THE EFFECTS OF ADDITIVES ON SUSPENSION POLYMERIZATION OF STYRENE AND ITS OPTIMIZATIONS

by

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ABSTRACT

THE EFFECTS OF ADDITIVES ON SUSPENSION POLYMERIZATION OF STYRENE AND ITS OPTIMIZATIONS

Nowadays, the incorporation of several novel additives such as colorants, flame retardants, and graphite into polystyrene is studied to tune its fire resistance, improve its cell structure, optimize its insulation properties, and give it an aesthetic look.

However, there are not many studies about the stabilization of suspension polymerization in the presence of different additives, which may alter different features of the reaction, such as its viscosity, its ionic strength, its reaction rate, etc.

The driving force of this study is to understand and optimize the reaction and the reaction conditions of incorporating different additives into polystyrene beads *via* suspension polymerization technique and free radical polymerization in the presence of graphite, colorant and flame retardants.

The impact of various additives on the polymerization was systematically investigated, focusing on parameters such as suspension stability, M_w, and T_g. It was observed that the incorporation of different additives caused different viscosity behaviors. The adverse effects of incorporation of different additives were overcome by the addition of polymeric suspension stabilizers and anionic surfactants.

ÖZET

KATKI MALZEMELERİNİN STİREN MONOMERİNİN SÜSPANSİYON POLİMERİZASYONUNA ETKİLERİ VE OPTİMİZASYONU

Günümüzde birçok polimer katkı maddesi kullanılmaktadır. Bunların en başında mor ötesi ışıktan koruyucu kimyasallar, ısı iletimini azaltıcı kimyasallar, renk vericiler, alev geciktiriciler ve biyo-bozunurluktan koruyucular gelmektedir. Polistiren sentezinde en çok kullanılan katkı malzemeleri; renk vericiler, alev geciktiriciler ve ısı yalıtımını artıran kimyasal bileşiklerdir. Bu katkı malzemeleri maddenin ısıya karşı direncini artırmak, hücre yapısını geliştirmek, maddenin ısı yalıtımını arttırmak ve maddeye estetik bir görüntü vermek için kullanılmaktadır.

Fakat, polistiren katkı malzemelerinin reaksiyonu nasıl etkilediği ve istikrarını ne yönde değiştirdiği hakkında denemeler pek az yapılmıştır. Farklı katkı malzemeleri reaksiyonun istikrarını farklı yönlerden etkiler. Örneğin reaksiyonun viskozitesinde istenmeyen artışlar olabilir, reaksiyonun iyonik gücü azalıp artabilir ya da reaksiyon hızı yavaşlayabilir. Bu değişimlerin sonucunda polistirenin ortalama tanecik boyutu ve tanecik boyutu dağılımı yüksek derecede etkilenmektedir.

Bu projenin amacı farkı katkı malzemelerinin süspansiyon polimerizasyonu esnasında reaksiyonun hızını ve reaksiyonun istikrarını nasıl değiştirdiğini gözlemlemek ve reaksiyonu optimize etmektir.

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LIST OF ACRONYMS/ABBREVIATIONS

BP15:3	Blue pigment 15:3
BPO	Benzoyl Peroxide
$CDCl_3$	Deuterated Chloroform
DI	Deionized Water
DSC	Differential Scanning Calorimetry
DSP	Disodium phosphate
EPS	Expandable Polystyrene
FR	Flame Retardant
G	Graphite
GPC	Gel-permeation Chromatography
HEC	Hydroxyethyl cellulose
HVAC	Heating, ventilation, and air conditioning
M_n	Number average molecular weight
M_w	Weight average molecular weight
PDI	Polydispersity Index
PEG	Polyethylene glycol
PVA	Polyvinyl alcohol
PVP-K90	Polyvinyl pyrrolidone
RPM	RPM Round per minute
Rxns	Reactions
SDBS	Sodium dodecylbenzene sulfonate
Sty	Styrene
T	Temperature
TCP	Tricalcium phosphate
THF	Tetrahydrofuran
VOCs	Volatile Organic Compounds
XPS	Extruded Polystyrene
T_g	Glass transition temperature

T_m	Crystalline melting temperature

1. INTRODUCTION

1.1. Polystyrene and Its Application Areas

Polystyrene is a resin that is made of styrene monomers in the presence of proper initiators. Extruded polystyrene (XPS) and expandable polystyrene (EPS) are two different polystyrene products that are commonly used in numerous industries, such as construction, heating, ventilating and air conditioning (HVAC), transportation, appliances, furniture, and packaging industries [1,2]. Micro-sphere polystyrene beads are used in the cosmetic industry to prepare cosmetic products [3].

Among them, EPS is the cheapest and most commonly used product, mainly in situations where humidity and water are not significant concerns since it is scarcely water-sensitive compared to XPS. In contrast, XPS is commonly preferred by end users for insulation when water-resistant blocks are required to build an economically viable construction in the long run.

One of EPS's significant advantages and environmentally friendly features is that it is almost 100% recyclable [4]. Nowadays, industries are compelled to use recyclable or biodegradable polymers due to the heightened environmental concern of the public, indicating that EPS blocks will continue to be a primary insulating substance in the industry. However, it should be noted that EPS recycling processes are not standard worldwide, and recycling efficiency should be another concern as well.

1.2. Polystyrene Synthesis Techniques

Polystyrene is a synthetic polymer that is produced through the polymerization of styrene in various conditions and techniques. Styrene molecule is the only monomer that can be polymerized through anionic, cationic, and free radical polymerization [5–7]. Polystyrene can be synthesized through melt, suspension, solution,

and emulsion polymerization techniques. The chemical properties and the end use of polystyrene alter depending on the production technique. The industry commonly applies suspension and melt polymerization techniques to produce lightweight insulation materials. Polystyrene micro-spheres are synthesized via the emulsion polymerization technique. They are utilized in the cosmetic industry since emulsion polymerization provides precise molecular weight distribution, low polydispersity index (PDI), and narrow particle size distribution compared to suspension polymerization and melt polymerization, which yields broadened product distribution.

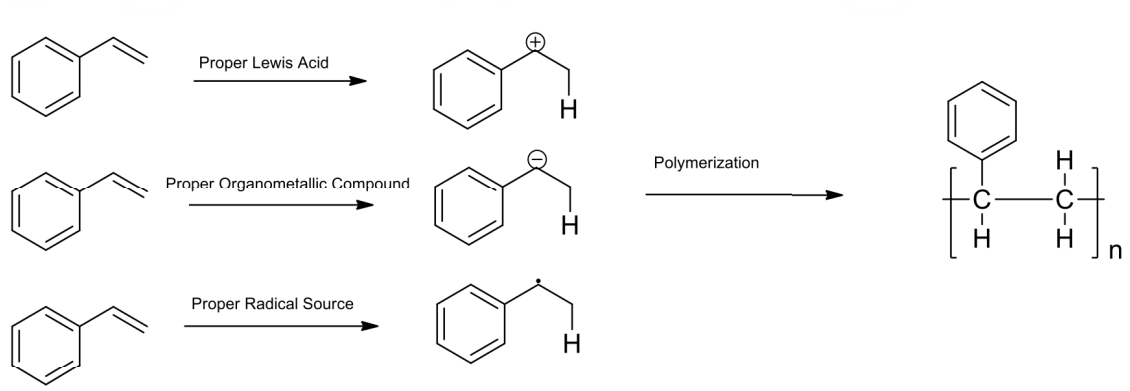


Figure 1.1. Syntheses mechanisms of polystyrene.

1.2.1. Polystyrene *via* Melt Polymerization

Extruded polystyrene foams are produced *via* extruders. Styrene and all the other reactants and additives are introduced from the hopper to the extruder to obtain extruded polystyrene, also called Styrofoam (XPS). Compared to EPS, XPS has a higher vapor diffusion resistance, compressive strength, and density. Due to its high resilience against water and humidity, it is commonly utilized in areas that require extreme water-resistance insulation, such as roofs [8].

1.2.2. Polystyrene *via* Suspension Polymerization

Suspension polymerization is a free radical polymerization process in which the monomer and liquid phases are immiscible and forced to form a suspension through

high agitation. As the viscosity of the monomer phase increases significantly during the reaction, the stability of the suspension drastically diminishes. Certain stabilizers are employed to stabilize the reaction by preventing the coalescence of micro-reactors. Polystyrene beads that are attained via suspension polymerization are further incorporated with volatile organic compounds (VOCs) to make them expandable polystyrene (EPS). Due to its high rigidity, low-density, high-volume percentage, low cost, and low mass, it is mainly utilized in insulation applications and food packaging. Furthermore, thanks to the high shock absorptivity of expanded polystyrene, it is also used to protect electrical devices until the first user unboxes them.

1.3. Synthesis Parameters of Suspension Polymerization of Styrene

1.3.1. Initiator

Initiators that are going to be employed in the suspension polymerization of styrene have to meet specific requirements. The primary prerequisite is to be monomer-soluble and water-insoluble. The decomposition temperature of the initiator is an essential parameter for producing a high-quality product due to its high impact on the reaction kinetics and polymer quality. The ratio of the initiator to the monomer exhibits a crucial role in the polymerization process and rate as well [9]. Typically, a single type of initiator is enough to run the polystyrene polymerization. However, Expandable polystyrene synthesis consists of two different stages; hence, it requires different initiators for each phase. The most common initiators are peroxide initiators such as dibenzoyl peroxide, dicumyl peroxide, and di(tert-butyl) peroxide. Besides them, peroxycarbonates, perketals, peresters, and azo compounds can also be utilized [10].

1.3.2. Suspending Agent

Suspending agents are substances utilized to stabilize suspensions through high agitation. High molecular weight polymers that contain hydrophilic and hydropho-

bic parts may be used in the suspension polymerization, such as polyvinyl alcohol, polyvinyl pyrrolidone, and hydroxyethyl cellulose [11, 12]. Similarly, colloidal particles that are not soluble neither in the water phase nor in the monomer phase are also utilized as suspending agents, such as tricalcium phosphate (TCP), magnesium pyrophosphate, and zinc oxide [13, 14]. Suspension polymerization involves numerous microreactors in suspension, and suspending agents significantly prevent the coalescence of two microreactors. They achieve this by providing electrostatic repulsion and a solid barrier around the microreactors. Colloidal particles that are insoluble in the liquid and monomer phases, along with surfactants and certain polymers, are used either individually or cooperatively with one another in the polymerization medium to yield adequate stabilization.

1.3.3. Oil to Water Ratio

Oil/Water ratio is a critical parameter in the design of a suspension polymerization reaction. The monomer concentration in the medium directly influences the reaction rate. Boosting the monomer ratio in the reactor can alter the reaction kinetics and impact the product quality. Moreover, the concentration ratio of the monomer to liquid phase also influences the coalescence of the microreactors during the polymerization as well as the heat removal from the microreactors [15]. The liquid phase supplies the reaction with the heat sinker, so reducing the water phase may cause localized heat problems and damage the stabilization.

1.3.4. Reactor Geometry and Shape

In a suspension polymerization system, reactor shape and geometry are the main characteristics that affect the size and shape of the formed beads. There are several types of reactors with different length-to-radius ratios and numbers of baffles [16]. However, the most common reactor geometry employed for suspension polymerization is two-baffled systems opposite each other. Baffles supply the suspension by alleviating heat transfer, promoting vortex formation, and providing uniform particle size

distribution and a proper shape for each bead. Furthermore, baffles aid in dispersing the monomer droplets throughout the reactor and prevent agglomeration, ensuring a good product at the end of the polymerization. The reactor selection depends on the reaction design and may change from recipe to recipe.

1.3.5. Impeller Shape

Impeller shape, just like the reactor geometry, plays a vital role in determining the quality of the products. Different impeller properties, including shape, radius, and length, can influence factors such as heat transfer, mass transfer, particle size distribution, *etc.* The appropriate mixer choice aims to optimize the conditions given above [16]. The most common impeller type for suspension polymerization in the presence of two-baffled systems that are opposite to each other is a two-pitched blade paddle impeller, which supplies the reaction with high homogeneity. Different reactor shapes may require different impeller shapes to succeed in suspension polymerization.

1.3.6. Agitation Speed

Agitation is utilized in order to form a suspension from two different immiscible liquids. Agitation speed is another determining factor for bead shape and size due to its effect on droplet coalescence and breakage. That is why it should be tuned so that the breakage overcomes the coalescence, eventually preventing the unwanted agglomerations [17].

1.3.7. Hydronium and Hydroxide Ion Concentration

The decomposition of the molecules that produce free radicals may change the pH significantly throughout the reaction. Some of the suspending agents are acid soluble, which causes condition change during the reaction since acidic media consume colloidal particles [16]. Some surfactants and polymers that may be used in suspension polymerization are acid and base susceptible to certain pH values, which is why the

pH of the reaction should be tuned with a proper buffer.

1.3.8. Additives

Monomeric flame retardants, polymeric flame retardants, metallic flame retardants, colorants, and thermal conductivity tuners can be incorporated into polystyrene beads during polymerization [18]. Each of the given compounds above may affect the reaction kinetics and the bead properties in a different manner due to their nature. In general, each additive incorporation into polystyrene beads requires a different study to fine-tune the reaction conditions.

1.4. Common Design Parameters of Polystyrene

1.4.1. Glass Transition Temperature (T_g)

The general design parameters of EPS include good thermal conductivity, uniform particle size distribution, expansion up to 98% of its volume, and resistance against humidity and flame. A good thermal conductivity is generally achieved by expanding polystyrene beads in the presence of heat. Polymer molecules become softened when exposed to enough heat to provide their amorphous part with flexibility. In the second stage, 120°C and high-pressure are applied to polystyrene to soften them. Softened polystyrene beads under high pressure are active in terms of diffusion, which are then permeated by n-pentane, which will be evaporated by the final user [19]. Blowing agents are trapped in the polystyrene above glass T_g and can be stored for a long time below T_g. Final use requires $T>T_g$ to evaporate the trapped blowing agents efficiently. That is why maintaining a proper range of T_g is necessary to facilitate easy release of the blowing agents while ensuring a long shelf life.

1.4.2. Molecular Weight (M_w) of Polymers

An excellent mechanical strength is naturally related to the molecular weight of the polymers for all polymers. That is why increasing the M_w of the polymer is going to supply the material with the required mechanical properties. Longer chains provide more entanglements and intermolecular forces, resulting in elevated mechanical properties such as increased tensile strength, modulus, and toughness [20].

2. AIM OF THE STUDY

The first objective of this study was to optimize the polymerization conditions of free radical suspension polymerization of polystyrene in the laboratory scale (1.0L).

Thereafter, different polymer additives such as graphite, colorants, and flame retardants are aimed to be incorporated into polystyrene beads by employing the optimized polymerization mentioned above.

3. EXPERIMENTAL

The polymerizations were carried out in a 2-baffled reactor (1L) that is oppositely placed. A 2-pitched blade paddle-type impeller was used in the studies. The reactor geometry and the mixer geometry were held constant throughout the studies.

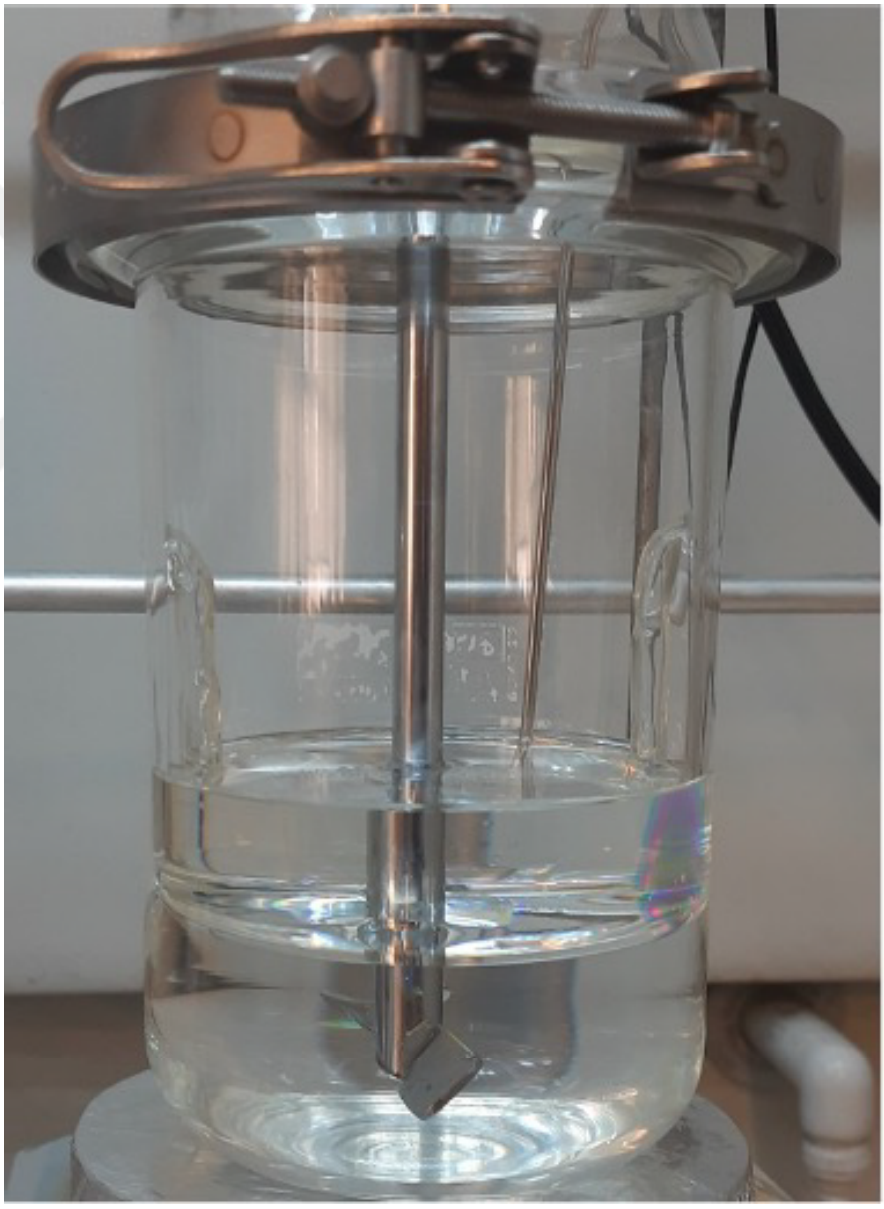


Figure 3.1. The reactor system employed in the suspension polymerization of styrene.

3.1. Materials

Styrene monomer (Sty), benzoyl peroxide (BPO), disodium phosphate (DSP), calcium chloride ($CaCl_2$), nacconol (SDBS), hydroxy ethyl cellulose (HEC), polyvinyl pyrrolidone K-90 (PVP-K90), and graphite (G), tricalcium phosphate (TCP) were obtained from CFN Kimya A.Ş. Aluminum and phosphate-based flame retardants were obtained from Isochemicals. Deionized water (DI) is prepared *via* a reverse-osmosis process.

3.2. Polystyrene Optimization

In all polymerizations, variables such as pH, temperature, the impeller shape and the reactor shape were held constant to isolate the effects of each alteration. All the reactants that are given in the below tables were introduced to the reaction vessel at the beginning of the polymerization. The reaction vessel (cylindrical five-necked glassware) was fitted with a condenser to prevent the loss of water from the reactor. The agitator was positioned 0.5 cm above from the bottom of the reaction vessel. The polymerization temperature was monitored with a thermocouple and the initial pH was adjusted by using a pH meter. After all the ingredients were introduced to the reaction vessel, the mixture was heated up to 90°C. The polymerization was assumed to begin at 90°C with the decomposition of the peroxide initiators. The polymerizations lasted for roughly 5 hours once the mixture reaches 90°C. The products were washed with deionized water to remove any residual suspension agents after the polymerization.

(i) Tricalcium phosphate (TCP) optimization reactions: TCP to water ratio (w/w) and the relative amounts of the initiator and the suspension agents were altered as shown below.

Table 3.1. TCP optimization reactions.

Rxns	Sty(g)	H2O(g)	TCP(g)	BPO(g)	DSP(g)	RPM	APS(mm)
pSt-3	200	400	0,8	0,638	0,0319	300	1,79
pSt-7	200	400	1,6	0,638	0,0319	300	>2
pSt-10	200	400	2,4	0,955	0,0319	300	1,53
pSt-11	200	400	0,8	0,955	0,0319	300	1,61
pSt-20	200	400	1,2	0,955	0,0319	300	1,52

(ii) Benzoyl Peroxide (BPO) ratio to monomer (mol/mol) was investigated while the other inputs were held constant.

Table 3.2. BPO optimization reactions.

Reactions	Sty(g)	H2O(g)	TCP(g)	BPO(g)	DSP(g)	RPM	APS(mm)
pSt-3	200	400	0,8	0,638	0,0319	300	1,79
pSt-11	200	400	0,8	0,955	0,0319	300	1,61
pSt-19	200	400	0,8	0,755	0,0319	300	>2
pSt-20	200	400	1,2	0,955	0,0319	300	1,52
pSt-22	200	400	1,2	1,4	0,0319	300	1,7

(iii) The difference between industrially obtained TCP and *in situ* TCP formation was investigated. *In situ* TCP was obtained by precipitating calcium chloride with disodium phosphate. Calcium chloride and disodium phosphate were introduced to the reaction vessel at the beginning of the polymerization.

Table 3.3. *In situ* TCP optimization reactions.

Rxns	Sty(g)	H2O(g)	TCP(g)	BPO(g)	$CaCl_2$(g)	DSP(g)	APS(mm)
pSt-12	200	400	0,8	0,955	0	0,0319	1,29
pSt-24	200	400	0	0,955	0,87	0,772	>2
pSt-25	200	400	0	1,1	0,87	0,772	1,46
pSt-37	200	400	0,8	1,1	0	0,0319	1,1

(iv) The alterations of agitator speed were investigated. Failures were observed when it was adjusted lower than 300 and over than 350.

Table 3.4. RPM optimization reactions.

Rxns	Sty(g)	H2O(g)	TCP(g)	BPO(g)	RPM	APS(mm)
pSt-11	200	400	0,8	0,955	300	1,61
pSt-13	200	400	1,1	0,955	350	1,15
pSt-14	200	400	0,9	0,955	325	1,13
pSt-Fail	200	400	0,8	0,955	400	N/A
pSt-Fail2	200	400	0,8	0,955	250	N/A

(v) Monomer/water ratio (w/w) was investigated. Throughout these experiments the mass ratio of monomer to benzoyl peroxide was held between 0.47 – 0.5%.

Table 3.5. Oil/water ratio optimization reactions.

Rxns	Sty(g)	H2O(g)	TCP(g)	BPO(g)	RPM	APS(mm)
pSt-11	200	400	0,8	0,955	300	1,61
pSt-15	100	400	1	0,4785	325	0,66
pSt-16	100	400	2,4	0,62	325	0,54
pSt-33	300	300	1,5	1,5	300	1,75
pSt-Fail3	300	300	0,8	1,5	300	N/A

3.3. Graphite Added Polystyrene

In all polymerizations, variables such as pH, temperature, the impeller shape and the reactor shape were held constant to isolate the effects of each alteration. Typical chemicals and procedures used in polystyrene synthesis were used. Differently, certain surfactants like PVP, HEC, or SDBS were introduced to reaction vessel at the beginning of the polymerization. Once the polymerization medium reached 90°C, it took 2 hours to add the master batch, which was comprised of graphite, BPO, St, and some surfactants such as PVP, HEC or SDBS. Typical purification steps employed in polystyrene synthesis were employed.

(i) Different suspension agents were employed throughout the optimization of the graphite incorporation such as polymeric suspension agents, anionic suspension agents, and colloidal suspension agents. All of them were introduced to the reaction vessel before the polymerization started.

Table 3.6. Suspension agents' ratio optimization for graphite incorporation reactions.

Rxns	Sty(g)	H2O(g)	TCP(g)	BPO(g)	PVP(g)	G	APS(mm)
pStG3	191+9	400	0,64	0,955	0,16	1	1,76
pStG4	191+9	400	0,56	0,955	0,24	1	1,62
pStG5	190+9	400	0,48	0,955	0,32	1	1,5
pStG6	190+9	400	0,4	0,955	0,4	1	1,47
pStG7	190+9	400	0,32	0,955	0,48	1	1,19

(ii) Different initiator ratios (mol/mol) were investigated due to initiator consumption throughout the polymerization by graphite.

Table 3.7. BPO optimization for graphite incorporation

Rxns	Sty(g)	H2O(g)	TCP(g)	BPO(g)	PVP(g)	G(g)	APS(mm)
pStG1	191+9	400	0,72	0,638	0,2	1	1,79
pStG3	191+9	400	0,64	0,955	0,16	1	1,76
pStG4	191+9	400	0,56	0,955	0,24	1	1,62

(ii) Different ionic strengths were investigated. To adjust ionic strength of the medium, KCl was introduced to the reaction vessel before the polymerization began.

Table 3.8. Salt effect for graphite incorporation.

Rxns	Sty(g)	H2O(g)	BPO(g)	PVP(g)	G(g)	KCl(g)	APS(mm)
pStG17	300+30	300	1,8	0,8+0,2	1,5	0	1,46
pStG18	300+30	300	1,8	0,8+0,2	1,5	1,1	1,58

(iv) The RPM change and its effect on polymerization was investigated due to the presence of graphite.

Table 3.9. RPM optimization for graphite incorporation

Rxns	Sty(g)	H2O(g)	TCP(g)	BPO(g)	PVP(g)	RPM	APS(mm)
pStG8	180+18	400	0,8	0,955	0,4	400	0,63
pStG12	190+9	400	0,8	0,955	0,2	300	1,72
pStG13	190+9	400	0	0,955	0,8	300	1,36
pStG17	300+27	300	0	1,8	0,8	350	1,46
pStG19	300+27	300	0	1,8	0,2+0,2	275	1,11
pStG20	300+27	300	0	1,8	0,8	275	¡0.5

(v) The difference between addition of the graphite after 2 hours and after 3 hours was investigated due to the change of the viscosity throughout the polymerization.

3.4. Metallic Flame Retardant Added Polystyrene

In these experiments, typical chemicals for polystyrene synthesis were used but flame retardants were added as the extra reagent. All the reactants were introduced to the reaction vessel including flame retardants before the polymerization began. The same procedure given in polystyrene synthesis was employed throughout polymerization and purification.

(i) The suspension agent nature of flame retardants was investigated.

Table 3.10. Suspension agent effect optimization of flame retardant incorporation reactions.

Rxns	Sty(g)	H2O(g)	TCP(g)	BPO(g)	FR(g)	APS(mm)
pStFr1.1.1	200	400	0,8	0,955	3,7	0,66
pStFr2.1.1	200	400	0,8	0,955	3,7	0,75
pStFr2.1.2	200	400	0	0,955	3,7	1,65
pStFr2.1.2	200	400	0	0,955	3,7	1,73

(ii) The addition of the flame retardants to polymerization recipe was investigated.

Table 3.11. Polystyrene reaction comparison with flame-retardant incorporated polystyrene reactions.

Rxns	Sty(g)	H2O(g)	TCP(g)	BPO(g)	FR(g)	APS(mm)
pSt-1	200	400	0,8	0,638	0	¿2
pSt-2	200	400	0,8	0,638	0	¿2
pStFr1.1	200	400	0,8	0,638	1,65	0,62
pStFr1.2	200	400	0,8	0,638	0,8	1,00

3.5. Colorant Added Polystyrene

One of the major challenges of the polymer industry is the incorporation of the colorants into polymers. In this chapter colorant incorporation into polystyrene is explored. A blue colorant namely phthalocyanine blue BP15:3 which is soluble in neither water nor suspended phase was used. The same procedure for both polymerization and purification for graphite addition is followed.

Table 3.12. Reactants in pigment incorporated polystyrene synthesis

Rxns	Sty(g)	H2O(g)	TCP(g)	BPO(g)	PVP(g)	Type	APS(mm)
pStB1	190+9	400	0,72	0,638	0,2	BP15:3	1,74
pStG1	190+9	400	0,72	0,638	0,2	G	1,79

3.6. Characterization

3.6.1. Gel Permeation Chromatography (GPC) Analysis

Viscotek VE2001 GPC instrument was utilized to determine the synthesized polymers' molecular weight. The temperature of the column was adjusted to 35°C, and tetrahydrofuran (THF) was chosen as a solvent. GPC samples were filtrated with a 0.45 mm filter, and the concentration was held at 4 mg/mL for all samples. The flow rate was adjusted to 0.5 mL/min for all samples.

3.6.2. Differential Scanning Calorimetry (DSC) Analysis

Exstar SII DSC 7020 instrument was used in order to determine the thermal characteristics of the synthesized polymers. During analyses, heating and cooling rates were held at a constant rate of 10°C/min. Methods are shown below:

3.6.3. Bead Size and Distribution Analysis

Retsch AS 200 was used in order to analyze the average bead size distribution.

4. RESULTS AND DISCUSSION

The results and discussion part will explore the polymerization kinetics, limitations and polymerization optimizations in terms of its M_w, and average particle size. First, optimization of styrene suspension polymerization will be discussed and then, polystyrene will be modified using graphite, flame retardants, and colorants.

4.1. Optimization of Suspension Polymerization of Styrene

Five different parameters were altered for the optimization of the suspension polymerization of styrene. The success of the polymerization was evaluated based on achieving specific criteria: a yield more than 95%, the formation of a spherical morphology, and a M_w at least 150 kDa.

4.1.1. Optimization of the TCP Amount

Colloidal TCP plays a crucial role in preventing the agglomeration of the suspended phase during the polymerization, ensuring the formation of spherical beads. The amount of TCP employed significantly influences polymerization conditions, impacting various aspects. An insufficient dosage of TCP may fail to provide the necessary stability for polymerization, leading to experimental failure as coalescences outnumber breakages. Conversely, an excessive dosage of TCP can negatively affect the average particle size due to oversaturation of the surface of the monomer droplets. Additionally, the size and shape of the TCP colloids are inherent factors that affect the suspension polymerization and should be taken care of before the experiments. In this section, the effects of the TCP amount on the polymerization will be addressed.

Experiments revealed that a TCP/water ratio higher than 0.2% (w/w) may result in the formation of large and immeasurable polystyrene beads, as observed in Table 4.1 (entry 2) whereas 0.2% yielded 1.79 mm (entry 1).

Table 4.1. Optimization of TCP amount

No	Rxns	Sty(g)	H2O(g)	TCP(g)	BPO(g)	RPM	APS(mm)
1	pSt3	200	400	0,8	0,638	300	1,79
2	pSt7	200	400	1,6	0,638	300	¿2
3	pSt10	200	400	2,4	0,955	300	1,53
4	pSt12	200	400	0,8	0,955	300	1,29
5	pSt20	200	400	1,2	0,955	300	1,52

Moreover, alterations in TCP were examined as the weight of BPO increased by a factor 1.5 in order to obtain the products (entries 3, 4, and 5) in a measurable range (0.5 – 2.0 mm). An increased TCP amount affected the average particle size adversely, as the average particle size increased after adding more than 0.2% of TCP to the reaction vessel. This adverse effect is ascribed to the infiltration of TCP substances into the monomer droplets.

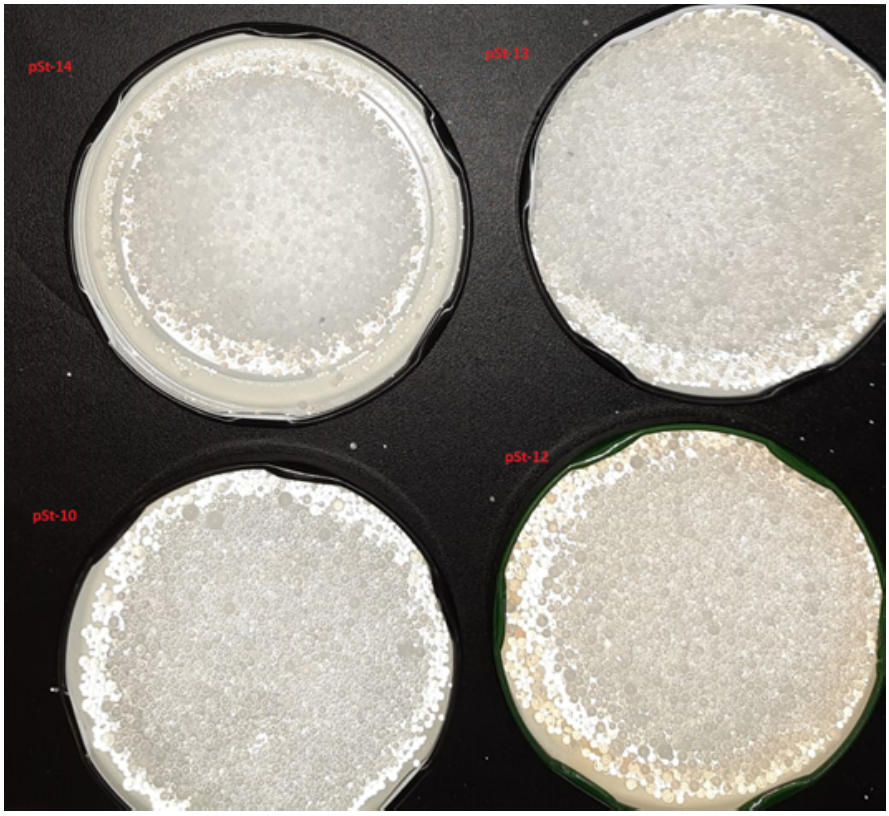


Figure 4.1. Pst-10, pst-12, pst-13, and pst-14 polymerization products.

4.1.2. Optimization of BPO, the Initiator Concentration

In the presence of sufficient heat, benzoyl peroxide (BPO) undergoes decomposition generating two free radicals that serve as initiators for polymerization by activating the benzylic position of styrene. The dosage of BPO plays an important role in this process, influencing the polymerization outcome. A lower BPO dosage yields high M_w polymers due to deficiency in the initiation step. However, it should be mentioned that increased levels of unreacted styrene monomers throughout the polymerization may cause problems. The presence of unreacted monomers dissolves the polystyrene causing an increase in the viscosity of the suspended phase and ultimately leading to an experimental failure. Conversely, a higher dosage of BPO restricts the polymer from having high M_w by consuming monomers rapidly. This results in mechanically poor polymer beads. Finding the balance in BPO dosage is essential to prevent experimental failure while enhancing the M_w of the polymer. The experiments were designed with an initiator/monomer mol ratio 0.1, and subsequent trials were conducted to assess if there exists an optimal ratio. Analysis of Table 4.2 (entries 1, 2 and 4, 5) reveals that an increase in the initiator amount correlates with a lower average particle size.

Table 4.2. Optimization of initiator amount

No	Rxns	Sty(g)	H2O(g)	TCp(g)	BPO(g)	RPM	APS(mm)
1	pSt1	200	400	0,8	0,638	300	> 2
2	pSt11	200	400	0,8	0,955	300	1,61
3	pSt18	200	400	0,8	0,755	300	> 2
4	pSt20	200	400	1,2	0,955	300	1,52
5	pSt23	200	400	1,2	1,11	300	1,17

Notably, dosages of 0.638, and 0.755 grams of BPO yielded large polymers (average particle size higher than 2.0 mm), whereas 0.955 grams of BPO produced sievable beads (average particle size lower than 2 mm) suitable for industrial purposes. A similar trend is observed with the variation in the amount of TCP up to 1.2 grams (entries

4 and 5). The addition of 0.955 grams of BPO resulted in an average particle size of 1.52 mm, whereas the addition of 1.11 grams of BPO decreased the average particle size to 1.17 mm. These findings highlight the significance of the initiator dosage for achieving desirable polymer properties in terms of size and quality.

4.2. *In situ* Tricalcium Phosphate Formation

Tricalcium phosphate is a colloidal solid substance that is neither soluble in water nor in the styrene monomer. The average particle size of the TCP and its distribution significantly affects the product quality. Commercially, 10 micron of average particle size and narrow particle size distribution is preferred[19]. In those experiments the difference between commercially available TCP and *in situ* generated TCP is addressed. Throughout the reactions RPM was held constant as 300. To attain *in situ* TCP, calcium chloride and disodium phosphate was employed at the beginning of the reaction. Analysing Table 4.3 (entries 1 and 2) where the BPO dosage is fixed at 0.955 grams, it is evident that commercially available TCP (entry 1) exhibits superiority over *in situ* TCP formation (entry 2) polymerization.

Table 4.3. Optimization of TCP use

No	Rxns	Sty(g)	H2O(g)	TCP(g)	BPO(g)	APS(mm)
1	pSt12	200	400	0,8	0,955	1,29
2	pSt24	200	400	0,8 *in situ*	0,955	¿2
3	pSt25	200	400	0,8 *in situ*	1,1	1,46
4	pSt37	200	400	0,8	1,1	1,10

Even though the polymerization conducted with commercially available TCP yielded 1.29 mm average particle size, *in situ* TCP formation polymerization yielded large particles that cannot be detectable with standard sieves. Similar results were obtained at higher BPO amounts at 1.1 grams (entry 3 compared to 4). It is certain that commercially available TCP demonstrated superiority in terms of effectiveness over

in situ generated TCP. This dominance can be attributed to the critical parameters governing the precipitation reaction of calcium chloride and disodium phosphate. The efficacy of the polymerization carried out with *in situ* TCP strictly depends on the formed TCP colloids. In the absence of a well-established precipitation reaction, the product quality may vary based on parameters such as temperature, concentration and the relative supersaturation which all need to be optimized.

4.2.1. Optimization of Stirring Rate: Revolution *per* Minute (RPM)

Revolution *per* minute (RPM) is a significant kinetic variable for the suspension polymerization of styrene. The agitation process facilitates the mixing of the suspension, resulting in the formation of suspension droplets within the aqueous medium. An excessively high stirring rate promotes the coalescence of these droplets rather than their breakages, ultimately causing an agglomeration of the suspended phase. In contrast, a low stirring rate might fail to sustain a stable suspended phase, potentially leading to the merging of monomer droplets causing agglomeration. It was observed that the suspension during the polymerization maintains its stability within the range of 300 to 350 RPM. However, insufficient stirring rate at 250 RPM and excessive stirring rate at 400 RPM led to experimental failures. Concurrently, higher agitation speeds require an increased amount of suspension agents to stabilize the polymerization. Analysis of Table 4.4 (entries 1,2 and 3) indicates that the polymerization conducted with 0.9 grams of TCP at 325 RPM exhibited superiority among the experiments by yielding the most desirable average particle size.

Table 4.4. Optimization of stirring rate

No	Rxns	Sty(g)	H2O(g)	TCP(g)	BPO(g)	RPM	APS(mm)
1	pSt13	200	400	1,1	0,955	350	1,15
2	pSt14	200	400	0,9	0,955	325	1,13
3	pSt11	200	400	0,8	0,955	300	1,61
4	pStFail	200	400	0,8	0955	400	N/A
5	pStFail2	200	400	0,8	0,955	250	N/A

4.2.2. Styrene to Water Ratio

The styrene to water ratio (w/w) ,which is also commonly expressed as oil/water ratio, is another critical parameter which influences product quality and process efficiency in styrene suspension polymerization. A low ratio offers an optimal particle size distribution though it limits the polymerization efficiency due to the lower dosage of styrene into the reaction vessel. Conversely, a high oil-water ratio significantly impairs heat removal efficiency due to limited heat absorption around the monomer droplets leading to large average particle size distribution. Heat-related challenges arise from the enthalpy-driven characteristics of the free radical polymerization. The sequential addition of each monomer to the polymer chain generates localized heat issues, particularly in the absence of an efficient heat removal mechanism surrounding the monomer droplets. An increased concentration of styrene monomer intensifies this challenge, as the efficiency of heat removal by the water diminishes significantly. This phenomenon results in the formation of polystyrene beads with irregular shapes. Polymerization up to a 1:2 oil/water ratio (w/w) does not require any additional co-stabilizers. However, higher ratios demand the incorporation of co-stabilizers to overcome localized heat and heat removal issues. In such instances, anionic surfactants like sodium dodecylbenzene sulfonate (SDBS) and non-ionic surfactants such as polyvinyl pyrrolidone are employed. The incorporation of these substances alleviates interfacial tension where TCP fails to stabilize, as it has no stabilization effects on interfacial tension. In Table 4.5 (entries 1 and 2), employing a 1:4 ratio (w/w) results in an average particle size distribution of approximately 0.6 mm.

Table 4.5. Optimization of oil/water ratio

No	Rxns	Sty(g)	H2O(g)	TCP(g)	BPO(g)	RPM	APS(mm)
1	pSt15	100	400	1	0,4785	325	0,66
2	pSt16	100	400	2,4	0,62	325	0,54
3	pSt11	200	400	0,80	0,955	300	1,61
4	pSt33	300	300	0,8	1,5	300	1,75
5	pStFail	300	300	0,8	1,5	300	N/A

Notably, an increase in the ratio up to 1:2 by weight produced slightly larger polymer beads, roughly 1.61 mm. In the presence of a co-stabilizer, 30 mg of SDBS and 0.2 gr of hydroxyethyl cellulose (HEC), the 1:1 ratio by weight (entry 4) yielded an average particle size distribution of 1.75 mm. However, without any co-stabilizer (entry 5), the polymerization failed.

4.3. Graphite Incorporated Polystyrene

Three different features of graphite incorporation to polystyrene polymerizations are investigated throughout the studies.

4.3.1. RPM Change

In Section 4.1.4 the investigation into the effects of RPM on the suspension polymerization was discussed. However, in polymerizations involving graphite incorporation, the addition of graphite introduced a viscosity-altering effect that required the employment of co-stabilizers such as HEC, PVP and SDBS to stabilize the suspended phase. It was observed that the inclusion of the surfactants also eased the RPM requirement which previously was effective only in a narrow range (section 4.1.4). Introduction of the surfactants to the reaction enhanced the tolerance of RPM range from 275 to 400 RPM. It should be noted that the shapes of the beads still depend on the agitation speed. Higher agitation speeds increase the shear force, leading to elongation and the formation of ellipsoidal polystyrene beads. Analysing Table 4.6 (entries 2 and 4) reveals that the average particle size is highly dependent on the surfactant amount rather than TCP amount.

Table 4.6. Optimization of the stirring rate for graphite incorporation

No	Rxns	St(g)	H2O(g)	TCP(g)	BPO(g)	PVP(g)	G(g)	APS(mm)
1	pStG2	200	400	0,72	0,638	0,2	1	1,79
2	pStG8	200	400	0,8	0,955	0,4	1	0,63
3	pStG19	300	300	0	1,8	0,2	1,5	1,11
4	pStG20	300	300	0	1,8	0,8	3	$< 0,5$

Undetectably small polymer beads are obtained when the surfactant/water ratio is adjusted up to 0.26% (w/w). In the first entry, where a 0.05% ratio (w/w) is employed, the average particle size was obtained 1.79 mm. Despite the fourth entry being conducted with 275 RPM, the amount of surfactant played a crucial role in determining particle size rather than RPM. The second entry demonstrates that polymerization at 400 RPM is stable with the employment of 0.1% (w/w) surfactant. In conclusion, the polymerization process is highly dependent on surfactant concentration rather than RPM in the presence of surfactant. In graphite incorporated polymerizations, where surfactants are consistently employed, it is essential to note that a precisely controlled agitation to achieve a stable suspended phase is not a requirement. Yet higher agitation rate should be avoided to prevent elongated products.

4.4. The Addition Time of Graphite

he successful incorporation of additives such as graphite into polystyrene during suspension polymerization is tied to the timing of the addition of the master batch (a mixture of BPO, St, graphite, and surfactant). Throughout the polymerization the viscosity of the medium changes. Introducing additive at the initiation of the polymerization may induce a sudden increase in viscosity, potentially leading to an experimental failure. Conversely, late introduction of the master batch prevents the incorporation of the additives into polystyrene beads due to insufficient concentration of monomer left. A critical viscosity threshold, identified as 1.5 to 2 hours into the reaction, must be reached to enable effective incorporation of graphite into polystyrene.

Low monomer availability and decreased viscosity beyond the 3 hours is the reason for inadequate incorporation of graphite into polystyrene (Figure 4.2).

Table 4.7. Optimization of the addition time of the graphite

No	Rxns	Sty(g)	H2O(g)	TCP(g)	BPO(g)	PVP(g)	G(g)	APS(mm)
1	pStG3hr	180	400	0,8	0,955	0	1	1,56
2	pStG2hr	191	400	0,72	0,638	0,2	1	1,79

Table 4.7 and the image below shows that the incorporation of the graphite into polystyrene is successful when the master batch is introduced to the reaction vessel after 2 hours.

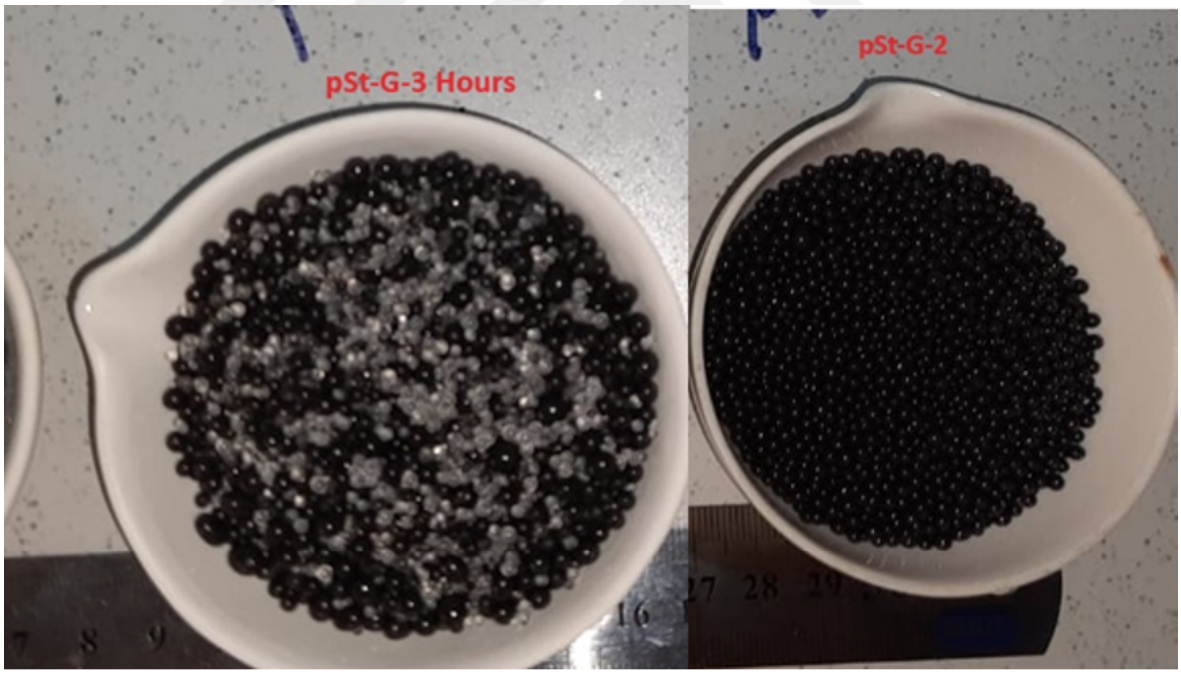


Figure 4.2. The difference between the addition of graphite into suspension polymerization after 2 hrs and after 3 hrs

4.4.1. Colloidal Polymeric Suspending Agent Ratio

In graphite incorporation trials, the inclusion of co-stabilizers becomes imperative to achieve a stable suspension and 325 RPM was held constant throughout the reactions. Colloidal suspension agents, such as TCP, are incapable of stabilizing the suspended phase when they are used alone. Therefore, colloidal suspension agents are commonly paired with either anionic surfactants or polymeric stabilizers. Notably, PVP and SDBS emerge as frequently employed reagents.

The experimental exploration involves varying the quantities of colloidal and polymeric reagents. Table 4.8 illuminates that a significant reduction in average particle size is achieved with increased PVP/TCP ratio (w/w).

Table 4.8. Optimization of collodial and polymeric suspension agent ratio

Rxns	Sty(g)	H2O(g)	TCP(g)	BPO(g)	PVP(g)	G(g)	APS(mm)
pStG3	190+9	400	0,64	0,955	0,16	1	1,76
pStG4	190+9	400	0,56	0,955	0,24	1	1,62
pStG5	190+9	400	0,48	0,955	0,32	1	1,5
pStG6	190+9	400	0,4	0,955	0,4	1	1,47
pStG7	190+9	400	0,32	0,955	0,48	1	1,19

This phenomenon arises from the superior efficacy of the polymeric stabilizers, such as PVP, particularly in highly viscous suspended phases where colloidal particles might be consumed by absorption. Experiments illuminate the dependence of the average particle size to the ratio of colloidal suspension agents to polymeric ones. The adjustment of the average particle size can easily be manipulated by the change of suspension agent ratio.

4.4.2. Optimization of BPO Amount for Graphite Incorporation

The effects of the initiator ratio in the suspension polymerization of polystyrene were discussed in Section 4.1.2. The presence of graphite introduces variability in the consumption of initiator amount, the viscosity and suspension stability. Graphite molecules are abundant in tertiary carbons that bear readily labile hydrogen atoms for free radicals.

Table 4.9. Optimization of the BPO amount for graphite incorporation

Rxns	Sty(g)	H2O(g)	TCP(g)	BPO(g)	PVP(g)	RPM	G(g)	APS(mm)
pStG1	190+9	400	0,72	0,638	0,2	300	1	1,79
pStG3	190+9	400	0,64	0,638	0,2	325	1	1,76
pStG4	190+9	400	0,56	0,955	0,24	325	1	1,62

The graphite surface may contain various functionalities such as carboxyl, carbonyl, and hydroxyl groups, contributing to a complex environment for hydrogen abstraction. It should be noted that the hydrogen abstraction mechanism is highly dependent on bond dissociation energy. That is why, even though the surface has many acidic hydrogens, the abstraction should proceed through tertiary hydrogen atoms due to its low bond dissociation energy. In other words, the addition of graphite into polymerization medium arises competition for free radicals. Some of the free radicals may then be consumed by the graphite molecules, leading to an insufficient BPO concentration in the polymerization. Consequently, in the presence of additives like graphite, deviation from the typical dosage should be expected.

4.4.3. Salt Effect

An increased dosage of suspension agent PVP, although is useful in stabilizing the suspension, it poses challenges such as wastewater treatment and the undesirable formation of ellipsoidal beads instead of the intended spherical ones. To enhance

both purification process efficiency and sphericity, potassium chloride (KCl) salt is commonly added to the polymerization. The idea behind this addition is to obtain high ionic strength which might force the droplets to stay more spherical. Contrary to expectations, the addition of KCl salt yields no significant positive effects on either particle shape or purification efficiency. Moreover, the particle size often drastically increases. The phenomenon can be attributed to the chloride anions (Cl^-) inducing chain scission reactions. The presence of chain scission reactions has an adverse impact on the particle size distribution. As an alternative strategy to attain the Pickering effect magnesium sulfate ($MgSO_4$) should have been used to avoid chain scission reactions and high polarity due to higher charges on its ions.

Table 4.10. Investigation of the salt addition effect in graphite incorporation reactions of polystyrene

Rxns	Sty(g)	H2O(g)	BPO(g)	PVP(g)	RPM	KCl(g)	APS(mm)
pStG17	300	300	1,8	0,8	310	0	1,46
pStG18	300	300	1,8	0,8	310	1,1	1,58

Table 4.10 reveals that 1.46 mm average particle size is obtained without using any salt, even though 1.58 mm average particle size is obtained in the presence of KCl salt.

4.5. Flame-Retardant Incorporated Polystyrene

Commercially, polystyrene often incorporates monomeric or polymeric organic flame retardants due to their high compatibility. However, these flame retardants typically contain halogen atoms, bearing environmental and health risks. As an alternative, metallic flame retardants are under contemporary study for their non-hazardous nature and high availability. This section aims to incorporate metallic flame retardants into polystyrene to overcome the adverse effects mentioned above.

4.5.1. Metallic Flame-Retardant Incorporated Polystyrene

This section aims to explore the difference between flame retardants employed polymerizations and pure polystyrene polymerizations. Flame retardants employed polymerizations significantly yielded smaller polystyrene products compared to those conducted without any flame retardants. This can be attributed to the inherent stabilization effect of flame retardants due to their colloidal nature. Their presence restricts the coalescence of monomer droplets and increases concentration of the suspension agent in the aqueous phase which decreases the average particle size.

Table 4.11. Investigation of metallic flame-retardants incorporated polystyrene reaction stabilities

Rxns	Sty(g)	H2O(g)	TCP(g)	BPO(g)	RPM	FR(g)	APS(mm)
pStFr1.1	200	400	0,8	0,638	300	1,65	0,62
pStFr1.2	200	400	0,8	0,638	300	0,8	1
pSt1	200	400	0,8	0,638	300	0	> 2
pSt2	200	400	0,8	0,638	300	0	> 2

According to Table 4.11, solely TCP used ones yielded products larger than 2 mm; conversely, the addition of 0.8 grams of FR yielded average particle size 1.00 mm and the addition of 1.65 grams of FR yielded 0.62 mm of average particle size.

4.5.2. Metallic Flame Retardants as Suspension Agents

This study focuses on incorporating water and styrene insoluble metallic flame retardants into polystyrene beads during the polymerization process. The RPM was held constant for each experiments as 325. Viscous stage of polymerization supplies the reacting polymers with high diffusivity, allowing the flame retardants to be absorbed by the polystyrene beads. To exploit this property and simplify the polymerization, experiments are conducted without any additional suspension agents, relying solely on

the flame retardants' stabilizing effect. However, compared to usual recipe using TCP substance, average particle size resulted in significantly larger, and the shape of the products tend to become ellipsoidal.

Table 4.12. Investigation of stabilizing effect of flame-retardants onto suspension polymerization

No	Rxns	Sty(g)	H2O(g)	TCP(g)	BPO(g)	FR(g)	APS(mm)
1	pStFr1.1.1	200	400	0,8	0,955	3,7	0,66
2	pStFr2.1.1	200	400	0,8	0,955	3,7	0,75
3	pStFr2.1.2	200	400	0	0,955	3,7	1,65
4	pStFr1.1.2	200	400	0	0,955	3,7	1,73

Table 4.12 reveals that the addition of flame retardants with TCP yielded products with diameters 0.65 to 0.75 mm. However, in the absence of the TCP, the average particle size of the products obtained is in the range of 1.65 to 1.75 mm. Evenly distributed particle size of flame retardants may simplify the polymerization since it might wipe off the requirement of TCP substances. At increased viscosity levels, the absorption of colloidal particles may become possible. A high dosage of metallic flame retardants is intended to enhance both the stability of the reaction before it reaches a viscous state and, thereafter the incorporation of flame retardants during the suspended phase, which shows high viscosity. It can be asserted that flame retardants can also stabilize the polymerization, as their presence in the recipe could yield an average particle size lower than 2 mm.

4.6. Colorant Incorporated Polystyrene

The incorporation of different additives into polystyrene beads serves various purposes. Coloring polystyrene beads after the production step is an additional and cost-ineffective step. Therefore, a blue pigment, namely phthalocyanine pigment, which is insoluble in both water and monomer is employed to achieve cost and time effective

polymerization. In those experiments, 300 RPM and 0,638 gr BPO were held constant. The mechanism of the addition mimics the graphite addition polymerization, and the parameters are kept consistent. Under the same conditions, the addition of colorant and graphite demonstrated similar kinetic behaviors in terms of both reactivity and stability.

Table 4.13. Colorant incorporation, graphite incorporation, and polystyrene reactions

Rxns	Sty(g)	H2O(g)	TCP(g)	PVP(g)	BP15:3	G	APS(mm)
pStBlue	190+9	400	0,72	0,2	1	0	1,74
pSt3	200	400	0,8	0	0	0	1,79
pStG1	191+9	400	0,72	0,2	0	1	1,79

The Table 4.13 indicates that the same inputs yielded similar average particle size for both graphite and colorant polymerizations respectively 1.79 mm and 1.74 mm.



Figure 4.3. Blue pigment incorporation, graphite incorporation and regular polystyrene reaction products

4.7. M_w of the Polystyrene and Its Relation to Initiator Amount

A linear correlation between M_w and initiator is observed throughout the experiments. As the employed initiator amount on the polymerization increased, the M_w of the polymers decreased. This linear correlation is also applicable to graphite incorporated ones. Consistent with expectations, recipes involving graphite yielded

higher M_w products compared to pure polystyrene. This outcome is attributed to the competition between tertiary carbon hydrogens of graphite and benzylic hydrogens of styrene monomer. The abstraction of tertiary hydrogens leads to a reduction in active free radicals, thereby resulting in higher M_w products in graphite incorporated polymerizations.

Table 4.14. Initiator dependency of the molecular weight and number of molecular weight

Reactions	BPO (g)	M_w(daltons)	M_n(daltons)
pStMix4	0,638	260303	153994
pSt11	0,955	191694	118290
pSt22	1,4	128804	83770
pStG1	0,638	482507	185683
pStG3	0,955	250279	121443
pStG8	0,99	233285	136384

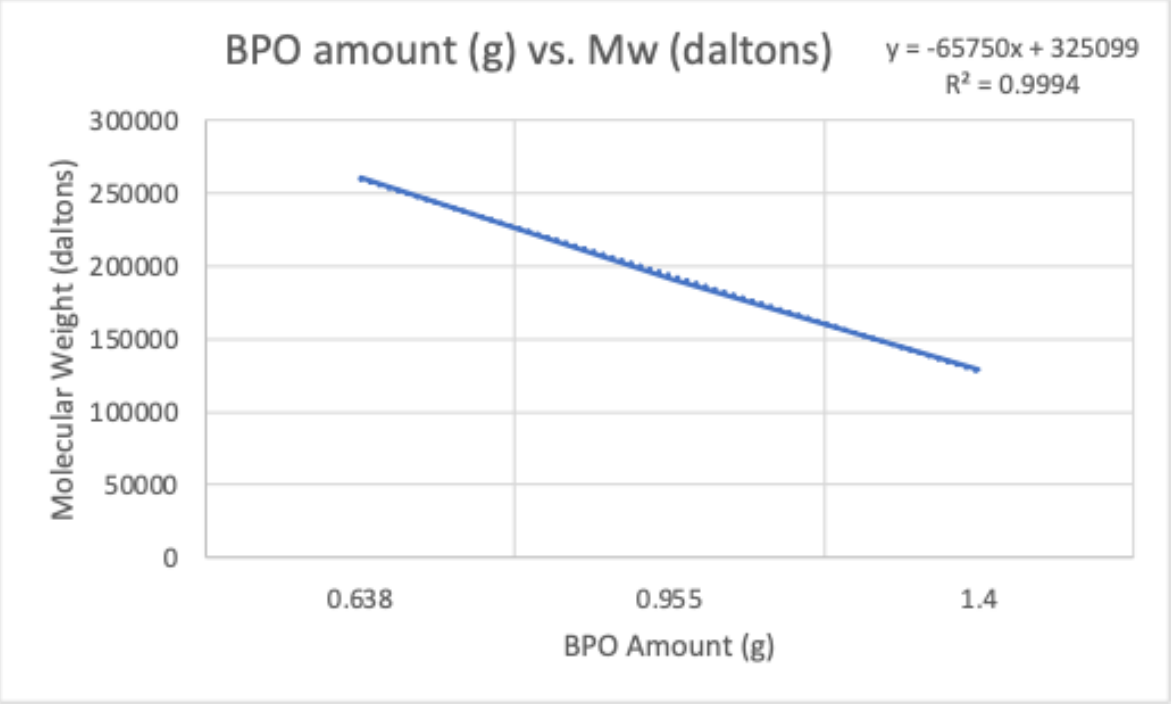


Figure 4.4. Linear dependency of M_w to initiator in polystyrene synthesis

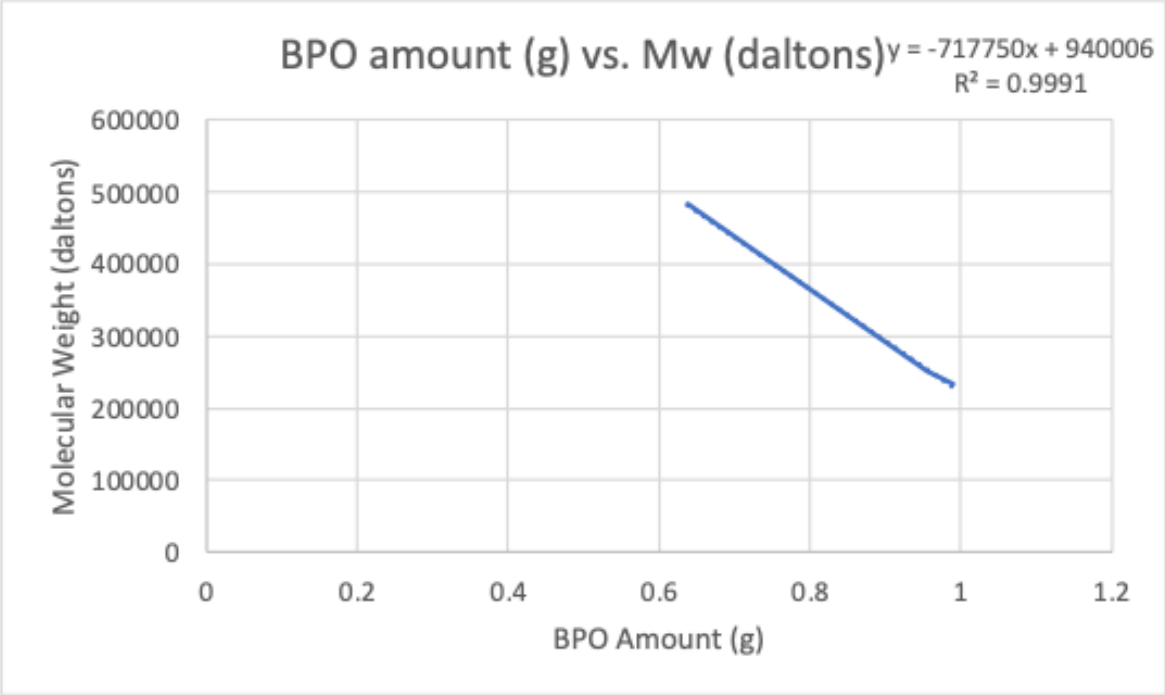


Figure 4.5. Linear dependency of M_w to initiator amount in graphite incorporated polystyrene synthesis

4.8. DSC Data and Their Processability

Studies using DSC data have shown that the incorporation of graphite into polystyrene increases the T_g of the polystyrene beads in comparison to pure polystyrene products by about 5°C. A lower T_g is generally desired for successful impregnation of VOCs into polystyrene beads after the first stage of polymerization. The diffusivity of the polystyrene beads is highly dependent on their T_g. A higher T_g shows lower diffusivity, conversely lower T_g enhances the diffusion process. The addition of lubricants to the polymerization process such as phthalate esters enhances flexibility of the polymers by expanding the free volume within them, allowing for increased rotational freedom. This in turn, reduces the T_g.

Table 4.15. Glass transition temperature of the products of polystyrene and graphite incorporated polystyrene.

Reaction	Glass Transition Temperature
pSt11	88
pSt13	89,4
pSt20	91,27
pStG4	95,18
pStG7	97,01
pStG16	98,16
pStG-FR	98,76

5. CONCLUSION

To conclude, the optimization of styrene polymerization depends on various factors, specifically the selection of reactants, their respective ratios, and certain kinetic factors such as impeller shape and reactor geometry. Additionally, the incorporation of additives such as graphite, flame retardants, and colorants also have a huge impact on the polymerization process, which has been the focus of optimization studies. The addition of reactants such as colorants and graphite led to an increase in the viscosity of the suspended phase, necessitating the incorporation of additional stabilizers, such as polymeric or anionic surfactants, which were required to decrease the interfacial tension. Whereas additives such as flame retardants have little amount of relation with interfacial tension and viscosity. They supplied the polymerization medium with increased amounts of insoluble colloids which prevent the monomer droplets from coalescence.

All these additives were incorporated into polystyrene beads *via* absorption. Furthermore, the alterations in $T_g$were investigated and the M_w of the particles were measured. It was found that certain reactants such as graphite can consume active ingredients and alter the process which should then be re-optimized.

6. FUTURE WORK

The addition of strong ionic compounds such as $MgSO_4$ may promote the formation of the spherical particles in the presence of polymeric co-stabilizers. Furthermore, continuous addition of additives, possibly allowing for better control over the polymerization rate and nucleation, is likely to improve production quality.

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APPENDIX A: SPECTROSCOPY DATA

The results of DSC analyses and GPC analyses are shown in this chapter. Necessary information are provided.

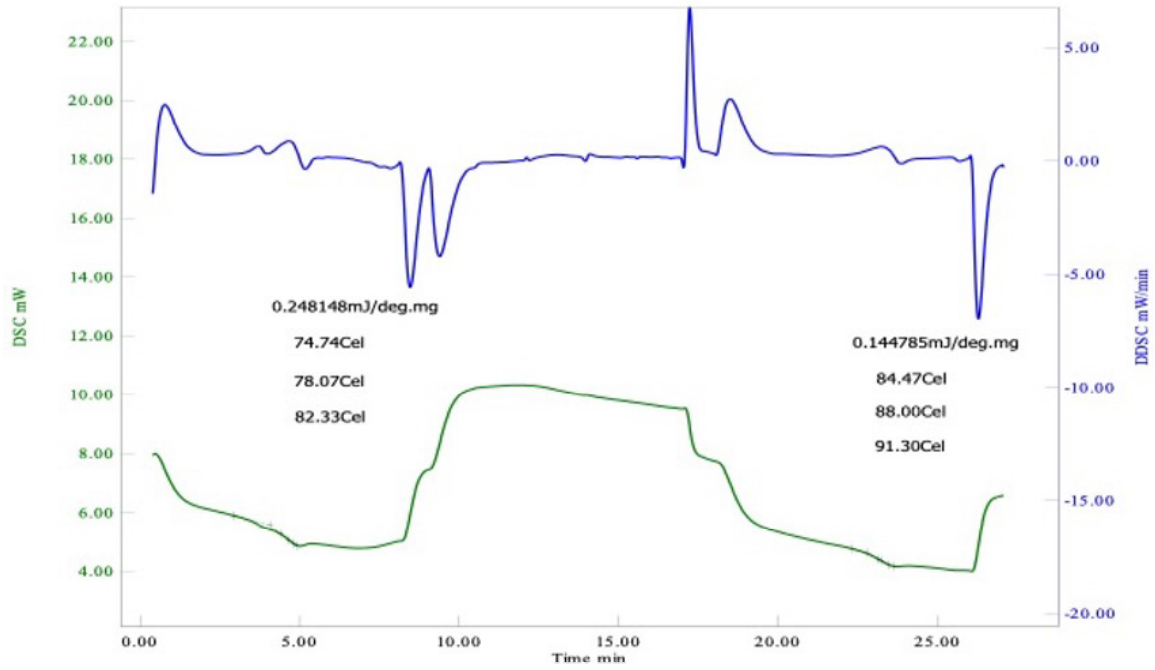


Figure A.1. DSC analysis of pSt-11.

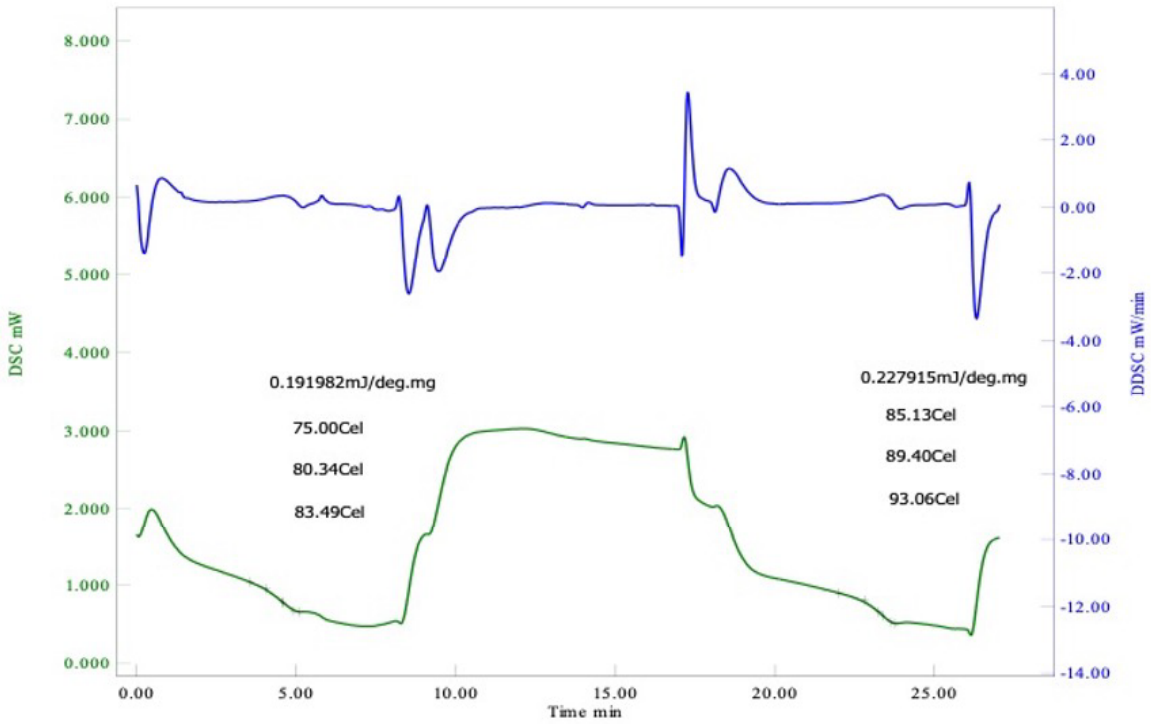


Figure A.2. DSC analysis of pSt-13.

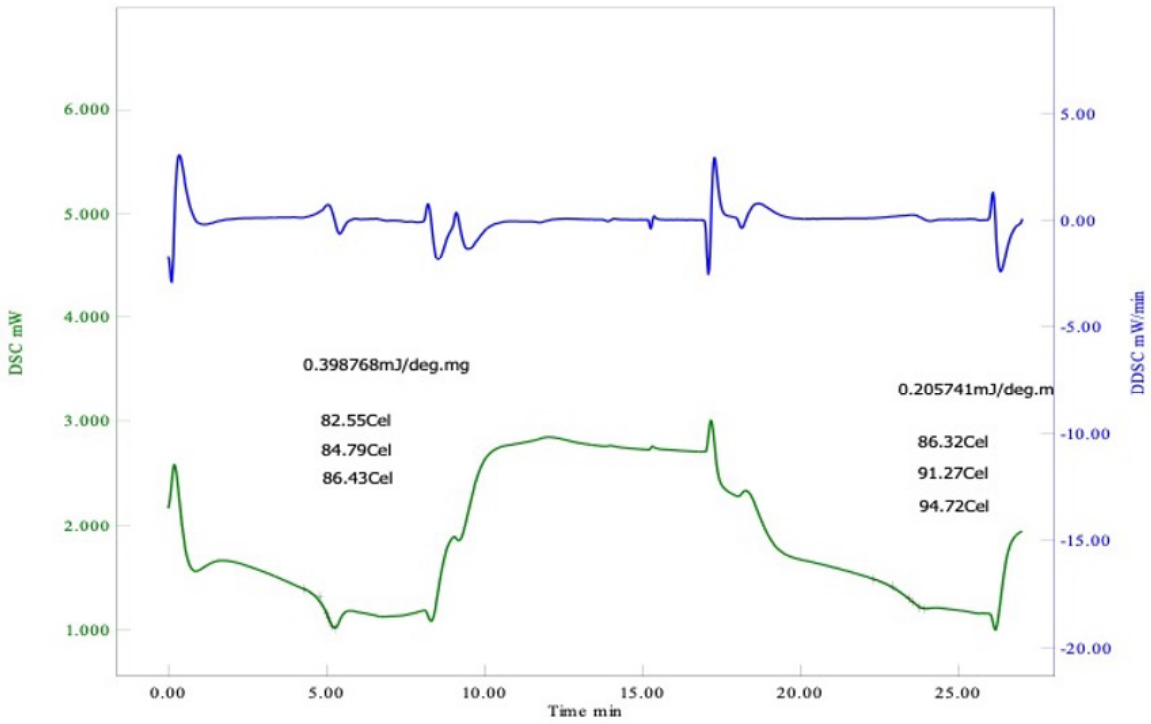


Figure A.3. DSC analysis of pSt-20

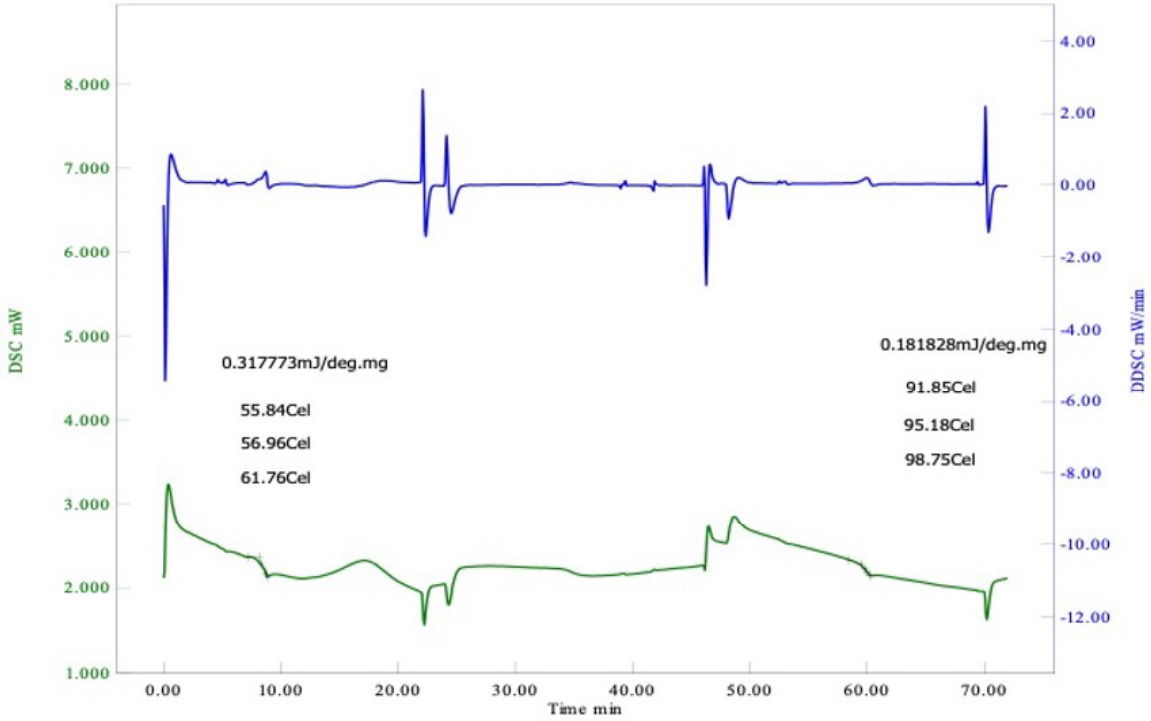


Figure A.4. DSC analysis of pSt-G-4

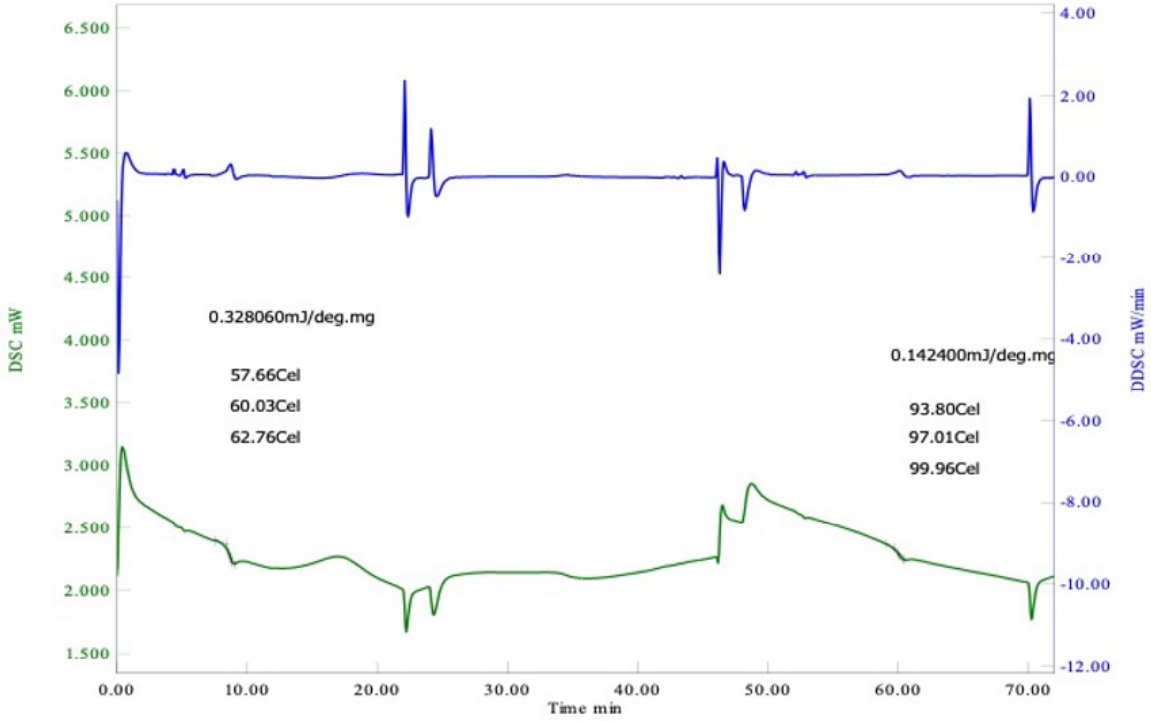


Figure A.5. DSC analysis of pSt-G-7

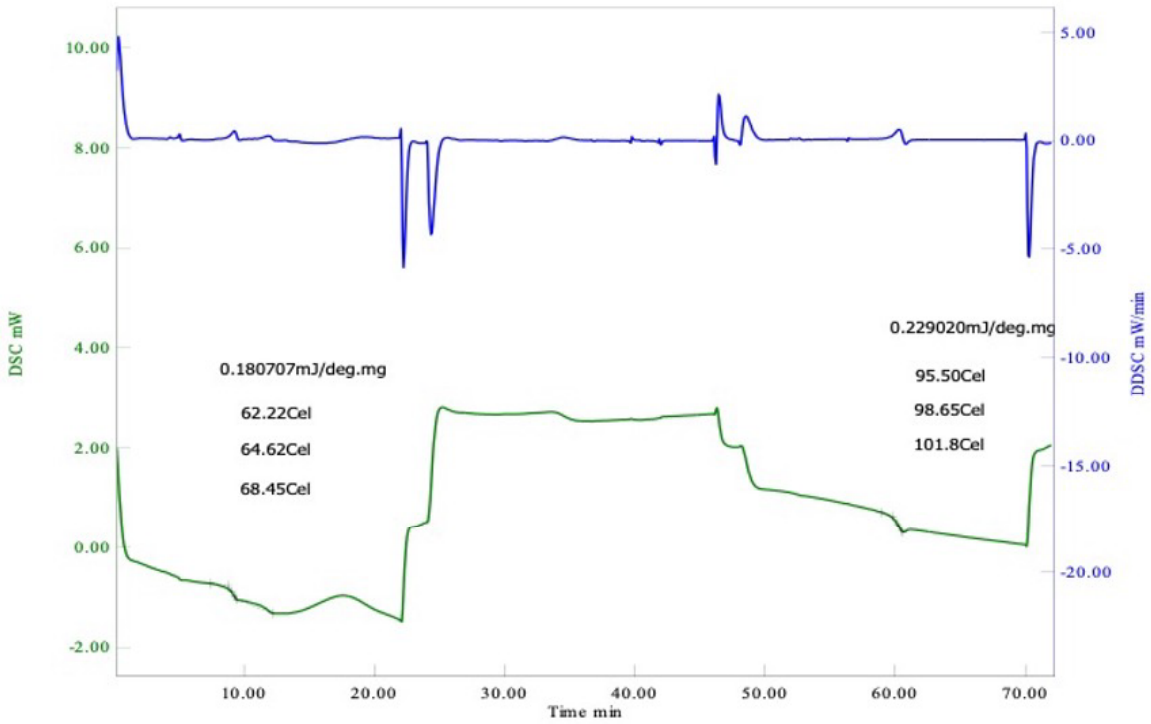


Figure A.6. DSC analysis of pSt-G-16

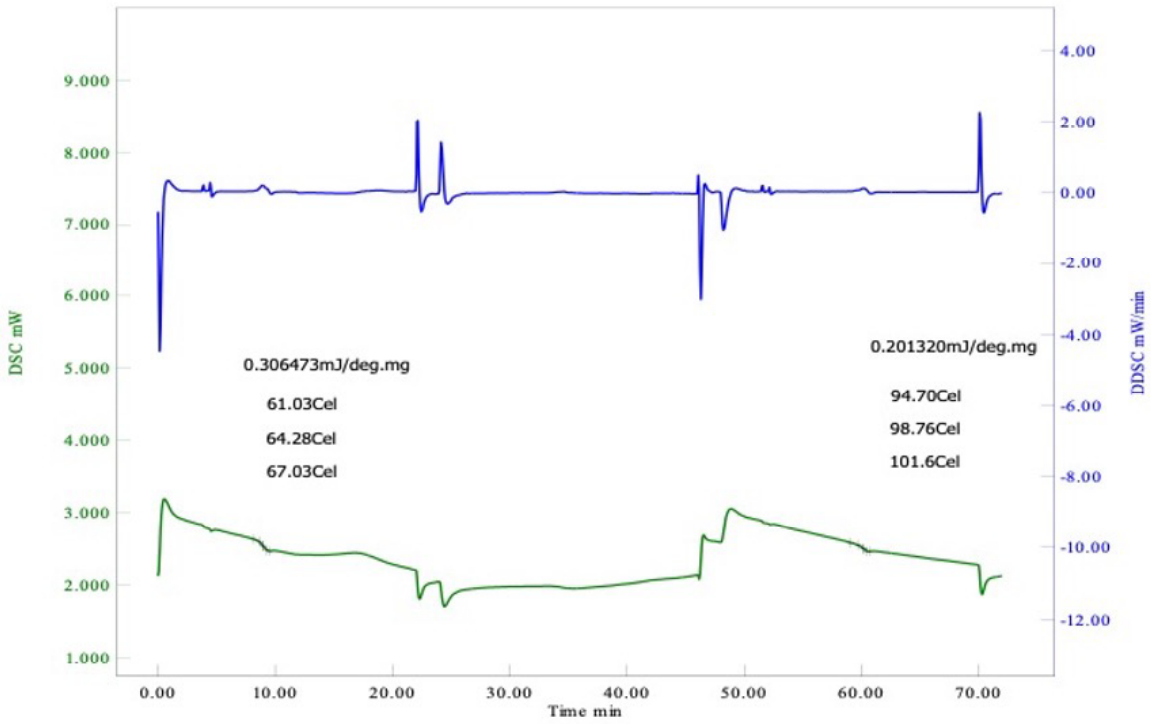


Figure A.7. DSC analysis of pSt-G-Fr

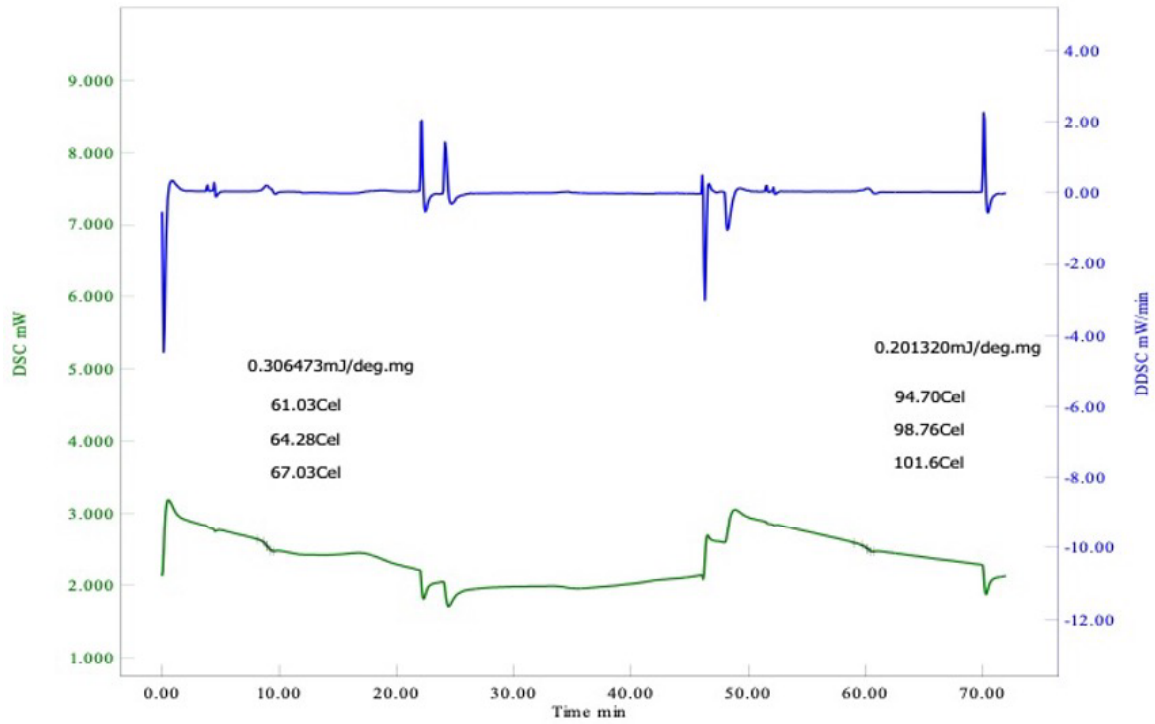


Figure A.8. GPC analysis of pSt-mix4

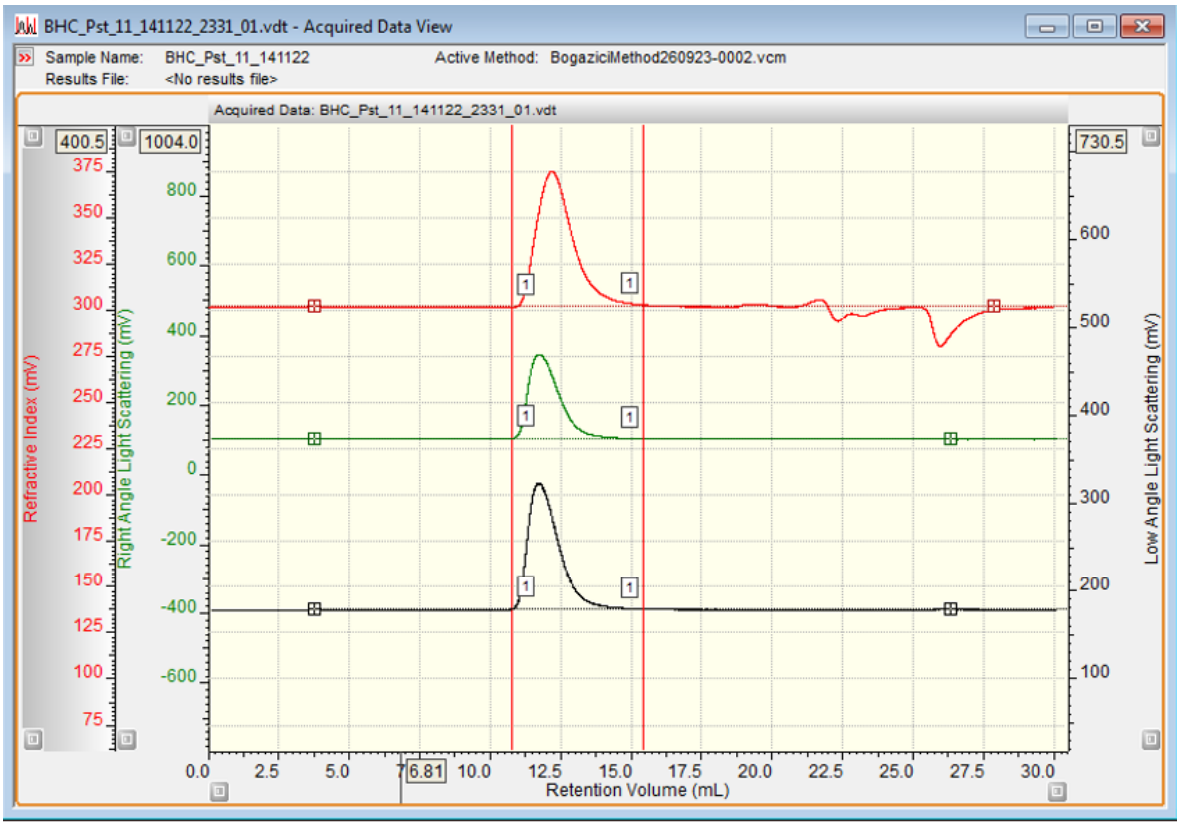


Figure A.9. GPC analysis of pSt-11

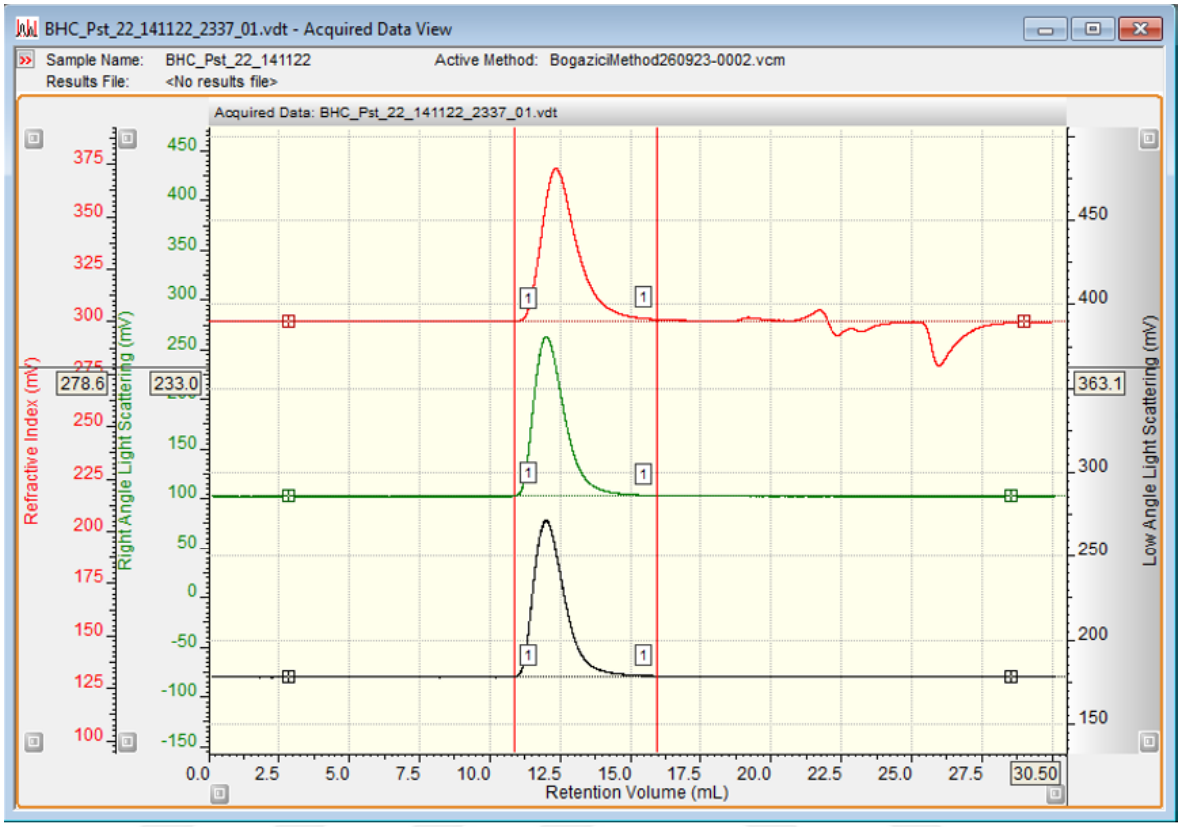


Figure A.10. GPC analysis of pSt-22

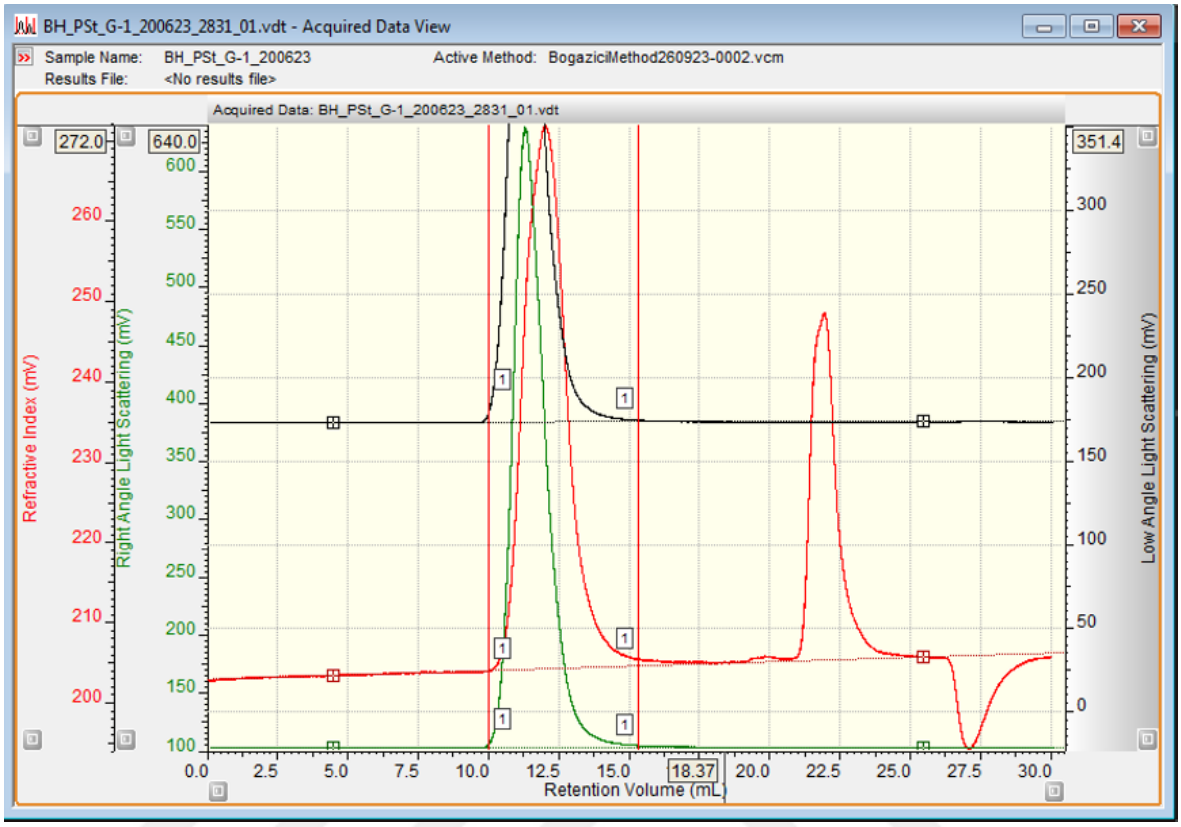


Figure A.11. GPC analysis of pSt-G-1

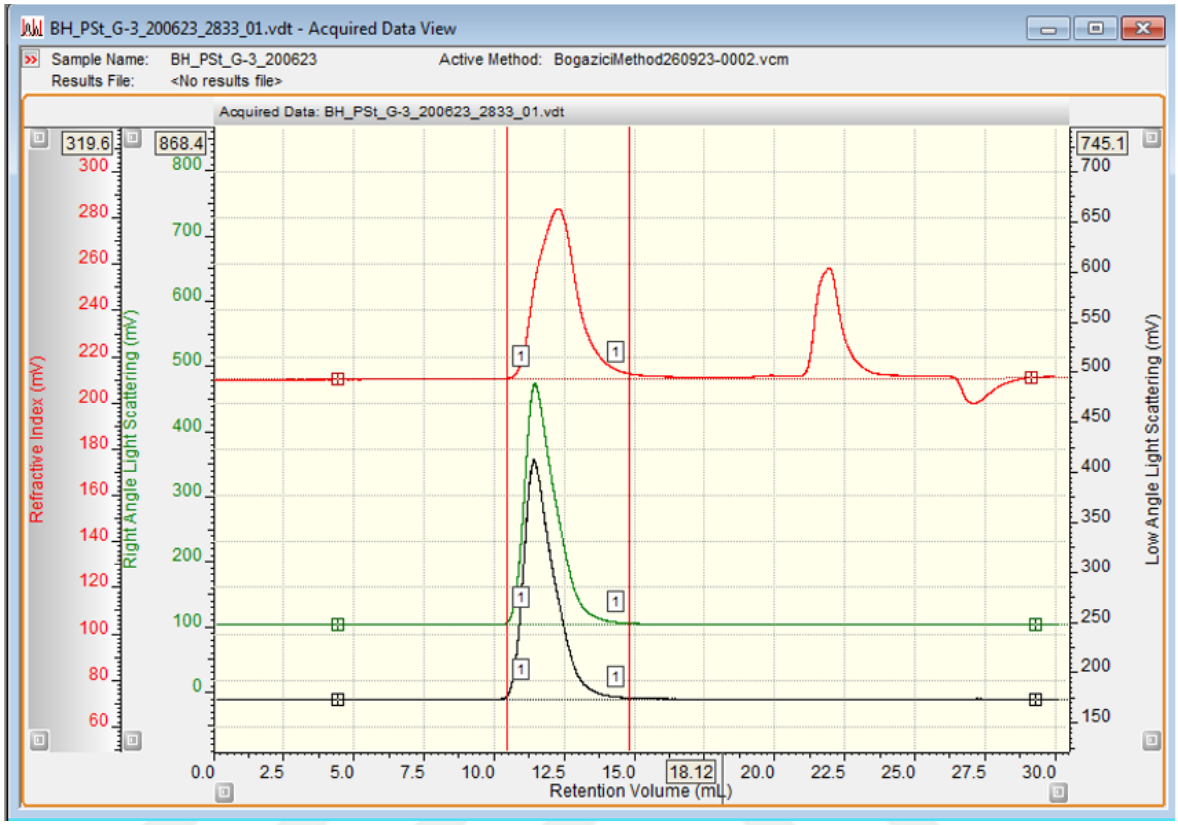


Figure A.12. GPC analysis of pSt-G-3

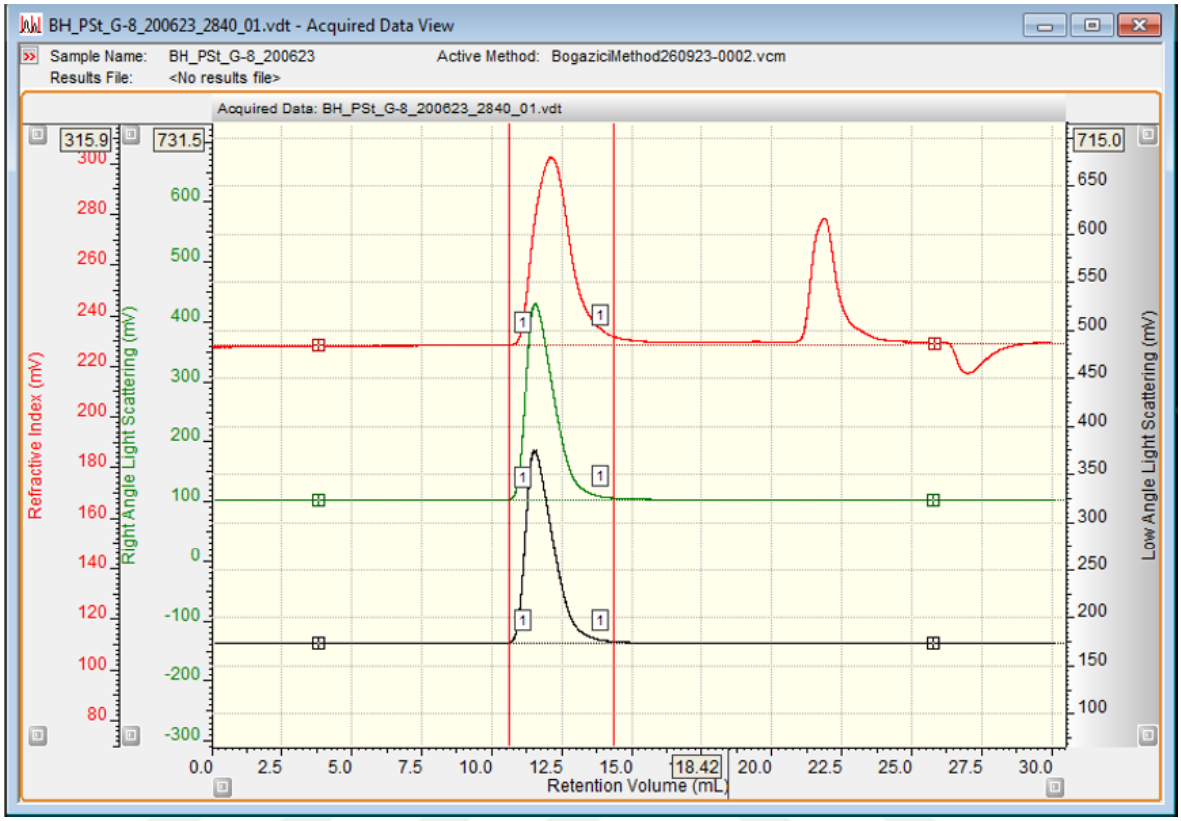


Figure A.13. GPC analysis of pSt-G-8