

Synthesis and Characterization of Poly Styrene-Co-Poly 2-Hydroxyethylmethacrylate (HEMA) Copolymer and an Investigation of Free-Radical Copolymerization Propagation Kinetics by Solvent Effects

Anaif M. Alhewaitey^{1,2*}, Ishrat Khan¹, Naif M. Alhawiti³

¹Department of Chemistry, Clark Atlanta University, Atlanta, USA

²Department of Chemistry, University of Tabuk, Tabuk, Saudi Arabia

³CAHFS, University of California Davis, Davis, California

Email: *dr.anaif369@gmail.com

How to cite this paper: Alhewaitey, A.M., Khan, I. and Alhawiti, N.M. (2024) Synthesis and Characterization of Poly Styrene-Co-Poly 2-Hydroxyethylmethacrylate (HEMA) Copolymer and an Investigation of Free-Radical Copolymerization Propagation Kinetics by Solvent Effects. *Open Journal of Polymer Chemistry*, **14**, 63-93.

<https://doi.org/10.4236/ojpchem.2024.141004>

Received: January 13, 2024

Accepted: February 26, 2024

Published: February 29, 2024

Copyright © 2024 by author(s) and Scientific Research Publishing Inc. This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

A series of homo and copolymers of styrene (ST) and 2-hydroxyethyl methacrylate (HEMA) in three different media (bulk, tetrahydrofuran, and benzene) have been investigated by free radical polymerization method. The samples obtained from the synthesis were characterized by Fourier Transform-Infrared spectroscopy (FT-IR), proton nuclear magnetic resonance spectroscopy (¹H NMR), atomic force microscopy (AFM), and differential scanning calorimetry (DSC). The results show that the synthesis of the polymers is more feasible under neat conditions rather than solvent directed reaction. Moreover, the DSC data shows that the polystyrene obtained is amorphous in nature and therefore displayed only a glass transition signal rather than crystallization and melting peaks. In addition, this study indicates that homopolymerization of styrene via free radical polymerization tends to be preferable in less polar solvents like THF than in non-polar solvents like benzene. Benzene might destabilize the formation of the reactive radicals leading to the formation of the products. In summary, the homopolymerization of styrene is more feasible than the homopolymerization 2-hydroxyethyl methacrylate under the experimental setup used. Styrene is more reactive than 2-hydroxyethyl methacrylate than free radical polymerization reaction due in part of the generation of the benzylic radical intermediate which is more stable leading to the formation of products than alkyl radical which are less stable. Furthermore, polymerization of styrene under neat conditions is preferable in solvent-assisted environments. The choice of solvent for the synthesis

of these polymers is crucial and therefore the selection of solvent that leads to the formation of a more stable reaction intermediate is more favorable. It is worth noting that the structure of the proposed copolymer consists of a highly polar and hydrophilic monomer, 2-hydroxyethyl methacrylate and a highly non-polar and hydrophobic monomer, styrene. These functionalities constitute an amphiphilic copolymer with diverse characteristics. A plausible explanation underlying our observations is that the reaction conditions employed in the synthesis of these copolymers might not be the right route required under free radical polymerization.

Keywords

2-Hydroxyethyl Methacrylate, Polymerization

1. Introduction

Among the many areas of chemistry, polymer science is a comparatively new field. The research dedicated to polymer nanocomposites has been intensely studied in the last ten years. Of all of the potential goals of materials science research, one of the ultimate objectives is the improvement of multi-functional materials. For example, Hybrid materials, which are materials consolidating a polymeric blend with other (natural, inorganic, or organic) material constituents play a significant role in future progressions in applications such as electronics, transportation, and bioengineering [1] [2]. These advances will rely upon polymer science to create materials that combine light weight and high mechanical stability with novel optical, electronic or thermal transport properties.

Polymer science, often known as macromolecular science, is a branch of materials science that studies polymers, particularly synthetic polymers like plastics and elastomers. Researchers from a variety of fields, including chemistry, physics, and engineering, work on the topic of polymer science. Polymers are modern materials that may be found in practically every item we use in our daily lives. Polymers' relevance has been emphasized in recent years due to their applications in several fields of research, technology, and industry, ranging from basic usage to biopolymers and medicinal polymers. Polymers, a word we hear a lot, are extremely important and one cannot fathom existence without them. Polymers are a wide class of materials that are made up of many small molecules called monomers that are bonded together to form lengthy chains and are utilized in a variety of everyday products and goods [1].

People have been using polymers in their lives for a long time, but they did not fully understand them until World War II. For the fabrication of the article required for civilized life, there were relatively few resources accessible. Steel, glass, wood, stone, brick, and concrete were utilized for the majority of the building, while cotton, wood, jute, and a few other agricultural items were employed to make apparel and fabrics.

The tremendous rise in demand for manufactured goods has resulted in the development of novel materials. Polymers are these new materials, and their impact on our current way of life is almost unfathomable. Clothing composed of synthetic fibers, polyethylene cups, fiberglass, nylon bearings, plastic bags, polymer-based paints, epoxy glue, polyurethane foam cushions, silicone heart valves, and Teflon-coated cookware are all examples of polymer-based products [2].

The word “polymer,” or “macromolecule,” comes from the Greek word poly, which means “many,” and meros, which means “parts.” The polymer molecule has a high molecular weight (between 10,000 and 1,000,000 g/mol) and is made up of many structural units that are usually joined by covalent connections [1] [3].

Polymers are made by combining monomers in a chemical process. Monomers can create polymer chains by reacting with another molecule of the same kind or another type under the right conditions. Natural polymers have resulted from this process in nature, but synthetic polymers are man-made.

Since the beginning of time, polymers have been present in the natural world (e.g., cellulose, starch, and natural rubber). Since the middle of the nineteenth century, man-made polymeric materials have been investigated. The polymer sector has grown quickly in recent years, and it now outnumbers copper, steel, aluminum, and a few other industries combined.

Both natural and synthetic polymers play an important role in human comfort and convenience, and are responsible for life itself, as well as medication, nourishment, communication, transportation, irrigation, containers, clothes, historical recording, structures, and roadways. Indeed, modern society would be difficult to comprehend without synthetic and natural polymers. Science has a significant role in giving solutions to essential problems such as food, clean and abundant water, air, energy, and health in our ever-increasing modern environment. Polymer knowledge and related texts provide both information and insights for a deeper understanding of polymers in our lives. Understanding polymers is aided by the information obtained from basic science classes. This data covers scientific notions that are factual, theoretical, and practical. It is useful for individuals who just want to be well educated, as well as those who wish to pursue medicine, engineering, physics, chemistry, biomedical sciences, law, and business, among other fields [2] [3].

Coatings, elastomers, adhesives, mixes, plastics, fibers, caulks, ceramics, and composites could all benefit from synthetic and natural polymers in the form of inorganic and organic polymers. The basic concepts that apply to one polymer category, as well as a few simple fundamental laws, are applicable to all other polymer categories. These fundamentals are woven into the polymer texts’ fabric [4].

Nearly all material scientists, more than half of all chemists and chemical engineers, a considerable number of physicists, textile technologists, mechanical engineers, pharmacists, and other scientific groups are participating in polymer research and development initiatives, which is not surprising [5]. Furthermore,

polymers and polymer chemistry play a vital role in the development of their new areas in pharmacy, biomedicine, molecular biology, biochemistry, and biophysics. It's easy to see why big molecule research is one of the most popular and fastest-growing topics of science. As a result, polymer appears to be a specialized multidisciplinary or branch of chemistry. Instead, it is a specialized, broad, and distinct subject that can encompass some aspects of chemistry as well as a variety of other scientific fields. When research organizations trained in one specialized discipline turn their attention to a related field, the domains of science have always become quite busy. This has always been true in polymer research and will continue to be so in the future. The application of ideas, chemical knowledge, and procedures to complicated materials and macromolecules is a necessity in polymers.

This is a crucial undertaking that necessitates the most advanced chemistry has to offer [6]. Perhaps more than any other subject of study, polymer chemistry bridges and slashes the traditional boundaries of chemistry, biology, physics, materials, engineering, pharmacy, and even medicine. In addition, a newbie to polymer science must have the ability to combine the extensive information from all of the aforementioned domains. As a result, this editorial was produced to demonstrate the critical and memorable functions that polymers play in human life [7] [8].

There are numerous polymerization processes and methods; one of the most prominent is free-radical polymerization (FRP), which is a polymerization method in which a polymer is formed by adding free-radical building blocks one at a time. Free radicals can be produced through a variety of methods, most of which require independent initiator molecules. The initiating free radical adds (nonradical) monomer units to the polymer chain once it is generated. Free-radical polymerization is a common synthesis method for a wide range of polymers and composite materials. Because free-radical chemical interactions are relatively non-specific; this is one of the most versatile forms of polymerization accessible, allowing for simple reactions between polymeric free-radical chain ends and other chemicals or substrates. Free-radical polymerization produced 40 billion pounds of the 110 billion pounds of polymers produced in the United States in 2001 [9].

Poly 2-hydroxyethylmethacrylate (pHEMA) is a linear polymer composed of very active hydroxyester units distributed uniformly on the polymeric chain. pHEMA is a biocompatible hydrophilic methacrylate polymer. In the dry state, the material is hard and glassy, but in polar media, the pendant hydroxyethyl group can extend outward, and the material becomes soft and flexible. pHEMA is soluble in common organic polar solvents such as lower alcohols; however, the polymer does not dissolve in water without a co-solvent. Instead, it will absorb water and swell.

This polymer is considered one of the most important hydrophilic polymers, biodegradable, and non-toxic materials. It forms an inert, water-stable, non-degradable hydrogel with high transparency. The physical properties of pHEMA

can be tuned by varying cross-linking density, incorporating different chemistries through copolymerization, and introducing mesoscopic pores [10]. **Figure 1** shows the chemical structures of Poly (2-hydroxyethyl methacrylate), and **Figure 2** shows the 2-hydroxyethyl methacrylate (HEMA) monomer.

Polystyrene is one of the most well-known polymers because it possesses a number of distinct characteristics, such as hardness and transparency, and because it is relatively inexpensive to manufacture. While on the other hand, it does have several shortcomings that limit the scope of its applicability [11] [12]. In order to fine-tune both the chemical and physical properties of polystyrene, which are critical for the vast range of applications for polymers [13] [14]. **Figure 3** shows the chemical structures of Polystyrene. And **Figure 4** shows polystyrene foam sheets.

Poly(2-hydroxyethyl methacrylate) : PHEMA

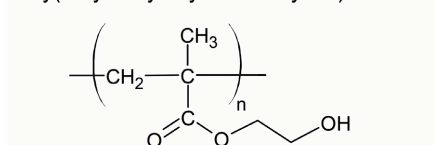


Figure 1. The chemical structures of Poly (2-hydroxyethyl methacrylate).



Figure 2. The 2-hydroxyethyl methacrylate (HEMA) monomer.

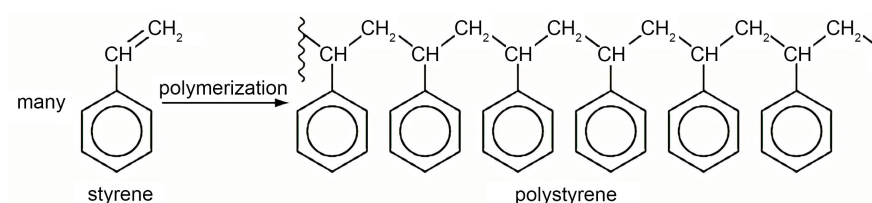


Figure 3. The chemical structures of polystyrene.



Figure 4. Polystyrene foam sheets.

2. Objective of the Study

Poly styrene-CO-Poly 2-Hydroxyethylmethacrylate (HEMA) COPOLYMER in three different media (bulk, tetrahydrofuran, and benzene) by the free radical polymerization method was used. This project is broken down into three parts. In the first part, The synthesis of the various homopolymers, Poly styrene (PS) and Poly 2-Hydroxyethylmethacrylate (PHEMA) For 6 hours and for 24 hours in three different media (bulk, tetrahydrofuran, and benzene) by free radical polymerization method. In the second part, Copolymer Poly (Styrene)-Co-Poly (2-hydroxyethyl methacrylate) was prepared by Free Radical Polymerization (FRPs). PS-Co-PHEMA for 6 hours and for 24 hours in three different media (bulk, tetrahydrofuran, and benzene) was investigated. The third part was to characterize the functionalized polymer using FT-IR, ¹H NMR, to confirm the structure of the product. The morphology of the surface has been examined by AFM instrument. In addition, the thermal stability was studied by DSC instruments.

3. Materials and Method

3.1. Polymerization

Materials

The chemicals were utilized exactly as they were received, with no further purification Calcium hydride (CaH₂) (40 mesh, 95%), sodium metal, benzophenone, The initiator Azobisisobutyronitrile (AIBN), Benzene (Aldrich, 99%, A.C.S. Reagent were purchased from Sigma Aldrich and used as received. Styrene (S), tetrahydrofuran (THF) and 2-hydroxyethyl methacrylate (HEMA, 99%, Aldrich), were purchased from Sigma-Aldrich Company as well and were purified before used. The procedures of purification are described below in detail. Methanol (MeOH) (99%, ACS) and Hexane were purchased from Fisher Chemical Company.

3.2. Materials Purification

Solvent

In a 1000 mL round-bottomed flask, tetrahydrofuran (THF) was purified by refluxing over sodium metal (**Figure 5**) in the presence of benzophenone. The THF turned a deep purple color, indicating the absence of oxygen and moisture in the solvent. Following are the purifying techniques.

All of the glassware used in this reaction was oven-dried, and the work space was completely dry. Pre-drying of tetrahydrofuran (THF) was done overnight using potassium hydroxide (KOH) or molecular sieves (3 or 4). The sodium was chopped into small pieces to fit in the flask's neck; smaller pieces also provide more surface area.

The boiling flask was filled with sodium particles weighing about 5 g, and the flask was sealed. To the boiling flask and restopper, 30 g of benzophenone was added to 2 liters of THF. The solution/mixture was refluxed under nitrogen until benzophenone ketyl produced a rich blue color (Na[Ph₂O]).

3.3. Monomers

For two days, styrene was swirled over finely powdered calcium hydride. Styrene was frozen, degassed, and thawed three times on the vacuum line before being distilled into ampoules with break-seals. The ampoules were then removed from the vacuum line and sealed with a hand torch before being stored in the refrigerator until they were needed (**Figure 6**).

Monomer 2-hydroxyethyl methacrylate (HEMA, 99%, Aldrich) was purified by washing an aqueous solution (50 vol % HEMA) of monomer with 150 ml of water then add hexanes (450 mL), salting the monomer out of the aqueous phase by addition of NaCl, drying over MgSO₄, and distilling under reduced pressure (**Figure 7**).



Figure 5. Purification of THF.



Figure 6. Purification of styrene.

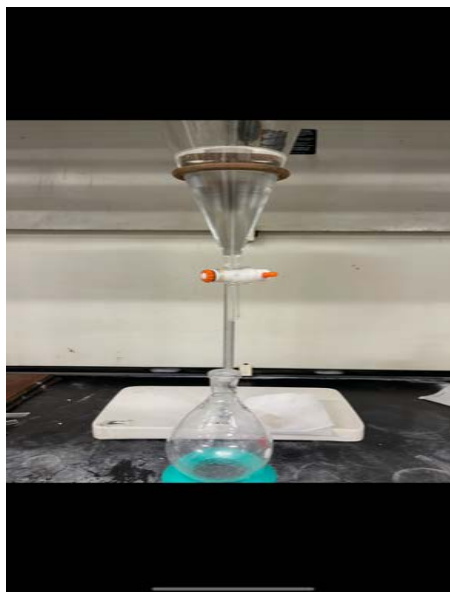


Figure 7. Purification of 2-hydroxyethyl methacrylate (HEMA).

The Azobisisobutyronitrile (AIBN) was purified by recrystallization in methanol. Approximately 5 g of AIBN were weighed on an analytical balance and transferred to an Erlenmeyer flask with cover, along with about 200 ml of methanol. The mixture was stirred, using a magnetic stirrer for 1 hour at room temperature. Then, filtration was performed using filter paper. The undissolved part was discarded while the filtrate was placed in the refrigerator for 24 hours. AIBN was recrystallized dried in the desiccator reduced and, after drying, was transferred to a pressure bottle with lid and stored in the freezer until use.

3.4. Procedures

Homopolymerization of Styrene (PS) for 24 hours (**Table 1**).

The styrene monomer was polymerized by the Free-radical polymerizations (FRPs) method.

Then all the samples were transferred to an oil bath maintained at 60°C and stirred for 24 hours. The polymer was obtained by precipitation of the reaction mixture into 500 ml Methanol drop by drop, vacuum filtered, and then dried in a vacuum oven at room temperature (**Figures 8-10**).

3.4.1. Homopolymerization of 2-Hydroxyethyl Methacrylate (P HEMA) for 24 Hours (**Table 2**)

The 2-hydroxyethyl methacrylate (HEMA) monomer was polymerized by the Free-radical polymerizations (FRPs) method.

Then all the samples were transferred to an oil bath maintained at 60°C and stirred for 24 hours, the polymer was obtained by precipitation of the reaction mixture into 500 ml Hexane drop by drop, vacuum filtered, and then dried in a vacuum oven at room temperature (**Figure 11** and **Figure 12**).



Figure 8. Homopolymerization of styrene in different solvents.



Figure 9. Homopolymerization of styrene in silicon oil bath at 60°C for 24 hours.

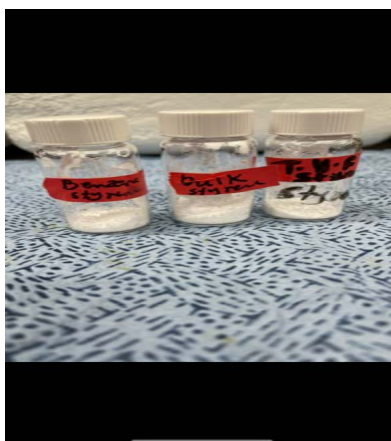


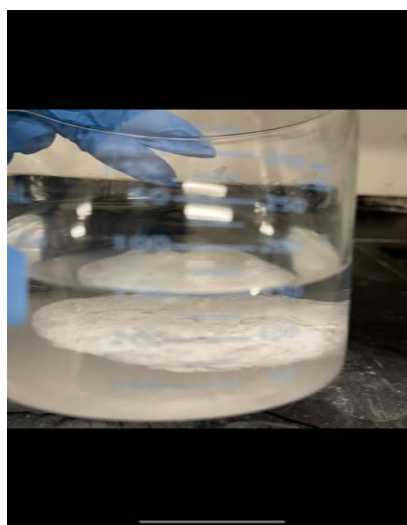
Figure 10. Homopolymerization of styrene after dried in a vacuum oven 24 hours.

Table 1. The experimental details of homopolymerization of styrene (PS) for 24 hours.

| Solvent | AIPN | Styrene |
|---------------|---------|---------|
| Bulk | 0.033 g | 1.02 g |
| T.H.F 10 ml | 0.033 g | 1.02 g |
| Benzene 10 ml | 0.033 g | 1.02 g |

Table 2. The experimental details of homopolymerization of HEMA for 24 hours.

| Solvent | AIPN | Hema |
|---------------|---------|--------|
| Bulk | 0.033 g | 1.02 g |
| T.H.F 10 ml | 0.033 g | 1.02 g |
| Benzene 10 ml | 0.033 g | 1.02 g |

**Figure 11.** Homopolymerization of HEMA after 24 hours.**Figure 12.** Homopolymerization of HEMA after dried in a vacuum oven 24 hours.

3.4.2. Synthesis of the Copolymer Poly (Styrene)-Co-Poly (2-Hydroxyethyl Methacrylate) by Free Radical Polymerization (FRPs). PS-Co-PHEMA for 24 Hours (Table 3)

All the samples were transferred to an oil bath maintained at 60°C and stirred for 24 hours. The polymer was obtained by precipitation of the reaction mixture into 500 ml Hexane drop by drop, vacuum filtered, and then dried in a vacuum oven at room temperature (Figure 13).

3.4.3. Homopolymerization of Styrene (PS) during 6 Hours (Table 4)

The styrene monomer was polymerized by the Free-radical polymerizations (FRPs) method.

Then all the samples were transferred to an oil bath maintained at 60°C and stirred for 6 hours, The polymer was obtained by precipitation of the reaction mixture into 500 ml Methanol drop by drop each one hour gradually 10 ml from the reaction mixture with T.H.F and Benzene while the Bulk 0.33 ml, vacuum filtered, and then dried in a vacuum oven at room temperature.

Table 3. The experimental details of synthesis of the PS-Co-PHEMA for 24 hours.

| Solvent | AIPN | Styrene | Hema |
|---------------|---------|---------|--------|
| Bulk | 0.033 g | 1.02 g | 1.02 g |
| T.H.F 10 ml | 0.033 g | 1.02 g | 1.02 g |
| Benzene 10 ml | 0.033 g | 1.02 g | 1.02 g |

Table 4. The experimental details of homopolymerization of styrene (PS) during 6 hours.

| Solvent | AIPN | Styrene |
|---------------|--------|---------|
| Bulk | 0.05 g | 2 g |
| T.H.F 60 ml | 0.05 g | 2 g |
| Benzene 60 ml | 0.05 g | 2 g |

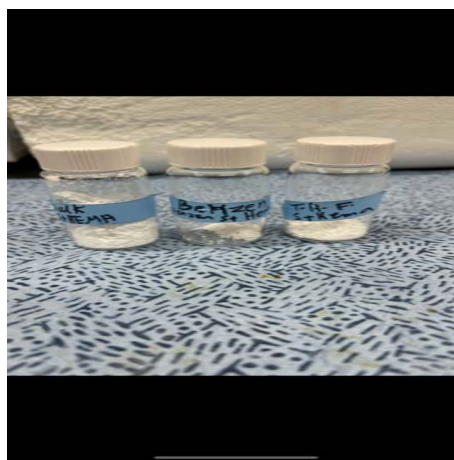


Figure 13. Synthesis of the copolymer PS-Co-PHEMA after dried in a vacuum oven 24 hours.

3.4.4. Homopolymerization of 2-Hydroxyethyl Methacrylate (P HEMA) during 6 Hours

The 2-hydroxyethyl methacrylate (HEMA) monomer was polymerized by the Free-radical polymerizations (FRPs) method. **Table 5** shows the experimental details of Homopolymerization of HEMA during 6 hours.

Then all the samples were transferred to an oil bath maintained at 60°C and stirred for 6 hours, The polymer was obtained by precipitation of the reaction mixture into 500 ml Hexane drop by drop each one hour gradually 10 ml from the reaction mixture with T.H.F and Benzene while the Bulk 0.66 ml, vacuum filtered, and then dried in a vacuum oven at room temperature.

3.4.5. Synthesis of the Copolymer Poly (Styrene)-Co-Poly (2-Hydroxyethyl Methacrylate) by Free Radical Polymerization (FRPs). PS-Co-PHEMA during 6 Hours (Table 6)

Then all the samples were transferred to an oil bath maintained at 60°C and stirred for 6 hours, The polymer was obtained by precipitation of the reaction mixture into 500 ml Methanol drop by drop each one hour gradually 10 ml from the reaction mixture with T.H.F and Benzene while the Bulk 1 ml, vacuum filtered, and then dried in a vacuum oven at room temperature (**Figures 14-19**).

Table 5. The experimental details of homopolymerization of HEMA during 6 hours.

| Solvent | AIPN | HEMA |
|---------------|--------|------|
| Bulk | 0.05 g | 4 g |
| T.H.F 60 ml | 0.05 g | 4 g |
| Benzene 60 ml | 0.05 g | 4 g |

Table 6. The experimental details of synthesis of the PS-Co-PHEMA during 6 hours.

| Solvent | AIPN | Styrene | Hema |
|---------------|--------|---------|------|
| Bulk | 0.05 g | 2 g | 4 g |
| T.H.F 60 ml | 0.05 g | 2 g | 4 g |
| Benzene 60 ml | 0.05 g | 2 g | 4 g |



Figure 14. Synthesis of the PS-Co-PHEMA after 1 hour.



Figure 15. Synthesis of the PS-Co-PHEMA after 2 hours.



Figure 16. Synthesis of the PS-Co-PHEMA after 3 hours.



Figure 17. Synthesis of the PS-Co-PHEMA after 4 hours.



Figure 18. Synthesis of the PS-Co-PHEMA after 5 hours.



Figure 19. Synthesis of the PS-Co-PHEMA after 6 hours.

3.5. Characterization

3.5.1. Nuclear Magnetic Resonance Spectroscopy

Proton and carbon NMR (^1H NMR, ^{13}C NMR) spectra were obtained in solution states at room temperature using deuterated chloroform (CDCl_3) as the solvent on a Bruker AVANCE III 500 MHz spectrometer and a Bruker 400 MHz spectrometer.

3.5.2. Fourier Transform Infrared (FT-IR) Spectroscopy

To confirm the functional group of the samples, FT-IR spectra were obtained on a Perkin-Elmer Spectrum 65 FT-IR spectrometer. The potassium bromide (KBr) ID card approach was used to manufacture some samples. On a KBr plate, the other samples were recorded.

3.5.3. Atomic Force Microscopy (AFM)

A Bruker Dimension Fast Scan Atomic Force Microscope was used to obtain AFM height images of samples created by drop-casting in various solvents on a silicon wafer and then air-drying them.

3.5.4. Differential Scanning Calorimetry (DSC)

The samples were thermally analyzed on a TA Instruments DSC Q 2000 under nitrogen environment at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ under nitrogen atmosphere. All samples were collected in T zero hermetic aluminum sample pans by weighing 5 - 15 mg and hermetically sealing them. The second heating cycle's thermal transition temperatures were reported.

4. Result and Discussion

4.1. Polymerization

Synthesis of Polystyrene: The synthesis of the various homopolymers were done by first reacting styrene in the presence of AIBN as initiator at an elevated temperature of 60°C neat as shown in Equation 1. The reaction was monitored for an extended period of about 6 h and the results obtained are depicted in **Table 7**. As seen from **Table 7**, within an hour homopolymer of polystyrene was formed and this continued until 3 h where a solid polymer was isolated.



Equation 1 Location

After successful synthesis of the homopolymer of polystyrene without the use of solvents, we proceeded to synthesize polystyrene in the benzene and tetrahydrofuran (THF) as shown in Equations 2 & 3. The same reaction conditions employed in the neat reaction were used for the reactions of the proposed homopolymer polystyrene.

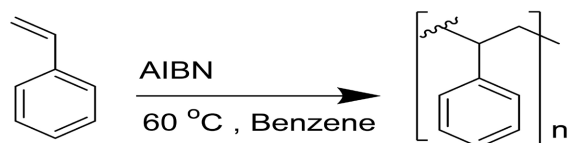


Equation 2 Location

As observed in **Table 7**, when THF was used as solvent for the homopolymerisation of reaction of styrene, no detectable homopolymer of styrene was observed within a period of 3 h. However, within 4 h a traceable amount of the polymer was obtained until the reaction was stop within 6 h. As depicted in **Table 7**, when the solvent was changed to benzene, no observable reaction was observed over the stipulated time investigated.

Table 7. Homopolymerization of Styrene (PS) during 6 hours.

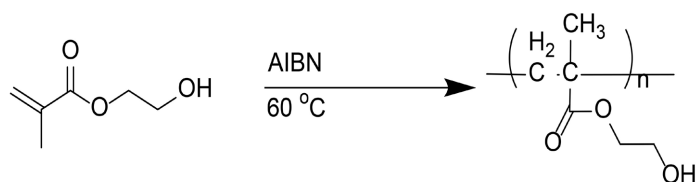
| Time | 1 hour | 2 hours | 3 hours | 4 hours | 5 hours | 6 hours |
|---------------|------------|------------|---------------|---|--------------|--------------|
| Bulk 0.33 ml | Polymer | Polymer | Solid polymer | - | - | - |
| T.H.F 10 ml | No polymer | No polymer | No polymer | A little amount of copolymer but can't collect it | Copolymer | Copolymer |
| Benzene 10 ml | No polymer | No polymer | No polymer | No copolymer | No copolymer | No copolymer |

**Equation 3 Location**

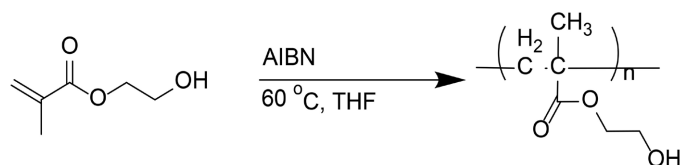
This data suggests that the use solvent has pronounced effect on the formation of titled homopolymer. As described above, without the use of solvent, the formation of homopolymer was achieved quickly and quantitative amount was obtained. However, when the reaction was carried out in less polar solvent (THF) and pure non polar solvent the yield of the product decreased with respect to THF and no recordable product for benzene. Since the reaction is presumed to occur *via* free polymerization, it could be that the generation of the intermediate radicals that leads to the formation of the products tends to be more stable under neat conditions rather than under solvent driven conditions. In addition, the results also indicate that, homopolymerization of styrene via free radical polymerization tends to be preferable in less polar solvent like THF than in non-polar solvent like benzene. Benzene might destabilize the formation of the reactive radicals leading to the formation of the products.

4.2. Homopolymerization of 2-Hydroxyethyl Methacrylate (P HEMA)

The synthesis and analysis of the homopolymerization of styrene prompted us to examine the behavior of 2-hydroxyethyl methacrylate (HEMA) under the same experimental setup. As observed in the structure of the 2-hydroxyethyl methacrylate, there is hydroxyl group (primary alcohol functionality), ester functional group and an alkene functional group. These diverse groups have pronounced effects on the reactivity of the monomer compared to the reactivity of the styrene where the functional groups were only an alkene substituted on an arene.

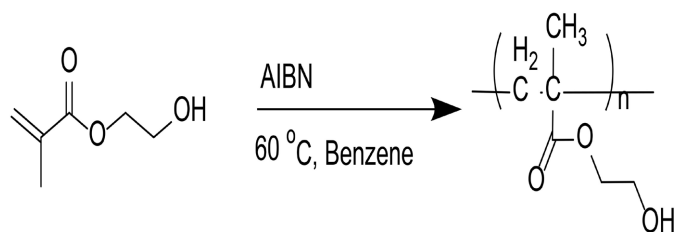
**Equation 4 Location**

For better comparison and to derive conclusive remarks, the same reaction conditions employed in the synthesis of the polystyrene were carried out for the synthesis of poly(2-hydroxyethyl methacrylate) (PHEMA). As seen in Equations 4-6, the reaction was first performed without the use of solvent and the synthesis was monitored for 6 h as described above.



Equation 5 Location

Likewise, THF was used and benzene as shown in Equations 4 and 6 respectively. All these reactions were monitored over a period of 6 h. The results obtained are shown in **Table 8**. As could be seen from **Table 8**, irrespective of the reaction's conditions employed in the proposed synthesis of the polymer no observable products were obtained within the time frame allotted.



Equation 6 Location

The underlying reason for not obtaining any polymer based on this reaction conditions may be that the 2-hydroxyethyl methacrylate might not be a good substrate for free radical polymerization. In addition, the generation of alkyl radicals under these reaction conditions might be stable and reactive enough to lead to the formation of product in comparison to the benzylic radicals generated in the polymerization of styrene. More so, the presence of other functional groups (alcohol and ester) could interfere with the generation and stabilization of the required radicals needed for the formation of the final products.

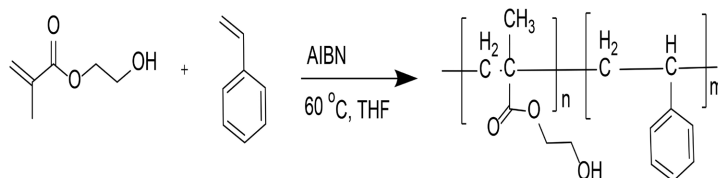
In summary, homopolymerization of styrene is more feasible than homopolymerization of 2-hydroxyethyl methacrylate under the experimental setup used. Styrene is more reactive than 2-hydroxyethyl methacrylate in free radical polymerization reactions due in part to the generation of benzylic radical intermediates which are more stable, leading to the formation of product, than alkyl radicals which are less stable. Furthermore, polymerization of styrene under neat conditions is more preferable than in solvent-assisted environments. The choice of solvent for the synthesis of these polymers is crucial and therefore the selection of a solvent that leads to the formation of a more stable reaction intermediate is more favorable.

Table 8. Homopolymerization of 2-hydroxyethyl methacrylate (P HEMA) during 6 hours.

| Time | 1 hour | 2 hours | 3 hours | 4 hours | 5 hours | 6 hours |
|---------------|------------|------------|------------|--------------|------------|------------|
| Bulk 0.33 ml | No polymer | No polymer | No polymer | No polymer | No polymer | No polymer |
| T.H.F 10 ml | No polymer | No polymer | No polymer | No polymer | No polymer | No polymer |
| Benzene 10 ml | No polymer | No polymer | No polymer | No copolymer | No polymer | No polymer |

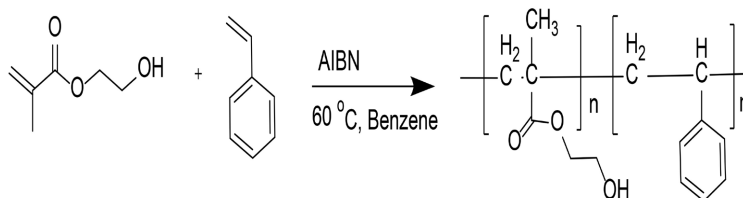
4.3. Copolymerization of 2-Hydroxyethyl Methacrylate (HEMA) and Styrene (ST)

Our initial experimental analysis on the synthesis of homopolymer prompted us to investigate further the synthesis of copolymerization reactions between 2-hydroxyethyl methacrylate (HEMA) and Styrene (ST). As shown in Equation 7, we began the synthesis by first reacting 2-hydroxyethyl methacrylate (HEMA) and Styrene (ST) under neat conditions using AIBN as initiator at an elevated temperature of 60°C. As the reaction was monitored for continuous 6 h, no formation of the proposed copolymer was observed in **Table 9**. We further performed the synthesis of the copolymer HEMA-ST under solvent directed conditions using THF and benzene as depicted in Equations 8 and 9 respectively. As seen from summarized data in **Table 9**, as the reaction was monitored for 6 h, no product was detected under the reaction conditions employed.



Equation 7 Location

It worth noted that the structure of the proposed copolymer consists of highly polar and hydrophilic monomer, 2-hydroxyethyl methacrylate and a highly non-polar and hydrophobic monomer, styrene. These functionalities constitute an amphiphilic copolymer with diverse characteristics. Plausible explanation underlying our observations is that, the reaction conditions employed in the synthesis of these copolymers might not be the right route required under free radical polymerization. In addition, the presence other functional groups (alcohol & ester) might interfere with the formation of the product. We also anticipate that the immiscibility of two reactant might also contribute to the inability of these monomer to react appreciably form the titled copolymers.



Equation 8 Location

Table 9. Synthesis of the copolymer poly (Styrene)-Co-Poly (2-hydroxyethyl methacrylate) by free radical polymerization (FRPs). PS-Co-PHEMA during 6 hours.

| Time | 1 hour | 2 hours | 3 hours | 4 hours | 5 hours | 6 hours |
|---------------|--------------|--------------|-----------------|------------|------------|------------|
| Bulk 1 ml | No copolymer | No copolymer | Solid copolymer | - | - | - |
| T.H.F 10 ml | No copolymer | No copolymer | No polymer | No polymer | No polymer | No polymer |
| Benzene 10 ml | No copolymer | No copolymer | No polymer | No polymer | No polymer | No polymer |

4.4. Characterization of Polymers

FT-IR

Fourier transform-infrared spectroscopy (FT-IR) is a powerful spectroscopic technique that enables the identification of the presence or absence of key functional groups in a molecule. As such it used to aid in the characterization of synthesized compounds. As result, after successful synthesis of the proposed polymers, the products were analyzed using FT-IR. The results obtained are shown in **Figures 20-28** under FT-IR results.

For example, FT-IR spectrum of polystyrene obtained under neat condition is shown in **Figure 20** was obtained by taking an aliquot amount of the sample and it was run using IR spectrophotometer. Since the structure of the polymer consists primarily of arene and carbon-carbon single and double bond, we expected these functionalities to present in the spectrum. As observed in the spectrum a very peak around $2850 - 2975 \text{ cm}^{-1}$ is seen for the C-H stretching of an alkane and also very weak of around 1650 cm^{-1} for the aromatic carbons.

In comparison to the spectra obtained from samples synthesized in THF and benzene (**Figure 21** & **Figure 22** respectively), no significant differences were observed with respect to the spectrum in **Figure 20**. Since the structure of the proposed polystyrene possess the same functional groups.

We also analyzed the homopolymer derived from 2-hydroxyethyl methacrylate using FT-IR. The results obtained are depicted in **Figures 23-25**. 2-hydroxyethyl methacrylate consists of hydroxyl group, a carbonyl moiety, an ester component and carbon-carbon double bond. We therefore anticipated the presence of these functional groups in the IR-spectra.

As observed in **Figure 23**, for example, the broad peak seen around $3400 - 3700 \text{ cm}^{-1}$ of the spectrum for the poly-2-hydroxyethyl methacrylate obtained under neat condition depicts the presence of alcohol functional group. The carbonyl of the ester functional group was observed as a sharp peak around 1702 cm^{-1} and a weak C-H stretching of an alkane was observed around 2850 cm^{-1} .

The poly-2-hydroxyethyl methacrylate sample synthesized in THF and benzene were also analyzed using FT-IR. The results obtained are depicted in **Figure 24** & **Figure 25**. As observed in **Figure 24** & **Figure 25**, there is no significant difference between the spectra as expected. The signals observed in the spectrum obtained for the sample under neat conditions. For example, the broad peaks found around $3400 - 3700 \text{ cm}^{-1}$ of the spectrum for the poly-2-hydroxyethyl methacrylate obtained in THF and benzene conditions depict the presence of alco-

hol functional group. The carbonyl of the ester functional group was observed as a sharp peak around 1702 cm^{-1} and a weak C-H stretching of an alkane were observed around 2850 cm^{-1} as reflected in **Figure 24** & **Figure 25**.

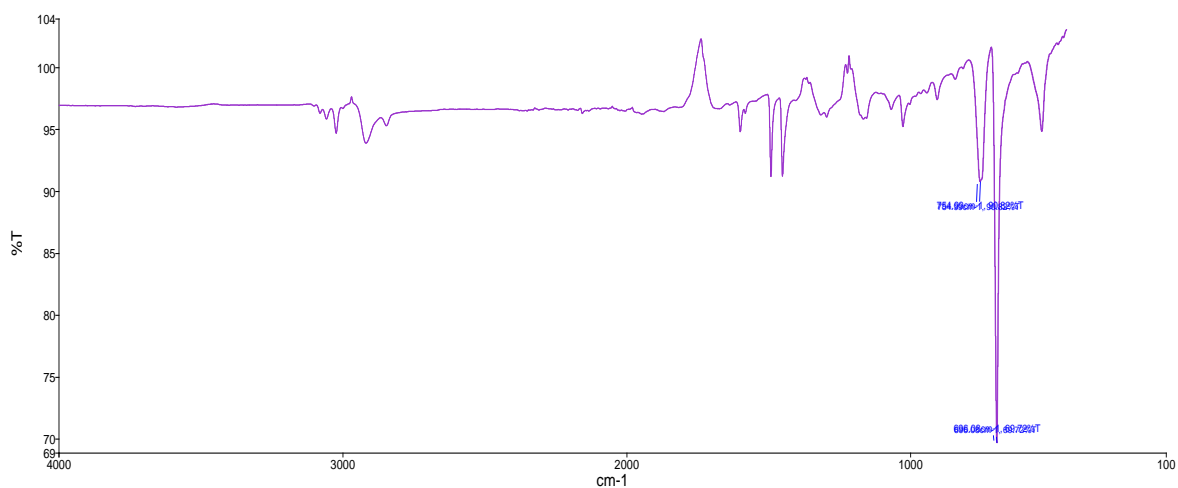


Figure 20. FT-IR spectrum of polystyrene under neat condition.

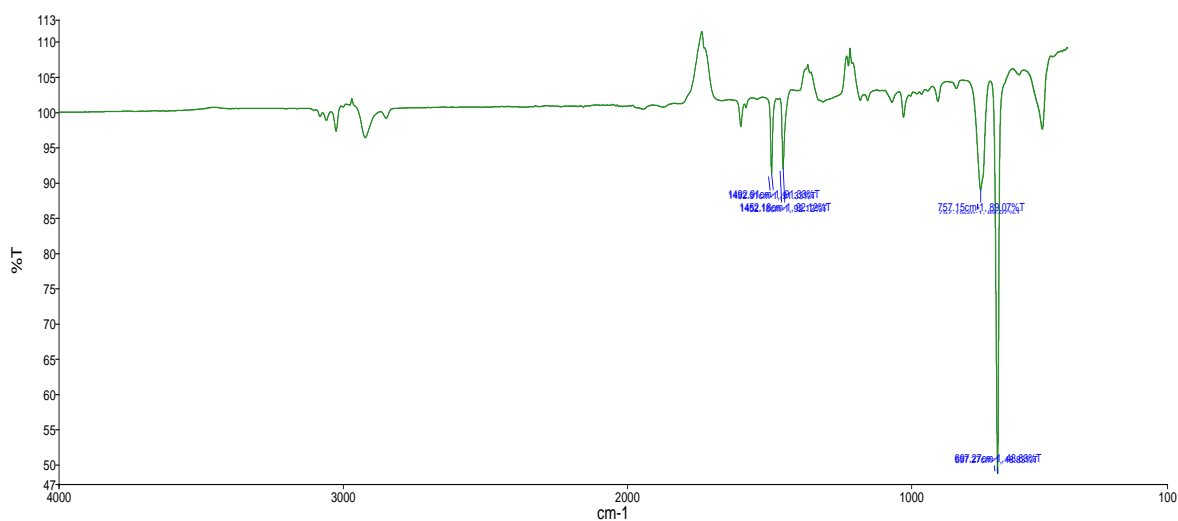


Figure 21. FT-IR spectrum of polystyrene in THF.

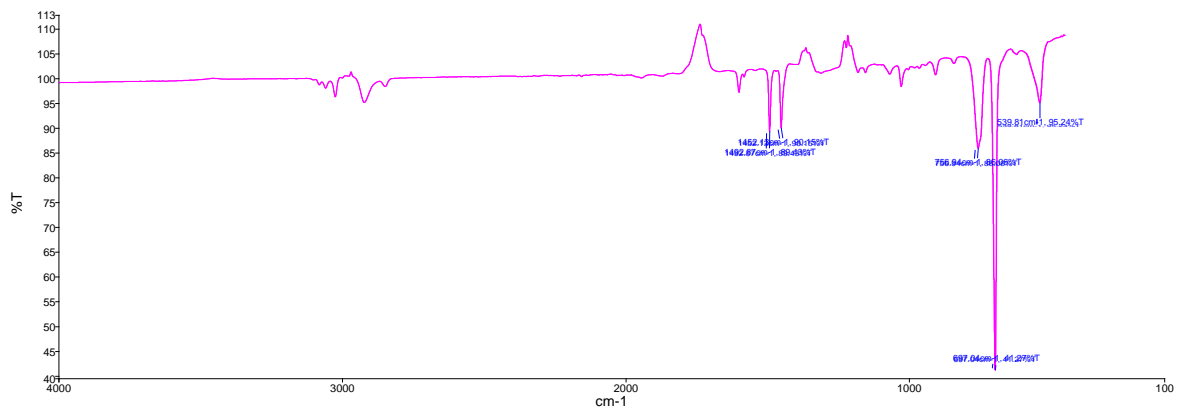


Figure 22. FT-IR spectrum of polystyrene in Benzene.

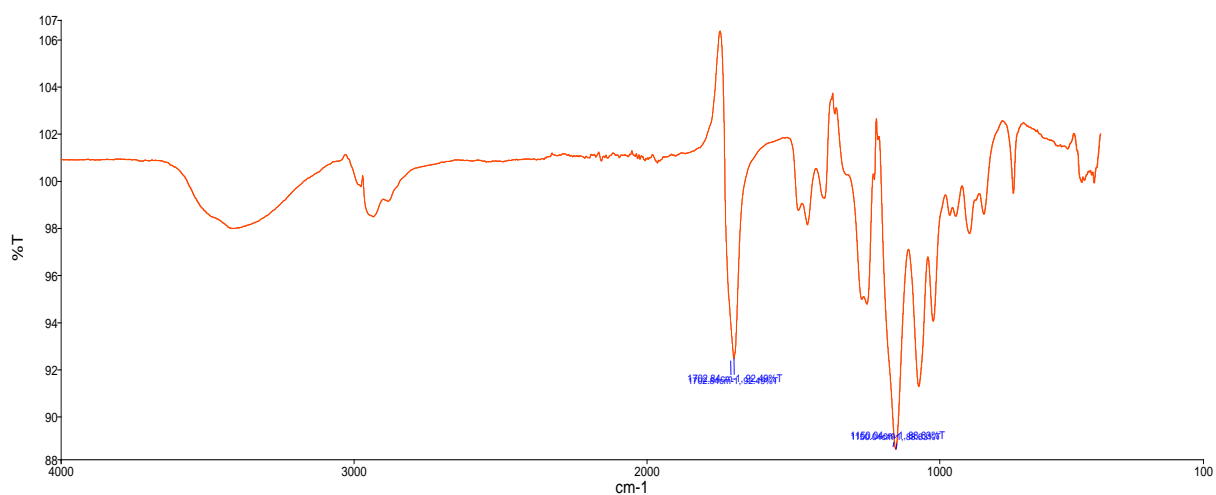


Figure 23. FT-IR spectrum of poly-2-hydroxyethyl methacrylate under neat condition.

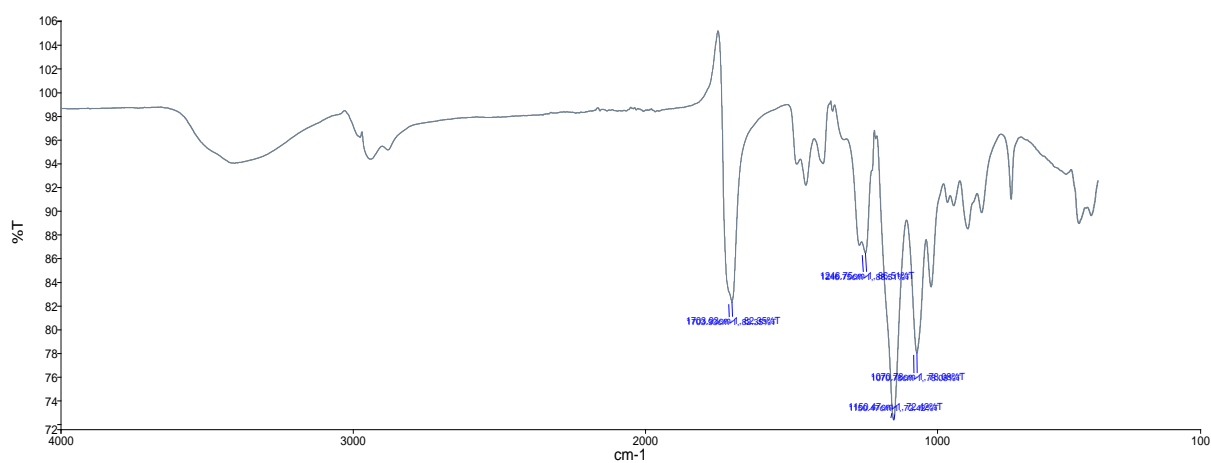


Figure 24. FT-IR spectrum of poly-2-hydroxyethyl methacrylate under in THF.

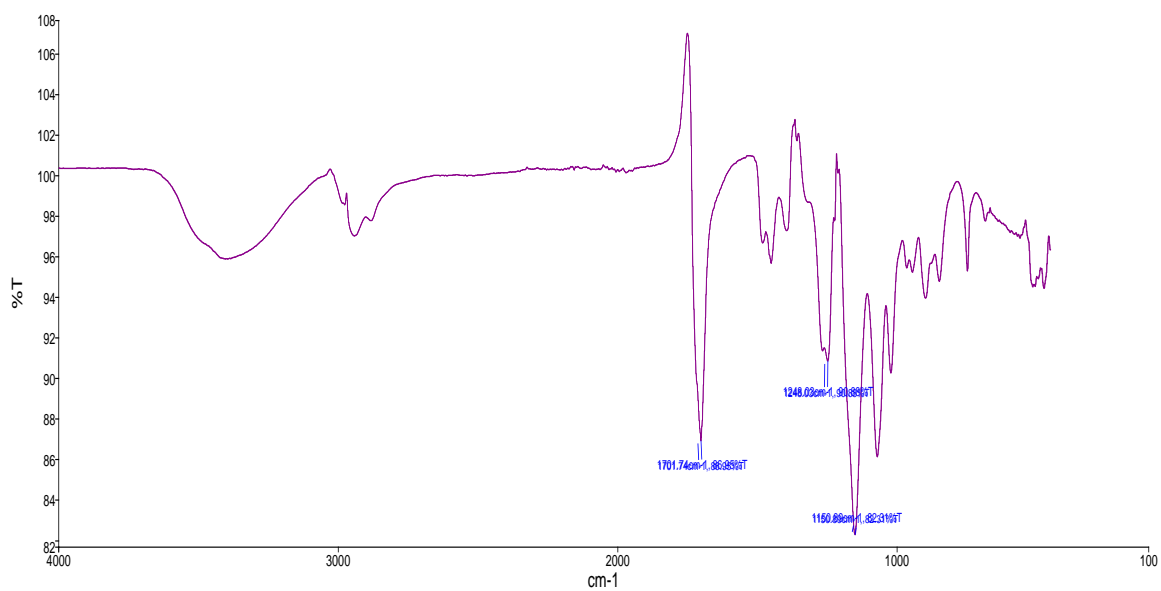


Figure 25. FT-IR spectrum of poly-2-hydroxyethyl methacrylate in Benzene.

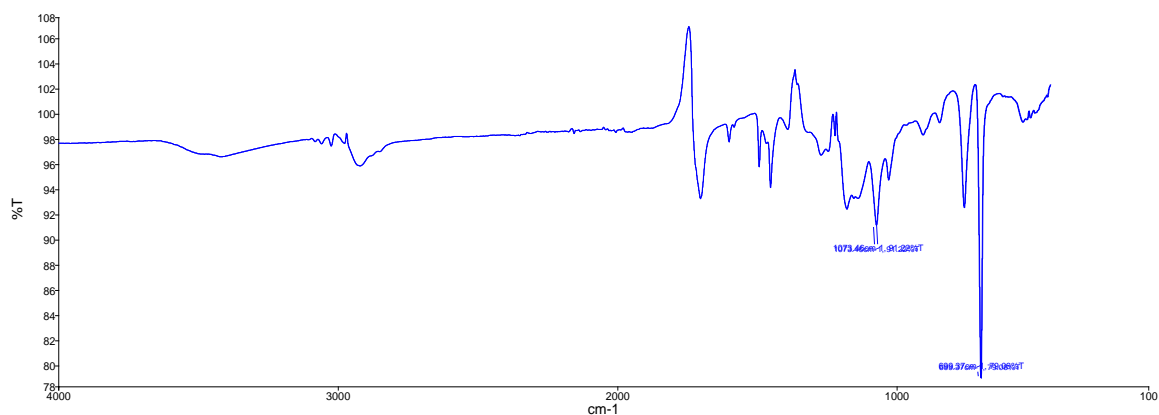


Figure 26. FT-IR spectrum of 2-hydroxyethyl methacrylate-styrene under neat conditions.

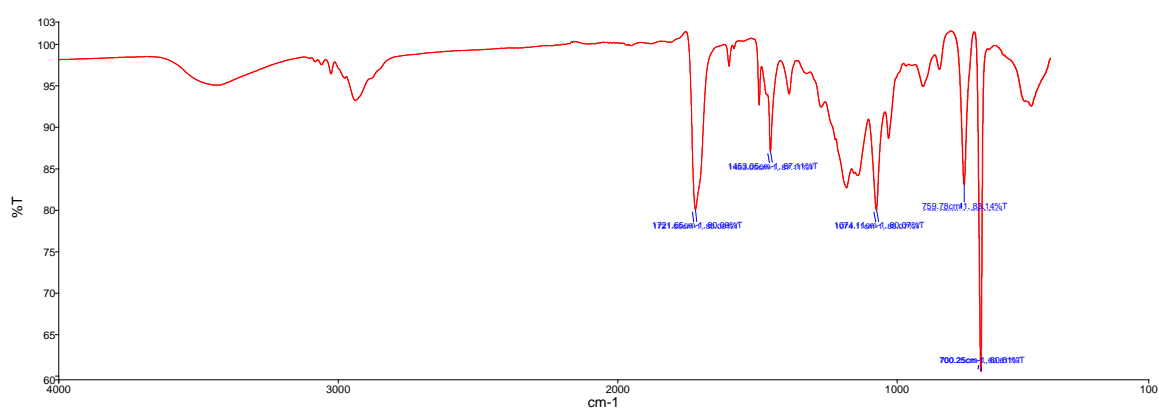


Figure 27. FT-IR spectrum of 2-hydroxyethyl methacrylate-styrene in THF.

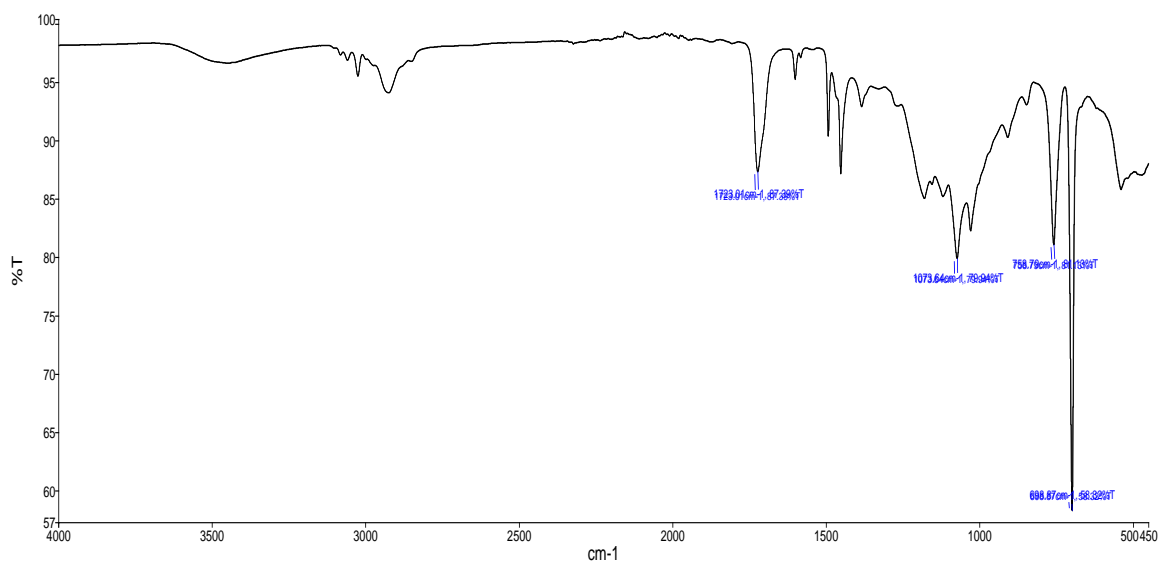


Figure 28. FT-IR spectrum of 2-hydroxyethyl methacrylate-styrene in benzene.

After careful analysis of the spectra obtained for all the homopolymers we also examined the three copolymers synthesized under the same experimental conditions. We first analyzed the copolymer 2-hydroxyethyl methacrylate-styrene

under neat conditions and spectrum obtained is shown in **Figure 26**. As observed in **Figure 26** a very peak around $2850 - 2975 \text{ cm}^{-1}$ is seen for the C-H stretching of an alkane and also very weak signal around 1650 cm^{-1} for the aromatic carbons. As observed in **Figure 26**, the broad peak but weak signal seen around $3400 - 3700 \text{ cm}^{-1}$ of the spectrum for the 2-hydroxyethyl methacrylate – styrene obtained under neat condition depicts the presence of alcohol functional group. The carbonyl of the ester functional group was observed as a sharp peak but weak signal around 1702 cm^{-1} and a weak C-H stretching of an alkane was observed around 2850 cm^{-1} .

The spectra obtained for the copolymers generated in THF and benzene are shown in **Figure 27** & **Figure 28** respectively. As observed in these Figures there are major differences with respect to the signals obtained.

However, in comparison to the spectrum obtained under neat conditions, the carbonyl signal of 2-hydroxyethyl methacrylate in the copolymer was to 1721 and 1723 cm^{-1} in THF and benzene respectively. In addition, these carbonyl signals of the ester tend to sharper than the signal obtained under neat conditions. In effect, there is no significant differences between the spectra recorded for all the proposed polymers, however, we do observe the key functional groups within the structures of the polymers.

4.5. Proton Nuclear Magnetic Resonance Spectroscopy. (The Results Obtained Are Shown in Figures 29-35 ^1H NMR Spectrum)

The elucidation of the structure of the synthesized polymers was also performed using the proton nuclear magnetic resonance spectroscopy. **Figure 29** depicts the ^1H NMR spectrum for the sample obtained under neat conditions. The sample was first dissolved in chloroform-d and the measurement was taken thereafter. As observed in the spectrum, a broad singlet peaks were observed at round 7.00 ppm and 12.60 ppm which correspond to the arene protons the sample. Since the proposed polystyrene consists mainly of benzene core, we anticipated such deshielded signals. As observed in the spectrum no other signals were seen up field. It quite interesting to know that the vinylic protons which are usually observed round 5.00 ppm is absent in the spectrum, depicting that it has been converted into saturated protons in the polymer. However, due to the poor solubility of the sample which leads to bad shimming of the nmr sample, we could not detect the signals of the aliphatic protons.

Similar analyses were performed on the sample obtained under THF and benzene assisted reactions. **Figure 30** & **Figure 31** depict the ^1H NMR spectra for the sample obtained under these conditions.

As describe above, the sample were first dissolved in chloroform-d and the measurement were taken thereafter. As observed in the spectra, a broad singlet peaks were observed at round 7.00 ppm and 12.60 ppm which correspond to the arene protons in the sample like the spectrum obtained under neat conditions.

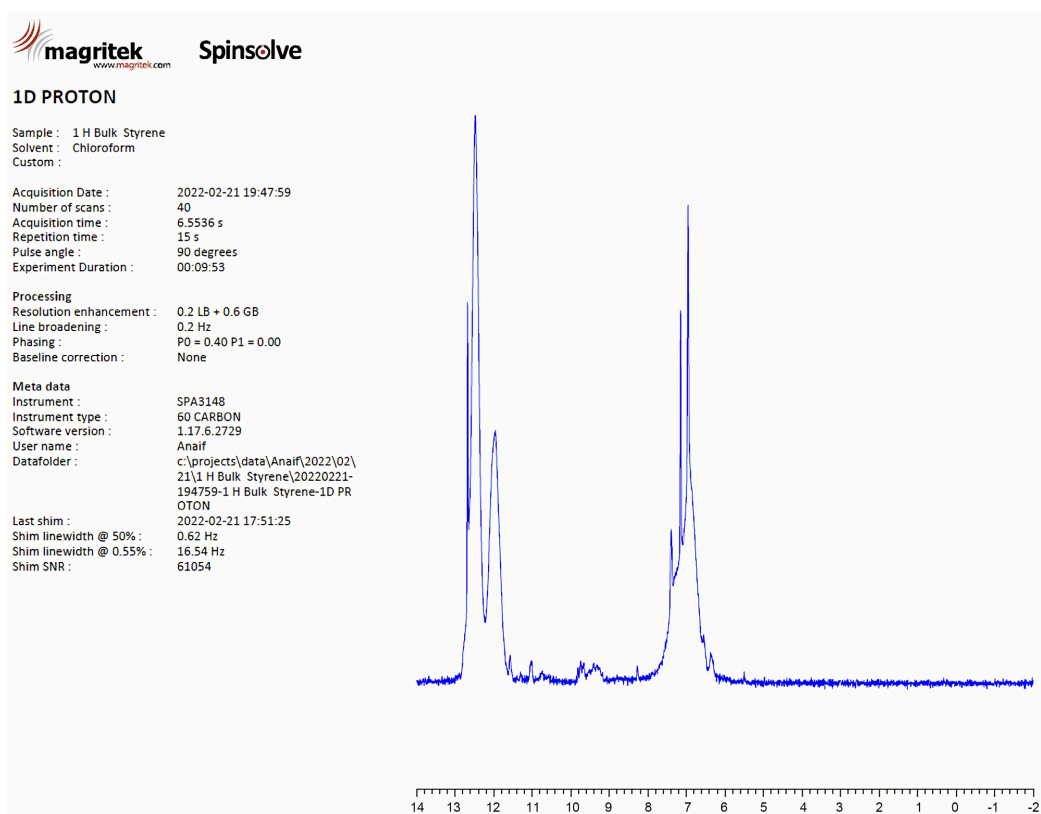


Figure 29. ^1H NMR spectrum of polystyrene under neat conditions.

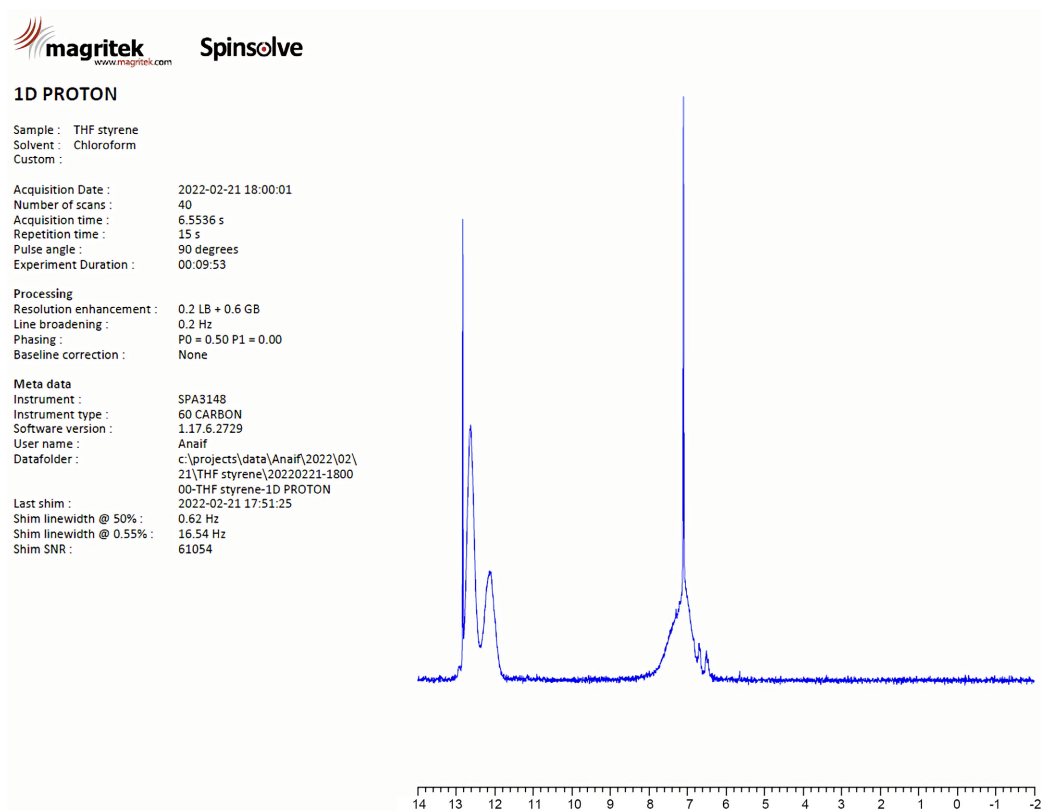


Figure 30. ^1H NMR spectrum of polystyrene under THF conditions.

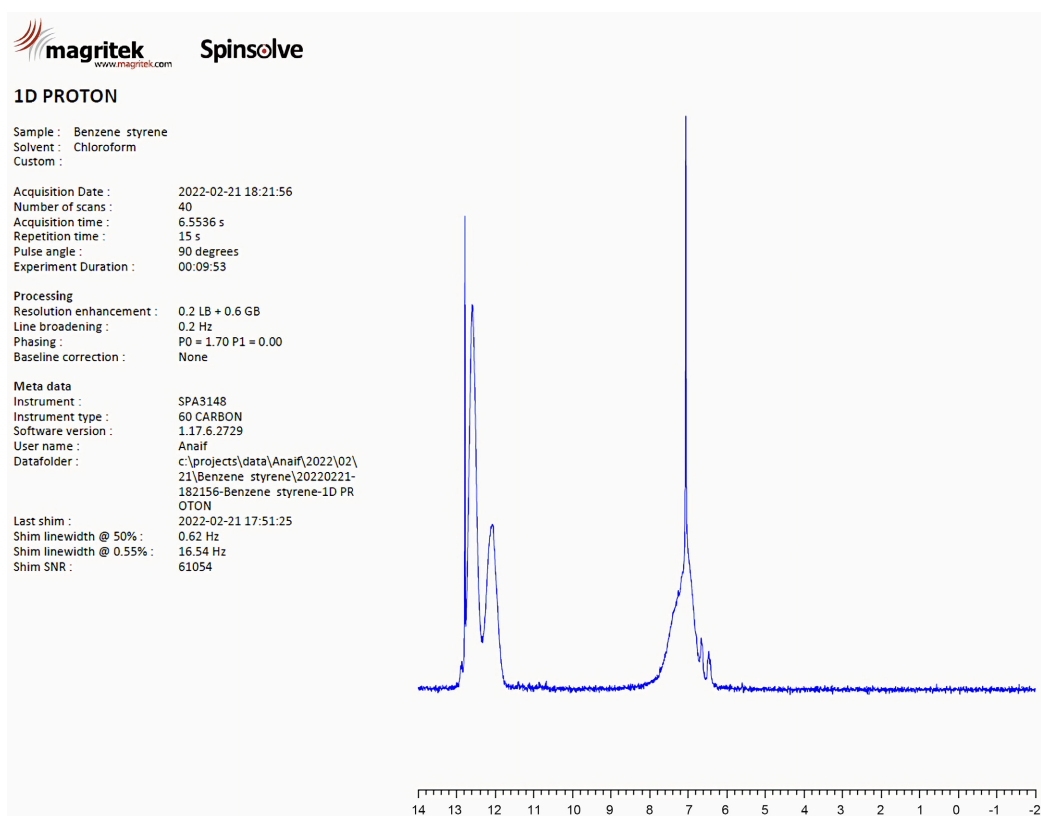


Figure 31. ^1H NMR spectrum of polystyrene under benzene conditions.

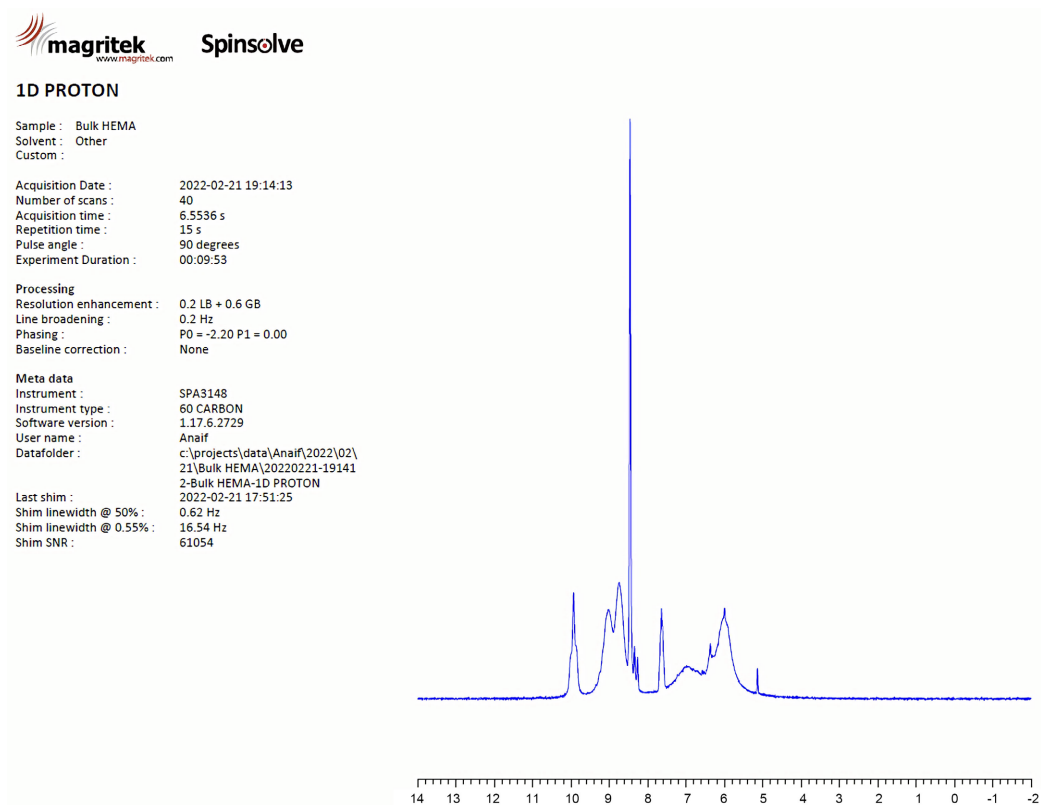


Figure 32. ^1H NMR spectrum of 2-hydroxyethyl methacrylate under neat conditions.

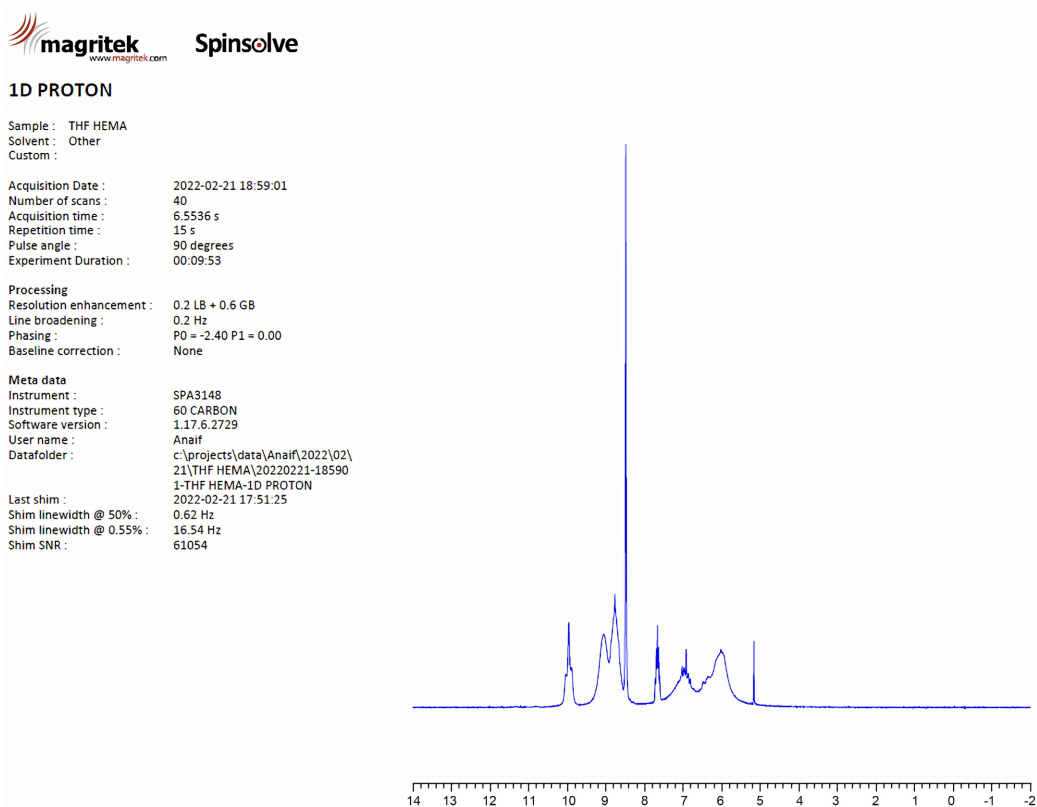


Figure 33. ^1H NMR spectrum of 2-hydroxyethyl methacrylate under THF conditions.

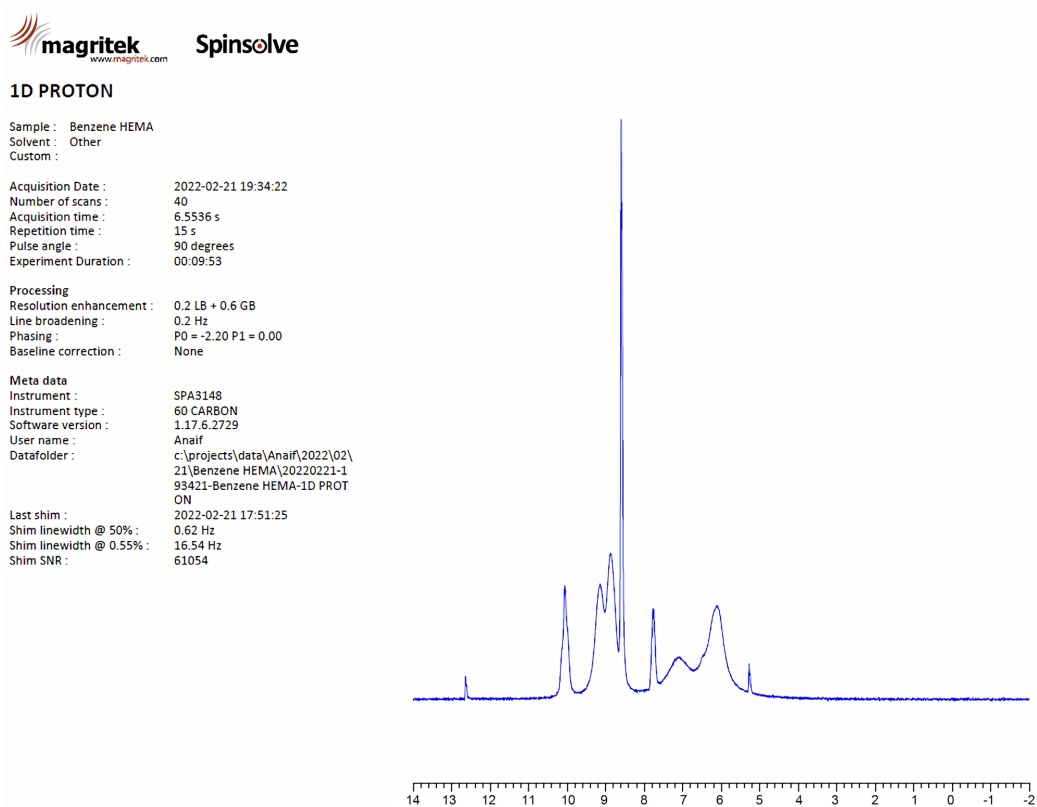


Figure 34. ^1H NMR spectrum of 2-hydroxyethyl methacrylate under benzene conditions.

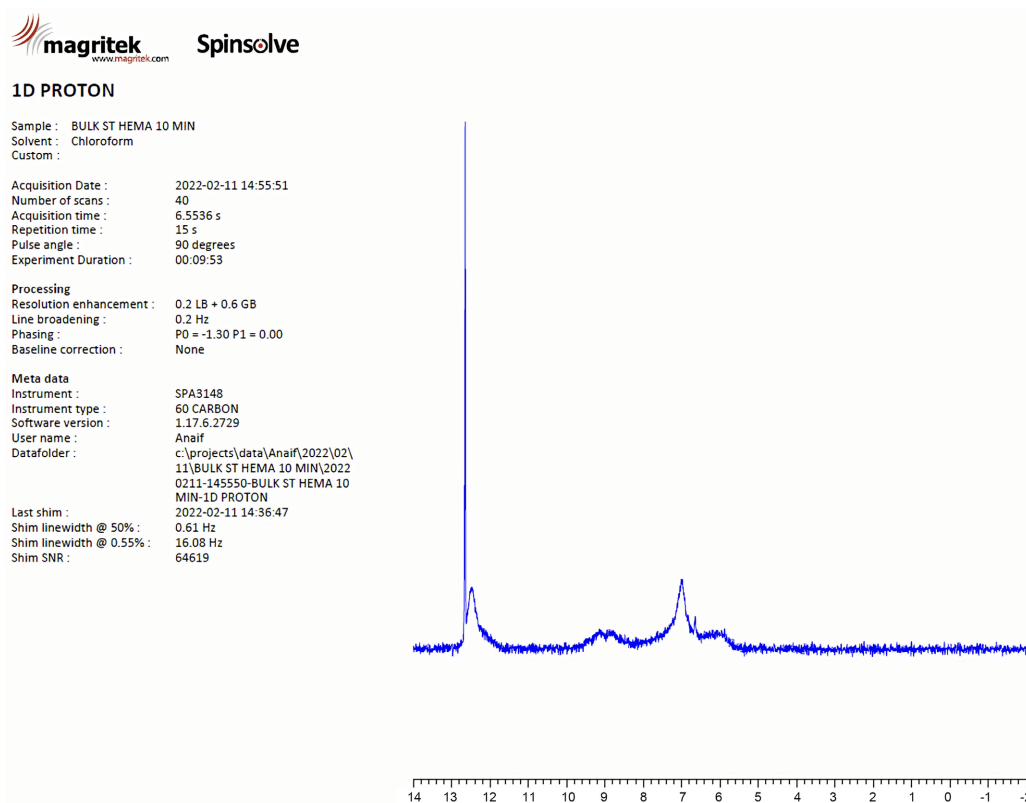


Figure 35. ^1H NMR spectrum of 2-hydroxyethyl methacrylate-ST under neat conditions.

We also analyzed the nmr sample of 2-hydroxyethyl methacrylate under neat, THF and benzene conditions. The spectra obtained are shown in **Figures 32-34**.

Due poor solubility of the sample in the deuterated solvent used the multiplicity of the aliphatic protons of the sample were not observed. However, broad peaks for example were observed at 6.00 ppm, 7.40 ppm and 10.00 ppm.

These observations is quite interesting because we anticipated such signals to be upfield since majoring of the protons in our proposed sample are aliphatic protons, since there were no observable reactions under these two conditions.

As observed in **Figure 33** & **Figure 34** similar spectra were obtained for the samples under THF and benzene assisted reactions as expected.

Poor solubility of the sample led to bad shimming of the nmr sample and this resulted in the broadening of the signals obtained for all the copolymerization samples under the three conditions used. Such no relevant information could be derived from the spectra for the three samples. We therefore used the spectrum obtained for the copolymer 2-hydroxyethyl methacrylate-ST under neat conditions to exemplify the result obtained as shown in **Figure 35**.

4.6. Atomic Force Microscopy

To better understand the actual composition and structure of our proposed copolymers, atomic force microscopy of our sample was studied to determine their detailed film morphology. Understanding the detailed morphology of polymeric materials especially heterogeneous materials are very crucial for determining

mechanical properties and hence the AFM images of our copolymers were carried-out. The data obtained for the copolymers 2-hydroxyethyl methacrylate-ST under neat, THF and benzene assisted are shown in **Figures 36(a)-(c)** respectively.

As seen in the AFM images, we observed similar patterns in the morphologies of the film casted indicating that there are no significant differences among the samples obtained under the three experimental conditions.

4.7. Differential Scanning Calorimetry (DSC) (The Results Obtained Are Shown in Figure 37 and Figure 38)

Differential scanning calorimetry (DSC) is a very prominent thermoanalytical technique used to explore the responses of polymers to heating. For example, DSC can be used to analyze the melting of a crystalline polymer or even the glass transition. As a result, in examining DSC data, three important parameters can be elucidated; glass transition temperature, T_g , crystallization temperature, T_c , and melting temperature, T_m . To analyze our sample using the DSC technique, the samples were thermally analyzed on a TA Instruments DSC Q 2000 under nitrogen environment at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under nitrogen atmosphere. All samples were collected in Tzero hermetic aluminum sample pans by weighing 5 - 15 mg and hermetically sealing them. The second heating cycle's thermal transition temperatures were reported. Since the reaction under neat condition leading to the formation of polystyrene was feasible, we investigated its thermal behavior and the result is depicted in **Figure 37**.

Figure 38 depicts the DSC data for the reference sample obtained from Sigma Aldrich. As it is known that most polymers in their molten state, when cooled would at some point reach its glass transition temperature (T_g) and this result in a change in the mechanical properties of the polymer with subsequent drastic change from those of an elastic material to those of a brittle one due to variations in the polymer chain mobility. As a result, when the polystyrene sample obtained under neat condition was examined using the DSC, we observed a gradual increase in the transition. As observed in **Figure 37**, It is essential to note that the transition does not occur abruptly at one unique temperature but rather over a extend range of temperatures.

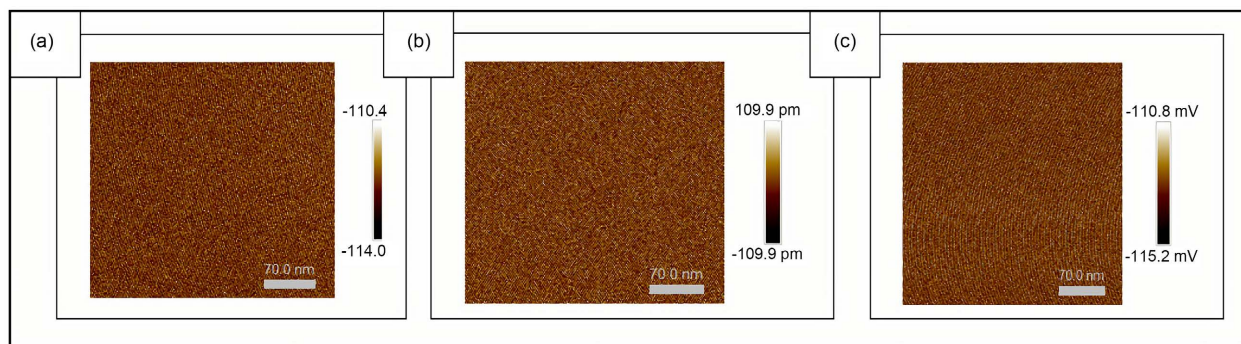


Figure 36. Atomic force microscopy images of copolymer of 2-hydroxyethyl methacrylate-ST under (a) neat (b) THF (c) Benzene conditions.

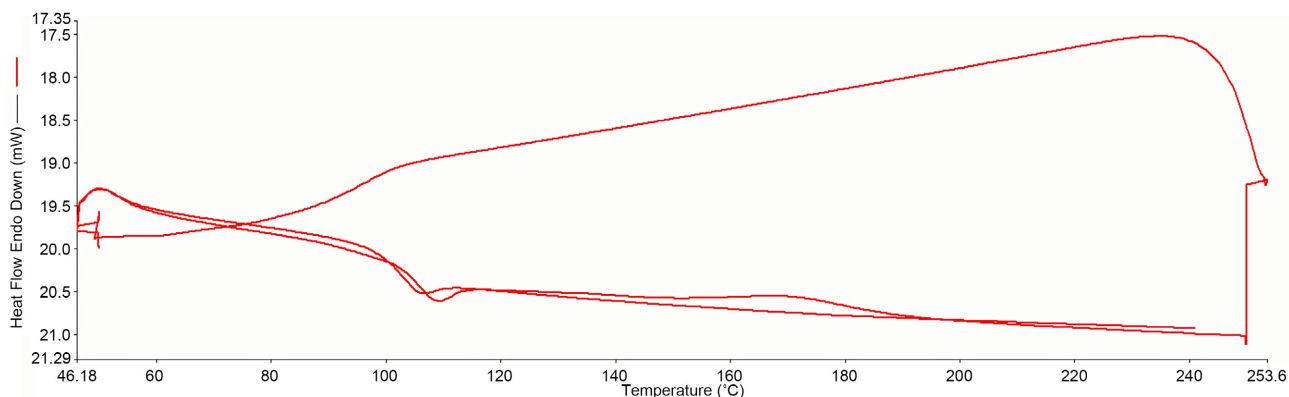


Figure 37. Differential scanning calorimetric response of polystyrene obtained under neat conditions.

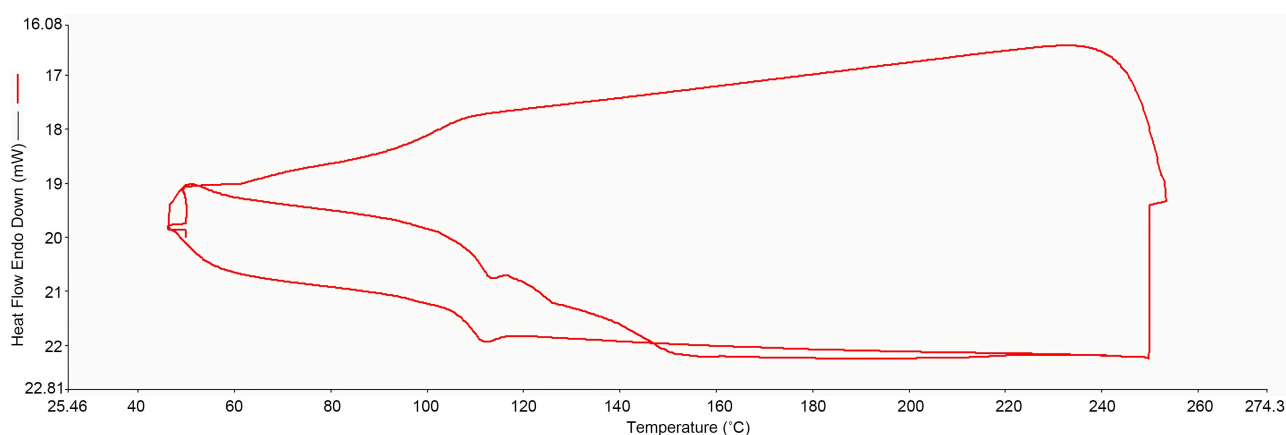


Figure 38. Differential scanning calorimetric response of polystyrene obtained from sigma used as a reference.

Above the glass transition temperature some polymer chains have high movement resulting in an increased in the kinetic energy of molecule which leads to crystals formation. Since crystallization is an exothermic process releasing heat released to the surroundings results in a decrease in the recorded heat flow and a dip in the plot of heat flow versus temperature. Such a crystallization peak is used to confirm that crystallization occurs in the sample, which enables the determination of crystallization temperature (T_c) and likewise latent heat of crystallization. However, our DSC data did not display such dip in the plot as a result our sample did not form a crystalline structure in the process and therefore could not determine the T_c . In addition, majority of polymer chains are capable to move around freely at the melting temperature (T_m) and thus increased the entropy of the polymeric material. Melting is an endothermic process, requiring the absorption of heat. The energy added during this time is used to melt the crystalline regions and does not increase the average kinetic energy of the chains that are already in the melt. In a plot of heat against temperature this appears as a jump discontinuity at the melting point. Unfortunately, such inflexion was not observed in our DSC analysis for both sample and the reference polymer as shown in **Figure 37** & **Figure 38**. In summary therefore, our synthesized polymer did not display all the three well-noted transitions during heating, that is,

glass transition, crystallization and melting. It can therefore be said that only polymers capable of forming crystals exhibit crystallization and melting peaks in their DSC analysis while purely amorphous polymers will only undergo a glass transition. Our sample therefore exhibit amorphous behavior.

5. Conclusion

We have performed a series of syntheses utilizing free radical polymerization methods. Two monomers with different functionalities within their core structures were used, which is styrene and 2-hydroxyethyl methacrylate. To develop a facile approach in the synthesis of their homo and copolymers three different media were employed-neat (bulk), tetrahydrofuran (THF) and benzene. After careful investigation of all the samples and the reaction conditions, only homopolymerization of styrene under neat conditions yielded an appreciable amount of the desired product. The samples obtained from the synthesis were characterized by Fourier Transform-Infrared spectroscopy (FT-IR), proton nuclear magnetic resonance spectroscopy (^1H NMR), atomic force microscopy (AFM), and differential scanning calorimetry (DSC). The results show that the synthesis of the polymers is more feasible under neat conditions rather than solvent assisted reaction. In addition, the DSC data shows that the polystyrene obtained is amorphous in nature and therefore displayed only a glass transition signal rather than crystallization and melting peaks. Further analysis might be needed to hasten the synthesis route for these homo and copolymers.

Conflicts of Interest

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

References

- [1] Elias, H.-G. (1997) *An Introduction to Polymer Science*. Wiley, Hoboken.
- [2] Belgacem, M.N. and Gandini, A. (2011) *Monomers, Polymers and Composites from Renewable Resources*. Elsevier Science, Oxford.
- [3] Billmeyer, F.W. (1971) *Textbook of Polymer Science*. 2nd Edition, Wiley-Interscience, New York.
- [4] Karak, N. (2009) *Fundamentals of Polymers: Raw Materials to Finish Products*. Eastern Economy Edition, PHI Learning Pvt Ltd, New Delhi.
- [5] Pillai, O. and Panchagnula, R. (2001) Polymers in Drug Delivery. *Current Opinion in Chemical Biology*, **5**, 447-451. [https://doi.org/10.1016/S1367-5931\(00\)00227-1](https://doi.org/10.1016/S1367-5931(00)00227-1)
- [6] Chanda, M. and Roy, S.K. (2008) *Industrial Polymers, Specialty Polymers, and Their Applications*. CRC Press, Boca Raton. <https://doi.org/10.1201/9781420080599>
- [7] Clayden, J., Greeves, N. and Warren, S.G. (2012) *Organic Chemistry*. 2nd Edition, Oxford University Press, Oxford, 1450-1466.
- [8] Ebdon, R.J. (1992) *Introduction to Polymers (Second Edition)* R.J. Young and P.A. Lovell Chapman and Hall, London, 1991. pp. 443, price £16.95. ISBN 0-412-30640-9 (PB); ISBN 0-412-30630-1 (HB). *Polymer International*, **27**, 207-208.

<https://doi.org/10.1002/pi.4990270217>

- [9] Odian, G. (2004) Principles of Polymerization. 4th Edition, Wiley-Interscience, New York.
- [10] Zare, M., Bigham, A., Zare, M., Luo, H., Rezvani Ghomi, E. and Ramakrishna, S. (2021) pHEMA: An Overview for Biomedical Applications. *International Journal of Molecular Sciences*, **22**, Article 6376. <https://doi.org/10.3390/ijms22126376>
- [11] Ku, P.L. (1988) Polystyrene and Styrene Copolymers: Their Manufacture and Application. II. *Advances in Polymer Technology Advances in Polymer Technology*, **8**, 201-223. <https://doi.org/10.1002/adv.1988.060080301>
- [12] Ku, P.L. (1988) Polystyrene and Styrene Copolymers. I. Their Manufacture and Application. *Advances in Polymer Technology Advances in Polymer Technology*, **8**, 177-196. <https://doi.org/10.1002/adv.1988.060080204>
- [13] Vasiliev, V.G., Rogovina, L.Z. and Slonimsky, G.L. (1985) Dependence of Properties of Swollen and Dry Polymer Networks on the Conditions of Their Formation in Solution. *Polymer*, **26**, 1667-1676. [https://doi.org/10.1016/0032-3861\(85\)90284-8](https://doi.org/10.1016/0032-3861(85)90284-8)
- [14] Rietsch, F., Daveloose, D. and Froelich, D. (1976) Glass Transition Temperature of Ideal Polymeric Networks. *Polymer*, **17**, 859-863. [https://doi.org/10.1016/0032-3861\(76\)90251-2](https://doi.org/10.1016/0032-3861(76)90251-2)