Full Length Research Paper

Synthesis of polymethyl methacrylate (PMMA) by batch emulsion polymerization

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Poly (methyl methacrylate) was synthesized by batch emulsion polymerization with Methyl Methacrylate as the monomer potassium peroxo-disulfate as the initiator, sodium stearate as the emulsifier and distilled water as a medium. The kinetics of free radical polymerization was studied. The kinetics has been modeled, assuming homogeneous nucleation and the resulting equation were solved using runge-kutta method. Degree of conversion and rate of polymerization were studied.

Key words: Polymethyl methacrylate, emulsion polymerization, free radical polymerization, homogeneous nucleation, emulsifier.

INTRODUCTION

PMMA is a versatile material and has been used in a wide range of fields and applications. The German chemist Fittig and Paul discovered in 1877 the polymerization process that turns Methyl Methacrylate into poly Methyl Methacrylate (Lovell 1997). PMMA is routinely produced by emulsion polymerization.

Water born polymerization such as emulsion polymerization are of great importance in industry application as they provide environmental friendly process, remove the reaction heat easily during polymerization and assume the feasible handling of the final product having a low viscosity. Research in controlled/free radical polymerization has been increased significantly during the past two decades (Wi et al., 2008).

Emulsion polymerization involves the propagation reaction of free radicals with monomer within the monomer–swollen polymer particle dispersed in the

hydrophobic particles are stabilized by surfactant sodium stearate. Micelles are formed when the level of surfactant is greater than its critical micelles concentration (CMC). Particle nuclea-tions are generated via the capture of radicals by micelles. These absorb monomer to achieve a critical chain length (Zhu and, 2008).

PMMA is often used as a light or shatter-resistant alternative to glass. It is an economical alternative to polycarbonate (PC) when extreme strength is not necessary. It is often preferred because of its moderate properties, easy handling and processing, and low cost. PMMA is a versatile material and has been used in a wide range of fields and applications as a substituent of glass, medical technologies and implants and aesthetic use as well. This properties and uses of PMMA motivated us to work on.

The main objective of this paper is synthesis of Poly Methyl Methacrylate by batch emulsion polymerization and to develop a model to describe the emulsion polymerization of Methyl Methacrylate in a batch reactor at steady state and the comparison of model predictions with experimental observations and characterization of PMMA polymer by estimation of properties of polymer solution. Recently, Arora and colleagues presented this work in a preliminary form and the detailed results are given in this study.

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Nomenclature: f, Initiator efficiency; P, concentration of polymer; I, initiator (mol/L); M, monomer (mol/L); R, primary radical; K_d, rate constant for initiator decomposition (min^{-1}); K_1, rate constant for Initiation (lit/mol min); K_p, rate constant for propagation (lit/mol min); Ktc, rate constant for termination by combination (L/mol min); Ktd, rate constant for termination by disproportionation (L/mol min); K_{trTA}, rate constant for transfer to monomer/Initiator (L/mol min); K_t, Overall rate coefficient for termination (L/mol min). aqueous phase. These discrete

EXPERIMENTAL SETUP

The schematic diagram of the experimental setup as shown in
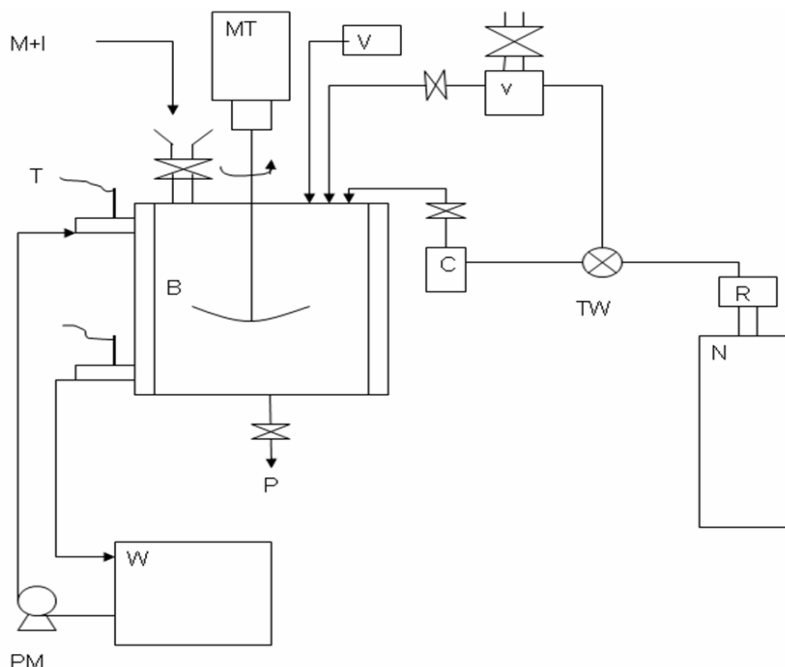
Figure 1. A schematic representation of batch emulsion polymerization process. B = batch reactor; N = N_2 gas cylinder; R = gas regulator; C = gas supply controller; TW = three way valve; v = initiator vessel; V= vacuum pump; MT = motor; T = thermometer; PM = pump; W = water tank; M = monomer; I = Initiator, P = Polymer.

Table 1. Recipe used in emulsion polymerization of PMMA (Flory, 1953).

Recipe	Quantity
Ion-exchanged double distilled water	180 ml
Methyl methacrylate	106 ml
Sodium stearate	2 gm
Potassium persulfate	1 gm
N_2 gas	supply at rate of 3 LPM
Hydroquinone	Present in Monomer
Temperature of reaction	70 ± 1°C
Stirring speed N	700 - 750 rpm

Figure 2. Picture of PMMA.

Figure 1. A jacketed batch reactor provided with a high speed mixer is used for emulsion polymerization. Proper arrangements are provided for the control of reaction temperature and the RPM of the mixer. Proper arrangements are provided for administering the initiator under inert atmosphere. Inhibitor is removed by heating Methyl Methacrylate at a temperature of 60°C, recipe used is given in Table 1.

Characterization

Viscosity of PMMA solutions varies from 1.07 to 1.42 cP with concentration of polymer solution. pH of PMMA solutions varies from 5.5 to 6.4 with concentration of polymer solution (Figure 2).

An electrical conductivity meter (EC meter) measures the electrical conductivity in a solution. Commonly used in hydroponics, aquaculture and freshwater systems to monitor the amount of nutrients, salts or impurities in the water.

The common laboratory conductivity meters employ a potentiometric method and four electrodes. Often, the electrodes are cylindrical and arranged concentrically. The electrodes are usually made of platinum metal. An alternating current is applied to the outer pair of the electrodes. The potential between the inner pair is measured. Conductivity could be determined in principle using the distance between the electrodes and their surface area using the Ohm's law but generally, for accuracy, a calibration is employed using electrolytes of well-known conductivity. The results as shown in Table 2.

Conductivity of PMMA solutions varies from 0.027 to 0.092 with concentration of polymer solution from 4.8 to 11.6 gm/lt (Jain,

Table 2. Results of viscosities of PMMA solution.

Beaker no.	Weight of polymer	Concentration in 50 ml benzene (gm/L)	Efflux time t for polymer solution	$\eta_{rel}=\eta/\eta_0 = t / t_0$	η in cp
1	0.24	4.8	4.08	1.07	1.075
2	0.32	6.4	4.12	1.08	1.085
3	0.42	8.4	4.51	1.18	1.186
4	0.48	9.6	5.03	1.32	1.326
5	0.58	11.6	5.43	1.42	1.427

Table 3. Reaction kinetic equations for batch emulsion polymerization.

Species	Mass balance equations for batch emulsion polymerization reactor
For initiator	$R_i = fd[I^\cdot]/dt = 2fK_d[I]$
For monomer	$R_p = -d[M]/dt = K_p(fK_d/K_t)^{1/2}[M][I]^{1/2}$
For polymer	$d[p]/dt = (fK_d/K_t)K_{tc}[I]+(fK_d/K_t)K_{td}[I]+(fK_d/K_t)^{1/2}K_{trM}[M][I]^{1/2}$ $+(fK_d/K_t)K_{trI}[I]^{3/2}$

Table 4. Rate constant for free radical polymerization of PMMA.

Constants	Value of constants
f	0.58
K_d	0.001834 min^{-1}
K_p	49876.54 l/mol min
K_{trM}	1.40813 l/mol min
K_1	K_p
K_{td}	K_t
K_{tc}	0.0
K_t	1.414 × 10^9 l/mol min

2008.). Conductivity of polymer solution is measured by conductivity meter. Conductivity meter is firstly calibrated with 0.1 N AgCl solution.

Modeling of batch emulsion polymerization for PMMA

The model is developed to describe the emulsion polymerization of Methyl Methacrylate in a batch reactor at steady state. Non-isothermal effects are considered by coupling the mass and energy balances through the Arrhenius dependence of the rate constants (Sangwai et al., 2005). Conservation of energy accounts for the heat generated by the propagation reaction and heat removal through the wall of the reactor and by convective fluid flow. The density of the mixture is a function of the conversion, the amount of solvent introduced in the feed and the temperature. Heat capacities of the monomer, solvent and polymer are taken to be constant, independent of temperature. Monomer and polymer are assumed to have the same heat capacity on a unit mass basis (Min and Ray, 1978; Zeaiter et al., 2002; Tefera et al., 1997). The set of coupled first order differential equations (Chern, 2006) is listed in Table 3. The Arrhenius expressions of the rate constants

are listed in Table 4. The calculated results are the conversion, initiator and PMMA concentration profiles and rate of polymerization. Model predictions for different operating conditions have been compared with experimental observations. Reaction kinetics equations for batch emulsion polymerization are following in Table 3.

Computation

Rate of change in Initiator I

$$R_i = fd[I^\cdot]/dt = 2fK_d[I] \tag{1}$$

Rate of change in Monomer M

$$R_p = -d[M]/dt = K_p(fK_d/K_t)^{1/2}[M][I]^{1/2} \tag{2}$$

Rate of change in polymer P

$$d[p]/dt = (fK_d/K_t)K_{tc}[I]+(fK_d/K_t)K_{td}[I]+(fK_d/K_t)^{1/2}K_{trM}[M][I]^{1/2}$$
$$+(fK_d/K_t)K_{trI}[I]^{3/2} \tag{3}$$

Initial condition:-

At t = 0,   I = Ii,   M = Mi,   P = 0,

Now, in order to solve the equations 1, 2 and 3 simultaneously we make use of the Runge-Kutta method for the solution of ordinary differential equations (Sangwai et al., 2005). We carry out the calculations for different values of I, M and P corresponding to time and using h = 0.001 s. Kinetics rate constant for free radical polymerization of PMMA is calculated at 70°C from literatures (Baillagou and Soong, 1985) (Tefera, 1997). Rate constant for free radical polymerization is shown in Table 4.

Table 5. Results of pH and conductivity of different concentration of PMMA solution.

Beaker no.	Concentration of PMMA solution gm/L	pH	Conductivity (mhos)
1	4.8	5.5	0.027
2	6.4	5.8	0.051
3	8.4	6.0	0.055
4	9.6	6.1	0.075
5	11.6	6.4	0.092

Table 6. Results of batch emulsion polymerization by simulation.

Time (min)	Initiator concentration (mol / L)	Monomer concentration (mol / L)	PMMA concentration (Mol / lt)
0	0.185	5.0	0.0
15	0.182078	2.652442	0.000037
30	0.179202	1.6993186	0.000074
45	0.176372	0.965976	0.000110
60	0.173586	0.360244	0.000146
75	0.170844	0.267043	0.000181
90	0.168146	0.163858	0.000213
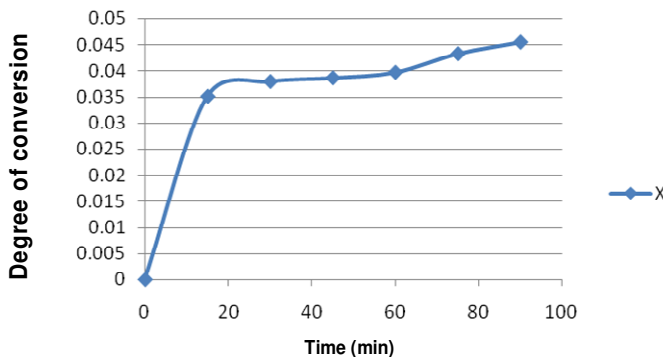
Figure 3. Degree of conversion with respect to time for emulsion polymerization of PMMA.

We have the equations

$$R_i = fd[R^\cdot]/dt = 2fK_d[I]$$ = f (t, I, M, P)

$$R_p = d[M]/dt = K_p(fK_d/K_t)^{1/2}[M][I]^{1/2}$$ = g (t, I, M, P)

$$d[p]/dt=(fK_d/K_t)K_{tc}[I]+(fK_d/K_t)K_{td}[I]+(fK_d/K_t)^{1/2}K_{trM}[M][I]^{1/2}$$
$$+(fK_d/K_t)K_{trI}[I]^{3/2}$$ =
p (t, I, M, P)

With the initial conditions:

At t = 0,   I = Ii,   M = Mi,   P = 0,

Now, using h = 0.001 sec we calculate the values of I, M and P at different intervals using Turbo C^{++} version 3.0 and simulate the data. The corresponding results were plotted graphically.

RESULTS AND DISCUSSION

pH of PMMA solution is measured by pH meter at 25°C. Conductivity of PMMA solution is measured by conductivity meter. pH and conductivity of different concentrated PMMA solutions are tabulated in Table 5. Dried polymer which is made in experiment runs is dissolved in 50 ml of benzene. Efflux time t_0 required for a specified volume of benzene solvent to flow through a capillary is measured by ostwald viscometer. Measured efflux time t_0 for benzene at 20°C is 3.81 s. Viscosity of benzene with respect to water is calculated by viscometer. η_0 = 1.005 cp, viscosity of samples are tabulated in Table 2.

Results of batch emulsion polymerization has been done by simulation Table 6. Degree of conversion × increase with time t initially and then equilibrates between 0.04 and 0.06 as shown in Figure 3, a sharp increase has been observed because of Trommsdorff effect, this was due to the localized increase in viscosity of the polymerizing system which caused the motion of the radical hindered to approach each other for the termination, hence it decrease the termination rate.

Figure 4 shows linear increase at conversion value of 0.03 and suddenly shoot up at value of 3.5 rate of polymerization R_p in very short time, data is given in Table 6. This could be because of exothermic nature of reaction and also auto-acceleration must be caused by the raised viscosity of the polymerization region when
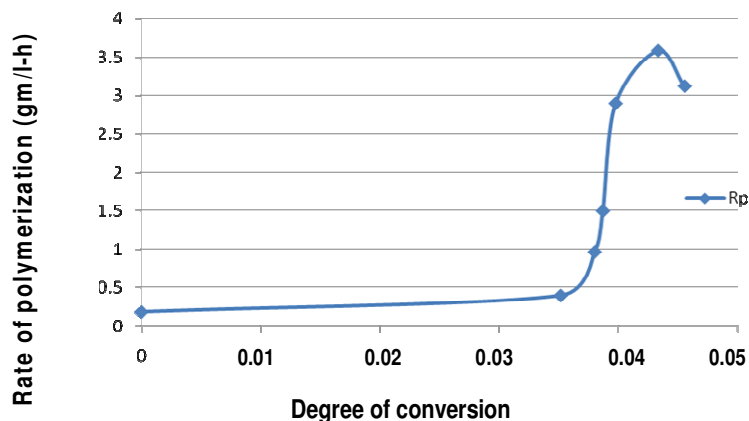
Figure 4. Rate of polymerization with respect to conversion for emulsion polymerization of PMMA.
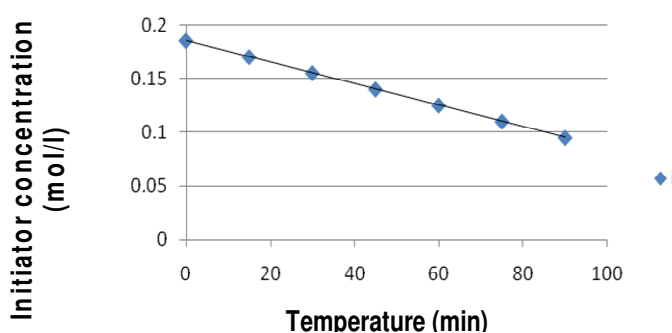
Figure 5. Initiator concentration profile in emulsion polymerization of Poly Methyl Methacrylate with respect to time.

the concentration of formed polymer molecules was increased and termination decreased from concentration 0.035 to 0.045. Initiator concentration profile in Figure 5 shows that the concentration of initiator decrease with time from concentration 0.185 - 0.168 mol/L, because the initiator radical combines with monomer particle and leads to chain propagation, which finally leads to formation of polymer. The faster the initiation rate the narrower should be the particle size distribution. Monomer concentration profile in Figure 6 shows that the concentrations of Methyl methacrylate monomer exponentially decrease with time from concentration 5.0 to 0.164 mol/L. This could be because the monomer is the raw material for the polymerization reaction, the concentration of monomer decreases as the reaction proceeds forward with time.

Polymer concentration in Figure 7 shows that the concentration of polymethyl methacrylate increases with time from concentration 0 to 0.000213 mol/L. As the reaction proceeds in the forward direction, the product's concentration increases with time.

We got the degree of conversion from 0 to 0.04553,

pH of the polymer solution varies from 5.5 to 6 and conductivity varies from 0.027 to 0.092 (mhos). Number average degree of polymerization for disproportion was 334.29 and its average molecular weight was 33429.21 gm/gmol. The kinetic chain length obtained was 334.29. Kinetic chain length is inversely proportional to the radical concentration. Increasing the radical concentration in radical polymerization leads to small sized polymer molecule.

Encountered difficulties in batch emulsion polymerization of PMMA

The following difficulties are encountered during batch emulsion polymerization of PMMA.

(1) In batch reactor, the outlet of the reactor is clogged during the polymerization process. It could be because of emulsifier particles.
(2) In batch emulsion polymerization process, it is difficult to maintain constant temperature during the process. Emulsion polymerization is exothermic reaction
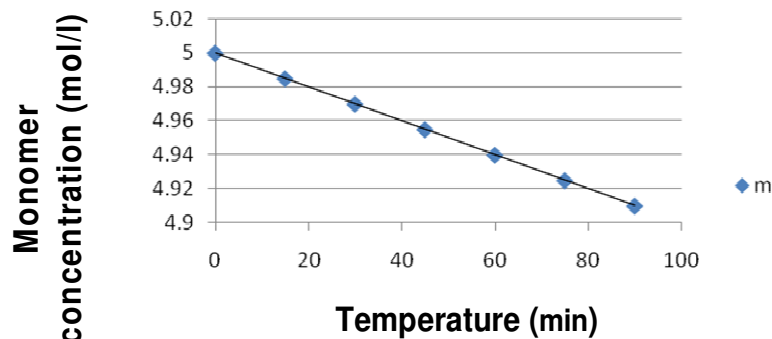
Figure 6. Monomer concentration profile in emulsion polymerization of MMA with respect to time.
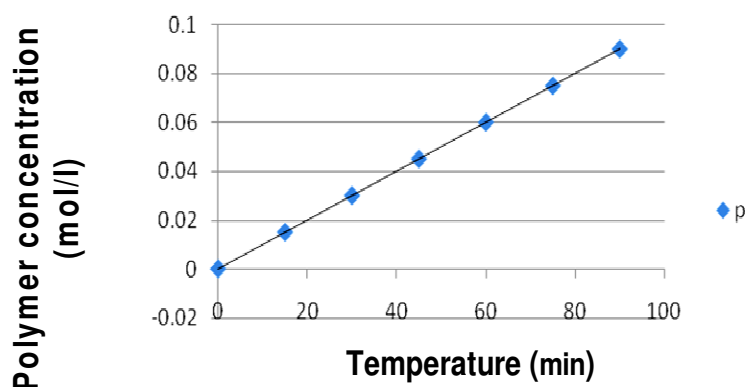
Figure 7. PMMA concentration profile in emulsion polymerization with respect to time.

so temperature of reaction goes higher than the desired temperature. For maintaining the constant temperature hot water is circulated through the jacket of the batch reactor.

Conclusion

PMMA polymer was successfully prepared by batch emulsion polymerization as shown in Figure 4 and characterized. The simulation of the process was carried out using Runge-Kutta algorithm on C++ computer language. Corresponding graphs were obtained for concentration of initiator, monomer, PMMA with time hence the complete analysis of batch polymerization process was done.

Degree of conversion and rate of polymerization is calculated at particular time which shows the trommsdorff effect. The graphs were plotted from results and discussed. With the successful synthesis of PMMA from emulsion polymerization, it is suggested that this technique can be extended for the preparation of other polymers as well.

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