Characterization of PMMA Polymer Particles by Light Diffraction Method: Effect of Monomer, Initiator and Dispersion Medium Concentration on Monodispersity

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ABSTRACT

In this research work, the micron size PMMA (Poly Methylmethacrylate) polymer particles were prepared by dispersion polymeraization. In order to acheive optimum conditions, different concentartiion of initiator, monomer and dispersion medium were used. The polymer particle size and size distribution were then investigated by using light diffraction & laser technique. Variation in concentration of initiator showed that mean particle size decreased as the concentration of initiator AIBN (2,2-Azobis Iso Butyro Nitrile) was increased. The particle size distribution became wider with increase in concentration of initiator. Monomer concentration increase shows increase in the particle size and broaden the size distribution. However, when monomer MMA (Methyl methacrylate) concentration was decreased the particle size also decreased whereas the particle size distribution is less wide as compared to concentration increased.

Key Words: **PMMA, Polymer, Characterization, Monodisperse, Monomer, Initiator.**

1. INTRODUCTION

Monodisperse polymer particles has become an important area of research because of its industrial importance. The total weight of colloids and particulate polymer produced world wide is of the order of 100-1000 tonnes per annum. The material has a broader applications including paints, coatings, plastic, catalyst and a variety of other industrial applications in addition to basic investigation of materials, instrument calliberation, determination of pore size, filters efficiency and chromatograph column packings. It also had an applications in the simulation of antibodies production and purification, for serological diagnostic tests (e.g. human pregnancy), as a model system in adsorption studies, in the manufacture of contact lenses, various electrical applications and many more which are not listed here. The level of success in each of these applications is eventually depends on the size of the particels, size distribution, morphlogy and surface characteristics in addition to other factors [1-3].

Control of particle size and its uniformity has been essential area of interest for the scientists. It has been difficult to prepare monodispersed micron size polymer particle. Bradford, et. al. [1] had prepared monodisperesed particle of polystyrene. Bhanti, et. al. [2] had generated polystyrene latex particle. Dispersion polymerization is

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the second approach for preparing polymer particles in micron size. This method was very thoroughly reviewed by Barrett, et. al. [3-4] and produced almost similar size of particles. The Method depends on incipient aggregation of the polymerising species at the initial stage of polymerisation, the number of particles were determined by the growing nuclei. The final size and size distribution were determined by the quantity of monomer used and the stabilizer capability for growing particles.

Almog, et. al. [5] had successfully produced monodispersed PMMA/polystyrene particles in size range of micrometer. The method involves stabiliser (polymeric steric) in addition to quaternary ammonium salt as a electrostatic costabiliser. Pendleton, P., et. al. [6] El-Aasser, et. al. [7] and Soomro, S.A., [8-10] successfully prepared monodispersed PMMA polymer particles in various particle sizes & size distribution; varying the concentration of monmer, stabilizer, costabilizer, initiator and dispersion medium in addition to scaling up the process. Nagao, D., et. al., [11] carried out polymerization using monomer (anionic), p-styrenesulfonate that improves polymerization stability of the polymer. Monodispersed PMMA narrow particle size distribution were produced by radiation-induced polymerization using alcohol as dispersion medium at room temperature in presence of steric stabilizer by Ye, Q., et. al. [12].

A work by Dai, Q., et. al., [13] were on the production of monodispersed PMMA polymer particles by radiation by using hexane-ethanol media in presence of vinyl terminus PSI (Polysiloxane) macromonomer (as stabilizer) at room temperature. One step, polymerization method that produced poly(methylmetahcrylate) particles in nano size (100nm) and high polymer yield were investigated by Camli, S.T., et. al. [14]. DLS (Dynamic Light Scattering) was used for polymer particles characterization. The effect of concentration of acetone, monomer and initiator were investigated for the optimization of average particle hydrodynamics diameter and polydispersity index. A review were carried out by Kim, J.W., et. al. [15] to reveal the seeded polymerization technique that synthesise different polymer colloids. A novel macromonomer of vinyl-terminated bifunctional polyurethane was synthesized by Cao K., et. al., [16] and was used for dispersion polymerization of methymethacrylate in ethanol.

The method for the current study was earlier used by Soomro, S.A., et. al. [8-10] for the preparation of monodisperse PMMA particle. The similar method was also reported by El-Aasser, et. al. [7]. Monodispersed PMMA polymer particle were prepared by varying the concentration of monomer, initiator and dispersion medium; keeping the other parameters constant. The effect of changing the concentration had been studied to investigate the polymer particles size and size distribution. The PMMA polymer particle were characterized by using light diffraction and laser techniques.

2. MATERIAL S AND METHOD

2.1 Chemicals Used

The chemicals used in the preparation of micron size PMMA polymer particle are shown below. The chemicals were used as supplied except methyl methacrylate which was further purified to remove the inhibitors. Methyl methacrylate were purified by distilling in the rotary vacuum evaporator in a constant temperature bath at 55°C [8-10].

- Methylmethacrylate
- PVP (Poly Vinylpyrolidon)
- Methyl tricaprylyl ammonium chloride (Aliquat 336)
- AIBN
- Methanol

The work on preparation of monodispersed PMMA polymer particles was reported by other workers using dispersion polymerization and emulsion polymerization.

They used various combination of dispersion medium,i.e. methanol, ethanol and hexane; with or with out water. In their work, various types of initiator were used in addition to change in concentrations. Concentrations of monomer (MMA) was also varied.

Lee, J., et. al., [17] had carried out work by changing the initiator and monomer concentrations; using methanol-water mixture as dispersion medium to prepare PMMA polymer particle. The ADVN (2-2 Azobis-2,4 Dimethylvaleronitrile) as an initiator was used. The results were compared with the conventional initiator, AIBN. Poly(dimethylsiloxane) containing macro-azo-initiator was also reported for the preparation of PMMA polymer particles, Tan, J., et. al. [18]. Dispersion polymerization was carried out using initiator, 2-2 -azobis[N-(2-carboxyethyl)-2-2-methylpropionamidine] and results were comaperd with AIBN and BPO (Benzoyl Peroxide) as an initiator in another study [17].

Tan, J., et. al. [18] used photoinitiated dispersion polymerization technique using ethanol-water mixture to produce PMMA polymer particles in presence of UV radiations at room temperature. Another work on preparation of PMMA was reported, Dai, Q., et. al. [13] using aqueous alcohol media using radiations at room temperature. Hexane-ethanol media was used for dispersion polymerization of MMA, Camli, S.T., et. al. [14]. A soap free emulsion polymerization of MMA was also reported using aqeous methanol media, Hong, J., et. al. [19].

2.2 PMMA Polymer Particle Preparation and Separation

The experimental set-up used for the preparation of PMMA ploymer particles consists of a three neck round bottom flask fitted with a stirrer. A 500ml flask was used for 125g sample. The three neck round bottom reaction flask was used in order to facilitate the purging of nitrogen through the system to eliminate oxygen from the system. The stirrer was fitted firstly in order to mix and disperse the reactants & polymer particles properly and secondly to hinder the settling of the polymer particles formed during reaction. The reaction mixture was then placed in a constant temperature bath at 55°C for 48 hours to complete the polymerization process. The concentration of monomer, initiator and dispersion medium were changed, keeping the stabilizer and costabilizer concentration constant. PMMA polymer particles were separated from the mixture by centrifuge for 10-20 minutes at 1500-4000 rpm at 20°C. The colloidal polymer particles (dry) obtained were redispersed in the methanol. Methanol were then separated by centrifuge technique. It was centrifuged twice to remove organic media (methanol). The product were allowed to dry in air, Soomro, [8- 10].

2.3 Characterization of PMMA Polymer Particles

Before characterization, the particles were resuspended in methanol and sonicated in an ultrasonic bath for 10 minutes in order to redisperse the polymer particles evenly. The analysis of the particle size and size distribution were carried out using two methods, namely; Coulter Counter and Malvern Autosizer.

2.3.1 Coulter Counter

The Coulter Counter is one of the best known methods of counting/sizing irregularly shaped and spherical particles irrespective of composition and refrective index. It is a direct method of measuring particle size as shown in Fig. 1. A dilute suspension of polymer particles & electrolyte solution were analyzed. The suspension was stirred in vessel and drawn through small apperture by means of a tap being opened to a vacuum source. Current passing through small apperture between two electrodes enable the particles to be sensed by the momentary changes in electrical impedence as they pass through the apertures, as each particle displaces its own volume of eletrolyte. The particle-generated pulses were amplified and measured. By this technique, thousand's of particles per seconds may individually be measured in terms of size and size distribution with accuray. Choice of electrolyte

depends upon the particle composition. The equipment was used especially for the measurement of the main polymerisation product, poly(methylmethyacrolate). The poly(methylmethyacrolate) polymer particles prepared were generally in the size range of 0.07-20μm as shown in Figs. 2-4 .

2.3.2 Malvern Autosizer

The Malvern unlike the Coulter Counter is an indirect method of particle size analysis that employs laser diffraction to measure the particle size range from sub-micron to micron of a variety of powders, suspensions

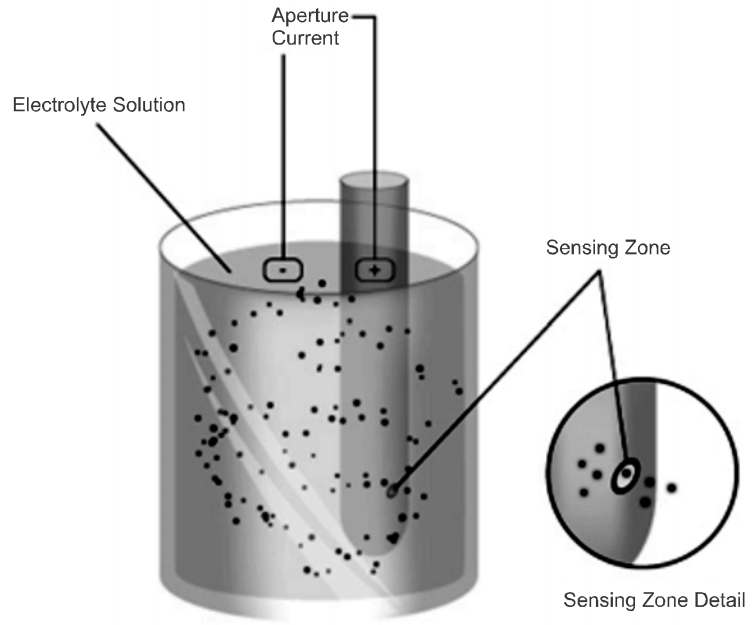

FIG. 1. COULTER COUNTER

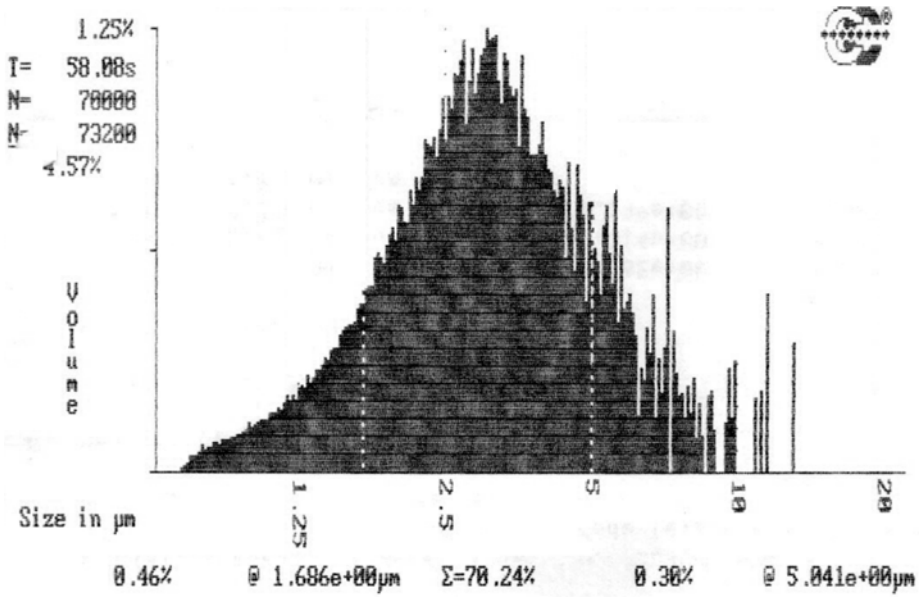

FIG. 2. CHARACTERIZATION OF PMMA POLYMER PARTICLE-EFFECT OF INITIATOR (AIBN) CONCENTRATION

and emulsions in a very fast analysis time of about 10 seconds. For this analysis, the particles were resuspended in the dispersion medium. In this work methanol was used as a dispersion medium. Care should be taken in making the sample for analysis. The sample should be well dispersed in the medium and also not very dilute or too concentrated. The sample prepared was then poured in to the cuvette and inserted via a small sliding lid into the top of the optical unit. The experimental details such as refractive index, viscosity, density and temperature etc. were selected according to the dispersion medium used.

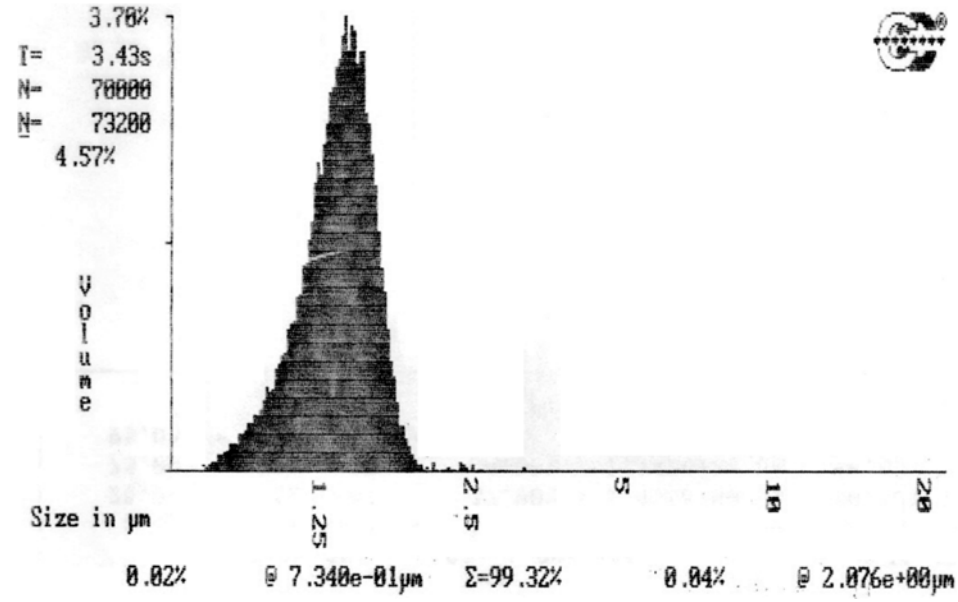

FIG. 3. CHARACTERIZATION OF PMMA POLYMER PARTICLE-EFFECT OF MONOMER (MMA) CONCENTRATION

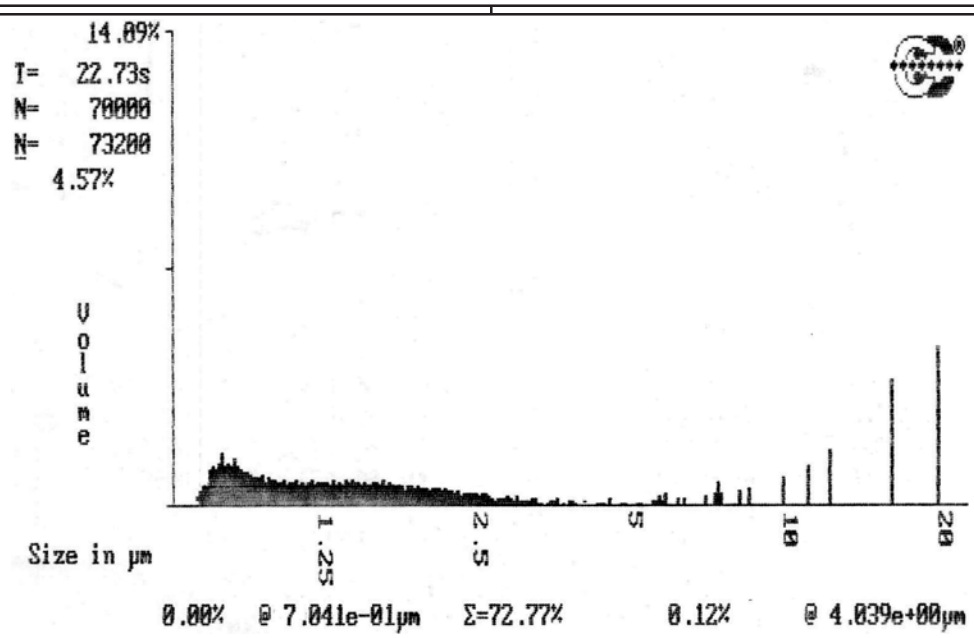

FIG. 4. CHARACTERIZATION OF PMMA POLYMER PARTICLE-EFFECT OF DISPERSION MEDIUM (METHANOL-WATER) CONCENTRATION

The instrument used was Malvern Autosizer IIc and consists mainly of three compartments, optical unit, the digital correlator and computer system. The instrument can measure the particle size range from 0.003-3.0µm (3-3000nm). The instrument was used to measure the particles in the waste and wash liquid. The particles were very small and were not settled with main product. Some times these tiny particles were in a substantial quantities and the waste and wash liquid was cloudy. These fine particles were about 500nm in size and cannot be measured by Coulter Counter.

3. RESULTS AND DISCUSSIUON

PMMA polymer particle size and size distribution plays an important role in the flow and quality of plastic and paint materials. This is strongly dependent on the concentration of monomer, initiator, stabilizer, costabilizer and dispersion medium. Also temperature plays an important role on polymer particle size and size distrbution. In this study, PMMA polymer partice size and size distribution were investigated by varying the concentrations of initiator, monomer and dispersion medium; keeping the other parametres constant. The resulting PMMA polymer particle were analyzed by Coulter Counter for particle size & particle size distribution. The results of the analysis are discussed as follows:

3.1 Effect of Initiator Concentration

The experiments were carried out to investigate the effect of varying initiator (AIBN) concentration to study the effect on the formation of PMMA polymer particle size. Also, particle size distribution was invstigated by coulter counter in order to have micron size PMMA polymer particles of uniform size. The concentration of the initiator, AIBN, were increased from 0.09- 0.50% as shown Table 1, Kohki, N., et. al. [20].

The mean particle size varied between 4.85-2.2µm, Fig. 5, as far as the particle size distribution were concerend, the two best results were observed at 90 and 65.18% concentration of initiator. The particle size were found between 4.2-5.2 and 1.6-4.5 µm respectively as shown in Table 1. Fig. 2 shows the wide particle size ditribution that is between 0.25-15µm.

3.2 Effect of Monomer Concentration

The effect of varying concentration of monomer were studied. Coulter Counter equipment were used to analyze the particle size and size distribution. Concentration of the monomer was gradually increased from 5-25% as shown in Table 2.

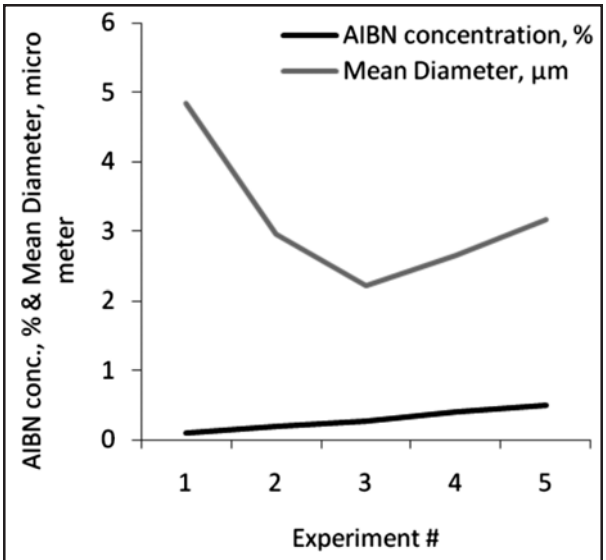

FIG. 5. CHARACTERIZATION OF PMMA POLYMER PARTICLE-EFFECT OF AIBN CONCENTRATION ON PMMA POLYMER PARTICLE MEAN SIZE

TABLE 1. EFFECT OF THE INITIATOR CONCENTRATION ON PMMA POLYMER PARTICLE SIZE AND SIZE DISTRIBUTION

Experiment No	1	2	3	4	5
AIBN Concentration	0.09%	0.18%	0.27%	0.40%	0.5%
Mean Diameter	4.85µm	2.96µm	2.21µm	2.65µm	3.16µm
Size Range	4.2-5.2µm	1.7-5.0µm	1.6-4.5µm	1.6-4.3µm	1.5-3.7µm
Weight	90%	70.2%	65.1%	63.1%	56.3%

Monomer concentration were increased from 5-25%. The mean particle size was decreased from 7.87-1.351µm which is substantial decrease in particle size as shown in Fig. 6. On the other hand, when concentration of the monomer was increased to 15%; the mean particle size also increases to 6.309µm. In both cases either at higher or lower concentration, the particles were polydispersed.

The size range of the polymer latex particles were also observed. When the monomer concentration was 5%, 99.32% particles was in between 0.07-2.07µm size. 82.65% of PMMA particles were in the size range of 5.04-8.07µm, when the concentration of the monomer was 15% (Table 2). The particle size distribution were 0.25-2.2µm, as shown in Fig. 3.

3.3 Effect of Methanol-Water as a Dispersant

Dispersion medium was the variable in the following experiments,Table 3. In these experiments, in addition to pure methanol; methanol-water mixture [7] was also used as dispersion medium to study the effects on polymer size and its distribution. Methanol-water mixture ratio used were 100:00, 80:20, 70:30, 55:45 and 40:60% as shown in Table 3.

The particle size distribution was not successful and a very small quantity of particles were produced as the ratio of water were increased, Fig. 7. The size distribution was very wide and also decrease in particle size was observed, as shown in Fig. 4.

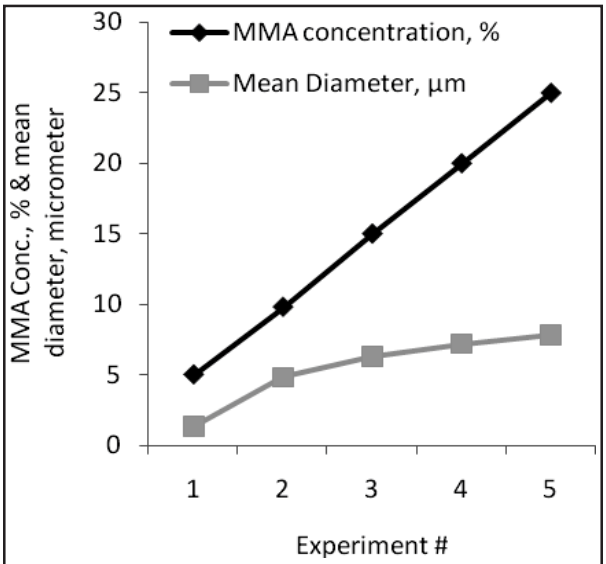

FIG. 6. CHARACTERIZATION OF PMMA POLYMER PARTICLE-EFFECT OF MMA CONCENTRATION ON MEAN PARTICLE SIZE

TABLE 2. EFFECT OF MONOMER CONCENTRATION ON PMMA POLYMER PARTICLE SIZE AND SIZE DISTRIBUTION

Experiment No.	1	2	3	4	5
MMA Concentration	5.0%	9.8%	15%	20%	25%
Mean Diameter	1.35µm	4.85µm	6.31µm	7.24µm	7.87µm
Size Range	0.07-2.07µm	4.2-5.2µm	5.04-8.07µm	3.56-8.67µm	3.12-9.67µm
Weight	99.32%	90%	82.65%	70%	60%

TABLE 3. EFFECT OF METHANOL-WATER AS A DISPERSANT ON PMMA POLYMER PARTICLE SIZE AND SIZE DISTRIBUTION

Experiment No.	1	2	3	4	5
Methanol	100%	80%	70%	55%	40%
Water	0%	20%	30%	45%	60%
Mean Diameter	4.85µm	3.12µm	1.21µm	1.39µm	2.56µm
Size Range	4.2-5.2µm	2.7-7.34µm	0.8-09.0µm	0.72-11.04µm	0.63-19.86µm
Weight	90.1%	73.42%	70.2%	72.8%	76.7%

In this study, monodispersed polymer particles were obtained at 55°C by varying the concentrations of initiator, mononmer and dispersion medium. The monodispersed PMMA particle were obtained at initiator concentration of 0.18%, monomer concentration of 9.8 and 100% concentrated methanol. The PMMA polymer particle size is strongly dependent on monomer-initiator concentration as well as on temperature while it is independent on the concentration of dispersant, Cao, K. et., al. [16], and Gijung, K., et. al. [21].

In the present work the 90% particles of PMMA polymer particle were obtained in size range of 4.2-5.2µm (Table 1) by using thermal induced polymerization at 55°C . Where as, Cao, K., et. al. [16] produced 2.0-4.0µm particle size range of PMMA using radiation induced polymerization reaction at room temperature. The current work shows narrow PMMA particle size distribution, i.e. 4.2-5.2µm.

Monodispersity of PMMA polymer particles were also achieved [18], using ethanol-water as dispersion medium in presence of UV radiations at room temperature.

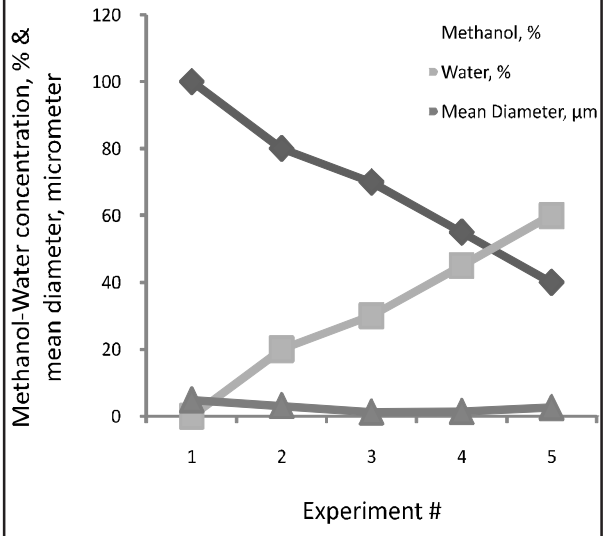

FIG. 7. EFFECT OF METHANOL-WATER CONCENTRATION ON PARTICLE SIZE

4. CONCLUSIONS

The experimental work was focused to study the formation of monodispersed PMMA polymer particles and characterization of polymer particle. Different experiments were carried out by varying concentrations of initiator, monomer and dispersion medium, keeping the other parameter constant viz. stabilizer, costabilizer concentration and temperature. The following conclusions had been made:

(i) The work shows that the initiator concentration affects the size of the particles and particle size distribution. Increase in the concentration of the initiator decreases the particle size and widens the size distribution. The similar pattern of particle size formation of PMMA has been reported by other researchers.

(ii) The monomer concentration affect in different way. The particle size of PMMA increases with increase in concentration of monomer. This happens because flocculation and coagulation occurs. The particle size distribution becomes wide as in the case of initiator concentration.

(iii) Finally the composition of dispersion medium was changed and instead of using methanol alone, methanol-water mixture as a dispersion medium was used. The mean particle size decreases as the concentration of methonol was decreased in the mixture. However, the particle size distribution becomes very wide. In contrast, the other researchers work shows no effect on particle size and size distribution, when they use Ethanol-water mixture in conjuction with photoinitiator.

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