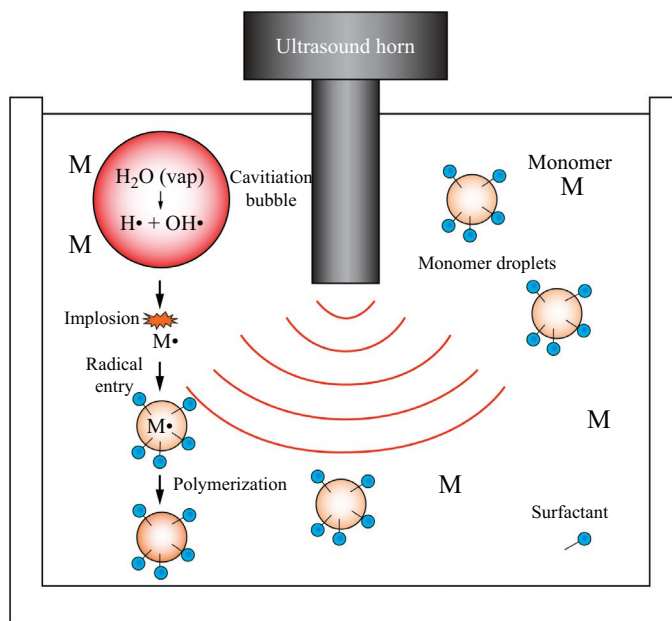


Fig. 1 Schematic diagram of the proposed emulsion polymerization process induced by ultrasound [8].

In an ambient atmosphere, by the usage of ultrasonic energy the emulsion polymerization of vinyl acetate can be initiated. This process (ultrasonic power plus a redox initiator) will result in a better and sufficient polymerization rate in which directing the particle size and molecular weight of vinyl acetate polymer is possible. Ultrasonic-assisted polymerization also generates a steady, milky white, dirty emulsion of vinyl acetate [10].

1.1 Ultrasound-assisted mini-emulsion polymerization system

The polymerization of poly(methyl methacrylate) and poly(butyl acrylate) by ultrasound in the presence of dodecyl trimethylammonium chloride as a cationic surfactant has

shown considerable changes in the polymerization rate. At 30°C, stable dispersions with a diameter of 40–150 nm and polymer molecular weight of 106 g mol⁻¹ are formed in the polymerization of mixed oil-in-water emulsions of monomeric forms, which was an initiator-free reaction. An ionic surface active agent as straightener will cause the creation of clear latex particles [6]. The obtained results reveal a mini-emulsion method, in which nucleation of particles continually occurs in the reactions of a monomer to polymer changing [9].

Under ambient conditions, the mini-emulsion polymerization of *n*-butyl methacrylate (BMA)-assisted with ultrasound using the mixtures of aliphatic and aromatic hydrocarbon liquids-is investigated to measure the monomer transformation percent and molecular weights of the BMA macromolecules. Also, the kinetics of the polymerization practice and resultant polymer features according to these measurements is studied. The results showed that the polymerization rate and molecular weights of the polymers were influenced by the nature of the organic liquid existent in the emulsion and its share in mixture content. As the experiments showed, there were no significant changes when using aliphatic organic liquids in the rates of BMA polymerization, whereas in the case of aromatic liquids a considerable reduction of the polymerization rate and decrease in polymer size were observed. Chain transfer reactions and creation of a radical complex among the propagating radical and the organic liquid in the oil blend effect the kinetics of the polymerization practice [11].

Further, the effect of free radicals in semibatch miniemulsion was studied wherein ultrasound and an external addition of initiator is used to produce free radicals. The effect of different reaction conditions was also reported in the literatures [7].

1.2 Ultrasonic initiation of aliphatic alcohols polymerization

Aliphatic alcohols as hydroxyl radical trappers increase the polymerization rate of ultrasonically initiated emulsion polymerization since these alcohols can release into cavitation bubbles and interact with $\cdot\text{OH}$ produced by the sonolysis of water, which can produce hydroxyalkyl radicals. Increasing the reaction system radicals is proved by the measurements of H₂O₂ yield and the rate of polymerization at the various aliphatic alcohols. For example, using methanol as one of these aliphatic alcohols will result in the following phenomena:

- Scavenge $\cdot\text{OH}$ to enhance the content of radicals
- Quench ultrasonic cavitation

The high temperature and high pressure result in the drop in the content of radicals which will reduce the polymerization rates. Methanol, by decreasing the ultrasonic cavitation temperature and pressure, causes the reaction to continue efficiently. In this case, it includes two reactions which affect the initialization of the polymerization and decides the optimized concentration which will have the fastest reaction rates (Fig. 2) [12].

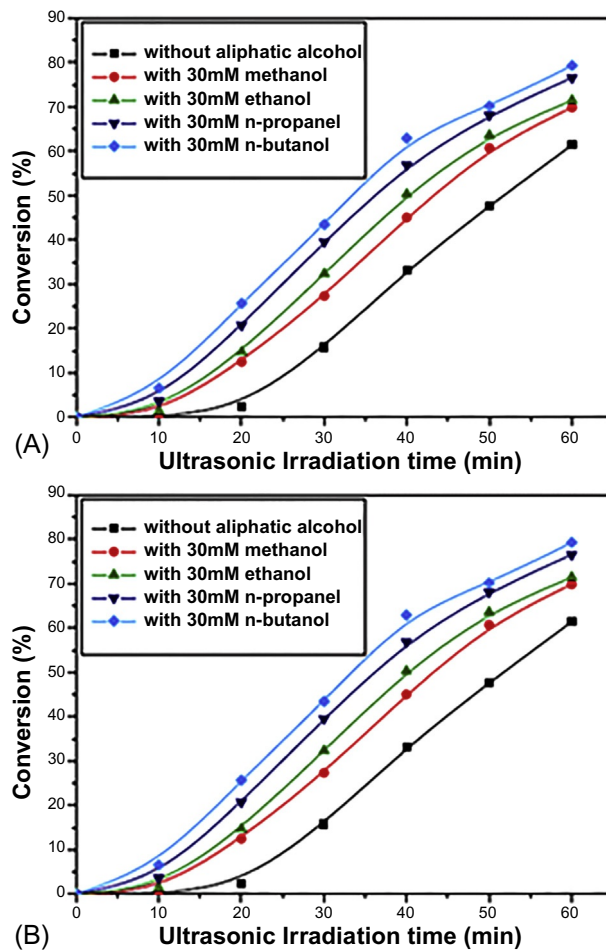


Fig. 2 (A) Conversions-ultrasonic irradiation time curves of ultrasonically initiated emulsion polymerization of styrene in the presence of various aliphatic alcohols. (B) Conversion-ultrasonic irradiation time curves with different amounts of methanol [12].

1.3 Liquid carbon dioxide systems

Ultrasound is used in the high-pressure liquid carbon dioxide systems. MMA-CO₂ and styrene-CO₂ medium have been the subjects of both polymerization and radical scavenger detection studies. UV-vis analysis determined the radical formation rate and the cavitation has been proven by the results. As mentioned before, the irradiation period (ultrasonic process) has a considerable impact on the molecular weight and its dispersal in a polymer. Also, the ratio of CO₂/monomer content has an influence on the molecular weight dispersion confirmed by the outcomes obtained from the polymerization process. A comparison of the SEM images revealed that ultrasound irradiation causes the steady

distribution polymerization in liquid CO₂, which proves that this polymerization can efficiently do without using a stabilizer. A handmade reactor was used for the purposes of this research. It is a cylindrical reactor with a 45-mL capacity, manufactured from stainless steel. Fig. 3 is a schematic illustration of the experiment. Two tempered steam gauge glass windows was equipped to the cell until detect the cavitation experience [13].

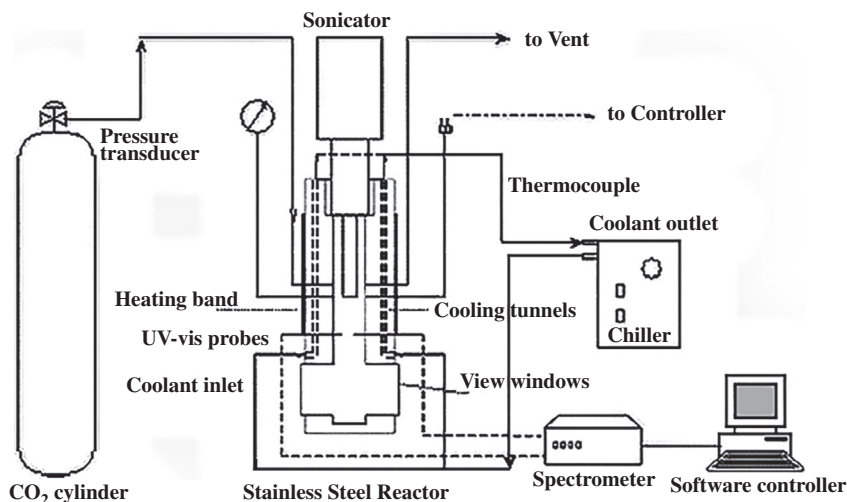


Fig. 3 Schematic representation of the experimental apparatus [13].

1.4 Indirect ultrasound-assisted emulsion polymerization

Frequency and the reactor's situation influenced the polymer yield and molecular weight of the produced polymer under indirect ultrasonic irradiation. The irradiation process is carried out in three stages and the effects of ultrasound on polymerization were investigated. It was concluded that, by the creation of a steady emulsion in the first step and changing the frequency of the sound and reactor's position in a parallel process with irradiation time in the next two stages, an improvement in polymer yield can be expected. Also, the molecular weight of the polymer was with altering the reactor's situation with irradiation in two steps was controlled, which in the second stage maintained low chain scission energy. This dynamic process, which includes the changes in irradiation manner over the way of the polymerization, is an effective application to intensify the emulsion polymerization practice. The complete experimental procedure is explained in Fig. 4. The temperature of the water bath was preserved steady at 30°C by a thermostatic stream of water. The nitrogen was constantly flowing through the reaction because of the gas needed for the ultrasound started emulsion polymerization of MMA [14].

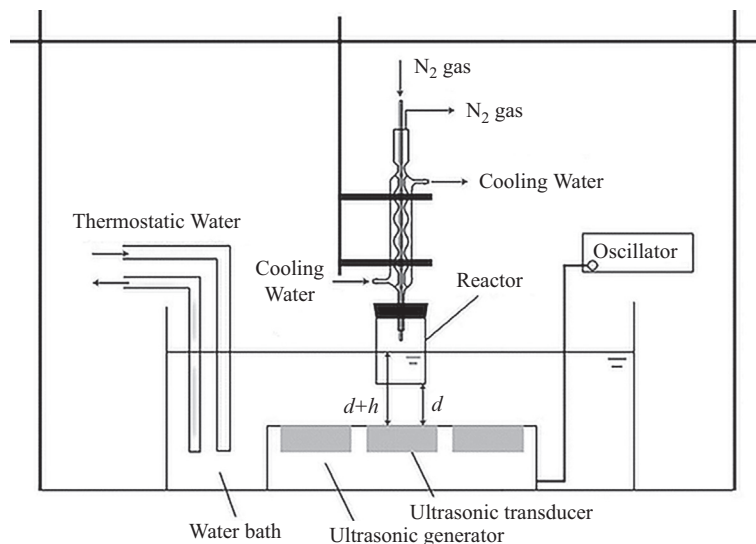


Fig. 4 Experimental setup [14].

1.5 Ultrasound-assisted emulsion polymerization to produce hydrogel polymer

The in situ emulsion polymerization of the three component system as a poly(acrylic acid)-bentonite-FeCo hydrogel nanocomposite *via* ultrasound is investigated. The physical properties of hydrogel are improved with the addition of delaminated bentonite clay sheets and the use of Fe-Co helped the adsorption of an organic pollutant [15].

1.6 Ultrasound-assisted emulsion copolymerization of butyl acrylate/vinyl acetate

As in the meaning of it, two different respiting units form a copolymer. Thus, the copolymerization process involves a simultaneous polymerization of two different monomers to form a single polymer chain [1].

Emulsion of butyl acrylate and vinyl acetate has been reacted under ultrasonic and without any added initiator. In this method, ultrasonic cavitation formed the radicals required for the polymerization. The kinetic studies of the reaction revealed that the polymerization rate at equivalent monomer concentrations of vinyl acetate have markedly lower values when compared to the butyl acrylate. The numbers of particle sizes and polymer molecular weight confirm that the monomer evaporation into the

cavities resulted from ultrasound effect, dampening the cavitation process to result in a lower radical density [16]. At higher ultrasonic power, the time of the reaction was shortened and the monomer conversion was at its highest level. These factor resulted in a diminution in the average molecular weight [17].

1.7 Ultrasound-assisted graft copolymerization of acrylic acid/poly(vinylidene fluoride)

Grafted Acrylic acid (AA) to the hollow fiber membrane of poly(vinylidene fluoride) (PVDF) was prepared by the ultrasound-assisted graft polymerization method (Fig. 5). In general, the attaching compactness improved with the rise of ultrasonic power, but the enhancement in the rate of the polymerization at the beginning was higher and the rate becomes lower as the reaction proceeds (Fig. 6B) in a way that, at an ultrasonic power of 1080 W, the attaching density had a steady value and no change was reported [18].

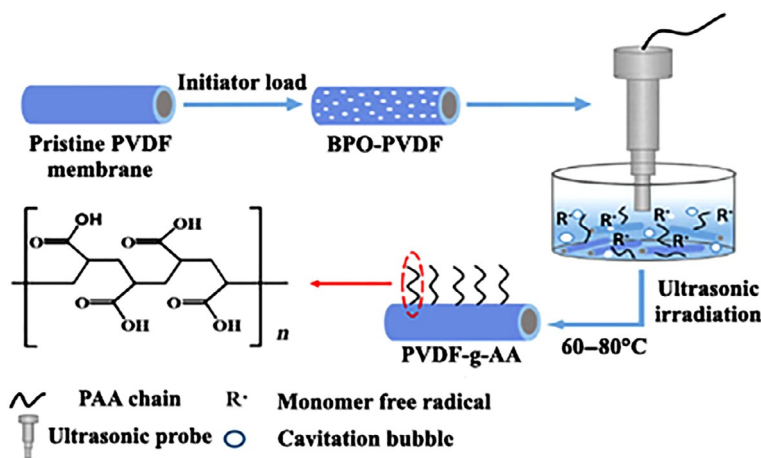


Fig. 5 Schematic representation of the modification process of PVDF hollow fiber membrane using AA as the graft monomer [18].

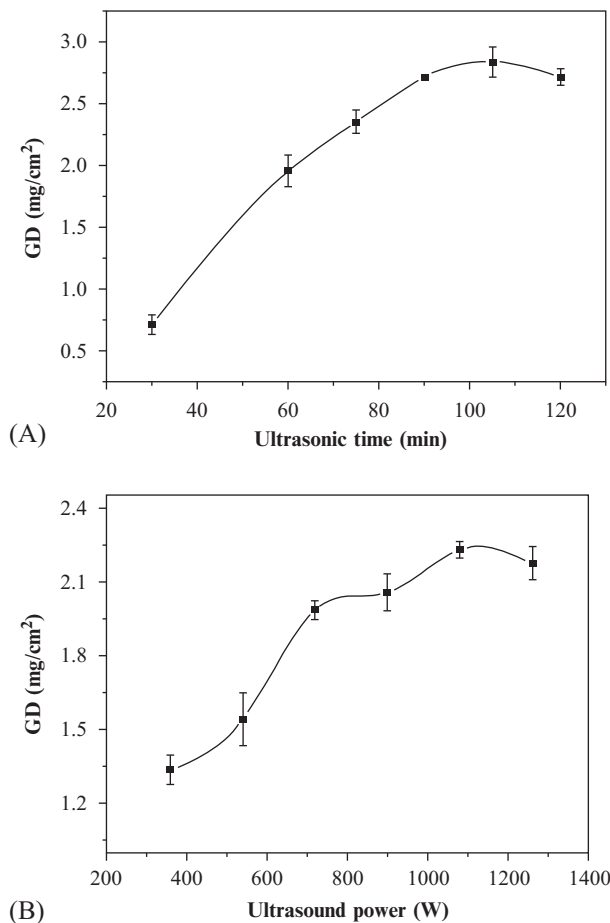


Fig. 6 Graft dispersity versus different conditions: (A) ultrasonic time, and (B) ultrasonic power [18].

1.8 Ultrasonic-assisted emulsion polymerization of polyaniline/nanostructure TiO₂ nanocomposites

Encapsulation or surface grafting of nano inorganic additives and polymers has been employed to produce polymer nanocomposites [19]. Various methods such as intercalative polymerization, suspension polymerization, emulsion polymerization, etc. are employed in the fabrication of nanocomposites [20, 21]. Along with these methodologies, ultrasonic irradiation was used to prepare some desired environment and effects in order to achieve a better dispersion of the nanocomposite component [22–26]. For example, the polymerization of polyaniline/nanostructure TiO₂ nanocomposite particles under ultrasonic was studied. Ultrasonic can reduce the assortment of nano TiO₂

particles, and so the nanoparticles are prepared accordingly to be dispersed in aqueous solution. Deposition of polyaniline on the surface of the nanoparticle will produce a core-shell form. In this process, conductivity of the samples increases when ultrasonic irradiation is used. Therefore, when the polyaniline content declines to $\sim 10\%$, the conductivity of the nanocomposite stays intact at $10^{-1} \text{ S cm}^{-1}$ (Fig. 7) [27].

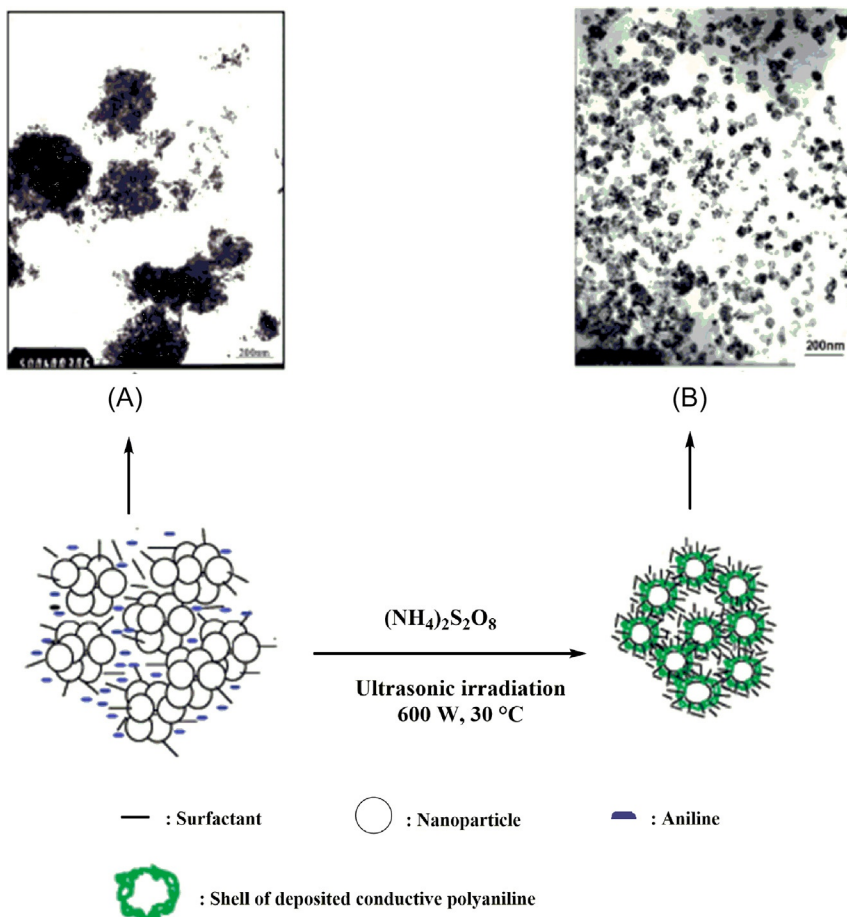


Fig. 7 Formation of core-shell polyaniline/nanocrystalline TiO_2 composite particles: (A) TEM photograph of aggregates of nanocrystalline TiO_2 in aqueous solution; (B) TEM photograph of polyaniline/nanocrystalline TiO_2 composites particles obtained through ultrasonic irradiation [27].

1.9 Ultrasound-assisted emulsion polymerization ZnO/poly(butyl methacrylate) nanocomposites

In another approach using the hydrothermal-sonochemical emulsion polymerization technique, zinc oxide (ZnO)/poly(butyl methacrylate) (PBMA) and PBMA/polyaniline (PANI)-ZnO latex nanocomposite were synthesized. This study had three main objectives:

- (1) Synthesis of modified ZnO nanoparticles by sonochemistry
- (2) ZnO-PBMA synthesis by sonochemical emulsion polymerization in green media
- (3) Enhancing the properties of ZnO-PBMA latex for anticorrosive applications [28].

1.10 Ultrasound-assisted emulsion polymerization of the poly(styrene-co-methyl methacrylate)/montmorillonite nanocomposite

The ultrasonic-assisted emulsion copolymerization of styrene and methyl methacrylate is studied. It has been observed that the ultrasound in the synthesis of the exfoliated structure poly(styrene-co-methyl methacrylate)/exfoliated montmorillonite (P(MMA-co-St)/O-MMT) nanocomposite lowers (at a fivefold faster polymerization rate) the time required for the polymerization to take place, along with the higher polymerization rate and better distribution of MMT in polymer latex. Fig. 8 is a schematic illustration of the exfoliated P(MMA-co-St)/OMMT nanocomposite synthesis mechanism. The first stage shows the mixing of O-MMT with styrene in the existence of the ultrasonic wave to create the exfoliated structure. Ultrasound and its cavitation effects create high shear levels that, related to strong confusion, will result in clay domination into single sheets, which make easier the dispersion of these platelets into the monomer phase. In the second stage, the polar carboxyl groups of the methyl acrylate and styrene react by the polar groups ($-OH$) existing on clay sheets leading to an establishment of steady emulsion droplets of monomers. Ultrasonic irradiations create the implosion of cavities, which is one of the reasons for the formation of the radicals throughout the polymerization process. This radical generation quantity also decreased the distribution resistance resulting from unstable conditions caused by the cavitation factors of ultrasonic, which will result in much faster polymerization rates. The diffusion resistance reduction increases the micro-vortex sign of the component, causing great effects in the reaction condition [29].

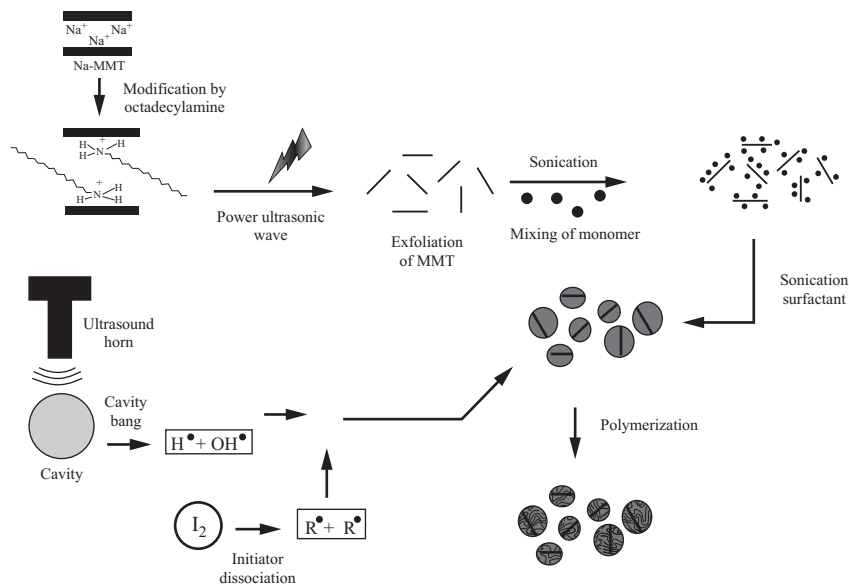


Fig. 8 Schematic mechanism for exfoliation of MMT and the formation process of P(MMA-co-St)/O-MMT nanocomposite [29].

1.11 Ultrasound-assisted mini-emulsion production of polypyrrole-ZnO (PPy/ZnO)

Oil-water mini-emulsion synthesis of PPy/ZnO by ultrasound was investigated. As was evident by the TEM images, uniform dispersion of ZnO nanoparticles in the polypyrrole medium was achieved due to the influence of ultrasonic energy on the polymerization medium. Ultrasound controlling the sizes of the particles improves the cooperation between ZnO and PPy nanoparticles. Fig. 9 demonstrates the reaction mechanism of a hybrid PPy/ZnO nanocomposite formation in the presence of ultrasound. As is obvious in Fig. 9, ultrasound produces cavitation conditions which are responsible for the creation of a mini-emulsion. Also, high temperature and pressure in the bubbles and intense shear energy in the medium are the results of the crumble in cavitation bubbles. Such forces can prepare such conditions prior to the uniform decomposition of ferric chloride into iron (ferric) and chloride ions and the production of identical and nanosized droplets. Furthermore, the shock waves of ultrasound cavitation caused destruction of the particles. This fragmentation breaks the particle aggregation, thus resulting in superior control over the size dispersal. Ultimately, the produced PPy/ZnO hybrid nanocomposite is stabilized with the surfactant SDBS. Py is the pyrrole monomer, and Py^+ is the radical cation which can dimerize by the elimination of H^+ with ultrasound, such as given below in reactions (1)–(4): [30]

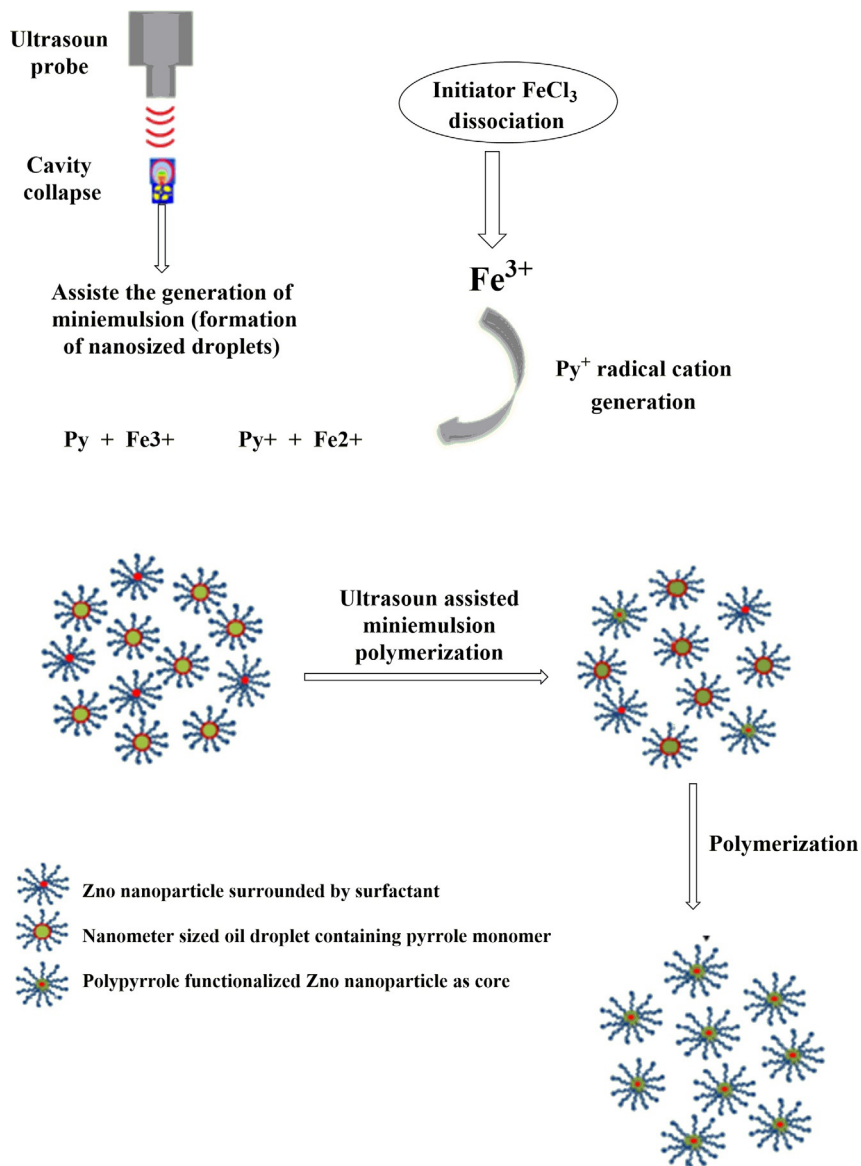
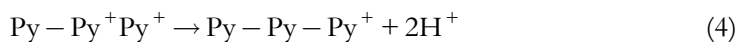
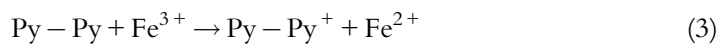


Fig. 9 Mechanism of functionalization of ZnO nanoparticles using polypyrrole in the presence of ultrasound during miniemulsion polymerization [30].



2. Bulk and suspension polymerization

A simple process in which the minimum of product contamination can be achieved in the polymerization of the pure monomer is called Bulk polymerization. In this polymerization, monomer suspends as droplets (discontinuous phase) (50–500 mm in diameter) in water (continuous phase) [1].

2.1 Ultrasound-assisted bulk polymerization of styrene

The results in the ultrasonic Bulk polymerization of styrene with AIBN as the initiator are listed and explained as follows:

1. Initiator concentration square root directly affects the rate of polymerization.
2. Enhancing net ultrasonic energy causes the total rate constant of polymerization to decrease linearly.
3. As sound energy is applied, an increase in average molecular weight is observed.
4. Ultrasonic waves affect the depression behavior of the gel.

The results also showed that the termination reaction rate rises and ultrasonic irradiation reduces the efficiency of the initiator [31].

2.2 Ultrasound-assisted bulk polymerization to fabrication of hydrogel macromolecules

Hydrogels are dense cross-linked polymers with three-dimensional network structures made from groups of functional hydrophilic which have significant water and solute molecules adsorbent ability. The swelling capability of the hydrogels is one of the key factors, considering the Polymerization methods, which is affected by functional units and the type of cross-linking agents, electric field, pH, ionic intensity, light, and temperature are the external affecting parameters that affect hydrogels [15].

Dispersions of monomer droplets and formation of free radicals were achieved by the assistance of ultrasound for initiation of polymerization of polymer hydrogel. Ultrasound irradiations create high shear gradients, which can control the molecular weights, and also through improvement in the adsorption ability of hydrogels and mechanical properties are able to enhance the particles dispersion in the polymer matrix [32].

Furthermore, initiation of bulk polymerization reactions to formation of polymer hydrogel by ultrasound-assisted synthesis from attachment of acrylamide and *N*-isopropyl acrylamide onto lignin by combination of montmorillonite with excellent swelling-deswelling property for the elimination of methylene blue from the aqueous medium is studied, and the results showed positive effects of ultrasonic on the polymerization process. Fig. 10 shows the schematic illustration of this process [32]. Also, in copolymers, the graft ratio, graft efficacy, and monomer conversion improved remarkably in ultrasound methods. Furthermore, the graft ratio and graft efficacy increased when one of the components and initiator were sonicated before the reaction prior to the addition of monomer [33].

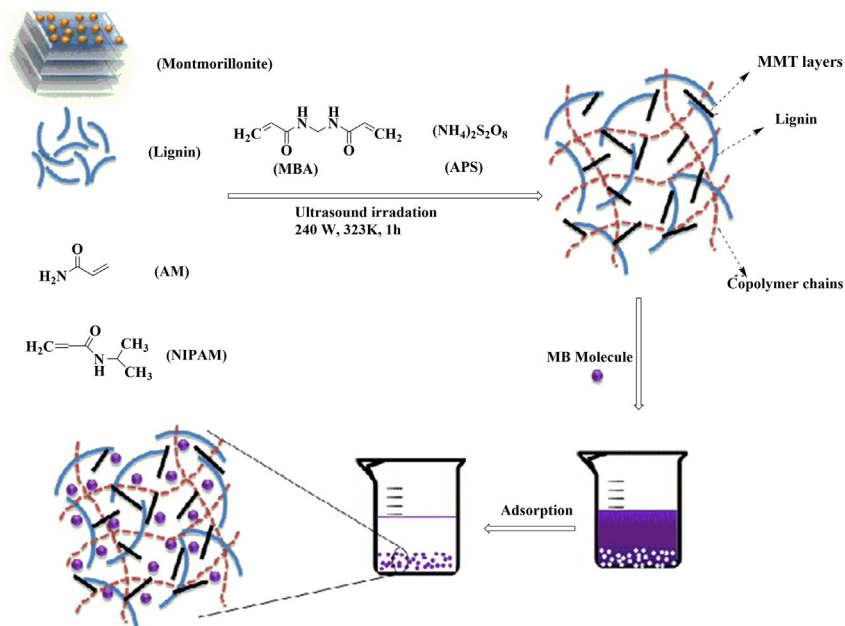


Fig. 10 Scheme for synthesis of hydrogel for the removal of methylene blue [32].

2.3 Ultrasound-assisted suspension polymerization of styrene

The suspension polymerization of styrene with the help of ultrasound is considered experimentally in a batch reactor and stirred continually. The following results are obtained from experiments:

1. Ultrasound prevents the agglomeration between droplets. Also, in batch and continuous reactors, it prevents the adhesive of droplets on the reactor wall during suspension polymerization.
2. The effect of the irradiation in the condition of 500 W at 400 kHz on the kinetics of suspension polymerization in batch operation was insignificantly unimportant, and so the rate equation of bulk polymerization under no irradiation represents the polymer yield and the average molecular weight of polymer.
3. The effects of the interactions between droplets in the reactor on monomer to polymer conversion and the average molecular weight in continuous operations by considering complete micro-mixing and complete segregation calculations were investigated. In micro-mixing, there are two stable steady states in a range of 6 where we can observe the gel effect, and also the droplet movements in the reactor will cause the interactions affecting the conversion and the average molecular weight of the polymer.
4. In the continuous operation, the results which occurred in between two very great conditions showed the considerable interaction between droplets [34].

2.4 Ultrasound-assisted suspension polymerization of 2-hydroxyethylmethacrylate/ethylene glycol dimethacrylate copolymer

As was illustrated before, the role of ultrasound in different kinds of polymerization is obvious. Here we study the suspension Copolymerization of 2-hydroxyethylmethacrylate and ethylene glycol dimethacrylate using ultrasound (20 kHz). Different aspects of the process and the products such as shape, particle size, and development of the physical features (surface area, pore volume), which are affected by ultrasound, were observed continually and reported in the paper. Using ultrasound, they were able to prepare both smaller particles (10 μm) or larger ones (100 μm) since either way a narrower polydispersity (PD) of sizes in the particles is possible [35].

3. Solution polymerization

In the solution polymerization process, the solvent acts as a diluent and supports the heat transfer process of polymerization reaction.

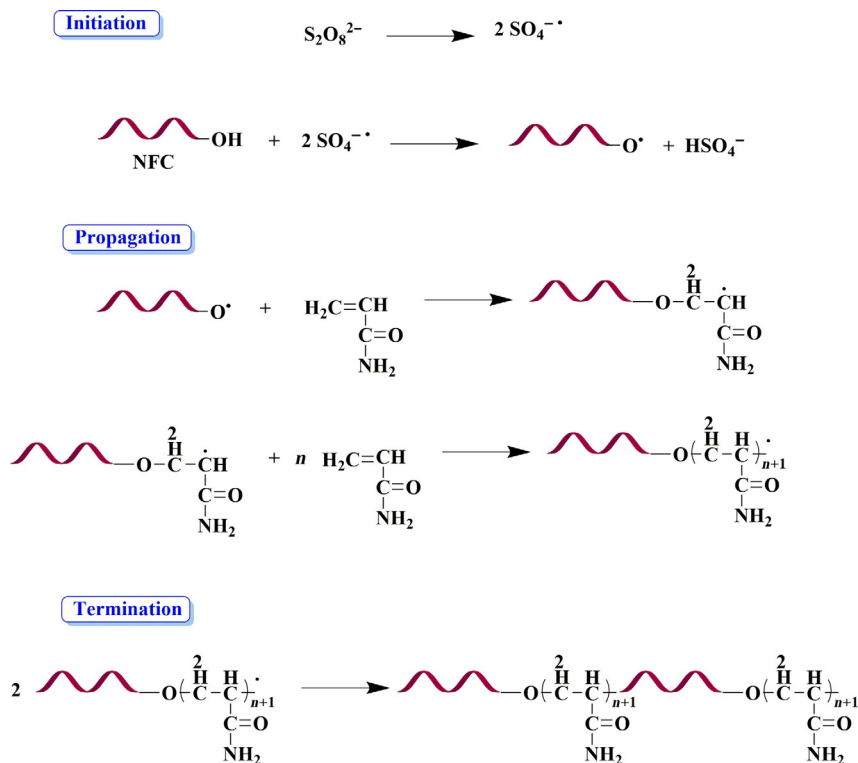
3.1 Ultrasound-assisted polymerization of acrylic hydrogels

In the preparation of acrylic hydrogels, ultrasound was employed to generate initiating radicals in the solutions of viscous aqueous monomer by glycerol, sorbitol, or glucose as potential additives in an open system at the temperature of 37°C [36].

Also, the cavitation effect of ultrasound in situ ultrasound-assisted polymerization of Polypropylene composite membrane with an acrylic hydrogel layer improves the attaching efficacy of acrylic acid on the membrane surface. It is necessary to mention that the ultrasound not only did not have a negative effect on the mechanical properties of modified membranes, but also there was a slight increase in mechanical characteristics of functionalized membranes owing to the presence of acrylic hydrogels, as was evident by the results of the experiment. This hydrogel can be a potential adsorbent for dyes and some salts in aqueous phases [37].

3.2 Ultrasound-assisted copolymerization of polyacrylamide/nano-fibrillated cellulose and acrylic acid/poly (vinylidene fluoride)

In the process of grafting the polyacrylamide onto nano-fibrillated cellulose (NFC-*g*-PAM) under ambient conditions, the ultrasound-assisted protocol had an intense influence in improving the attachment of PAM onto NFC (Scheme 1). Persulfate initiator and the ultrasound irradiation interactions causing the synergistic effect accelerate the creation of sulfate ion radicals as can be seen in Scheme 1. These radicals are responsible for the initiation and propagation of the polymerization practice [38]. In AA grafting onto PVDF, the grafting density of the reaction mixture could be controlled by changing the time and power of ultrasonic waves, monomer, and initiator concentration.



Scheme 1 Schematic representation for synthesis of NFC-*g*-PAM via an ultrasound-assisted method [38].

3.3 Ultrasound-assisted polymerization of poly (*N*-isopropylacrylamide-*co*-2-hydroxyethyl methacrylate)

Toward preparation of the copolymers with lower polydispersity index and with consideration to the polymerization rate and polydispersity of molecular weight, in the ultrasound-assisted polymerization of poly (*N*-isopropylacrylamide-*co*-2-hydroxyethyl methacrylate), without chemical initiator, the optimum volume fraction of ethanol was 60 vol%. The faster polymerization rate and lower molecular weight were achieved in advanced ultrasonic energy force, which was due to the higher number of radicals prepared in the reaction. In all the ultrasonic power intensities, the polydispersity was less than 1.5, so while maintaining low polydispersity, the molecular weight can be managed with ultrasonic energy force [39].

4. Phase-transfer catalysis polymerization

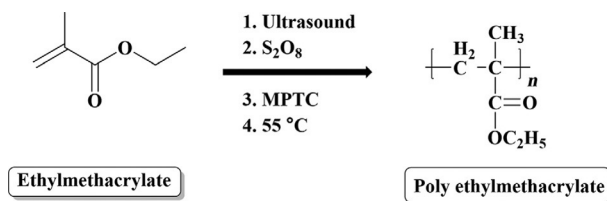
Phase-transfer catalysis (PTC) is important and such a convenient tool owing to its high conversion, simplicity, and high selectivity in different conditions and environments. Because of such properties, PTC can handle the interactions between immiscible lipophilic and hydrophilic reactants [40].

4.1 Ultrasound-assisted polymerization of butyl acrylate using crown ethers as PTC

The first study on this method was described by Rasmussen and Smith. They investigated the polymerization of butyl acrylate with several crown ethers as a PTC and initiators named potassium peroxydisulfate ($K_2S_2O_8$) which is soluble in water [41]. It was shown that the ultrasound improves the PTC efficiency with the production of high interfacial space through emulsification reaction that to enhance the interfacial contact area can create extremely fine emulsions. The reactivity of the reaction in a synergetic of PTC along with ultrasound is considered appropriate, which can result in some beneficial products [42].

4.2 Ultrasonic-assisted free radical polymerization of ethyl methacrylate using PTC

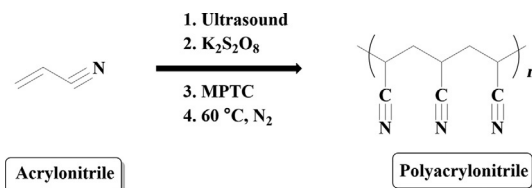
A novel dual-function, 1,4-dihexadecylpyrazine-1,4-dium dibromide was synthesized and was applied as PTC in the free radical polymerization of ethyl methacrylate assisted via ultrasound. The data of the experiment exhibited that the rate of polymerization enhances almost three to eightfold with 28 kHz (300 W) and 40 kHz (300 W), respectively, under ultrasonic medium (Scheme 2) [43].



Scheme 2 Reaction of polymerization of ethyl methacrylate [41].

4.3 Ultrasound-assisted radical polymerization of acrylonitrile using PTC

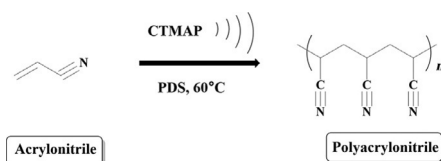
Selvaraj et al. reported the radical polymerization of acrylonitrile (AN) using ultrasound in a water/chlorobenzene biphasic system at 60°C assisted with multi-position phase-transfer catalysis. As mentioned above, the parameters involved in the polymerization rate revealed that the R_p enhances three to eightfold with 28 and 40 kHz underneath ultrasonic waves-assisted (Scheme 3) [44].



Scheme 3 Polymerization of acrylonitrile [44].

4.4 Ultrasound-assisted radical polymerization of acrylonitrile using PTC

Another study confirmed the importance of PTC and ultrasound combined techniques in active radical polymerization of acrylonitrile in two-phase conditions. The results of this study too showed the ultrasound effect on the rate of polymerization. The significant enhancement on the R_p was obvious by varying the experimental parameter under ultrasonic conditions. Ultrasound condition causes the fast dissociation of the initiator so that the production of more free radicals is possible and also the mixing of two phases can be improved. The polymerization of acrylonitrile (M) initiated using $K_2S_2O_8$ /PTC in ethyl acetate/water is shown in Scheme 4. In the two-phase system, the PCT role ($Q^+ X^-$) is to transfer the anion (Y^-) of the aqueous phase to the organic phase, at an area among the phases. Then, in situ reformed $Q^+ X^-$ in the aqueous phase is able to preserve the PTC polymerization practice as revealed in Fig. 11. Cavitations generated by the chemical effects of ultrasound are responsible for the generation of free radicals [45].



Scheme 4 Ultrasound-assisted phase-transfer catalyzed polymerization of acrylonitrile [45].

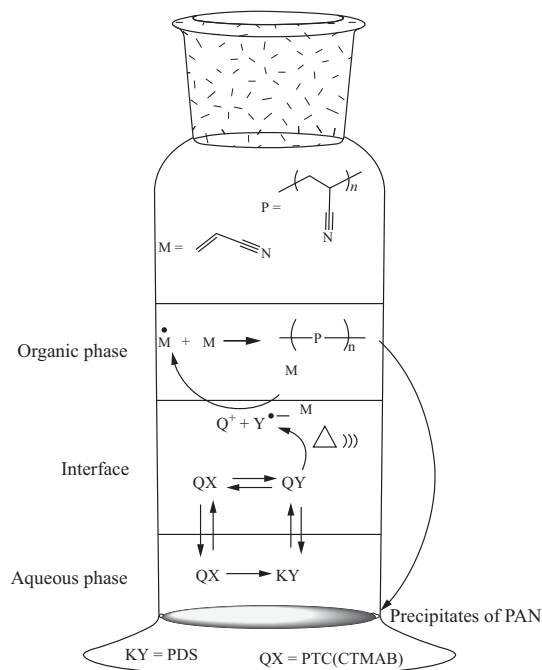


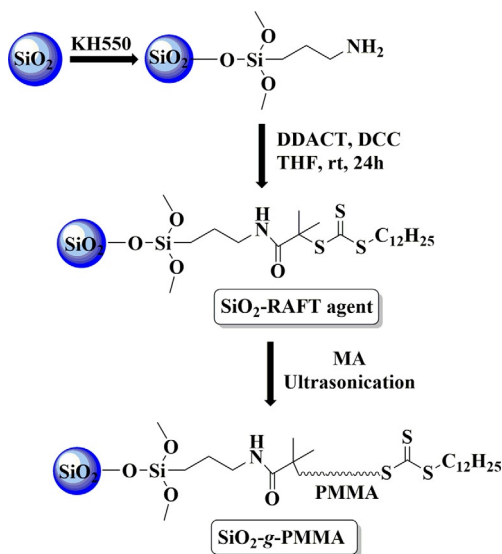
Fig. 11 Kinetic model of an ultrasound and PTC-assisted polymerization of acrylonitrile in a two-phase system [45].

5. Reversible addition-fragmentation chain transfer

Reversible addition-fragmentation chain transfer (RAFT) polymerization is defined as a living radical polymerization consisting of sets of reversible stages which work based on the degenerative chain transfer to convert suspended chains to an active propagating radical in a controlled reaction process [1].

5.1 Ultrasound-assisted graft modification of silica gel by RAFT polymerization

Silica gel graft modification with RAFT polymerization underneath ultrasonic waves has been investigated (Scheme 5) [46].



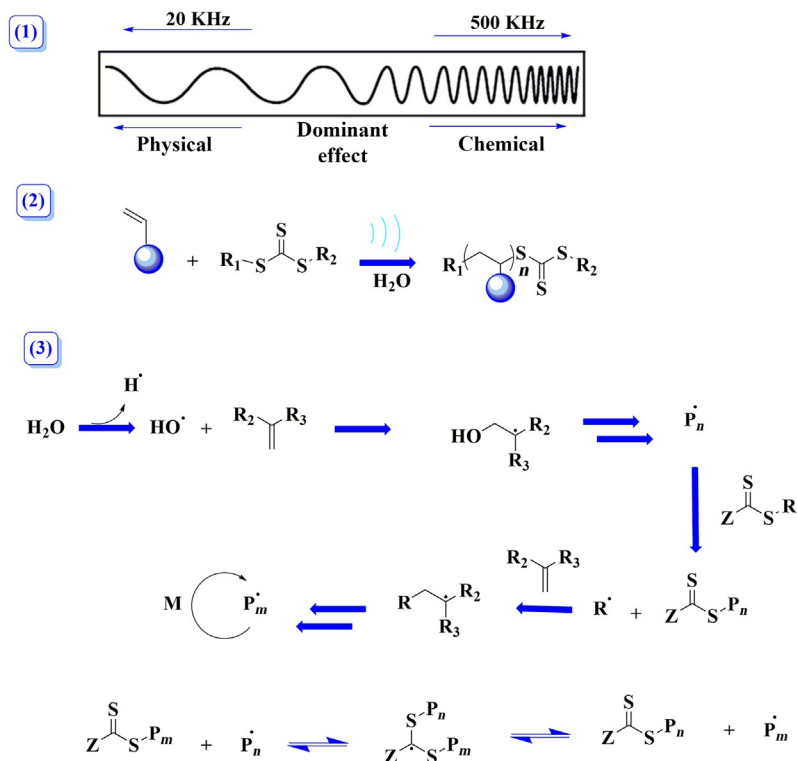
Scheme 5 The modification and graft polymerization of silica gel [46].

Ultrasound can be a proper source to initiate the radicals of a controlled radical polymerization when it occurs in the existence of a (RAFT) agent. This method is considered as a highly “green” approach of externally regulated/controlled polymerization which is able to directly point monomers or polymer structures in the process of polymerization. As was mentioned before, ultrasound causes the vaporization of liquid molecules into cavitation bubbles, which in fact will result in the formation of radical species, so that the growth of these species will eventually bring a collapse in the system. This anomaly is responsible for the generation of extreme localized pressures along with the areal heats, hence enabling the vaporization of so-called molecules into their related radicals.

Generally, there are two important effects of ultrasound needs to be mentioned:

- Physical strengths (i.e., high shear)
- Chemical effects (i.e., radical generation)

The frequency of the irradiation directly determines the extent of physical and chemical effects in a way that at low frequencies (~ 20 kHz) physical strengths are in the ascendant by the minimal chemical effects, while at higher frequencies (> 200 kHz) we can observe the opposite behavior prior to the high frequency in the system (Scheme 6) [47].



Scheme 6 (1) Schematic representation of sonochemically induced RAFT polymerization (sonoRAFT); (2) proposed mechanism for sonochemical initiation of RAFT process; and (3) representation of forces generated under different ultrasonic frequencies [47].

5.2 Ultrasound-assisted RAFT polymerization-induced self-assembly (Sono-RAFT-PISA)

Reversible addition-fragmentation chain transfer by the polymerization-induced self-assembly process assisted with ultrasound (Sono-RAFT-PISA) is a “green” method in which the high-frequency (490 kHz) ultrasound is used. This reaction is done in the

existence of water as initiator and also as a solvent instead of organic initiator, namely *inisolv*, which can target the poly(*N*-isopropylacrylamide-*co*-*N,N'*-methylenebis(acrylamide)) P(NIPAM-*co*-MBA) as core and poly(poly(ethylene glycol) methyl ether acrylate) PPEGMA as shell-based thermosensitive nanogels (Scheme 7).



Scheme 7 Synthesis of thermosensitive nanogels-based on PPEGMA-*b*-P(NIPAM-*co*-MBA) [48].

Here some of the advantages of the Sono-RAFT-PISA approach are mentioned:

- Total monomer conversion
- Low temperature
- High polymerization rate
- Temporal control over the polymerization
- Usage of water as *inisolv*
- Lack of unused organic compound in the nanogels

The RAFT-PISA process, which is assisted with high-frequency ultrasounds, can acquire some benefits like:

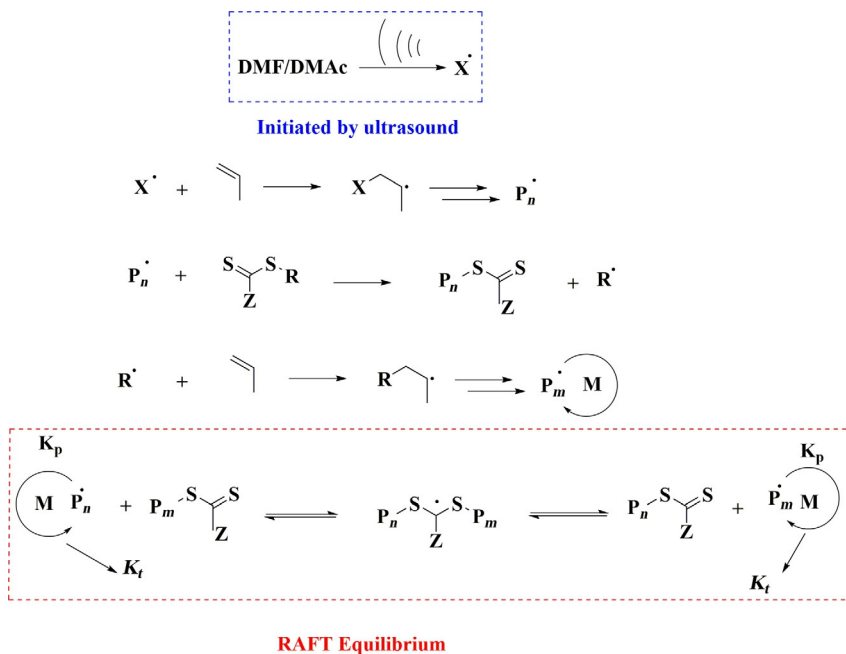
- (1) Low reaction temperature
- (2) Complete monomer conversion
- (3) Lack of additional initiator

Schematic illustration of the RAFT-PISA process is presented as follows [48].

5.3 Ultrasound-assisted Sono-RAFT polymerization in organic solvents

Sono-RAFT in organic solvents such as DMF and DMAc with high-frequency ultrasonic power (490 kHz) showed that the polymerizations were commonly well managed by low dispersity of produced polymers. Monomer vapor pressure, solvent, and polymer nature influence the final monomer conversion and molecular weight association. In summary, the sono-RAFT process offers an ultrasound-assisted controlled polymer synthesis without the need for additives or common radical initiators [49].

The radicals (e.g., methyl radicals) which were produced via high-frequency (490 kHz)-stimulated pyrolysis of organic solvents (X^{\bullet} in Scheme 8) can also initiate a polymerization. In this way, controlled sono-RAFT polymerization without the use of external additives or initiators in organic solvents is possible of being achieved (Scheme 8) [49].



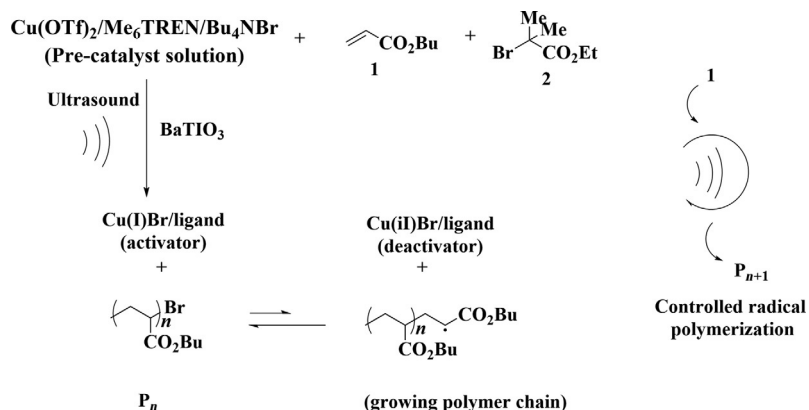
Scheme 8 Proposed mechanism of organic SonoRAFT [49].

6. Atom transfer radical polymerization

Atom transfer radical polymerization (ATRP) is referred to as a method in which the generation of a carbon-carbon bond by a transition metal catalyst is possible. The polymerization from this process is described as atom transfer radical addition polymerization (ATRAP) [1].

6.1 Ultrasound-assisted polymerization of acrylate by (ATRP) method

As an example, the polymerization of acrylate monomers provided by ultrasonic agitation is studied. Piezo-chemical reduction of Cu(II) in the attendance of a monomer of *n*-butyl acrylate and ethyl α -bromoisobutyrate used as the initiator will produce a low dispersity poly(*n*-butyl acrylate). Having a continuous increase of the polymer chain requires a continual ultrasonic activation of the chains during the process which is schematically presented as follows (Scheme 9) [50].



Scheme 9 Ultrasound-induced controlled radical polymerization of *n*-butyl acrylate 1. Sonochemical reduction of the Cu(II)/Me₆TREN complex at the interface of the piezoelectric nanoparticle (BaTiO₃) leads to the formation of the activator for ATRP. The polymeric chain growth starts from the alkyl halide initiator 2 and successive addition of 1 to the growing polymeric chain P_n occurs in a controlled fashion. The final polymer P_{n+1} is obtained after chain termination. P represents a polymeric chain with a degree of polymerization *n* [50].

6.2 Ultrasound-assisted polymerization of acrylate by (ATRP) method

Also, Methyl acrylate (mechanoATRP)^a with low ppm of the CuBr₂/tris(2-pyridylmethyl)amine catalyst was carried out in an ultrasound chamber with narrow molecular weight distribution as can be seen in Fig. 12. [51].

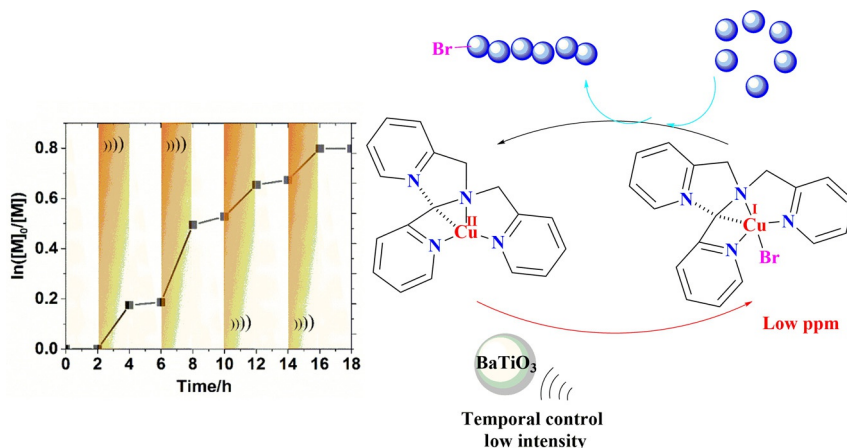


Fig. 12 Temporal control in mechanoATRP using BaTiO₃ nanoparticle (tetragonal, 200nm) as a mechano-electric transducer under ultrasound agitation through intermittent switching on/off the ultrasound bath [51].

^a Mechanically controlled atom transfer radical polymerization.

7. Ring-opening polymerization

Ring-opening polymerization (ROP) is another type of polymerization in which monomers such as amides, acetals esters, cyclic ethers, and siloxanes are used [1].

Ultrasonic of ring-opening polymerization in cyclic Bisphenol A polycarbonate oligomer can initiate the polymerization process and continually improves the reaction conditions; thus, no added chemical initiator is needed (Fig. 13.). Although having a chemical initiator in ultrasound-assisted polymerizations can significantly improve the polymerization rate compared to the initiator-free reactions, for example, if lithium salicylate is used as the initiator, the time of reaction would be reduced and the reaction would be conducted seven times faster than in initiator-free reactions [52].

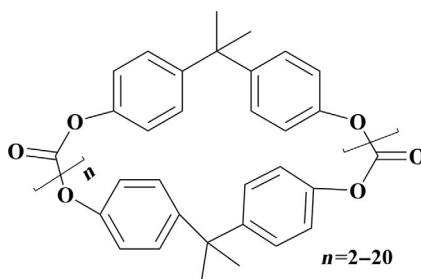


Fig. 13 Cyclic oligomeric bisphenol A polycarbonate [52].

In another research, ultrasound with higher intensities was used in δ -valerolactone and ϵ -caprolactone ring-opening polymerization with dibutyl tin dilaurate used as a catalyzer in this reaction (Fig. 14). It was observed that the sonication creates better reaction conditions and accelerates the polymerization rate. In δ -valerolactone polymerization, using sonication can also improve depolymerization reactions which cause the molecular weight to drop during the reaction. The δ -valerolactone sequences caused the incorporation of ϵ -caprolactone into the products which was the result of ultrasound usage in the reaction. This incorporation led to synthesizing copolymers from the so-called monomers [53].

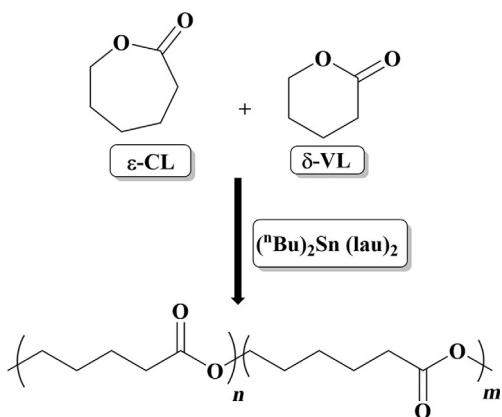


Fig. 14 Ring-opening polymerization of δ -valerolactone and ϵ -caprolactone [53].

Gumel et al. reported the conversion of the γ -caprolactone to poly-6-hydroxyhexanoate and investigated the ring-opening polymerization process of this reaction. The initiation of the reaction is achieved through the lactone ring opening by the H_2O molecule in the complex media in which the molecule performs as a nucleophile on the intermediate complex of acyl carbon from acyl-enzyme in order to create hydroxyl carboxylic acid. The additional propagation of polymer causes the back side attack of the terminal hydroxyl unit on the complex which then results in the chain elongation process in which the monomer to polymer conversion occurs. This steps in this reaction are intensified in the presence of ultrasound that affects the catalytic behavior, chain propagation steps rate, and the process of monomer synthesis, and thus the polymerization rate is improved. Enhanced micro-streaming confirmed by the results of characterization, revealed that the sonication synthesizes a polymer with excellent crystalline structure compared to the sonication-free process in which the crystallinity is 61% and 21%, respectively. This micro-streaming provides an alignment of polymer molecules in the presence of ultrasonic irradiation. As results after 90 hrs, the poly-6-hydroxy hexanoate polymer molecular weight was much higher (twice) in sonicated conditions than non-sonicated ones [54].

8. Conclusion

The chapter mainly focused on characterizing the different aspects of the energy resulting from ultrasonic which mostly causes the degradation of polymer chains in a case where the produced radicals are the keys for the polymerization process to be started. The discussion here included some ultrasound-assisted polymerization processes such as Emulsion Polymerization, Bulk and Suspension Polymerization, Ring-Opening Polymerization, etc. To conclude, ultrasonic waves are one of the most used approaches for the dispersion of monomer into the medium of complex solutions where there is no need for excess or any chemical initiator. The results reveal that the process of ultrasonic-assisted polymerization is easily controlled by the properties provided by means of ultrasonic waves in which case there is no need for chemical stabilizers. Also, according to the kinetic studies mentioned in the chapter, the polymerization rate, decrease in polymer size, and molecular weight distribution are directly influenced by the properties of the ultrasonic energy so that the consideration of different outcomes of the reaction products can be manipulated along with the engineering of the ultrasonic energy to form a condition which will result in a most efficient product.

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