
IONIC LIQUIDS AND THEIR ROLE AND EFFECTS AS REACTION MEDIA IN POLYMERIZATION PROCESSES

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Abstract: *This article reviews the application of ionic liquids as alternative reaction media in polymer synthesis, with a particular emphasis on the radical polymerization and copolymerization of methyl methacrylate (MMA). It examines how the unique physicochemical properties of ionic liquids influence key aspects of the process, including reaction pathways, rate behavior, and phenomena such as autoacceleration (gel effect). In contrast to traditional organic solvents, ionic liquids provide a more controllable reaction environment, which supports the formation of polymers with increased molecular weight and improved structural regularity. The study also considers how ionic media affect the microstructure and resulting properties of copolymers obtained from MMA in combination with different comonomers. Attention is given to the role of intermolecular interactions and medium polarity in determining polymer growth and architecture. Due to their negligible vapor pressure, reusability, and tunable nature, ionic liquids are increasingly regarded as efficient and sustainable media for advanced polymerization processes.*

Keywords: *ionic liquids, methyl methacrylate, radical polymerization, copolymerization, gel effect.*

INTRODUCTION

One of the central challenges in modern chemistry and chemical engineering is the replacement of conventional organic solvents with safer and more environmentally benign alternatives. Most organic solvents are characterized by high volatility, toxicity, and flammability, which makes their use at both laboratory and industrial scales potentially harmful to human health and the environment. In this context, the substitution of toxic and explosion-prone reaction media with alternative systems such as supercritical fluids or ionic liquids has, in recent years, become a major research direction aligned with the principles of green chemistry [1,2].

Ionic liquids are a class of salts with melting points typically below 100 °C, and in many cases, they exist in a liquid state at room temperature. They are composed of organic or inorganic cations and anions and, unlike classical molecular solvents, possess a fully ionic structure. This feature largely determines their distinctive physicochemical properties. Theoretically, an extensive variety of ionic liquids can be synthesized by combining different cations and anions, allowing their properties to be tailored for specific applications [3].

Although the first reports on ionic liquids date back to the late nineteenth century, a significant milestone was achieved in 1914, when P. Walden synthesized the first ionic liquid with a low melting point [4]. Earlier studies had also reported compounds such as ethanolanmonium nitrate. In 1934, the potential application of ionic liquids was first highlighted in a patent concerning cellulose dissolution at low temperatures [5]. While various ionic liquids were synthesized between the 1940s and 1980s, substantial interest in this field emerged only after the 1990s, leading to a rapid expansion of research, patents, and review publications [6].

The growing interest in ionic liquids is primarily attributed to their unique properties, including a wide liquid-phase temperature range, negligible vapor pressure, non-volatility, non-flammability, minimal explosion risk, and high thermal and chemical stability. In addition, ionic liquids exhibit high polarity and ionic conductivity, enabling them to dissolve a broad spectrum of substances, including organic, inorganic, and organometallic compounds, as well as natural and synthetic polymers. These characteristics have facilitated their widespread application in catalysis, electrochemistry, energy technologies, analytical chemistry, and materials science [7–12].

Ionic liquids are typically synthesized through three main approaches: ion-exchange reactions involving halogenated precursors, quaternization processes, and reactions conducted on ion-exchange materials [9,10]. At the same time, alternative synthesis routes that avoid halogen-containing components are attracting increasing attention, as such components may adversely affect the electrochemical and catalytic properties of ionic liquids [13].

At present, ionic liquids are regarded not only as passive solvents but also as active media capable of influencing the course of chemical reactions. They can affect reaction rates, selectivity, and product yields, and may even alter reaction mechanisms. This behavior is particularly evident in catalytic processes and organic synthesis [14].

Initially, the application of ionic liquids in polymer chemistry was limited, primarily focusing on olefin polymerization using Ziegler–Natta-type catalysts and the electrochemical synthesis of conducting polymers [15–17]. However, the development of chemically stable ionic liquids based on imidazolium cations and fluorinated anions has significantly expanded their applicability. As a result, ionic liquids are now widely employed in polymerization and polycondensation processes [18].

In recent years, particular attention has been given to the role of ionic liquids in radical polymerization processes. The radical polymerization of methyl methacrylate (MMA) is of considerable industrial importance, yielding poly(methyl methacrylate) (PMMA), a material known for its high transparency, mechanical strength, and resistance to environmental factors. When used as reaction media, ionic liquids can influence polymerization rates, chain growth mechanisms, and especially the characteristics of the gel effect (Trommsdorff effect), thereby enabling control over the molecular weight and structure of the resulting polymer [19].

In addition, the copolymerization of MMA with other monomers is widely investigated for the development of functional materials. For instance, copolymers of MMA with acrylonitrile (AN) exhibit favorable mechanical, thermal, and chemical properties. The presence of ionic liquids in such systems modifies the reaction medium, affecting copolymer composition, chain architecture, and phase behavior [20].

More recently, the synthesis of ionic liquid-based monomers and their subsequent polymerization has led to the emergence of a new class of materials known as polymerized ionic liquids (poly(ionic liquids)). These materials are of considerable interest due to their ionic conductivity, thermal stability, and functional versatility, and are regarded as a promising direction in advanced materials science [21].

The structure of ionic liquids plays a critical role in polymerization processes. Variations in cation–anion combinations influence key parameters such as polarity, viscosity, and ionic strength, thereby affecting reaction kinetics and mechanisms. For example, ionic liquids synthesized from N-methylpyrrolidone and phosphoric acid exhibit high polarity and strong solvating ability, making them effective media for polymerization. In contrast, ionic liquids derived from morpholine and sulfuric acid are distinguished by their proton conductivity and catalytic activity, rendering them promising for processes involving both radical and ionic mechanisms [22,23].

Studies indicate that the involvement of ionic liquids in polymerization processes not only enhances reaction rates but also affects the pore structure, morphology, and electrical conductivity of the resulting polymers. By selecting appropriate cation–anion combinations, it is possible to achieve high selectivity and improved product yields [24].

In summary, polymerization and copolymerization processes conducted in ionic liquid media are of significant importance from both fundamental and applied perspectives. The aim of this review is to systematically analyze the role of ionic liquids in polymer synthesis, particularly in the radical polymerization of MMA and the formation of MMA-based copolymers, to summarize their influence on polymer structure and properties, and to evaluate the application potential of various types of ionic liquids.

Properties of ionic liquids

Ionic liquids constitute a class of substances distinguished by unique physicochemical properties and broad applicability in modern chemistry. These properties are governed by their ionic nature and the diversity of cation–anion combinations. For this reason, ionic liquids are often described as “designer solvents,” as their characteristics can be deliberately tuned for specific purposes [25].

One of the key features of ionic liquids is their wide liquid-phase temperature range. They typically exhibit low melting points (below 100 °C) and remain in the liquid state until thermal decomposition occurs at elevated temperatures. However, predicting melting points is nontrivial, as they are strongly influenced by factors such as

cation asymmetry, alkyl chain length and branching, and the size and structure of the anion [26].

Asymmetric cations and bulky anions reduce crystallinity, leading to lower melting temperatures. Moreover, many ionic liquids tend to form glassy states, which complicates the experimental determination of their melting points [27].

Another important property is their negligible vapor pressure, which effectively eliminates volatility and minimizes the emission of hazardous substances into the atmosphere. In addition, ionic liquids are generally non-flammable and present minimal explosion risk, enhancing their suitability for industrial applications [28].

Thermal stability is a critical parameter for ionic liquids. Their upper operating temperature is defined by thermal decomposition. In protic ionic liquids, thermal stability is often correlated with the difference in acid–base strength (ΔpK_a); an increase in ΔpK_a generally corresponds to enhanced stability [29]. In other systems, decomposition mechanisms are largely determined by chemical interactions between the cation and anion [30].

Ionic liquids are also characterized by high polarity and ionic conductivity, which underpin their widespread use in electrochemical systems and catalytic processes. They are capable of dissolving a wide range of substances, including organic, inorganic, and organometallic compounds, as well as polymers, making them versatile solvents [31].

Viscosity is another important parameter influencing their application. Ionic liquids are typically highly viscous, which affects diffusion processes and reaction kinetics. Other physical properties, such as density, surface tension, and conductivity, are likewise determined by ion size, shape, and intermolecular interactions [32].

Various theoretical approaches have been developed to predict the physical properties of ionic liquids. Methods based on molecular volume and quantum chemical calculations have provided insights into parameters such as density and viscosity. However, these models primarily capture general trends and remain limited in predictive accuracy for specific systems [33].

Structurally, ionic liquids can be classified into several categories. Based on the cation type, common classes include imidazolium-, pyridinium-, ammonium-, phosphonium-, and morpholinium-based systems. According to the anion, they may contain halides, tetrafluoroborate, hexafluorophosphate, sulfate, and other species. Additionally, ionic liquids are categorized as protic or aprotic, depending on their synthesis mechanism and proton transfer capability [34].

From an acid–base perspective, ionic liquids are divided into protic and aprotic systems. Protic ionic liquids are formed through proton transfer between a Brønsted acid and base, typically via a direct interaction that simplifies synthesis and does not require significant energy input. The presence of hydrogen bonding in such systems influences their structural dynamics, leading to notable changes in viscosity, ionic conductivity, and chemical reactivity [35]. In contrast, aprotic ionic liquids are generally obtained through quaternization of organic bases followed by anion exchange. These systems exhibit higher structural stability and a wider electrochemical window, making them more suitable for electrochemical applications, catalysis, and radical polymerization processes [36].

The hydrophilic or hydrophobic character of ionic liquids depends largely on their ionic composition, particularly the size and polarity of the constituent ions. Hydrophilic ionic liquids readily mix with water to form homogeneous phases and typically contain small, highly polar anions such as acetate or halides, making them suitable for aqueous

and biochemical applications [37]. In contrast, hydrophobic ionic liquids are immiscible with water due to the presence of large, weakly coordinating anions such as PF_6^- and BF_4^- . These systems are advantageous for biphasic processes, including extraction and selective separation [38].

Functional ionic liquids are specifically designed systems in which functional groups are incorporated at the molecular level to impart targeted properties. Catalytically active ionic liquids can act as reaction media and active sites, enhancing both reaction rate and selectivity. In polymerization processes, ionic liquids may function not only as solvents but also as structure-directing agents, influencing polymer morphology and functional characteristics [39]. Additionally, ionic liquids with low toxicity and good biocompatibility are increasingly applied in pharmaceutical and biotechnological fields [40].

Recent studies have also focused on ionic liquids with tailored structures. For instance, systems synthesized from N-methylpyrrolidone and phosphoric acid exhibit high polarity and strong solvating ability, whereas those based on morpholine and sulfuric acid are notable for their proton conductivity and catalytic activity. These properties make them promising candidates for various chemical processes, including polymerization.

In summary, the physicochemical properties of ionic liquids are intrinsically linked to their structure, and the ability to modulate these properties enables their effective application across a wide range of fields, particularly in polymer synthesis.

Polymerization in Ionic Liquids – Mechanism and Gel Effect

Free-radical polymerization carried out in ionic liquid media is an effective approach widely used for the synthesis of vinyl monomers. In such systems, polymerization behavior differs significantly from that observed in conventional organic solvents, primarily due to the ionic nature of the reaction medium [41]. Studies indicate that during the synthesis of polystyrene (PS), poly(methyl methacrylate) (PMMA), and their copolymers in ionic liquids, both the reaction rate and the molecular characteristics of the resulting polymers exhibit notable variations.

The radical polymerization mechanism generally consists of three fundamental stages:

1. chain initiation,
2. chain propagation,
3. chain termination.

However, the high polarity and structural organization of ionic liquids directly influence the kinetics of these steps. In particular, an increase in the propagation rate combined with a reduction in termination reactions often leads to the formation of polymers with higher molecular weights [42].

From a kinetic perspective, an increase in the propagation rate constant (k_p) and a viscosity-controlled limitation of the termination rate constant (k_t) are commonly observed in ionic liquid media [43]. Although increasing temperature accelerates the overall reaction, a higher ionic liquid content raises system viscosity, thereby reducing molecular diffusion. This, in turn, lowers the probability of radical–radical collisions and suppresses termination processes.

Under such conditions, a diffusion-controlled kinetic regime emerges, commonly referred to as the gel effect (Trommsdorff–Norrish effect). As the reaction progresses, system viscosity increases sharply, restricting macroradical mobility and hindering their recombination. Consequently, the termination rate decreases while chain growth

accelerates, resulting in a rapid increase in molecular weight [44].

The structural characteristics of ionic liquids—such as alkyl chain length of the cation, degree of symmetry, and coordinating ability of the anion—play a crucial role in polymerization behavior. Longer alkyl chains typically increase viscosity, thereby affecting both reaction kinetics and polymer molecular weight. The nature of the anion, in turn, governs the polarity and catalytic stability of the ionic medium [45].

Controlled radical polymerization techniques, particularly atom transfer radical polymerization (ATRP), can be effectively implemented in ionic liquids. The good solubility of catalysts in the ionic medium and the formation of homogeneous phases enable precise control over molecular weight and its distribution [46]. In some cases, the stability of catalytic complexes in ionic liquids allows polymerization to proceed at lower temperatures.

Another important mechanism, reversible addition–fragmentation chain transfer (RAFT) polymerization, exhibits “living” polymerization characteristics in ionic liquid media due to the balanced progression of chain transfer reactions. In this case, the concentration of active radicals remains low, and termination reactions are minimized, resulting in polymers with narrow molecular weight distributions [47].

In addition, direct polymerization of ionic liquid-based monomers is possible. In such systems, ionic liquid fragments become incorporated into the polymer backbone, leading to materials with intrinsic ionic conductivity and specialized functional properties [48]. Depending on monomer structure, linear, branched, or three-dimensional network polymers can be obtained.

Overall, radical polymerization in ionic liquid media is characterized by higher reaction rates, increased molecular weights, and distinct kinetic behavior compared to classical systems. These features are closely associated with the high polarity, viscosity, and radical stabilization capacity of ionic liquids, often accompanied by an enhanced gel effect.

Methyl methacrylate (MMA) and Its polymerization in ionic liquid media

Methyl methacrylate (MMA) is one of the most widely used vinyl monomers, particularly in the synthesis of optical materials, coating systems, and functional polymers. The radical polymerization of MMA in ionic liquid media exhibits behavior that differs significantly from conventional organic solvents, both in kinetic and structural terms. These differences are primarily associated with the high ionic strength, low vapor pressure, and structural stability of ionic liquids.

Research shows that the radical polymerization of MMA in ionic liquids (for example, imidazolium-based systems containing bis(trifluoromethanesulfonyl)imide or triflate anions) can be efficiently initiated using thermal initiators such as AIBN. In such systems, polymerization may be conducted either in molecular solvents such as DMF or directly in the ionic liquid phase, with high monomer conversion achieved in both cases [49].

A key feature of MMA polymerization in ionic liquid media is the strong influence of the reaction environment on both molecular weight and polymer yield. Specifically, PMMA obtained in ionic liquid systems often shows higher productivity and more stable structural characteristics. In addition, ionic liquids alter the solubility behavior of both the monomer and the growing polymer chains, thereby affecting the overall homogeneity of the reaction medium [50].

The polymerization proceeds via a classical free-radical chain mechanism. In the

initiation step, AIBN decomposes to generate active radical species, which then add to MMA molecules, initiating chain growth. In ionic liquid media, the propagation stage occurs under more stabilized conditions, as the ionic environment can partially stabilize radical centers. This, in turn, influences both the overall reaction rate and the lifetime of growing chains.

The type of ionic liquid has a pronounced effect on MMA polymerization outcomes. Systems containing anions such as NTf_2^- , BF_4^- , FAP^- , and triflate exhibit distinct polymerization behaviors. These differences are reflected in variations in molecular weight and thermal properties of the resulting PMMA. At the same time, the viscosity and structural organization of ionic liquids restrict termination reactions, facilitating the formation of higher-molecular-weight polymers [51].

Experimental results indicate that MMA polymerization in ionic liquids often exhibits behavior close to a “pseudo-living” character. This is evidenced by an almost linear relationship between molecular weight and conversion, suggesting a relatively controlled chain growth process [52].

Furthermore, the copolymerization of MMA with other vinyl monomers in ionic liquid media has been extensively investigated. In such systems, ionic liquids act not only as reaction media but also as factors influencing polymer microstructure. As a result, the thermal stability, mechanical properties, and ionic conductivity of the resulting copolymers can be significantly modified.

Effect of ionic liquids

Ionic liquids in radical polymerization systems do not function solely as solvents; they also modify the ionic character of the reaction medium and thereby influence both reaction kinetics and the mechanism of polymer chain formation. This effect becomes particularly pronounced in the polymerization of methacrylate-based ionic monomers.

Studies indicate that in ionic liquid media, stabilization of active radical centers together with altered solvation behavior of monomers at the microenvironment level leads to changes in both conversion degree and chain growth rate. Under these conditions, a higher degree of reaction control can be achieved compared to conventional organic solvents.

In particular, ionic liquids based on the bis(trifluoromethylsulfonyl)imide (NTf_2^-) anion, such as EMImTFSI-type systems, provide a more stable ionic environment during polymer chain formation. This can result in increased molecular weight and narrower molecular weight distributions in both homopolymerization and copolymerization of MMA [53].

Furthermore, the cationic and anionic structure of ionic liquids can influence the reactivity ratios of monomers, leading to changes in copolymer composition. In this sense, ionic liquids act not only as reaction media but also as elements of selectivity control and structural regulation [54].

In MMA copolymerization systems, it has been observed that ionic liquid media alter the mutual reactivity of monomers, thereby affecting the composition ratios of the resulting copolymers. This behavior has been particularly reported in imidazolium- and ammonium-based ionic liquid systems [55].

Overall, ionic liquids are considered highly functional reaction media for the polymerization of methacrylate-based monomers, capable of regulating both reaction kinetics and the structural characteristics of the final polymer products.

Copolymerization reactions

In homopolymers obtained from ionic liquid-based monomers, each repeating

structural unit contains an ionic liquid-derived fragment. During copolymerization of such monomers, ionic functional groups may be incorporated into the polymer chain in either a random or partially controlled manner, which directly influences the physicochemical properties of the final material [56,57].

According to literature data, copolymerization of 1-vinyl-3-butylimidazolium halides with N-vinyl-2-pyrrolidone has been carried out in methanol at 60 °C using AIBN as an initiator. The resulting copolymers exhibited a statistical distribution of ionic liquid fragments along the chain, and this structural feature was found to enhance their solubility in ionic liquid media, particularly in 1-butyl-3-methylimidazolium tetraborate systems. At the same time, these copolymers demonstrated potential as bifunctional stabilizers [58].

Copolymerization of ionic monomers based on methacrylate and styrene with other vinyl monomers has also been extensively investigated [59].

In a study by T. Endo and co-workers, radical copolymerization of 1-(2-methacryloyloxyethyl)-3-methylimidazolium bis (trifluoromethanesulfonyl) imide with methyl methacrylate (MMA) was performed in DMF using AIBN as an initiator. Ionic liquid EMImTFSI was also used as a reaction medium. The results indicated that the reactivity of the ionic monomer toward MMA was lower in both DMF and ionic liquid media [60].

In addition, copolymerization of HMA with [MEBIM][BF₄]-based ionic monomers led to the synthesis of statistical copolymers [61]. It was observed that increasing the HMA content decreases the glass transition temperature, while simultaneously enhancing ionic conductivity, which is attributed to the mobility of ionic functional groups within the polymer matrix.

Anion exchange processes have also been reported in similar systems. In particular, substitution of BF₄⁻ anions with LiTFSI in [MEBIM][BF₄] homopolymers resulted in changes in ionic conductivity and enabled the formation of new functional materials [62].

One of the important application areas of ionic liquid-based polymers is their use as gas sorbents. The high CO₂ solubility of imidazolium-based ionic liquids is of particular interest in this context [63]. In some systems, the mass fraction of dissolved CO₂ at room temperature can reach up to 7.4% [64].

Upon transition to the polymeric state, the CO₂ uptake capacity can increase further compared to ionic liquids, enabling their application in membrane and sorbent technologies [65]. This makes ionic liquid-based polymers promising materials for gas separation and storage applications.

At the same time, the synthesis of various ionic liquid monomers and their copolymerization behavior has been widely studied. For example, monomers such as [VBBIM][BF₄] and [BIMEMA][BF₄] have been synthesized and their radical polymerization and CO₂ adsorption properties have been evaluated [66].

Block copolymers in ionic liquid media have been prepared via atom transfer radical polymerization (ATRP) using a stepwise monomer addition strategy. In this approach, one monomer is first polymerized, and after reaching a certain conversion level, a second monomer is introduced into the system. This method enables the formation of block structures by preserving active chain ends [67].

In styrene–MMA systems, ionic liquid (BMIm)PF₆ has been used as the reaction medium, and radical polymerization was initiated using AIBN or other initiators. The results showed that both composition and molecular weight of the resulting copolymers

differ significantly from those obtained in conventional organic solvents [68].

In particular, the high polarity, relatively high viscosity, and good compatibility of the ionic liquid with MMA, combined with limited miscibility with polystyrene, were identified as key factors influencing reactivity ratios. As a result, noticeable changes in the reactivity parameters of MMA and styrene were observed [69].

Furthermore, copolymerization of styrene with N-substituted maleimides in ionic liquid media led to more ordered polymer structures. At the same time, the possibility of catalyst reuse improved the economic and environmental efficiency of the process [70].

The copolymerization of methyl methacrylate (MMA) with acrylic acid (AA) is a classical system proceeding via a radical mechanism. Such copolymers are widely used due to their ability to balance hydrophilic–hydrophobic properties and introduce functional groups into the polymer chain.

Typically, the copolymerization is carried out using radical initiators such as AIBN in solvents like DMF, dioxane, or ionic liquid-based media. During the reaction, MMA provides hydrophobic methacrylate units, while acrylic acid introduces ionic character through carboxyl (-COOH) groups. As a result, the obtained copolymers exhibit properties such as pH-responsive swelling, complex formation ability, and metal ion binding [71].

In ionic liquid media, the highly polar nature of the system enhances interactions between monomers, leading to a more homogeneous distribution along the copolymer chain. In addition, ionic liquids reduce side reactions and contribute to narrower molecular weight distributions [72].

CONCLUSION

The literature review indicates that ionic liquids play a significant role as efficient reaction media in polymerization processes. Their high polarity and ionic character influence the kinetics of radical polymerization by accelerating chain propagation and suppressing termination reactions, which ultimately leads to the formation of polymers with higher molecular weights.

During the polymerization of methyl methacrylate in ionic liquid media, an intensified gel effect and improved control over the reaction process are observed. At the same time, in copolymerization systems, ionic liquids affect both the structure and properties of the resulting polymers, enabling a certain degree of selective control over composition and architecture.

Overall, ionic liquids represent environmentally safer and reusable reaction media with considerable potential for wide application in modern polymer synthesis.

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