

Impact of Impeller Type on Methyl Methacrylate Emulsion Polymerization in a Batch Reactor

Shideh Fathi Roudsari, Ramdhane Dhib, Farhad Ein-Mozaffari

Department of Chemical Engineering, Ryerson University, Toronto, Ontario, Canada M5B 2K3

Correspondence to: F. Ein-Mozaffari (E-mail: fmozaffa@ryerson.ca)

ABSTRACT: The emulsion polymerization of methyl methacrylate (MMA) was carried out in a lab-scale reactor, which was equipped with a top-entry agitator, four wall baffles, a U-shaped cooling coil, and a temperature controller. Potassium persulfate and sodium dodecyl sulfate were used as the initiator and the surfactant, respectively. The experimental investigation demonstrated the impact of the impeller type (45° six pitched-blade turbine and Rushton impeller), number of impellers (single and double impellers), and impeller speed (100–350 rpm) on the monomer conversion, polymer particles size, molecular weight, and glass transition temperature. The results revealed that the effect of the impeller speed on the characteristics of the polymer attained using the pitched-blade turbine was more prominent than that for the Rushton turbine. It was also found that the impact of the impeller speed on the polymer characteristics was much more pronounced for the double pitched-blade turbines rather than for the double Rushton turbines. However, more uniform size distribution was achieved with the Rushton turbine. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40496.

KEYWORDS: emulsion polymerization; micelles; glass transition

Received 6 October 2013; accepted 22 January 2014

DOI: 10.1002/app.40496

INTRODUCTION

Mixing plays a vital role in the dispersion of the immiscible oil (monomer) phase in the continuous aqueous phase and the creation of a uniform temperature distribution inside the reactor vessel. In the stirred dispersion, deformation of the droplets occurs as a result of the shear forces in the turbulent flow field. The droplets experience viscous shear stresses, pressure variations along their surface, and turbulent velocity fluctuations.^{1,2} The impact of mixing on polymerization has been the subject of a few studies.^{3–5}

In an emulsion polymerization system, mixing can play a significant role in the kinetics of the chemical reaction. In the first two stages of the emulsion polymerization, reaction is controlled by diffusion mechanism; that is, the monomer is supplied by diffusion to the growing submicron polymer particles. In case of very low agitation rates, larger droplets are generated and phase separation may occur which will limit diffusion mechanism.⁶ In contrast, vigorous agitation can result in reduced nucleation of particles. In spite of the influence of mixing on emulsion polymerization kinetics, it has not been largely debated in the open literature. However, in some reported cases, conflicting results were obtained by different researchers on the effect of stirring on the rate of polymerization reaction.^{7,8} It has been reported⁷ that at low solid content, changing the impeller

type from the A310 hydrofoil (an axial-flow impeller) to the Rushton turbine (a radial-flow impeller) did not affect the polymerization rate. However, at high solid content, using the A310 hydrofoil resulted in a slower polymerization rate with a more distinct second population of particles compared to the runs that the Rushton impeller was employed. Some researchers⁸ reported an optimum range of stirring speed over which the polymerization rate was not affected by the speed.

A study⁹ on the colloidal stability of polystyrene and polyvinyl acetate latex systems showed that a large turbine impeller provided the highest heat transfer coefficient rate as compared with a pitched-blade impeller under the same conditions and no dependency of the coagulation behavior on process conditions in terms of energy dissipation, reactor scale, impeller type, and impeller diameter was observed. According to literature,¹⁰ the slope of coagulum formation versus impeller speed was higher for the Rushton turbine rather than the hydrofoil impeller. It was reported that the hydrofoil impeller, with a lower shear, produced a more stable reaction mixture. In another study, researchers¹¹ investigated the emulsion polymerization of vinyl acetate, ethylene, and *N*-methylol acrylamide using the Rushton and hydrofoil impellers. According to these researchers, the emulsions synthesized using the Rushton impeller had a larger particle size than those prepared using the hydrofoil impeller

due to the higher shear generated with the Rushton turbine. It was shown that¹² the axial-flow impellers were more energy efficient for the gas–liquid–liquid macromixing than the radial-flow impellers. Furthermore, the performances of the multi-impellers were investigated by some researchers.¹³ In fact, it has been reported the multiple impellers have great potential applications for the single-and two-phase systems due to their advantages over the single impeller. A flow analysis¹⁴ in slim reactors revealed multiple impellers should be used rather than the single impeller to save power and allow complete dispersion especially for reactors with the ratios of liquid level to reactor diameter >3 .

In addition, latex particle size is an important factor in emulsion polymerization. Some studies^{15,16} indicated that the overall rate of the monomer conversion decreased as the particle size got larger for both macro and mini emulsions. The formation of larger particle sizes at low conversion was also reported¹⁷ for MMA emulsion polymerization in a batch reactor with a redox initiator system. It was claimed that the particles may have become increasingly swollen by the monomer or by the occurrence of an eventual coalescence prior to the sample analysis.¹⁷ However, in the aforementioned studies little information has been provided regarding the detailed mixing characterization in emulsion polymerization. Nevertheless, it was reported¹⁰ that the number of particles decreased by using a larger impeller diameter and faster speed. This was attributed to the shear stress and its effect on the nucleation mechanism, and the aggregation of the unstable nuclei. In general, important characteristics of the latex products are particle size, molecular weight, and their relative distributions, chemical composition distribution, and of course the fragility properties. The choice of the recipe, reactor configuration, and the process conditions strongly determine the quality of the latex product. The ability to control the emulsion polymerization process is essential to guarantee constant product properties.¹⁸ In particular, many other studies focused on polymer chemistry and incorporation of chemical additives.^{17–19} Even though significant advances have been achieved in emulsion polymerization in recent decades, the basic concept of mixing, which is the basis for the formation of emulsion mixture, has not been fully delineated yet. The impact of stirring becomes more pronounced as the reactor size increases and the creation of the effective mixing throughout the reactor becomes a hard task. Therefore, an appropriate criterion should be considered for the scale-up of the mixing system.²⁰ Different scale-up criteria such as constant power/volume and constant tip velocity have been proposed in the literature while the geometric similarity exists between the small-scale and large-scale mechanically agitated reactors.^{21,22} However, these scale-up criteria are not compatible with each other. For instance, at constant power/volume, the agitation speed and shear rate are altered considerably.^{23–25} For liquid-liquid dispersions, Baldyga et al.²⁶ showed that the scale-up resulted in an increase in Reynolds number, larger turbulent fluctuations, and smaller drops. Some researchers believed that the scale-up criterion based on the same mixing time is not reliable and proposed two dimensionless groups as a function of the Reynolds number for a variety of impeller-vessel configurations.²⁷

For the emulsion polymerization scale-up, the goal is to produce at commercial scale latexes of the same quality as those developed in the laboratory. Because of geometric considerations, the larger the volume of the reactor, the smaller is its heat transfer area/volume ratio. Therefore, larger reactors require longer process times to carry out the process under good thermal control. Although agitation may improve the heat transfer, the range of the mixing intensity is limited because a vigorous agitation may cause shear induced coagulation. In large-scale reactors, it is difficult to reproduce uniform mixing similar to that in small reactors, and this is a common source of variability in particle nucleation and hence in particle size distribution. The size distribution affects the radical distribution, which in turn influences the molecular weight distribution and polymer architecture, and consequently latex properties. Besides, most researches are performed using jacket cooling on a lab-scale reactor. However, for large reactors, jacket cooling is not always sufficient to obtain reasonably short batch times and supplemental heat removal through external heat exchangers, internal cooling coils, and baffles must be used.²⁸

For the progress in future commercial latex products, it is essential to develop the cost efficient methods to control the polymer colloid properties as well as the polymer chemistry researches. In this study, the emphasis is to elucidate important aspects of operating conditions such as impeller configuration and speed that can affect the monomer conversion, the polymer molecular weight, and particle size distributions as well the transition glass temperature.

EXPERIMENTAL

Reactor Set Up

Figure 1 shows the schematic diagram of the experimental set up which is comprised of a PARR reactor vessel connected to a temperature controller heating/cooling bath and also temperature control unit (series 4530) and impeller speed controller. The reactor is a flat bottomed cylindrical tank with a diameter of 10.16 cm and a height of 26.67 cm with a total capacity of 2 L. The reactor vessel is equipped with one or two impellers of the following types: 45° pitched-blade turbine with a diameter of 5.00 cm, or Rushton impeller with a diameter of 5.00 cm. The off-bottom clearance is 1.3 cm and the inner distance is 8.00 cm between two impellers. The pitched-blade turbine is an axial-flow impeller, which generates flow along the impeller axis. The axial-flow impellers have been design to generate high bulk flow with low turbulence. The turbine impeller is a radial-flow impeller, which discharges flow along the impeller radius. The radial-flow impellers have been designed to produce high shear and turbulence within the mixing vessels.²⁰ Thus, in this study, we selected these two types of impellers to explore the effect of flow type and pattern on the emulsion polymerization. Besides, a U-shaped cooling coil connected to the circulator bath, a thermocouple jacket, and inlet and outlet pipes for sampling and gas purging were attached to the reactor. The power of motor is $\frac{1}{4}$ hp.

Materials

The following reagents were used in the polymerization: methyl methacrylate (MMA) with purity of 99% as monomer,

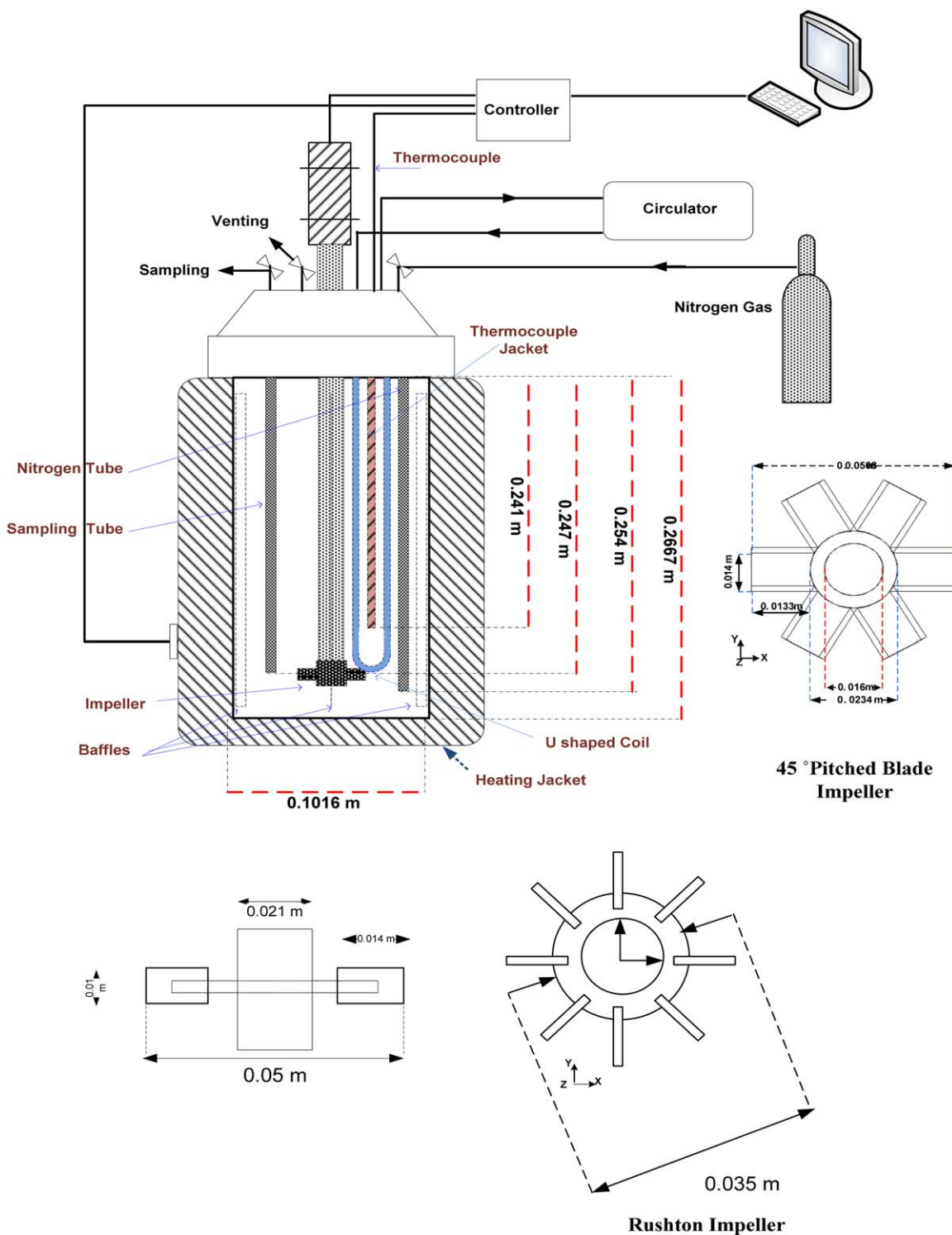


Figure 1. Schematic diagram of the experimental set up. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sodium dodecyl sulfate (SDS) with purity over 99% as surfactant, deionized (DI) water, potassium persulfate as initiator, and hydroquinone with 99% purity as inhibitor. All reagents were supplied by Sigma Aldrich Canada and used as received. Emulsions were prepared according to the following recipe: 700 g water, 250 g MMA, 8.64 g of SDS, and 0.5455 g of potassium

persulfate. The volumetric ratio of monomer to water was 4/10.²⁹ The desired amount of SDS was dissolved in 80 g of water while being stirred by means of magnetic stirrer bar. The SDS concentration was chosen to be above the critical micelle concentration which is reported to be 7.9×10^{-3} mole/L.²⁹

Table I. Experimental Ranges and Levels of Factors

Factor	Levels	Values
Speed	3	100, 250, 350
Impeller Type	2	Rushton, Pitched
Number of Impellers	2	1, 2

A mass of 600 g of water and the SDS aqueous solution were poured into the reactor, to which were added 250 g of MMA. The reactor temperature was set to 50 or 60°C and the reactor vessel was sealed and purged with nitrogen for 20 min. The venting valve was opened and closed several times for a completed air purge from the reactor tank. The impeller speed was varied from 100 to 350 ± 2 rpm. The potassium persulfate (i.e., initiator) was dissolved in 20 g of water at 55°C and then injected into the reactor by means of a syringe for the reactor set point of 60°C.

Samples (20 mL) were started to be taken 5 min after adding the initiator. The sampling procedure continued at an interval time of 10–15 min for a total reaction time of 130 min. Each sample was poured into a vial and 2 drops of 1% hydroquinone solution was immediately added to it to stop the reaction. The vials were placed in tray of ice and then put into the refrigerator. An aliquot of each sample in the vials was transferred directly into a dry and clean aluminum cup and was weighed and then dried in an oven at 40°C for 24 h. The conversion was calculated using the gravimetric method. Knowing that the particle size and particle size distribution can significantly impact on the quality and applications of the latex product, both variables were determined using Microtrac Particle Analyzer (Model S3000/S3500). The measurements of the polymer molecular weight were performed using GPC (Viscotek, Model 302-040) equipped with a triple detector array in which tetrahydrofuran was used as the mobile phase at a nominal rate of 1.0 mL/min. The molecular weight averages were obtained using universal

calibration and calibration with PMMA standards. Differential Scanning Calorimeter (DSC; Model Q2000 V24.10 Build 122) was used to measure the glass temperature of polymer samples under a nitrogen atmosphere (50.0 mL/min). The scan rate was 10°C/min over the temperature range 40–190°C. The T_g values for the dried polymer samples were determined from the second scan of the DSC curve.

Experimental Design

Minitab-16 was employed for statistical design of experiments and data analysis. After the preliminary tests, the selected ranges for the impeller speed, impeller type, and number of impellers are given in Table I. The experimental design and results obtained for the final conversion, molecular weight, and particle size are illustrated in Table II. The experiments were replicated for the Rushton impeller at the rotational speeds of 100, 250, and 350 rpm, and for the pitched impeller at the rotational speed of 250 rpm. Since the conversion profiles had the same trend for the replicated experiments, we concluded that repeating all the tests was not necessary as the chemical recipe and the temperature were the same for all the experiments.

RESULTS AND DISCUSSION

This study thoroughly discusses the effects of the stirring rate, type of impeller and single/double impellers on the monomer conversion, mean particle size, average molecular weight, and glass transition temperature. Generally, the emulsification and nucleation govern the course of the process at the beginning of the polymerization. The nucleation mechanism can be both micellar and homogenous nucleation for the partially soluble monomers.^{30–33} The MMA solubility in water is known to be 1.5 g/100 mL.²⁸ Hence, under the polymerization conditions (i.e., concentration of the initiator and the emulsifier) employed in this study, the micellar mechanism prevailed, and the homogeneous nucleation mechanism was negligible.

Besides, the rate of polymerization is mainly due to the intrinsic reaction rates involved and the transport of monomer to the

Table II. Experimental Design of the Experiments with Measured Values for Final Conversion, Molecular Weight, and Particle Size

No. ^a	Impeller type	Impeller speed (rpm)	Number of impellers	Conversion (%)	Molecular weight × 10 ⁻⁴ (g/mol)	Particle size (nm)
1	Rushton	250	Single	68	75	96
2	Pitched	250	Single	78	112	110
3	Pitched	100	Double	66	65	104.5
4	Rushton	100	Single	59	63.9	91
5	Pitched	100	Single	53	23	103
6	Pitched	350	Single	71	80	106
7	Pitched	250	Double	81	115	115
8	Rushton	100	Double	62	66	94
9	Pitched	350	Double	74	90	107
10	Rushton	350	Double	76	80	98
11	Rushton	350	Single	72.66	76	98
12	Rushton	250	Double	70	78	98

^aExperiments 1, 2, 4, and 11 were repeated three times.

growing particles.³⁴ In this research, the experiments were performed from low to high agitation rates at a fixed chemical recipe at isothermal reactor temperature, that is, 60°C while baffles were installed in the reactor in all experiments. Sampling was started 5 min after adding initiator at 5°C below the set point and a total of 13 samples were taken for each run. The monomer conversion profiles versus time at different impeller speeds are shown for the single and double pitched-blade [Figure 2(a)] and Rushton [Figure 2(b)] impellers. In Figure 2(a), the conversion was low at the impeller speed of 100 rpm with the use of single pitched impeller. With increase in the stirring rate to 250 rpm, the conversion reached to its maximum value and further increase in agitation led to reduction in the monomer conversion. The axial flow impellers produce a constant pumping action toward the bottom of the tank followed by circulation to the top and a relatively rapid return to the impeller zone.^{35,36} The short circulation time produced by the axial flow impeller increases the frequency of exposure to the high intensity shear in the impeller zone, where turbulent energy dissipation rates are much larger than in the bulk zone.^{36,37} The turbulent energy

up to the speed of 250 rpm produced the optimum collision of reactants and homogeneity of bulk flow to reach to the maximum conversion. However, further increase in the impeller speed to 350 rpm reduced conversion of monomer. It can be due to formation of vortices and instability and thus formation of dead zones in the bulk mixture at this extent of agitation in our system. Furthermore, in Figure 2(a), the monomer conversion was clearly increased at low impeller speed of 100 rpm when two pitched-blade impellers were employed. The conversion increase due to use of double pitched-blade compared to use of single one was less significant at higher impeller speeds at 250 and 350 rpm.

Generally, multiple impellers are often employed to improve circulation and narrow the distribution of shear and energy dissipation by forming more circulation loops within the tank mixture.²⁵ Therefore, more circulation loops at the impeller speed of 100 rpm helped to form better homogeneity of the reaction mixture and improved nucleation mechanism and growth process and thus the conversion was increased.

At higher impeller speeds, that is, 250–350 rpm, the conversion enhancement with installation of two pitched-blade was not very significant. Therefore, it can be resulted that the pumping action produced by single pitched-blade were strong to produce bulk homogeneity through the reaction mixture and use of double pitched-blade impellers only resulted in insignificant increment in conversion. Therefore, the limiting conversion even with the use of double pitched impeller should be sought in other factors, which will be shortly discussed here.

In Figure 2(b), the monomer conversion at low impeller speed of 100 rpm was higher with the use of Rushton impeller compared to the pitched-blade turbine. Using Rushton impeller was more efficient at low impeller speed of 100 rpm. The Rushton impeller creates fluid flow directed radially outward of the impeller and produces two circulating loops one below and one above the impeller. Mixing occurs between the two loops but less intensely within each loop.²⁵ With increase in the Rushton impeller speed the conversion was enhanced at 250 and 350 rpm. However, the increase was not very significant compared to the runs with the pitched-blade impeller. The radially fluid flow produced by the Rushton impeller mostly circulates into the region above the impeller. These recirculated fluid mixture then slowly return to the impeller zone. In contrast, the axial flow impeller produces a strong pumping action and a relatively rapid return to the impeller zone. Therefore, increase in the Rushton impeller speed majorly produced more shear near the impeller region and the conversion increase can be attributed to this region at low impeller speed of 100 rpm. However, less mixture homogeneity was achieved by Rushton impeller due to insufficient pumping action. Besides, the use of double Rushton impellers as shown in Figure 2(b) was not so effective. By employment of two Rushton impellers, more circulating loops are produced while mixing majorly occurs between the loops.²⁵ Therefore, the enhancement in the monomer conversion was not very significant by the two Rushton impellers at different speeds. It must be mentioned that the computational fluid dynamics (CFD) analysis of the current experimental work is

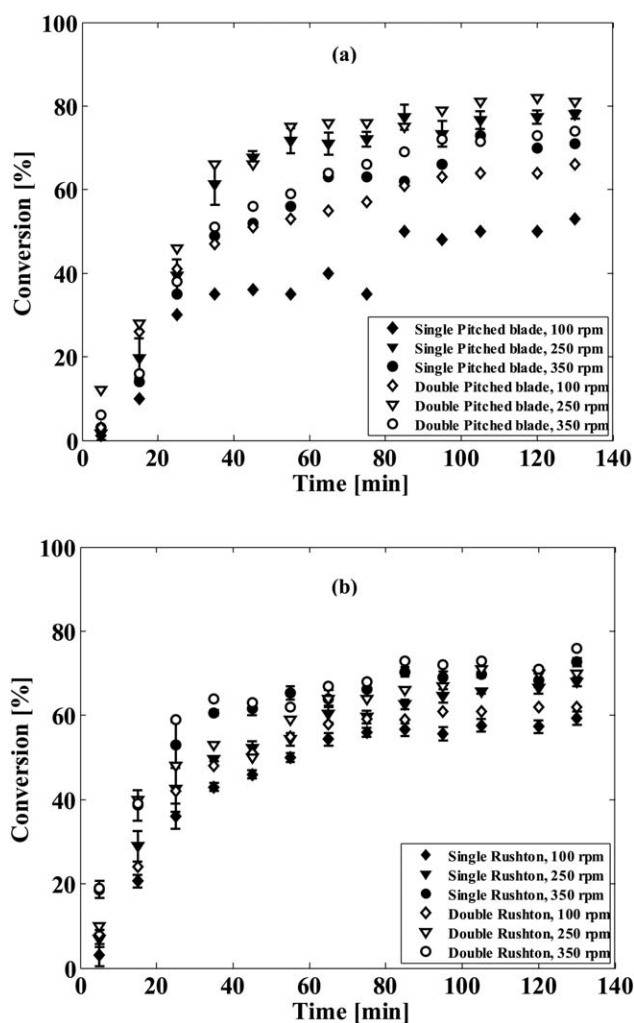


Figure 2. Monomer conversion versus reaction time for (a) pitched blade turbine and (b) Rushton impeller at the speeds of 100–350 rpm using both single and double impellers.

being conducted in our research laboratory to elucidate the homogeneity, turbulence, and flow pattern throughout the reactor vessel.

Figure 3 depicts the monomer conversion of the last samples versus impeller speed for single and double pitched-blade and Rushton impellers, at the reaction time of 130 min. The variation of conversion with speed was more observed for the runs using the pitched-blade turbine rather than the Rushton impeller. Moreover, installation of two pitched-blade improved the conversion at low impeller speed of 100 rpm. The complete conversion could not be achieved in the experiments. It has often been noted³⁸ that polymerizations carried out at temperatures significantly below the glass transition temperature of the pure polymer do not appear to reach full conversion. Besides, the limiting conversions can be attributed to the decreased initiator efficiency and decrease in the decomposition rate of the initiator at the isothermal reaction temperature.³⁹ Furthermore, in our study, the monomer was not purified as it was intended to resemble the actual industrial case. Therefore, all the mentioned reasons can be attributed to the limited conversion as observed in Figure 3.

The weight average molecular weight versus conversion at different impeller speeds are plotted for the single and double pitched-blade [Figure 4(a)] and Rushton [Figure 4(b)] impellers. The samples were taken at reaction times of 25, 75, and 130 min.

In Figure 4(a), at low impeller speed of 100 rpm, the weight average molecular weight was low. It means that due to low pumping action of the pitched-blade impeller at low speed, the emulsification was not sufficient and therefore the polymerization reaction was not significant. When the stirring rate was raised, the maximum molecular weight (M_w) was achieved at the rotational speed of 250 rpm and further increase in the speed up to 350 rpm decreased M_w , compared with the values at 250 rpm. Again, similar to the conversion-time profiles, the

most efficient pumping action of the pitched-blade occurred at the speed of 250 rpm with the rapid return of fluid to the impeller zone.^{35,36} It can be concluded that at 250 rpm the homogeneity of the mixture was at its optimum when the pitched-blade turbine was employed. Drop in the molecular weight at the pitched-blade speed of 350 rpm compared with 250 rpm are due to the instability and formation of vortices and dead zones in the bulk mixture at vigorous stirring rate. As mentioned earlier in this discussion, for MMA monomer, the nucleation mechanism can be considered micellar which means the growth of polymer chain can occur inside the micelles. The emulsification and homogeneity of dispersion is very important in the final molecular weight of polymers as it raises the probability of absorption of monomer into the micelles. In Figure 4(a), with employment of two pitched-blade impeller, the weight average molecular weight at low stirring rate of 100 rpm was significantly elevated. Use of the two pitched-blade impellers increased M_w at higher agitation rates of 250 and 350 rpm,

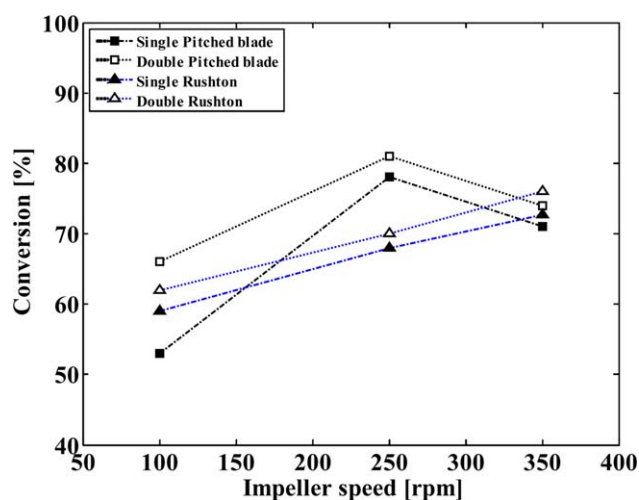


Figure 3. Final monomer conversion versus impeller speed at reaction time of 130 min for single/double pitched blade and Rushton impellers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

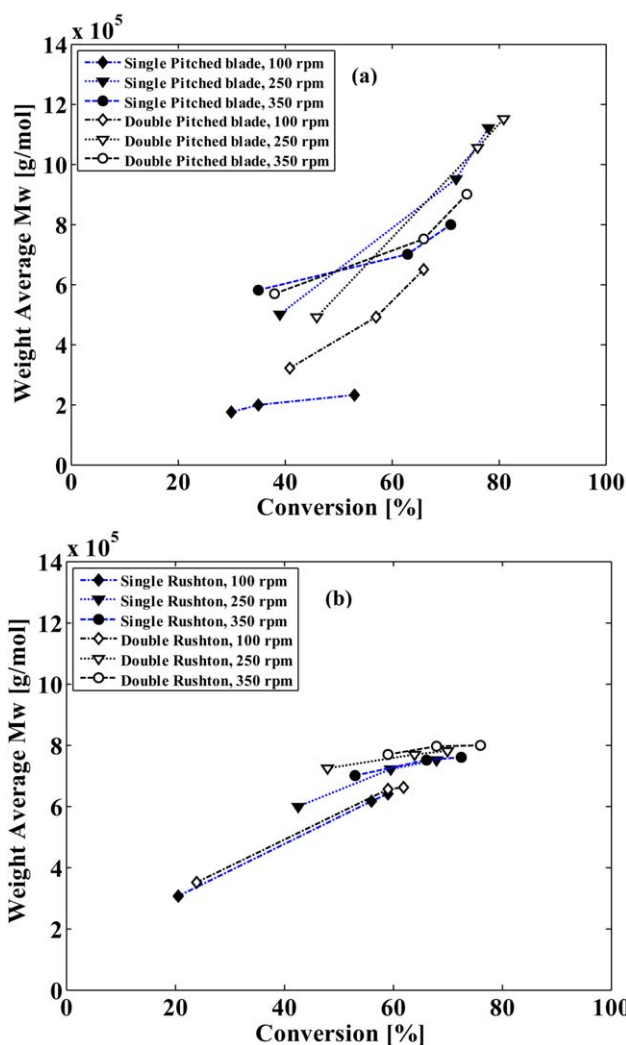


Figure 4. Weight average molecular weight versus monomer conversion for (a) pitched blade turbine and (b) Rushton impeller at the speeds of 100–350 rpm using both single and double impellers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

but not as much as the increment seen at the low agitation rate of 100 rpm. Again, similar to the conversion profile trends, it can be resulted that bulk homogeneity did not have much change with the use of double pitched-blade instead of single one at higher impeller speeds.

In Figure 4(b), the weight average molecular weight was higher at the Rushton impeller speed of 100 rpm compared with the similar profile using the pitched-blade turbine. The radial flow near the impeller region created a relatively good shear at low speed of 100 rpm. With increment in the Rushton impeller speed, the weight average molecular weight was enhanced at 250 and 350 rpm due to formation of higher shear near the impeller region and the improved mixing between the two loops. However, the increase in M_w with variation of speed was not eloquent compared with the runs with the pitched-blade impeller. Powerful pumping of the axial flow impeller, that is, the pitched-blade was more efficient at high impeller speeds to increase the growth rate of polymeric chain. Besides, the use of double Rushton impellers as shown in Figure 4(b) contributed to the increase in molecular weight, but it was trivial. Therefore, producing more circulating loops didn't result in a drastic increase in molecular weight. According to the data depicted in Figure 4(b), when the Rushton impeller was engaged, the slope of M_w versus conversion was decreased for conversions beyond 40%. However, the raise in molecular weight was still perceived after the 40% conversion with a very small slope. A polymer chain grows until a second radical enters into the polymer particle to terminate with the growing one. Therefore, the chain length is inversely proportional to the radical entry frequency. For a given initiator concentration, the frequency of radical entry decreases with the number of particles, therefore the molecular weight increases.²⁸ Figure 4 shows that when the pitched impeller was used, the molecular weight gradient was greater at higher impeller speeds compared with those achieved with the Rushton impeller. It can be inferred that the entry of radicals into particle was less pronounced when the pitched impeller was used compared with that measured for the Rushton impeller.

Figure 5 shows the weight average molecular weight of the last polymer samples at the reaction time of 130 min versus impeller speed for both single and double of pitched-blade and Rushton impellers. The variation of M_w with the impeller speed is more pronounced when the pitched-blade turbine is employed. The use of double impeller was more observed at low impeller speed of 100 rpm and for the pitched-blade impeller.

Figure 6 shows plots of polydispersity (PDI) of the last polymer samples obtained by GPC analysis at the end of polymerization (i.e., the reaction time of 130 min) for both pitched-blade and Rushton impellers.

The polymers produced in the reactor equipped with the Rushton impeller had a lower PDI compared with the samples obtained using the pitched-blade turbine. This demonstrates that the narrower molecular weight distribution can be attained using the radial-flow Rushton impeller even though the molecular weight is lower. In other words, the molecular weight was better controlled by the use of the radial-flow Rushton turbine

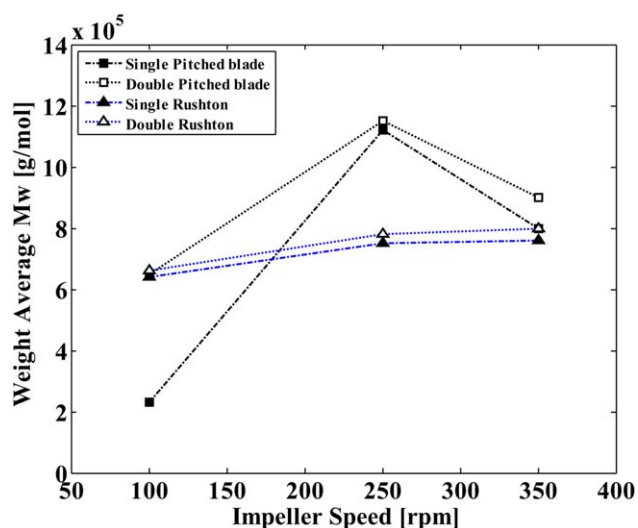


Figure 5. Final weight average molecular weight versus impeller speed at reaction time of 130 min for single/double pitched blade and Rushton impellers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

as the impeller. Besides, a uniform distribution of the molecular weight was achieved at the optimum speed of 250 rpm for the pitched impeller. It can be implied that the existence of radicals in the particles was well-proportioned throughout the particles at this agitation rate. Therefore, it can be postulated the growth of polymer chains and termination of polymerization were uniform in the population of particles. In other words, only the better mixing and more uniform distribution of reaction mixture in the reactor can describe this peculiarity in our system. Yet, the GPC sampling purification method might influence this result as well.

Figure 7 depicts the data trend of the particles size profiles versus conversion at different impeller speeds for the single and

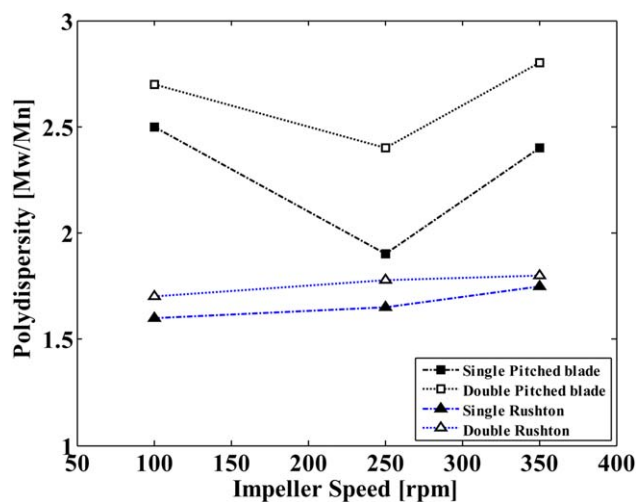


Figure 6. Final polymer poly dispersity versus impeller speed at reaction time of 130 min for single/double pitched blade and Rushton impellers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

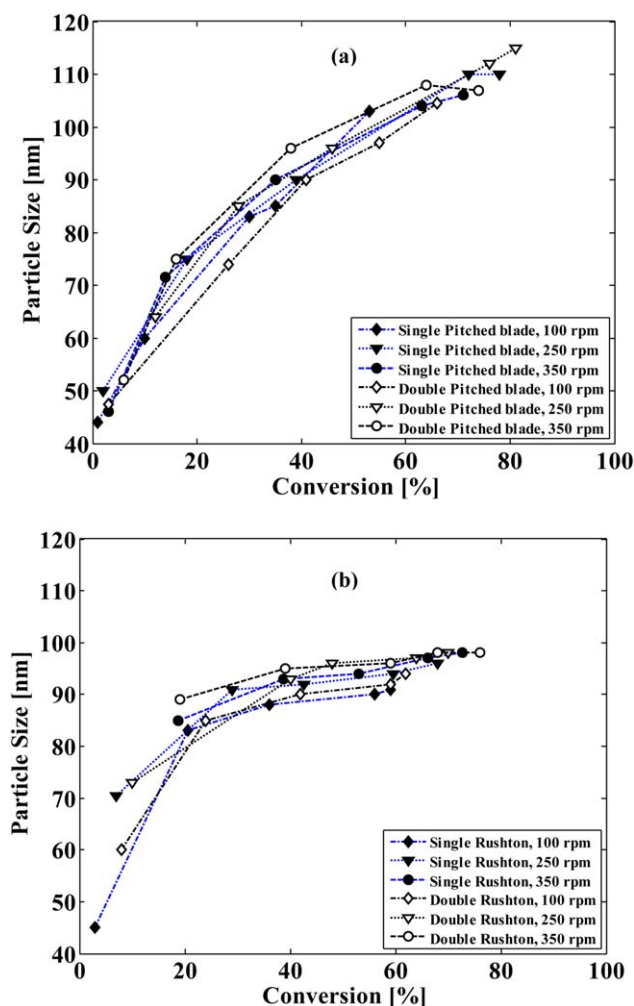


Figure 7. Mean particle size versus monomer conversion for (a) pitched blade turbine and (b) Rushton impeller at the speeds of 100–350 rpm using both single and double impellers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

double pitched-blade [Figure 7(a)] and Rushton [Figure 7(b)] impellers. The samples were taken at reaction times of 5, 25, 75, and 130 min.

In Figure 7, the trend of dependence of particle size on variation of speed was similar to the profiles of molecular weight. In Figure 7(a), at the agitation rate of 100 rpm, the mean particle size was low. Again, it was attributed to weak pumping of fluid and poor emulsification at this stirring rate when the pitched-blade is used. The emulsifier or surfactant molecules required to stabilize the primary particles come from those dissolved in the continuous aqueous phase and those adsorbed on the emulsified monomer droplet surfaces.⁴⁰ In Figure 7(a), when the single pitched impeller was engaged, the larger particle size was observed at the agitation rate of 250 rpm compared with the single pitched impeller at the higher speed rate, that is, 350 rpm. The maximum particle size was observed at the agitation rate of 250 rpm rather than 350 rpm.

At 250 rpm, the strong pumping capacity increased bulk flow and incorporated more monomer for the top layer of the reac-

tion mixture in the reactor vessel. In microscale, agitation at 250 rpm increased the growth of polymer chains by diffusion of monomer into the micelles. At the speed of 350 rpm, as discussed before, the excessive speed produced vortices that dropped the particle sizes. Also, employment of two pitched-blade impellers increased particle sizes at higher agitation rates of 250 and 350 rpm, but the increment seen at the low agitation rate of 100 rpm was more significant. In Figure 7(b), the particle size was higher at the Rushton impeller speed of 100 rpm compared with the same speed using the pitched-blade turbine [Figure 7(a)]. Again, the relatively good mixing in the impeller region resulted in better growth of particles. However, increase in the particle size in higher speed of 250 and 350 rpm compared with the sizes in 100 rpm was trivial. The particle size changes from the beginning to the end of the experiment were more significant for the experiments performed with the pitched impeller. When Rushton impeller was employed the slope of the particle size versus conversion drastically decreased after 20% conversion and the particles size reached a plateau after reaction times of 130 min. In contrast, with the use of the pitched impeller, the trend of the particle size profile showed a continuous increase with a raise in conversion. Therefore, the impact of impeller configuration on the trend of particle size is more eloquent when the pitched impeller is employed.

Figure 8 shows the last mean polymer particle size versus impeller speed for both pitched-blade and Rushton impellers (single and double) at reaction time of 130 min. The highest particle size was seen at the pitched-blade impeller speed of 250 rpm and moreover, using two impellers at this agitation rate resulted in a considerable increase in the mean particle sizes. Nevertheless, by comparing the final weight average molecular weight of polymers in Figure 5 with the final mean particle size of samples in Figure 8, we notice while the elevation in particle size by double pitched-blade at 250 rpm was considerable (Figure 8), the gain in molecular weight with double pitched-blade at 250 rpm was not very significant (Figure 5). Therefore, it is possible

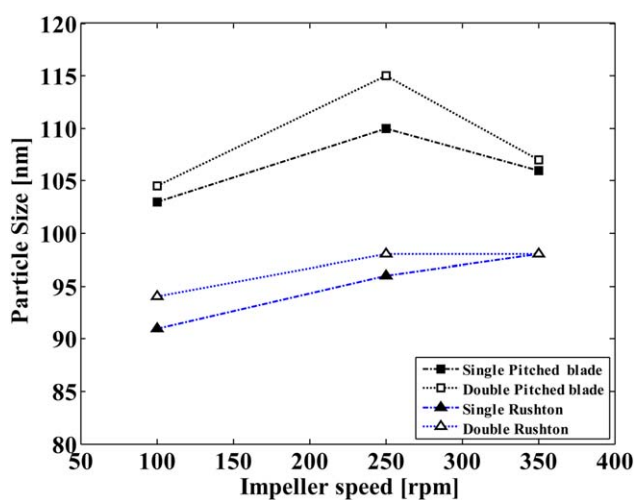


Figure 8. Final mean particle size versus impeller speed at reaction time of 130 min for single/double pitched blade and Rushton impellers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

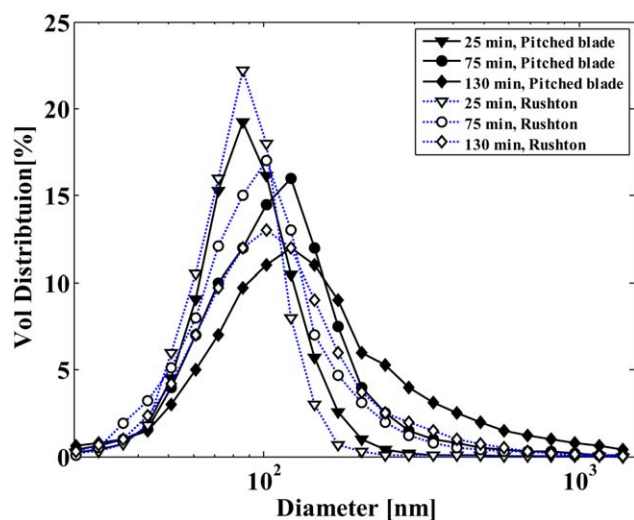


Figure 9. Particle size distribution at reaction times of 25, 75, and 130 min using pitched blade impeller and Rushton turbine at the impeller speed of 250 rpm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that agglomeration occurred at 250 rpm when double pitched impeller was employed. However, at higher speed, that is, 350 rpm, there is no significant difference between single and double pitched impellers. Figure 9 shows the particle size distribution at the reaction time of 25, 75, and 130 min for the pitched-blade and Rushton turbine at the impeller speed of 250 rpm. With increase in reaction time, the particle size distribution became broader as a wide variety of polymer particles were produced by both types of impellers. Using the Rushton impeller resulted in lower particle size compared with the pitched-blade turbine as discussed earlier. Nevertheless, with the Rushton impeller, the particle size distribution was narrower compared to that achieved using the pitched-blade turbine. This can be due to more intense energy dissipation in the Rushton swept volume, resulting in more stability in particle size distribution and less coalescence.⁴¹ Moreover, although the Rushton impeller results in a lower frequency of exposure to the impeller zone in the stirred tank than the pitched-blade turbine, the higher shearing action of radial than the axial impeller in the impeller zone can result in more uniform particle size distribution.³⁶ According to the Microtrac Particle Analyzer manual, the standard deviation can be used to evaluate the width of the particle size distribution. This value for the measurement with the pitched impeller was 1.5, 0.7, and 1.0 for the impeller speed of 100, 250, and 350 rpm, which is interpreted as poorly sorted, moderately well sorted, and moderately sorted particle size distribution. For the measurements with the Rushton impeller, the standard deviation values were all in the range of 0.5–0.71, which is interpreted as moderately well sorted size distribution.

The glass transition temperature (T_g), which is an important characteristic of polymers, defines the transition region in which the polymer changes from soft to brittle, and then hard states. The T_g values for the dried polymer samples were determined from the second scan of the DSC curve. Figure 10 shows the heat flow versus temperature for polymer samples obtained

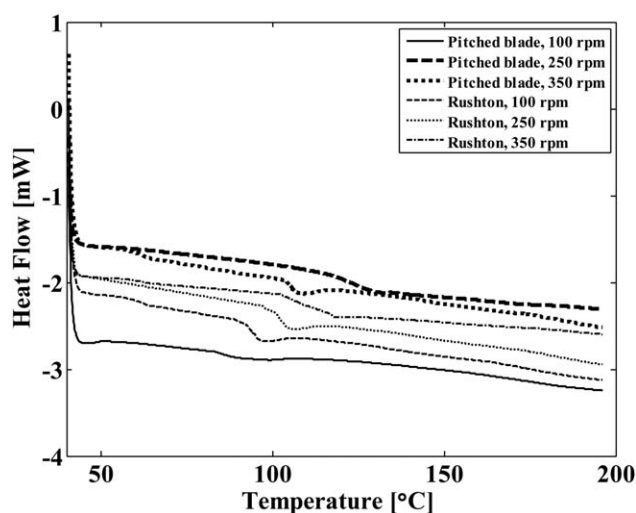


Figure 10. Heat flow versus temperature for final polymer at the impeller speeds of 100–350 rpm using pitched blade turbine and Rushton impeller.

using the pitched-blade and Rushton impellers at speeds of 100–350 rpm. The variation in glass temperature (T_g) values were recorded for the runs conducted using the pitched-blade turbine at 82.65, 115.44, and 103.35°C at the impeller speeds of 100, 250, and 350 rpm, respectively. The trend of gain in T_g up to 250 rpm and then decrease at the 350 rpm with the use of the pitched-blade turbine is similar to the trend of molecular weight as discussed earlier. However, the glass temperatures of PMMA samples produced by employing the Rushton turbine were less affected by the impeller speed variation. The glass temperature was recorded at 89.5, 96.06, and 101.53°C at the impeller speeds of 100, 250, and 350 rpm, respectively. The dependence of glass temperature with the average molecular has been reported in literature as well.⁴²

A general linear model was performed using Minitab-16 to generate the analysis of variance (ANOVA) tables for conversion, molecular weight, and particle size, respectively. The P -value was used to judge whether F-statistics was large enough to indicate statistical significance. A P -value < 0.05 indicates that the model is considered to be statistically significant.⁴³ Table III demonstrates that the impeller speed was a statistically significant factor for the conversion response while the impeller type, number of impellers, and interaction factors were insignificant. For the molecular weight response, according to Table IV, all factors and their interactions were insignificant. However, the reanalysis of the design revealed the significance of the impeller speed on the molecular weight response. Finally, according to Table V, the impeller type and speed were statistically significant on the particle size response while their interaction factor was insignificant.

Figure 11 shows the scanning electron microscopy (SEM) image (Model: Hitachi SU8000) of the dried end product latex, which was obtained at the Rushton turbine speed of 250 rpm. This image shows the size and shape distributions of the dried polymer particles. The information obtained in this study will enable us to combine the mixing phenomena with polymer chemistry to progress the emulsion polymerization process

Table III. ANOVA Results for the Final Conversion Response

Source	Degrees of freedom	Sequential sum of squares	Adjusted sum of squares	Adjusted mean square	F-statistic	P-value
Impeller speed	2	511.629	511.629	255.815	32.36	0.030
Impeller type	1	19.610	19.610	19.610	2.48	0.256
Number of impellers	1	62.290	62.290	62.290	7.88	0.107
Speed * Impeller type	2	94.989	94.989	47.495	6.01	0.143
Speed * Number of impellers	2	18.009	18.009	9.005	1.14	0.467
Impeller type * Number of impellers	1	9.470	9.470	9.470	1.20	0.388
Error	2	15.809	15.809	7.905		
Total	11	731.806				
Standard deviation = 2.81152; $R^2 = 97.84\%$; R^2 (adjusted) = 88.12%						
Regression model: Conversion = 69.2217 – 9.222 * (Impeller speed) – 1.2783 * (Impeller type) – 2.2783 * (Number of impellers) – 3.972 * (Impeller type) * (Impeller speed) – 1.722 * (Impeller speed) * (Number of impellers) + 0.8883 * (Impeller type) * (Number of impellers)						
After Re-analysis						
Impeller speed	2	511.63	511.63	255.81	10.46	0.004
Error	9	220.18	220.18	24.46		
Total	11	731.81				
Standard deviation = 4.94612; $R^2 = 69.91\%$; R^2 (adjusted) = 63.23%						
Regression model: Conversion = 55.9395 + 0.0569237 * (Impeller speed)						

to a point where industrial applications such as scale up and reactor design are much more feasible. We are currently using the CFD modeling in our research group to study the details of mixing such as shear forces, turbulence, and flow

pattern within the reaction mixture. The CFD study will enable us to analyze the scale-up of the emulsion polymerization. These results will be reported in our next article in the near future.

Table IV. ANOVA Results for the Final Molecular Weight Response

Source	Degrees of freedom	Sequential sum of squares	Adjusted sum of squares	Adjusted mean square	F-statistic	P-value
Impeller speed	2	3.4065 e +11	3.4065 e +11	1.7033 e +11	14.72	0.064
Impeller type	1	1.771 e +10	1.771 e +10	1.771 e +10	1.53	0.342
Number of impellers	1	3.424 e +11	3.424 e +11	3.424 e +11	2.96	0.228
Speed * Impeller type	2	1.6798 e +11	1.6798 e +11	8.399 e +10	7.26	0.121
Speed * Number of impellers	2	2.018 e +10	2.018 e +10	1.009 e +10	0.87	0.534
Impeller type * Number of impellers	1	1.756 e +10	1.756 e +10	1.756 e +10	1.52	0.343
Error	2	2.314 e +10	2.314 e +10	115.7		
Total	11	6.2146 e +11				
Standard deviation = 107,572; $R^2 = 96.28\%$; R^2 (adjusted) = 79.52%						
Regression model: Molecular weight = 769,917 – 225,167 * (Impeller speed) + 38,417 * (Impeller type) + 53,417 * (Number of impellers) + 146,583 * (Impeller type) * (Impeller speed) + 56,833 * (Impeller speed) * (Number of impellers) + 38,250 * (Impeller type) * (Number of impellers)						
After Re-analysis						
Impeller speed	2	3.40650 e +11	3.40650 e +11	1.70325 e +11	5.46	0.028
Error	9	2.80811 e +11	2.80811 e +11	3.1201 e +11		
Total	11	6.21461 e +11				
Standard deviation = 176,639; $R^2 = 54.81\%$; R^2 (adjusted) = 44.77%						
Regression model: Molecular weight = 769,917 – 225,167 * (Impeller speed)						

Table V. ANOVA Results for the Final Particle Size Response

Source	Degrees of freedom	Sequential sum of squares	Adjusted sum of squares	Adjusted mean square	F-statistic	P-value
Impeller speed	2	89.542	89.542	44.771	35.23	0.028
Impeller type	1	414.188	414.188	414.188	325.92	0.003
Number of impellers	1	13.021	13.021	13.021	10.25	0.085
Speed * Impeller type	2	24.875	24.875	12.438	9.79	0.093
Speed * Number of impellers	2	4.542	4.542	2.271	1.79	0.359
Impeller Type * Number of impellers	1	0.521	0.521	0.521	0.41	0.588
Error	2	2.542	2.542	1.271		
Total	11	549.229				
Standard deviation = 1.12731; $R^2 = 99.54\%$; R^2 (adjusted) = 97.45%						
Regression model: Particle size = 101.708 – 3.5833 * (Impeller speed) + 5.8750 * (Impeller type) + 1.0417 * (Number of impellers) – 0.2500 * (Impeller type) * (Impeller speed) – 1.722 * (Impeller speed) * (Number of impellers) + 0.8883 * (Impeller type) * (Number of impellers)						
After Reanalysis						
Impeller type	1	414.19	414.19	414.19	120.49	0.000
Impeller speed	2	89.54	89.54	44.77	13.02	0.007
Impeller Type*Impeller speed	2	24.88	24.88	12.44	3.62	0.093
Error	6	20.63	20.63	3.44		
Total	11	549.23				
Standard deviation = 1.85405; $R^2 = 96.24\%$; R^2 (adjusted) = 93.12%						
Regression model: Particle size = 101.708 + 5.8750 * (Impeller type) – 3.5833 * (Impeller speed) + 1.8750 * (Impeller type)*(Impeller speed).						

CONCLUSIONS

Emulsion polymerization of MMA was carried out in a 2 L laboratory reactor equipment with two different impeller types, a six pitched-blade and Rushton impeller. The effects of number of impellers, speed, and type of impellers on MMA conversion, molecular weight, particles size, and glass temperature were investigated. Stirring rate was varied from 100 to 350 rpm and single or double impeller were mounted on the shaft. Using the pitched-blade turbine reduced the monomer conversion, M_w , mean particle size and glass temperature at low agitation rate of

100 rpm. The maximum monomer conversion, M_w , mean particle size and glass temperature values were obtained at 250 rpm and further increase in speed, declined the mentioned properties.

Using the Rushton impeller showed relatively higher values for conversion, M_w , particle size and glass temperature compared with the values obtained using the pitched-blade turbine at 100 rpm; however, the increase in the mentioned properties with the elevation of impeller speed was less significant than the gain obtained using the pitched-blade turbine.

With employment of two pitched-blade impeller, the monomer conversion, M_w and particle size at low stirring rate of 100 rpm were elevated compared to values obtained using single pitched-blade impeller. However, at higher agitation rates, the increments were insignificant. Employment of double Rushton impellers was not so effective in increasing the monomer conversion, M_w and particle size. Using Rushton impeller resulted in the narrower molecular weight and particle size distribution compared with the pitched-blade turbine.

The finding of this study has the potential to contribute to the development of the novel polymerization processes where the adjustment of polymer characteristics can be obtained by suitable configuration design.

ACKNOWLEDGMENTS

The authors thank the Natural Sciences and Engineering Research Council of Canada (NSERC) and Ryerson University for the financial support.

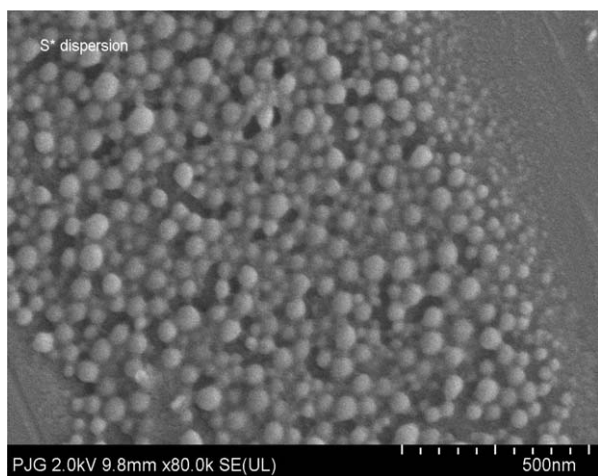


Figure 11. SEM image of final polymer product using Rushton turbine at impeller speed 250 rpm.

REFERENCES

1. Fathi Roudsari, S.; Turcotte, G.; Dhib, R.; Ein-Mozaffari, F. *Comput. Chem. Eng.* **2012**, *45*, 124.
2. Shinnar, R. *J. Fluid Mech.* **1961**, *10*, 259.
3. Patel, H.; Dhib, R.; Ein-Mozaffari, F. *Chem. Eng. Technol.* **2010**, *33*, 258.
4. Patel, H.; Ein-Mozaffari, F.; Dhib, R. *Comput. Chem. Eng.* **2010**, *34*, 421.
5. Fathi Roudsari, S.; Ein-Mozaffari, F.; Dhib, R. *Chem. Eng. J.* **2013**, *219*, 429.
6. Kemmere, M. F.; Meuldijk, J.; Drinkenburg, A.A.H.; German, A. L. *J. Appl. Polym. Sci.* **1999**, *74*, 3225.
7. Ozdeger, E.; Sudol, E. D.; El-Aasser M. S.; Klein, A. *J. Appl. Polym. Sci.* **1998**, *69*, 2277.
8. Nomura, M.; Harada, M.; Eguchi, W.; Nagata, S. *J. Appl. Polym. Sci.* **1972**, *16*, 835.
9. Kemmere, M. F.; Meuldijk, J.; Drinkenburg, A. A. H.; German, A. L. *Polym. React. Eng.* **1998**, *6*, 243.
10. Hong, J. PhD Thesis, Lehigh University, Bethlehem, USA, **2008**.
11. Choi, Y.; Lee, W. *Ind. Eng. Chem. Res.* **2010**, *16*, 431.
12. Cheng, D.; Cheng, J.; Li, X.; Wang, X.; Yang, C.; Mao, Z. *Chem. Eng. Sci.* **2012**, *75*, 256.
13. Zhang, L.; Pan, Q.; Rempel, G. L. *Ind. Eng. Chem. Res.* **2007**, *46*, 3538.
14. Maaß, S.; Eppinger, T.; Altwasser, S.; Rehm, T.; Kraume, M. *Chem. Eng. Technol.* **2011**, *34*, 1215.
15. Fontenot, K.; Schork, F.J. *J. Appl. Polym. Sci.* **1993**, *49*, 633.
16. Yu, Z.; Li, B.; Cai, M.; Li, B.; Cao, K. *J. Appl. Polym. Sci.* **1995**, *55*, 1209.
17. Parker, H. Y.; Westmoreland, D. G.; Chang, H. R. *Macromolecules* **1996**, *29*, 5119.
18. Congalidis, J. P.; Richards, J. R. *Polym. React. Eng.* **1998**, *6*, 71.
19. Sood, A. *J. Appl. Polym. Sci.* **2004**, *92*, 2884.
20. Oldshue, J. Y. *Chem. Eng. Prog.* **1989**, *85*, 33.
21. Okufi, S.; Perez de Ortiz, E. S.; Sawistowski, H. *Can. J. Chem. Eng.* **1990**, *68*, 400.
22. El-Hamouz, A.; Cooke, M.; Kowalski, A.; Sharratt, P. *Chem. Eng. Process.* **2009**, *42*, 633.
23. Afshar Ghotli, R.; Raman, A. A. A.; Ibrahim, S.; Baroutian, S. *Chem. Eng. Commun.* **2013**, *200*, 595.
24. Holland, F. A.; Bragg, R. *Fluid Flow for Chemical Engineers*, 2nd ed.; Butterworth-Heinemann: Oxford, UK, **1995**.
25. Paul, E. L.; Atiemo-Obeng, V.A.; Kresta, S. M. *Handbook of Industrial Mixing - Science and Practice*; Wiley: Hoboken, New Jersey, **2004**.
26. Baldyga, J.; Bourne, J. R.; Pacek, A. W.; Amanullah, A.; Nienow, A. W. *Chem. Eng. Sci.* **2001**, *56*, 3377.
27. Nere, N. K.; Patwardhan, A. W.; Joshi, J. B. *Ind. Eng. Chem. Res.* **2003**, *42*, 2661.
28. Asua, J. M. *Polymer Reaction Engineering*; Blackwell Publishing: Oxford, UK, **2007**.
29. Penlidis, A. *Polymer Reactor Design, Optimization and Control in Latex Production Technology*; McMaster University: Hamilton, **1986**.
30. Hansen, F. K.; Ugelstad, J. *J. Polym. Sci. Polym. Chem. Ed.* **1978**, *16*, 1953.
31. Hansen, F. K.; Ugelstad, J. *J. Polym. Sci. Polym. Chem. Ed.* **1979**, *17*, 3033.
32. Hansen, F. K.; Ugelstad, J. *J. Polym. Sci. Polym. Chem. Ed.* **1979**, *17*, 3047.
33. Hansen, F. K.; Ugelstad, J. *J. Polym. Sci. Polym. Chem. Ed.* **1979**, *17*, 3069.
34. Ohmura, N.; Nagamitsu, M.; Kondo, K.; Yano, T.; Usui, H. *J. Chem. Eng. Jpn.* **2005**, *38*, 722.
35. Holland, F. A.; Chapman, F. S. *Liquid Mixing and Processing in Stirred Tanks*; Reinhold: New York, **1966**.
36. Spicer, P. T.; Keller, W.; Pratsinis, S. E. *J. Colloid Interface Sci.* **1996**, *184*, 112.
37. Kim, Y. H.; Glasgow, L. A. *Ind. Eng. Chem. Res.* **1987**, *26*, 1604.
38. Soh, S. K.; Sundberg, D. C. *J. Polym. Sci. Polym. Chem. Ed.* **1982**, *20*, 1331.
39. Faldi, A.; Tirrell, M. *Macromolecules* **1994**, *27*, 4184.
40. Chern, C. S. *Prog. Polym. Sci.* **2006**, *31*, 443.
41. Pacek, A.W.; Chamsart, S.; Nienow, A.W.; Bakker, A. *Chem. Eng. Sci.* **1999**, *54*, 4211.
42. Blanchard, L.; Hesse, J.; Malhotra, S. L. *Can. J. Chem.* **1974**, *52*, 3170.
43. Tshukudu, T.; Zheng, H.; Hua, X.; Yang, J.; Tan, M.; Ma, J.; Sun, Y.; Zhu, G. *Korean J. Chem. Eng.* **2013**, *30*, 649.