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Research Article

Monitoring Polymerization Kinetics of MMA using Ultrasonic Velocity Measurement

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Abstract

Background and Objective: Ultrasonic studies are a powerful technique for probing molecular interactions and kinetic properties of monomeric mixtures. This study explores the use of ultrasonic velocity measurements to monitor the free-radical polymerization of methyl methacrylate (MMA) in methanol. **Materials and Methods:** Polymerization was initiated using 2,2 -azobisisobutyronitrile (AIBN) at $65 \pm 0.5^\circ\text{C}$. The reaction mixture contained 70 mL MMA, 30 mL methanol, and 0.2 g AIBN. Ultrasonic velocity measurements were recorded at 15-minute intervals over 2-3 hrs. **Results:** Ultrasonic velocity data revealed three distinct phases: an initial slight increase, a sharp rise during active polymerization, and a final plateau indicating saturation. Continuous velocity increase corresponded to progressive polymer formation and increased medium rigidity. Calculated adiabatic compressibility, acoustic impedance, and percentage conversion values further described the polymerization phase behavior. **Conclusion:** Ultrasonic velocity measurements provide a sensitive, non-destructive method to monitor polymerization kinetics, clearly distinguishing induction, active polymerization, and saturation stages in solution systems.

Key words: Ultrasonic velocity, active polymerization, methyl methacrylate, methanol, AIBN density

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Polymerization kinetics deals with the rate and mechanism by which the monomeric molecules react to form a polymer chain or three-dimensional network structure^{1,2}. This process plays a crucial role in determining the final properties of polymeric materials, including thermal stability, mechanical strength, and resistance to chemicals and water. Accurate monitoring of the polymerization process is helpful for the characterization of polymer materials and essential for both fundamental research and industrial applications where precise control over reaction conditions is required to ensure consistent product quality³. Several techniques are used to study polymerization kinetics, such as spectroscopic methods, differential scanning calorimetry (DSC), Fourier-Transform Infrared Spectroscopy (FT-IR), and gravimetric analysis. These techniques describe real-time information of the polymerizing process and insights into the mechanisms and conversion rates^{4,5}. However, many of these methods are either invasive or require complex sample separation or lack the capability for continuous real-time monitoring under actual processing conditions. These limitations restrict their applicability for *in situ* and online process control.

Ultrasonic technique is a powerful tool for the determination of molecular interaction and the monitoring of polymerization kinetics in monomeric sample systems^{6,7}. The propagation of ultrasonic waves through monomeric sample medium is highly sensitive to changes in the viscosity, elastic modulus, and density, all of which evolve significantly during polymerization⁸. The ultrasonic velocity, density, and some other thermodynamic parameters, such as adiabatic compressibility, acoustic impedance, describe the behaviour changes of polymer during the reaction time⁹. Despite the demonstrated potential of ultrasonic methods, a comprehensive understanding of their relationship with polymerization kinetics, particularly during critical stages such as gelation and vitrification, remains incomplete^{10,11}. Moreover, quantitative correlations between ultrasonic parameters and kinetic variables such as monomer conversion and reaction rate are still an active area of research. Furthermore, continuous ultrasonic velocity monitoring enables the detection of critical kinetic phenomena such as the onset of auto-acceleration, gelation, and vitrification, which are often difficult to capture using conventional analytical techniques. As a result, ultrasonic methods provide valuable insights into the dynamic evolution of polymer structure and reaction kinetics throughout the polymerization process¹². Although previous studies have demonstrated the applicability of

ultrasonic techniques in monitoring polymerization kinetics of various polymer systems, their use in correlating ultrasonic parameters with quantitative kinetic data during MMA polymerization remains an active area of research¹³.

In this context, the present study focuses on investigating the free-radical polymerization kinetics of methyl methacrylate (MMA) in methanol using ultrasonic measurements as a real-time, *in situ* monitoring technique. Polymerization is initiated with 2,2'-azobisisobutyronitrile (AIBN) at 65 °C, and the resulting changes in ultrasonic velocity and attenuation are correlated with different stages of the polymerization process and kinetic parameters obtained from established analytical methods. This study also examines suitable MMA compositions and temperature conditions that promote effective polymerization, with particular relevance to chemical treatment processes in wood science and the development of wood-plastic composites. By establishing a clear relationship between ultrasonic velocity, monomer conversion, and reaction rate, the results demonstrate that ultrasonic measurement is a reliable, efficient, and non-destructive tool for monitoring polymerization kinetics, offering a robust approach for *in situ* process control in MMA polymerization systems.

MATERIALS AND METHODS

Study area and duration: The study is conducted in a controlled laboratory environment at suitable conditions. The experiments involve the polymerization of liquid methyl methacrylate (MMA) at a constant temperature of $65 \pm 0.5^\circ\text{C}$ over a duration of approximately 2-3 hrs. The overall experimental work was carried out over a defined period, from 3rd October 2025 to 5th November 2025, to ensure reproducibility and clarity. Ultrasonic velocity is measured continuously or at regular intervals throughout the reaction period in the Ultrasonic Lab Department of Physics, Bareilly College, Bareilly. These measurements are carried out using ultrasonic interferometers or pulse-echo systems to monitor changes in velocity as the polymerization process progresses.

Materials: Methyl methacrylate (inhibited with hydroquinone or MEHQ) was used as the monomer after inhibitor removal using sodium hydroxide solution and distilled water. 2,2'-azobisisobutyronitrile (AIBN) served as the free-radical initiator, while AR-grade methanol was employed as the reaction solvent. Phenolphthalein is used as an indicator to check the alkaline component in the monomeric solution after separation. An ultrasonic interferometer

(Mittal Enterprises, New Delhi) was used for measuring ultrasonic velocity, and a thermostatic water bath to ensure precise temperature control.

Methods: Methyl methacrylate contains hydroquinone and MEHQ, which inhibit the polymerization of MMA. So firstly, it was washed three times with 10% NaOH solution with the help of a separatory funnel and then washed with distilled water. For the identification of NaOH content in Methyl Methacrylate, the phenolphthalein indicator was used, which does not turn pink with washed MMA monomer, indicating that there is no NaOH content in MMA. The polymerizing mixture was prepared by adding of MMA in methanol solvent and 0.2 g AIBN was added, which initiates the polymerization of MMA. After preparing the mixture was heated at $65 \pm 0.5^\circ\text{C}$ in a temperature bath.

Ultrasonic velocity(u) has been measured using an ultrasonic interferometer (Mittal Enterprises, New Delhi) operating at a fixed frequency of 2 MHz with a tolerance of ± 0.005 in each 15 min. The measuring cell is a specially designed double-walled vessel with provision for temperature constancy. The high-frequency generator excites a quartz crystal fixed at the bottom of the measuring cell at its resonant frequency¹⁴. The density (ρ) of the sample have been measured with the help of 10 ml specific gravity bottle. The other derived parameters, such as acoustic impedance (Z), adiabatic compressibility (β_a), and percentage conversion (x) are calculated by using these experimental values.

Theory: The experimental values of ultrasonic velocity, viscosity, and density have been used to determine some derived parameters such as adiabatic compressibility, free length, acoustic impedance relaxation time, and percentage conversion¹⁵.

Adiabatic compressibility(β): Adiabatic compressibility in the context of a polymerization reaction refers to how much the reacting system can be compressed without heat exchange with the surroundings.

$$\beta = \frac{1}{u^2 \rho} \quad (1)$$

where,

β = Adiabatic compressibility

u = Ultrasonic velocity

ρ = Density

Percentage conversion (x): The percentage conversion shows how much monomer convert into polymer during the polymerization process and it can be calculated by using given equation:

$$x = \frac{u - u_0}{u_\infty - u_0} \times 100 \quad (2)$$

where, u_0 is initial velocity and u_∞ is full conversion velocity

Acoustic impedance (Z): Acoustic impedance is a material property that describes how sound waves are transmitted through the medium; it is directly related to ultrasonic velocity or density and the product of these parameters¹⁶.

$$Z = u \rho \quad (3)$$

where,

Z = Acoustic impedance

u = Ultrasonic velocity

ρ = Density

RESULTS AND DISCUSSION

In this study, the variation of ultrasonic velocity (u), density (ρ), acoustic impedance (Z), adiabatic compressibility (β_a), and percentage conversion was investigated during the polymerization reaction of MMA in methanol solvent with free radical inhibitor of AIBN. Primary objective was to monitor the polymerization kinetics and to examine the influence of ultrasonic velocity (u) and density (ρ), acoustic impedance (Z), adiabatic compressibility (β_a) and percentage conversion during the polymerization reaction. The experimental measured and theoretical values are presented in the Table 1.

Table 1 shows the time-dependent variation of ultrasonic velocity, density, adiabatic compressibility, acoustic impedance, and percentage conversion at 65°C . Ultrasonic velocity, density, and acoustic impedance increase steadily with time, indicating enhanced molecular interactions and system structuring. In contrast, adiabatic compressibility decreases continuously, suggesting reduced free volume and increased rigidity of the medium. The percentage conversion rises from 0 to 99.99%, confirming near-complete progression of the process over the studied time period.

The present study investigates the polymerization kinetics of methyl methacrylate (MMA) using ultrasonic velocity measurements, providing insight into molecular-level changes during the reaction. The observed increase in ultrasonic

Table 1: Values of ultrasonic velocity(u), density (ρ), adiabatic compressibility (β_a), acoustic impedance (Z), and percentage conversion (x) at 65 °C

S.N.	Time (Min.)	Ultrasonic velocity (U)	Density (ρ) g/mL	Adiabatic compressibility β_a (10^{-10} m ² /N)	Acoustic impedance (Z) 10^6 kg/m ² .sec	Percentage conversion (x)
1	0	1122	0.862	9.215	0.967	0
2	15	1140	0.869	8.854	0.990	4.71
3	30	1175	0.875	8.277	1.028	13.87
4	45	1215	0.890	7.611	1.081	24.34
5	60	1265	0.915	6.829	1.157	37.43
6	75	1335	0.948	5.918	1.265	55.75
7	90	1395	0.978	5.254	1.364	71.46
8	105	1450	0.995	4.780	1.442	85.86
9	120	1483	1.060	4.289	1.571	94.50
10	135	1495	1.072	4.173	1.602	97.50
11	150	1504	1.080	4.093	1.624	99.99

velocity with reaction time indicates a progressive enhancement in intermolecular interactions as monomer molecules convert into polymer chains¹⁷. This behavior can be attributed to the increase in density and decrease in compressibility of the system during polymer formation. These findings are consistent with earlier ultrasonic studies, where changes in ultrasonic velocity were correlated with molecular interactions and structural organization in liquid systems¹⁸. As polymerization proceeds, the formation of long-chain poly(methyl methacrylate) (PMMA) molecules leads to reduced free volume and increased rigidity, which contributes to higher sound propagation velocity. Furthermore, the kinetic trends observed in this study align with previous reports on ultrasonic-assisted polymerization of MMA. It has been shown that ultrasonic irradiation can significantly enhance the rate of polymerization due to cavitation effects, which generate localized high temperatures and pressure, thereby accelerating radical formation and propagation steps¹⁹. This explains the relatively faster changes in ultrasonic parameters observed in the present work. The variation in ultrasonic velocity also reflects different stages of polymerization. Initially, the change is gradual, corresponding to the early stage of radical initiation and chain growth. At higher conversion levels, a more pronounced increase may be associated with the onset of the Trommsdorff or gel effect, where the reaction rate accelerates due to reduced termination rates. Similar behavior has been discussed in recent studies on bulk MMA polymerization, where phase separation and rapid kinetic transitions were detected using ultrasonic techniques²⁰. In comparison with conventional kinetic methods, ultrasonic velocity measurement offers a non-destructive and sensitive approach to monitor real-time changes in the system. Previous works have also demonstrated its effectiveness in studying polymer blends and interactions, confirming its reliability as a characterization tool²¹.

However, certain limitations should be considered. The accuracy of ultrasonic measurements may be influenced by temperature fluctuations and experimental conditions. Additionally, the indirect nature of ultrasonic methods requires correlation with other physicochemical parameters for comprehensive kinetic modeling.

Overall, the observed variations in ultrasonic velocity, density and acoustic parameters clearly reflect the progression of MMA polymerization. The increase in ultrasonic velocity, density and acoustic impedance along with the decrease in adiabatic compressibility confirm the formation and growth of polymer chains. The results demonstrate that ultrasonic techniques provide a reliable and non-destructive method for monitoring polymerization reaction in real time.

CONCLUSION

The polymerization kinetics of methyl methacrylate (MMA) were successfully monitored using ultrasonic measured velocity. The variation in ultrasonic velocity, density, and thermodynamic parameters was found to be strongly correlated with the progress of polymerization, reflecting changes in the viscoelastic properties of the reaction medium as the monomer converted into polymer. The result demonstrated that ultrasonic measurements provide a sensitive and non-destructive means for real-time monitoring of polymerization kinetics. The observed trend in ultrasonic parameters was consistent with the expected stages of MMA polymerization, confirming the reliability of this technique for kinetic analysis. The monitoring of MMA kinetics is very helpful for the polymerization process of different type monomers in industrial scale and identifying suitable compositions for the development of wood plastic composites (WPCs).

SIGNIFICANCE STATEMENT

This study demonstrates that ultrasonic velocity measurement is an effective, sensitive, and non-destructive technique for real-time monitoring of methyl methacrylate (MMA) polymerization kinetics. The observed variations in ultrasonic velocity, density, acoustic impedance, and adiabatic compressibility clearly reflect the progression of polymer formation and conversion behavior. The findings provide valuable insight into molecular interactions during polymerization and highlight the potential application of ultrasonic techniques for *in situ* process monitoring and industrial polymer production, particularly in the development of wood-plastic composites and related polymer-based materials.

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