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Mini-emulsion preparation, kinetics of reaction and physical properties of acrylic terpolymer lattices

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ABSTRACT

In this study, stable lattices of terpolymer butyl acrylate, methyl methacrylate, and styrene were synthesized by a mini-emulsion polymerization technique using tert-butyl hydroperoxide (TBHP)/Fe^{2+}/ ethylenediaminetetraacetic acid/sodium formaldehyde sulfoxylate redox initiators. The effects of water content, initiator concentration and reaction temperature on kinetics of the polymerization reaction were investigated. The reaction rate was determined by periodic sampling. The chemical composition of the samples was determined by FT-IR technique. The molecular weight distribution and polydispersity index (PDI) of polymers were determined by gel permeation chromatography (Mw ranges between 1.25 to 1.81 million g/mol, PDI ranges between 1.31 and 6.64). The size distribution of the polymers in the lattices was investigated by dynamic light scattering technique (position of peaks of different samples varied from 10 to 70 nanometers). Based on the glass-transition temperatures extracted from DSC thermograms, it was inferred that copolymerization produces a micro-structure of special blocks and that this particular terpolymer shows two glass-transition temperatures. Prog. Color Colorants Coat. 9 (2016), 269-279© Institute for Color Science and Technology.

1. Introduction

Acrylic resins are polymers formed from acrylic or methacrylic esters that are sometimes modified with monomers such as acrylonitrile and Styrene [1]. Acrylic resins are used as hybrid resins in combination with polyurethanes, epoxies, and silicones [2]. In many cases, the homo and emulsion co-polymerizations of one or more acrylate monomer are used to synthesize polymers for specific applications. Acryl polymers are used in the dye and coating industries, paper making, production of glue and sealant compounds, textile, leather, and due to their high external stability, high adhesion to under layer, proper wettability of pigments, they can be used as a veneer [3-5]. Also, these materials are used as additives in concrete construction, coating materials in agriculture, and in the structure of ion exchange resins [4]. The co-polymers resulting from Styrene (Sty)/methyl methacrylate (MMA) have found wide application in industry and medicine. Poly methylmethacrylate, due to its optical clarity and resistance to UV, is widely used as a glazer compound for (steel) sheet, optical lenses, and collectors of

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fluorescence. Polystyrene has acceptable mechanical and thermal properties with a high refractive index. However, its resistance to external environmental factors is weak, and it is easily yellowed in moisture [6]. Styrene is used as a co-monomer with butyl acrylate (BA) to improve hardness, resistance to strain, water and alkali, and also to modify the reflection of veneer and the glossiness of the surface [7]. MMA is one of the monomers of hard acrylate, and significant amounts of flexibilizer monomers are required when the copolymer of the monomer is being made. Flexibilizer monomers are the result of internal plasticizers that include acrylic esters. The esters used include flexible ethylhexyl acrylate, BA, and ethyl acrylate. These monomers should be used with Sty or MMA [8]. The emulsion acrylic resins are divided into thermoset and thermoplastic groups [9]. The difference between thermoplastic and thermoset acrylic resins are: the molecular weight of thermoplastic acrylic resin is higher than that of thermoset resins; thermoplastic acrylic resins do not have chemically active agents on the polymer chains, whereas there are active chemical agents such as hydroxyl, acid, amine etc on the thermoplastic acrylic resin chain; and the normal thermoplastic resins are used in normal dry air while the thermoset resins are used in a furnace [10]. The acrylic polymers are mostly produced by bulk, solution, and emulsion methods. However, the use of the emulsion polymerization is preferred as it has many advantages compared to other methods [3, 11]. Acrylic polymers have a block structure and are relatively soft; they form polymers in liquids with high boiling points and copolymers with a variety of monomers. From the standpoint of synthetic organic chemistry, the method of emulsion polymerization is one of the most important methods of polymerization. It is reported in the study conducted by Ganji et al. [12] who have used emulsion polymerization of pressure sensitive acrylics to produce acrylic polymers.

The emulsion polymerization usually runs at relatively high temperatures (70°C) for the production of commercial latex. For this reason, the use of redox initiators reduces the temperature of polymerization and can also make use of the heat from the reaction [13]. In BA semi-batch polymerization, Asua et al. [14] found that as the primer concentration is higher and the process is longer, the level of the branches was higher, but the gel was independent of the process conditions.

The total amount of consumed monomers, emulsifiers, initiators, and other solid materials to raw materials is used to determine the percentage of the final solid. The maximum solid percentage that can be achieved in an emulsion synthesis is limited by the viscosity and also depends on factors such as latex ion properties, particle size, and size distribution [15]. The polymeric properties of the product determine its performance. These properties include the mean molecular weight, particle size distribution, and conversion. Emulsion copolymerization of MMA and BA by the semi-batch method in water has been reported by Afghani et al. The results of this study showed that increasing the amount of emulsifiers in the feed favored the forward polymerization rate [16].

Various studies in the field of preparation of acrylic resins have been conducted with different methods. The most commonly used method in recent years is mini-emulsion copolymerization of free radicals of acrylic monomers in the presence of an alkyd resin. Nabuurs et al. [17] prepared an alkyd-acrylic hybrid system by this method and obtained a stable product using MMA as the acrylic monomer. They reported that the presence of an alkyd resin lowers the speed of polymerization and reduces the final conversion rate. They did not use any stabilizer in their study. Wang et al. [18] studied the macro and micro emulsion polymerization of acrylic monomers in the presence of alkyd resins and reported the deterrent effect of alkyd resins. They also used poly methyl methacrylate as a stabilizer, which was apparently very effective.

The same researchers in 1998 analyzed the copolymerization kinetics of Sty and BA mini-emulsion started by redox primer $(NH_4)_2S_2O_8/NaHSO_3$ at low temperatures (45°C). Then, in terms of the polymerization rate, it was concluded that the primer concentration plays a more important role in mini-emulsion polymerization than in normal emulsion polymerization [19]. Zhang et al. [20] succeeded to produce a latex containing concentrated and stable emulsions of MMA/BA with sodium dodecyl sulfate (SDS) and cetyl alcohol (CA) as surfactants, poly(vinyl alcohol) as the main amplifier of the liquid film with a redox based benzoyl peroxide/N,N'-dimethyl phenyl amine added to concentrated emulsions, and polymer particles with different shapes and sizes with low initial temperature. Experimental results showed that the surfactants and primer concentrations, liquid film amplifier categories, temperatures, etc., are responsible

for the stability of polymerization and polymerization rate.

A chain transfer agent such as dodecyl mercaptan is used as the costablizer in mini emulsion polymerizations of MMA [21] and Sty [22]. Although it can interfere with the stabilization of the drops and the polymerization rate, it does lead to the production of polymers of low molecular weight. In the following years, there have been many studies in the field of emulsion polymerization focusing on reaction kinetics, seed emulsion, and mass emulsions (suspension), as well as the synthesis of Sty/MMA, Sty/BA, and alkyd-acrylic hybrids by batch and semi-batch methods using thermal and redox primers at lower temperatures [23-29].

However, none of the conducted studies have used a formulation based on all three monomers (i.e., Sty/MMA/BA), and none have used the same molar ratios or tert-butyl hydroperoxide (TBHP) /Fe^{2+} /ethylenediaminetetraacetic acid (EDTA)/ sodium formaldehyde sulfoxylate (SFS) redox initiators as mentioned in this paper. In this work, we set out to obtain acrylic resins by the mini-emulsion technique with the appropriate physical properties for application in various industries and also to investigate the kinetic and properties of the synthetized resins.

2. Experimental

2.1. Materials

MMA, BA, and Sty were purchased from Simab Resin Company and were used without further purification. The anionic surfactants SDS and SFS were purchased from Merck Company. CA, TBHP, ferrous sulfate ($FeSO_4.7H_2O$), and EDTA were purchased from.

2.2. Procedures

The emulsifier and co-stabilizers, along with a given amount of distillated water, were mixed in a four-necked reactor to which monomers were then added. The prepared pre-emulsion was placed for 30 min in homogenizer. The redox initiators with metallic catalyst and chelating agent were used in determined amount, separately. In order to prevent a temperature increase during the reaction time, we placed the reactor in an ice bath. All the lattices were synthesized in a glass reactor mechanically stirred at 430 rpm for 4 h by the mini-emulsion polymerization technique and using the batch feeding method at specific temperatures. Table 1 reports the amount of starting materials, namely, emulsifiers, co-stabilizer, monomers and initiator, as well as reaction temperatures.

Table 1: The main features of synthesized latex.

Polymer	Conversion (%)	Solid Content(%)	Temperature (°C)	Initiator TBHP:SFS	M_w*10^{-6}	PDI	particle size (nm)	Surfactant SDS:CA (g)
#1	97	50	32	0/0529:0/79	1.25	2.45	-	5/089:10/089
#2	100	52	35	0/0627:1/0301	-	-	-	5/0428:10/0613
#3	43	22	-	0/0523:0/9736	-	-	-	5/0189:10/0173
#4	99.8	35	46	0/0609:0/99	-	-	-	2/5128:5/0208
#5	-	-	-	0/05:0/98	-	-	72	2/5094:5/0233
#6	99	43	33	0/0641:0/9968	-	-	-	3/0055:6/0016
#7	100	45	60	0/0595:0/9913	1.32	2.03	16.2	3/0018:6/0012
#8	100	45	60	0/0576:0/9889	1.51	2.33	12.5	3/0087:6/0037
#9	100	51	64	0/0574:0/99	-	-	-	3/0058:6/0062
#10	96	49	44	0/0292:0/3648	1.33	6.64	13	3/0054:6/0092
#11	92	42	30	0/0274:0/3627	1.81	1.31	10.2	3/002:6/0007

To create a sample, a polymer film of 30 or 120 μm in thickness was prepared using a film applicator, and then, in order to remove the remaining water, the resulting film was left at room temperature. Finally, the film was analyzed using GPC, FT-IR, and DSC.

Within various time intervals after the addition of the primer, samples were taken from the reactor of all the prepared lattices, placed in vacuum ovens at a temperature of 80°C, and the dry latex was weighed again to calculate the solid percentage (M) and the amount of reaction conversion based on equation 1. The reaction conversion is among the factors that have been used in determination of the reaction rate and the amount of unreacted monomer.

$$M = \frac{100\,(C - A)}{B - A} \qquad (1)$$

where M is the real solid content, A is the weight of the glass containers, B is the weight of the glass containers and the resin to be tested, and C is the weight of the glass containers and dry resin at the end of the test. In the above equation, solid percentage in theory is calculated from the total weight of the raw materials.

$$Conversion = \frac{real\ solid\ content}{theoretical\ solid\ content} \qquad (2)$$

For the determination of the glass-transition temperature, a differential scanning calorimeter DSC-1 (Mettler Toledo Company, Switzerland) was used. The samples were placed under a nitrogen flow and heated from 10 to 105°C. In order to measure the molecular weight of the resin, a gel permeation chromatograph (Agilent 1100 GPC model) was used. A chromatography column containing PL gel, 10 μm, 300×7.5 mm from Agilent Company was employed. The column temperature and mobile phase rate were 30°C and 1 mL/min, respectively. THF was used as the solvent. For identification of the resulting copolymer's composition, FT-IR spectrophotometry using an Equinox55 model (Bruker Company, Germany) was conducted in the wave number range of 400–4000 cm^{-1} and a tolerance of 4 cm^{-1}. To measure the mean and distribution size of resulted latex particles, dynamic light scattering (DLS) instrument (SEM model, SEMATech, France) was used.

3. Results and discussion

3.1. Reaction kinetics analysis

The practical solid content and monomer conversion percentage are summarized in Table 1. In this table, the effect of various parameters such as water content, the amount of primer, and temperature are presented. These parameters were investigated as follows.

3.1.1. The effect of water content

The results of effect of water content on reaction conversion are reported in Table 1 and conversion advancements for samples #2 an #7 are shown in Figure 1. In the synthesized UB sample in which the maximum amount of water was used, the conversion percentage is higher than for the rest of the synthesized samples. By reducing the water content, the average number of polymer particles per unit volume is increased. This leads to an increase in the polymerization rate and final conversion percentage. The aqueous phase acts as a medium in which droplets containing monomers and radicals formed by decomposition of the primer can come together to form oligomers. Emulsifier molecules accumulate in the water and form micelles; these are considered as the main location of polymerization [16].

3.1.2. Effect of the amount of initiator

Increasing the initiator concentration increases the presence of free radicals, and the rate of the starting phase of polymerization is thus increased . This results in higher conversion percentages, as shown in Table 1 and Figure 2.

3.1.3. Temperature effect

If the reaction temperature is increased, the speed of reaction initiation and the concentration of free radicals are increased. The amount of product formed in the micelles is usually increased by the emulsifier, the direct result of which is the increased production of latex particles. Also, the penetration rate of monomer droplets suspended in water into latex particles increases, and the monomer concentration in latex particles increases. This, combined with the increased penetration rate of free radicals into the particles, causes an increase in the polymerization rate. The effect of reaction temperature on polymerization conversion are shown in Figure 3.

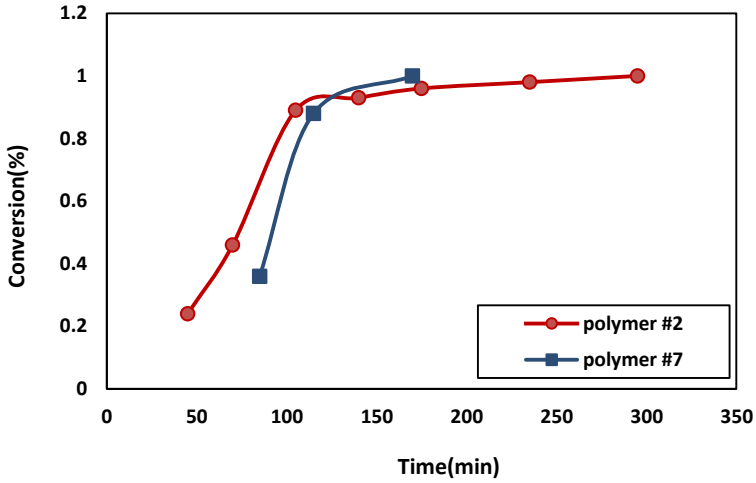

Figure 1:The effect of water content on reaction conversion.

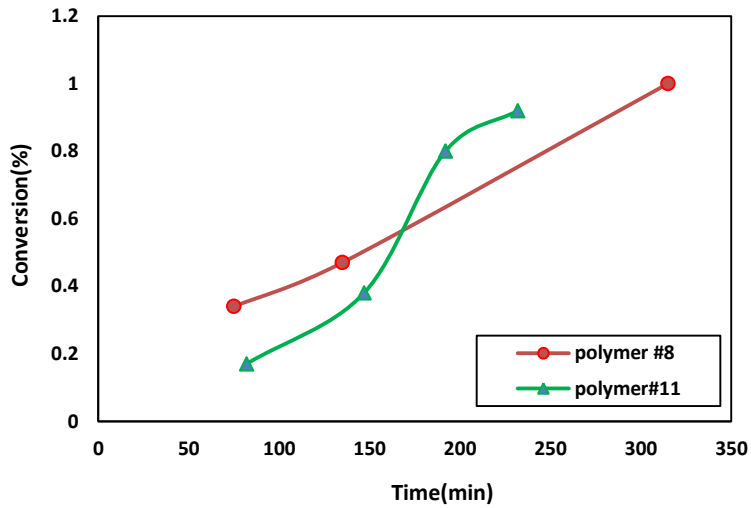

Figure 2: Effect of initiator concentration on reaction conversion.

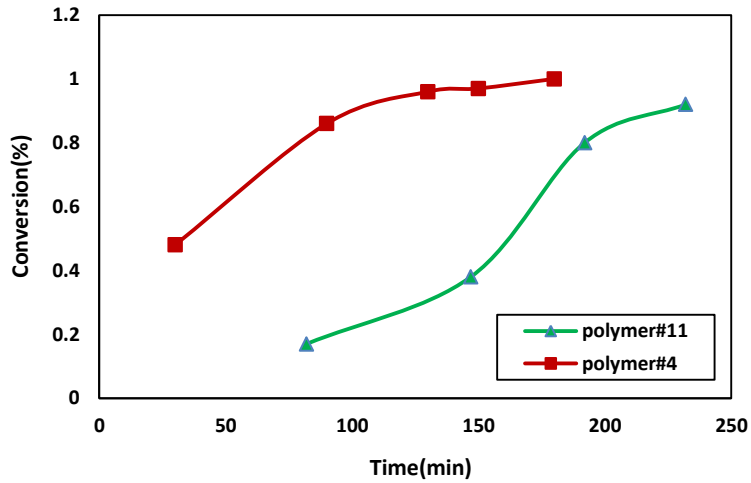

Figure 3: Effect of reaction temperature on polymerization conversion.

3.2. Identifying the structure of terpolymer by FT-IR

In order to confirm the chemical structure of the synthesized terpolymer, FT-IR analysis was carried out. In Figure 4, the bands at wavenumbers of 702, 756, and 834 cm^{-1} indicate a single-substituent of the Sty benzene ring, the band at 1167.18 cm^{-1} relates to C-O groups, the bands at 1238.54 and 1737.13 cm^{-1} are related to the acrylic ester agent, and the band at 3443.31 cm^{-1} is assigned to the hydroxyl group.

3.3. DSC Analysis

The first run DSC thermograms of samples 7 and 8 are represented in Figure 5a. As we observe in the figure, the T_g inclination points are very close to each other. This proximity of T_g values results in peaks similar to that of first order transition melting peaks. However, in the second run (Figure 5b), the DSC traces show a different behavior and only one transition at a lower temperature compared to those of the first run traces are observed. This observation indicates a different re-ordering of copolymer chains under experimental conditions. Using the FOX equation, we can obtain the combination of the co-polymers that have a predictable glass-transition temperature, T_g.

$$\frac{1}{T_g} = \sum_{i=1}^{n} \frac{w_i}{T_{gi}} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} + \frac{w_3}{T_{g3}} + ... + \frac{w_n}{T_{gn}} \qquad (2)$$

in which T_g is the glass-transition temperature of the co-polymer, T_{g1}, T_{g2}, T_{g3}, and T_{gn} are the glass-transition temperatures of the related homo-polymers, and W_1, W_2, W_3, and W_n are the weight fractions of related groups. With respect to the obtained image for samples 1, 2, 3, and 4, it can be observed that there are two distinct glass-transition temperatures for each film, which are presented in Table 2.

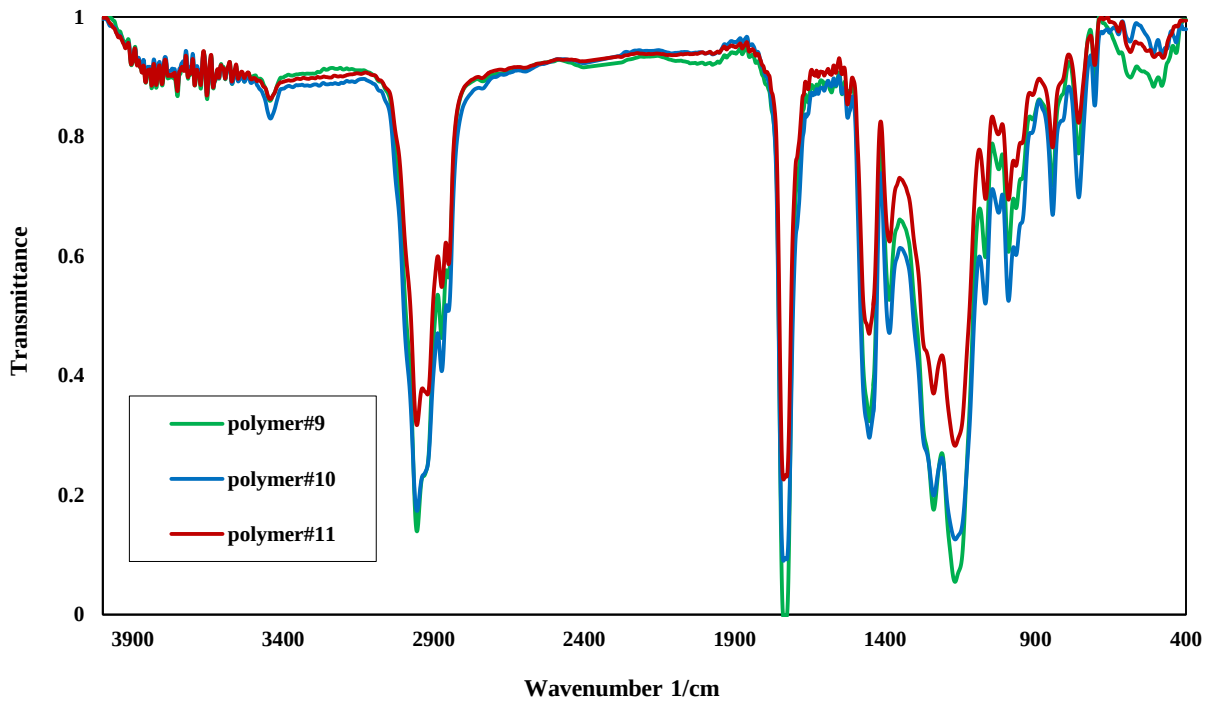

Figure 4: FT-IR spectra of different terpolymers of styrene, methyl (meth)acrylate and butyl acrylate.

Table 2: The glass-transition temperature of prepared samples.

polymer	Composition W_{Sty}:W_{MMA}:W_{BA}	Theoretical Value of Tg	Measured Value of Tg1	Measured Value of Tg2
#1	0.053:0.484:0.464	8.08	57.35	88.91
#2	0.047:0.54:0.414	0	58.08	82.28
#7	0.035:0.494:0.473	6.40	54.77	87.83
#8	0.036:0.493:0.472	6.75	51/45	83.66

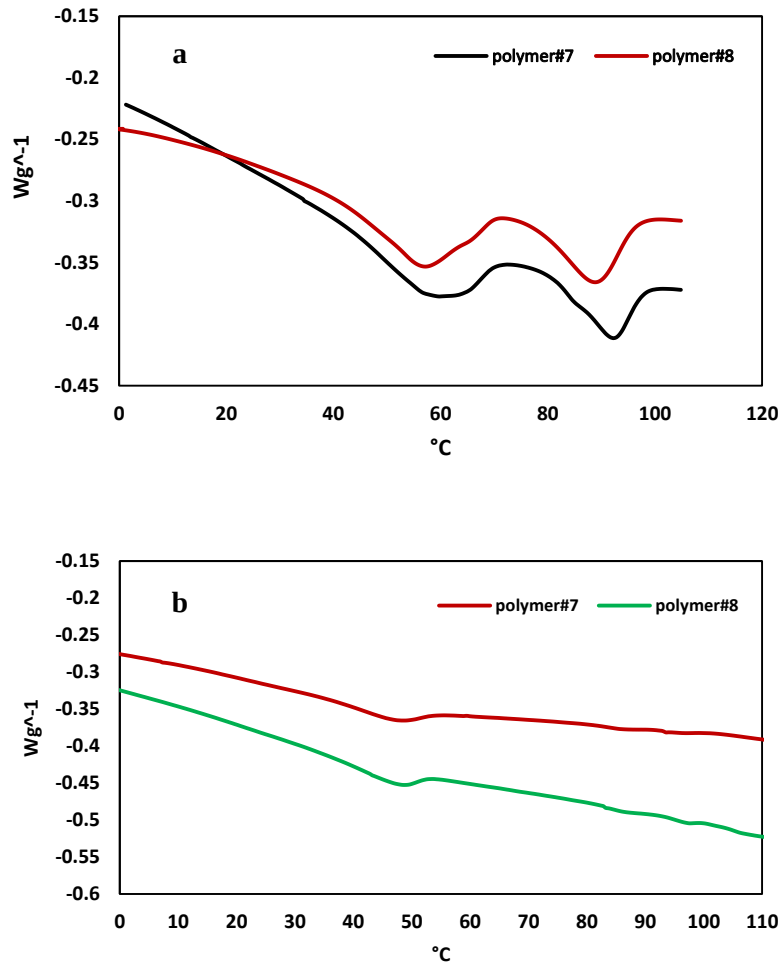

Figure 5: DSC thermograms of terpolymers of styrene, methyl (meth)acrylate and butyl acrylate a) the first run and b) the second run.

The presence of two glass-transition temperatures indicates that polymerization produces a special block structure. In Tables 3 and 4, the mole fractions of the monomers in the co-polymer are presented in terms of T_g. The rate of monomer activity in the co-polymerization reaction is shown in Table 5 [31].

According to Table 5, it can be observed that Sty and MMA have the same tendency to copolymerization with each other. So, if the end of the growing radical chain is on the Sty and MMA, it does not make a difference whether it reacts with Sty or MMA. Sty and MMA have different affinities for BA, and when BA is added, it was found that the main composite formed is the Sty-MMA copolymer. In this copolymerization reaction, the possibility of Sty radical copolymerization with Sty monomers or MMA is 80 % and that of Sty radical copolymerization with BA is 20 %. There was a 90% possibility that the MMA radical reacted with Sty and MMA monomers a 10 % possibility that it reacted with BA. This low level of BA incorporation into the polymers (10 or 20 %) accounts for the T_g measurements obtained by DSC.

3.4. Gel permeation chromatography (GPC)

The molecular weight of the polymers in a resin is an effective way to determine many properties, such as adhesion, mechanical properties, and acrylic latex film glossiness. The lowest molecular weight required for enough chain entanglements and good toughness of the film is about 50 kg/mol [15]. The molecular weight of acrylic resins is generally higher than 100,000 [23]. The closer the polydispersity index (PDI) to unity, the narrower is the distribution of molecular weight, which is desirable in some applications.

In emulsion polymerization, due to the separation of the radicals due to their distribution within the polymer particles, it is possible to simultaneously attain high molecular weights and polymerization rates. Emulsion polymerization is a method that presents polymers of high molecular weight and gives flexibility in preparing the copolymers. It is also reproducible, gives a quick response and a high monomer conversion, and is low in cost compared to other polymerization methods. The molecular weight distribution of synthesized samples are shown in Figure 6.

Table 3: Molar fractions of the monomers in terpolymer in terms of observed experimental T_{g1}.

polymer	Measured Value of Tg1	Composition W_{Sty}:W_{BA}	Composition W_{MMA}:W_{BA}	Composition W_{Sty}:W_{MMA}	Composition W_{MMA}:W_{BA}:W_{Sty}
#1	57.35	0.807:0.197	0.783:0.211	0.31:0.83	0.18:0.09:0.809
#2	58.08	0.813:0.192	0.767:0.219	0.31:0.83	0.19:0.08:0.815
#7	54.77	0.787:0.214	0.78:0.218	0.312:0.841	0.191:0.09:0.809
#8	51/45	0.794:0.217	0.77:0.231	0.324:0841	0.198:0.09:0.813

Table 4: Molar fractions of the monomers in terpolymer in terms of observed experimental T_{g2}.

polymer	Measured Value of Tg2	Composition W_{Sty}:W_{BA}	Composition W_{MMA}:W_{BA}	Composition W_{Sty}:W_{MMA}	Composition W_{MMA}:W_{BA}:W_{Sty}
#1	88.91	0.933:0.065	0.892:0.089	0.209:0.836	0.12:0.065:0.814
#2	82.28	0.949:0.067	0.941:0.072	0.212:0.852	0.14:0.067:0.81
#7	87.83	0. 928:0.07	0.892:0.091	0.211:0.837	0.12:0.07:0.81
#8	83.66	0.93:0.076	0.93:0.076	0.209:0.851	0.14:0.064:0.81

Table 5: Monomer activities in copolymerization [30].

Monomer (1)	Monomer (2)	r_1	r_2
MMA	Sty	0.5	0.5
Sty	BA	0.79	0.25
MMA	BA	0.92	0.13

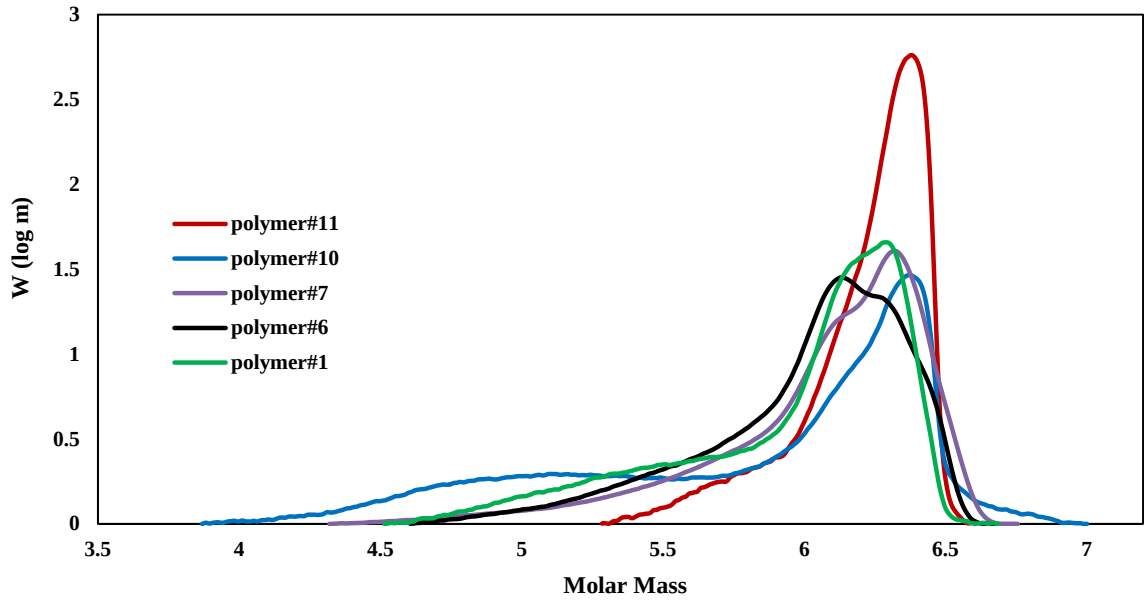

Figure 6: Molecular weight distribution of synthesized samples.

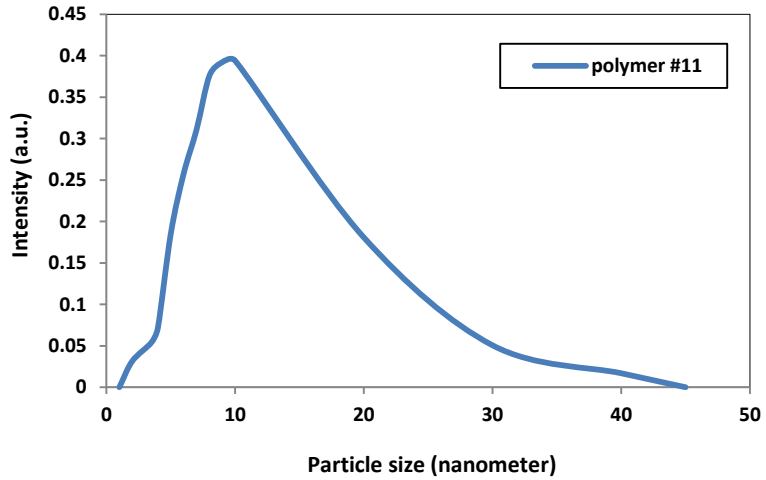

Figure 7: The size distribution of latex particles of polymer #11.

3.5. Particle size distribution of lattices

To measure the average particle size of latex particles and their particle size distribution, a laser light scattering device was used. Latex particles do not have necessarily the same size; however it is possible to produce particles with the same size. Latex particle size affects several final properties such as the rheological, optical, and mechanical properties, and these properties, e.g., viscosity, affect the formation of the film and the flatness of the surface after the film formation [15]. When the concentration of surfactant in mini-emulsion polymerization is very high, many micelles can be formed. As a result, some primary particles can be derived from micelle nucleation. Therefore, although the main location of the particle nucleation is in the monomer droplets instead of the micelle, homogeneous and micelle nucleation can also occur in mini-emulsion polymerization [29].

Mini-emulsion is obtained by shearing which converts greater monomeric droplets into 10–500 nm monomeric droplets, forming a range of monomeric particles by mini-emulsion polymerization. In this study, when the emulsion is sheared by ultrasound and a mechanical homogenizer, small droplets appear in the liquid medium. According to the droplet size distribution, if the monomer is slightly soluble in the

continuous phase, it tends to migrate from small to large droplets to reduce particle surface. This is evident from the data presented in Table 1 and by comparing the surfactant concentration and particle size of the sample. The size distribution of latex particles of polymer #11 are shown in Figure 7.

4. Conclusion

1) By reducing the amount of water, the amount of polymer existing in the environment and the conversion percentage of the monomers are increased.
2) The increased concentration of the initiator increases the conversion percentage of the monomers.
3) The rate of polymerization increases with temperature.
4) FT-IR spectra obtained for the pure monomer and the product confirms the formation of terpolymer
5) The thermal behavior of films observed in the DSC analysis was investigated. It was observed that co-polymerization produces a special block structure. We expected a random terpolymer structure with a single glass-transition temperature, while two distinct T_g temperatures were observed for these polymers. It shows that there are two different structural sections along the co-polymer chain, and based on the rate of activity of the monomers and their mole fraction, we formed co-polymers with low percentages of BA.

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