

Dispersion Polymerization of Methyl Methacrylate: Effect of Stabilizer Concentration

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ABSTRACT: In dispersion polymerizations of methyl methacrylate (MMA), little difference was found in the polymerization kinetics with varying stabilizer (PVP K-30) concentration, indicating that in contrast to emulsion polymerization, the kinetics of these dispersion polymerizations are independent of the number of particles. Comparing MMA precipitation and dispersion polymerizations revealed that nuclei formation in the latter results from precipitation polymerization occurring in the continuous phase, which can contribute significantly to the kinetics,

and especially to the molecular weight distributions. No change was found in the molecular weight distribution of the PVP during a dispersion polymerization, nor was there any measurable difference between using fresh and recycled stabilizer. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2453–2458, 2008

Key words: dispersion polymerization; radical polymerization; particle nucleation; stabilization; grafting; particle size distribution; molecular weight distribution

INTRODUCTION

Dispersion polymerization is an attractive method for producing micron-size polymer particles with a narrow size distribution in a single step. It was first developed in 1950s to fill a need for nonaqueous dispersion coating technologies for automotive paints.¹ Differing from emulsion or suspension polymerization, dispersion polymerization is defined as a process by which stable colloidal polymer particles are formed in a continuous liquid medium through polymerization of a monomer, which is completely miscible with this medium and in which a stabilizer has been initially dissolved.² That is, dispersion polymerization starts from a homogeneous solution and becomes heterogeneous during the reaction, since the medium is a poor solvent for the polymer being produced. This is similar to precipitation polymerization except that the precipitated polymers are stabilized to form fine particles.

A stabilizer is important for providing colloidal stability and control of particle size and size distribution in dispersion polymerization. Homopolymers, such as poly(vinyl pyrrolidone) (PVP), hydroxy propyl cellulose (HPC), and poly(acrylic acid),¹ have been successfully applied as steric stabilizers in dispersion polymerizations. A common characteristic of these stabilizers is that they all contain labile hydrogen atoms.

During a reaction, the hydrogen atoms are readily abstracted, which allows grafting of the monomer to form an amphipathic copolymer. This *in-situ* graft polymer may act as the real stabilizer by anchoring on the particle surface, providing steric stabilization. The existence of these *in-situ* graft polymer have been studied using infra-red (IR) spectroscopy,³ NMR,⁴ and electron microscopy.⁵ A mathematical model has also been proposed to predict the particle size by considering that the stabilization is only attributable to the graft polymer.^{6,7}

In dispersion polymerization, increasing the stabilizer concentration or its molecular weight generally decreases the particle size.^{4,8–10} However, there are a few studies that have suggested that the molecular weight of the stabilizer has little or no effect on the particle size.^{11,12} Costabilizers are sometimes added to achieve desired narrow particle size distributions. These are generally low molecular weight compounds, such as anionic, cationic, and nonionic surfactants^{8,10} (e.g., Aerosol OT, Aliquat 336, and Triton N-57), or long chain alcohols (e.g., cetyl alcohol).¹³ The efficiency of the costabilizer is closely related to how it competes with the stabilizer for adsorption onto the surface of the polymer particles. Although early studies almost always used a costabilizer to produce monodisperse particles, later investigations showed that it was only necessary when the concentration of stabilizer was low.⁸

In this study, the effect of stabilizer on the kinetics of dispersion polymerization has been investigated using reaction calorimetry. Comparisons are made

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TABLE I
Recipe for Dispersion Polymerization in the RC1 (70°C, 400 rpm)^a

Ingredient	Weight (g)	Amount ^a (%)
MMA	50.54	100
AIBN ^b	0.2527	0.5
PVP K-30 ^c	Varied	10–20
Methanol/water (70/30 wt/wt)	449.38	–

^a Based on monomer.

^b 2,2'-Azobis(isobutyronitrile).

^c Poly(vinyl pyrrolidone), PVP K-30, MW = 40,000 g/mol.

between dispersion and precipitation polymerizations to better understand the mechanism of dispersion polymerization.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA; Fisher, Pittsburgh, PA) monomer was purified via distillation at reduced pressure. The initiator, 2,2'-azobis(isobutyronitrile) (AIBN; Sigma-Aldrich, St. Louis, MO), was used without further purification. All other materials were used without further purification, including methanol (VWR, Bridgeport, NJ), and poly(vinylpyrrolidone) (PVP K-30; Sigma-Aldrich). Deionized (DI) water was used in all experiments.

Polymerization and characterization

Dispersion and precipitation polymerizations were carried out in a reaction calorimeter (Mettler RC1, MP10, 1 L reactor; Mettler-Toledo, Columbia, MD) to follow the kinetics. The recipes are shown in Table I. The solid contents of the polymer particles formed in the dispersion polymerization were kept at 9.80 wt %, the same as the standard recipe in previous studies.¹⁴ In the case of precipitation polymerization, the same recipe excluding the stabilizer (PVP K-30) was used. The procedure for using the RC1 to monitor the reaction kinetics is reported elsewhere.¹⁴

Particle size characterization

Scanning electron microscopy (SEM, Jeol 6300F; Peabody, MA) was used to determine the particle size distribution of the particles. The latex was diluted to about 1 wt % with a methanol/water mixture (weight ratio = 70/30), and one drop of the diluted latex was placed on an aluminum stub and dried in a hood at room temperature. The accelerating voltage applied was 1 kV and no coating was applied.

Molecular weight analysis

The molecular weight distributions of the PMMA were measured by gel permeation chromatography (GPC,

Waters 2487 dual absorbance UV detector ($\lambda = 235$ nm) and/or Waters 410 differential refractometer detector; Milford, MA). THF was used as the mobile phase. The THF flow rate was 1.0 mL/min. Waters HR3, HR4, and HR6 Styragel columns were used. Samples were filtered through 0.45 μ m filters before injection. Polystyrene narrow molecular weight standards were used for calibration. The following Mark–Howink constants were used to obtain the molecular weights: $K = 14.1$, $\alpha = 0.70$ for PSt, $K = 7.5$, $\alpha = 0.72$ for PMMA,¹⁵ all in THF.

For analysis of the molecular weight distributions of the PVP and recovered stabilizer samples, aqueous GPC was used. The mobile phase comprised a 0.01M NaNO₂ solution in a mixture of acetonitrile (20% v/v) and water (0.7 mL/min). Two mixed packed columns (TSK-Gel GMPWXL; TosoHaas, Montgomeryville, PA) were used. All samples were filtered through 0.45 μ m filters before injection.

RESULTS AND DISCUSSION

An initiator concentration of 2.5 mM AIBN was employed to carry out MMA dispersion polymerizations using different PVP K-30 stabilizer concentrations. Figure 1 shows the polymerization kinetics for

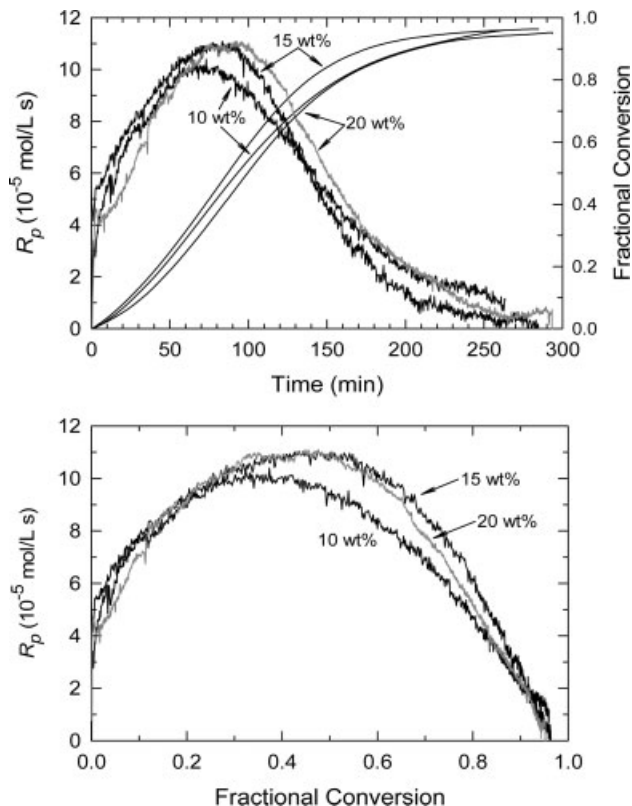


Figure 1 Kinetics of MMA dispersion polymerizations with different PVP K-30 concentrations. Top: reaction rate and fractional conversion vs. time; bottom: reaction rate vs. fractional conversion. [AIBN] = 2.5 mM, $T_r = 70^\circ\text{C}$, 400 rpm in the RC1 reactor.

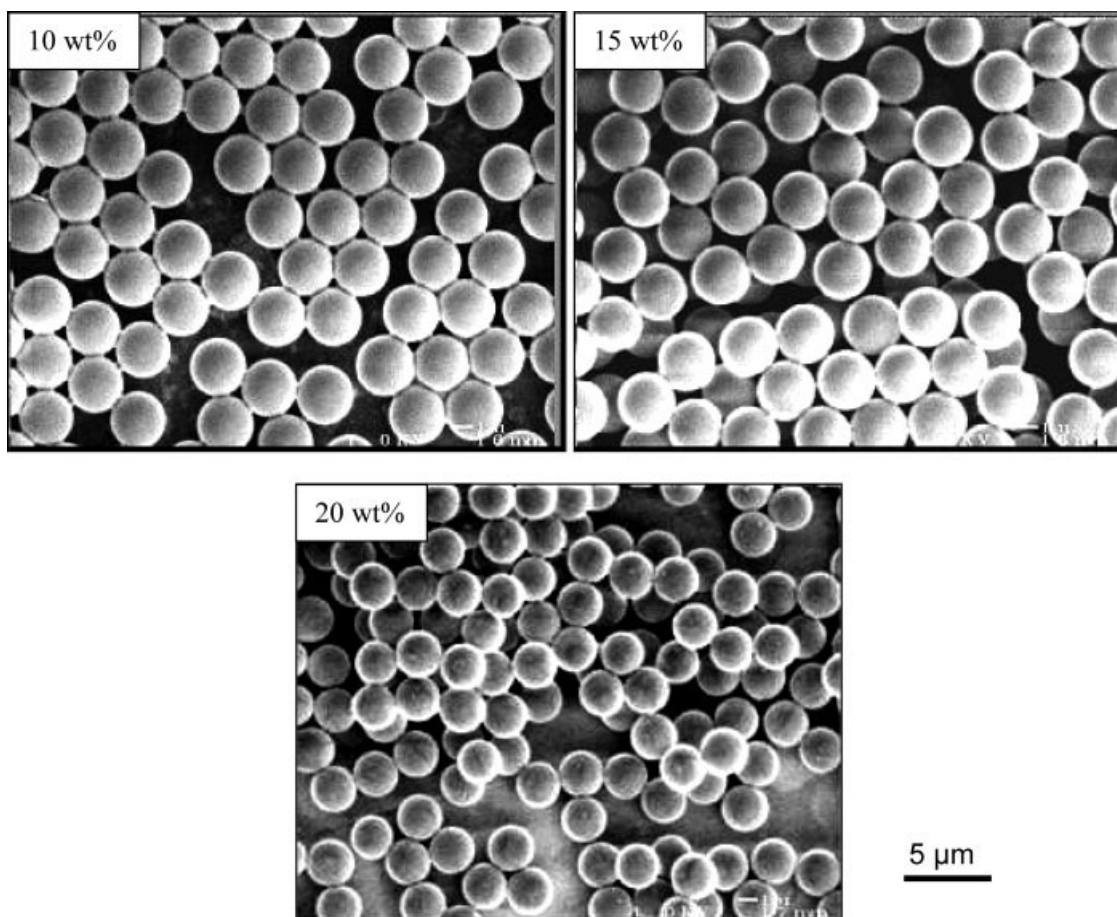


Figure 2 SEM images of PMMA particles prepared by dispersion polymerization with different PVP K-30 concentrations. [AIBN] = 2.5 mM, $T_r = 70^\circ\text{C}$, 400 rpm in the RC1 reactor.

reactions employing 10, 15, and 20 wt % PVP K-30 (based on monomer). All these reactions resulted in micron-size PMMA particles with narrow size distributions, as shown by the micrographs in Figure 2. The number-average particle diameter (D_n) and corresponding number of particles (N_p) are shown as a function of the stabilizer concentration in Figure 3. The reaction kinetics for these stabilizer concentrations are similar: a quick rise in rate occurs upon addition of the AIBN, followed by a long rise to a maximum and then a decrease as monomer is depleted in the system. No clear trend can be seen despite the significantly smaller particles (higher N_p) that were produced with 20 wt % PVP K-30. The fact that the reaction rate does not depend significantly on the number of particles is unlike most emulsion polymerizations where the reaction rate is proportional to N_p . This can be explained by the high number of radicals per polymer particle, which would be described as Smith-Ewart case 3 kinetics in emulsion polymerization. This differs from the more usual case 1 or case 2 kinetics where the average number of radicals per particle (\bar{n}) is $\frac{1}{2}$ or less. Dispersion polymerizations behave more like “pseudo-bulk” polymerizations where the reac-

tion rate is not significantly affected by a changing number of particles.

Kinetics of precipitation polymerization

When no stabilizer is present in the system, the reaction is a precipitation polymerization; the polymer formed is

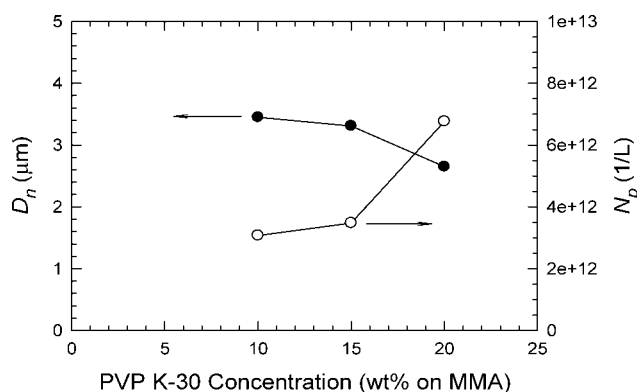


Figure 3 Particle size and particle number concentration as a function of PVP K-30 concentration in dispersion polymerizations of MMA.

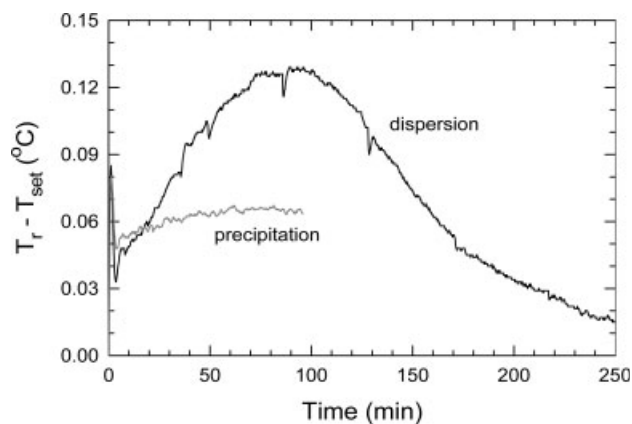


Figure 4 Relative temperature increase ($T_r - T_{set}$) in dispersion and precipitation polymerizations of MMA. [AIBN] = 2.5 mM; methanol/water = 70/30 (wt/wt); $T_r = 70^\circ\text{C}$; 400 rpm in the RC1 reactor.

not soluble in the medium and precipitates forming a macroscopic polymer phase. Obtaining an accurate reaction rate for the precipitation polymerization using the RC1 was not possible since the calibration required at the end of the reaction was not reliable because of the large amount of polymer precipitated on the temperature sensor. Therefore, instead of using the reaction rate, the temperature profiles obtained during the dispersion and precipitation polymerizations are compared, since the temperature profile is related to the rate of heat generation during the polymerizations. The results are presented in Figure 4 as ($T_r - T_{set}$) versus time. It can be seen that during the first 20 min, the reaction rate profile for the precipitation polymerization was about the same as the parallel dispersion polymerization. After that, the rates diverged with the precipitation polymerization becoming significantly slower than the dispersion polymerization.

The evolution of the molecular weight distribution in a MMA precipitation polymerization was monitored by carrying out parallel experiments in 20 mL

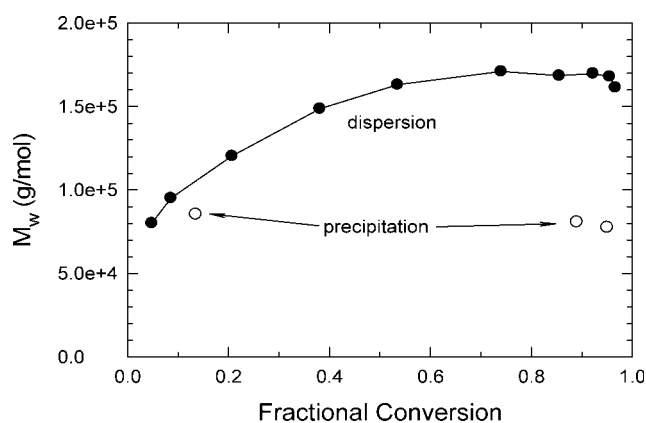


Figure 5 Evolution of weight-average molecular weight with conversion in precipitation and dispersion polymerizations.

vials, in a bottle polymerizer (45 rpm, end-over-end rotation) using a 5.0 mM initiator concentration. Since the agitation in a bottle polymerization differs from that in the RC1 reactor, a dispersion polymerization was also carried out in the same manner. Figure 5 shows the evolution of the weight-average molecular weight (M_w) with conversion. It can be seen that at low conversion (<15%), M_w of the polymer formed in the precipitation polymerization was similar to that formed in the dispersion polymerization. At the end of the reaction, however, it had not changed significantly and was much lower than in the dispersion polymerization, which increased throughout much of the reaction. To further compare these reactions, Figure 6 shows the molecular weight distributions of the polymers sampled at low and high conversions. The numbers on the left side of the graph represent the conversions of the samples taken in the precipitation polymerization, while the others are for the dispersion polymerization. As can be seen, the molecular weight distributions diverge at high conversion primarily because of the increased molecular weight in the dispersion polymerization. In precipitation polymerization, most of the polymer is formed by the continuous precipitation from the continuous phase, while in dispersion polymerization the polymer is largely formed in the polymer particles. This produces the differences in the molecular weight distributions. More interestingly, these also provide information regarding the molecular weight of unstable nuclei formed in dispersion polymerization since the polymer formed in the early stages of a dispersion polymerization should largely originate from the unstable nuclei. The high molecular weight side of the molecular weight distribution in the dispersion polymerization comes from the

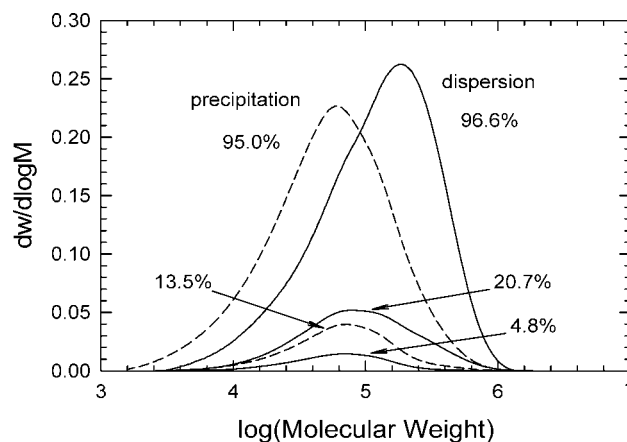


Figure 6 Comparison of molecular weight distributions of PMMA produced in precipitation and dispersion polymerizations at low and high conversions. The polymerizations were carried out under identical conditions except that the dispersion polymerization contains 20 wt % PVP K30 (based on monomer) in the recipe.

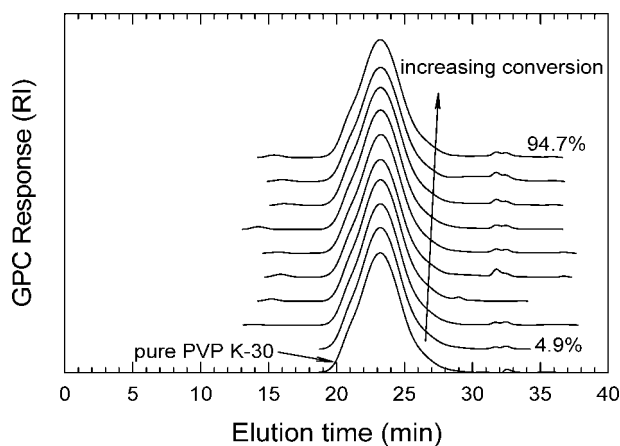


Figure 7 Evolution of molecular weight distribution of the stabilizer in the continuous phase during the dispersion polymerization of MMA. $[AIBN] = 5.0 \text{ mM}$, $[PVP \text{ K-30}] = 20 \text{ wt \%}$ based on MMA, methanol/water = 70/30 (wt/wt), $T_r = 70^\circ\text{C}$. Reaction was carried out in a bottle polymerizer.

polymerization in the polymer particles, which have a high internal viscosity (high weight fraction of polymer) resulting in a reduced termination rate (Trommsdorff gel effect). Polymerization inside the particles leads to the formation of an increasing molecular weight population with conversion and an increasing average molecular weight.

Comparing precipitation and dispersion polymerizations, it is clear that the kinetics in the early stages of the dispersion polymerization are similar to that of the precipitation polymerization. The nuclei in a dispersion polymerization are the consequence of polymer chains precipitated from the continuous phase, and they have lower molecular weights compared with polymers formed by polymerization inside the particles. It is clear that nuclei formation can contribute significantly to the kinetics and the molecular weight distribution of the final polymer particles. This was indicated previously in studies of the effect of initiator concentration in dispersion polymerization.¹⁴

Evolution of molecular weight distribution of the stabilizer during dispersion polymerization

The serum solids were recovered from samples taken throughout a dispersion polymerization of MMA and characterized by aqueous phase GPC. Figure 7 shows the evolution of the molecular weight distribution of the stabilizer where the bottom curve represents pure PVP K-30. No significant change in the molecular weight distribution was found. It was expected that if grafting of PMMA onto the PVP was significant, the high and low molecular weight portions of the PVP would contribute differently to the formation of the graft polymers and their adsorption onto the particle surfaces, and this would result in a change in the

observed molecular weight distributions. However, the results in Figure 7 show no measurable changes in the PVP molecular weight distributions. This may not be definitive, however, since even if graft polymers are present in the recovered stabilizer their amount should be relatively small. Moreover, the amount of PVP that is retained on the surface of the particles is typically less than 1% of the total PVP.

Characterization of recycled stabilizer

The use of recycled stabilizer has been reported in MMA dispersion polymerizations in methanol where it was found that recycled stabilizer (reclaimed by removing only the polymer particles from the final dispersion) does not differ significantly from pure stabilizer in that they both produce almost the same particle size and distribution.¹⁰ In contrast, when recycled stabilizer was used in *n*-BuA dispersion polymerizations in methanol/water, it was found that recycled stabilizer produced much smaller and polydisperse PBA particles compared with the narrow particle size distribution produced using the original stabilizer. In this research, further effort was made to see if in this system, recycled PVP affected the resulting particle size and distribution as compared with pure PVP.

The serum of a latex prepared by batch dispersion polymerization of MMA was first separated by sedimentation of the particles. This was dried overnight in a 75°C oven to obtain the recycled stabilizer (recycled PVP) and any other nonvolatile materials (e.g., initiator residue, oligomers). It is of interest to know how much medium-soluble PMMA is present at any time during a dispersion polymerization since it can be a precursor to the formation of nuclei during the reaction, and can possibly impact the nucleation when using recycled stabilizer. The 70/30 methanol/water mixture is a poor solvent for PMMA, as shown by the extremely low concentrations of medium-soluble PMMA compared with the stabilizer and even the residual initiator. The amount of medium-soluble PMMA was measured by repeated washing of the recovered medium-soluble solids with water followed by centrifugation. It should be noted that only water-insoluble materials remain after this procedure. Any grafted PVP would also be washed out (any water-insoluble grafted PVP would be adsorbed on the particles and be removed with them). The content of medium-soluble PMMA was determined to be 0.004 wt % and 0.016 wt % at 7% and 72% conversion, respectively (based on the continuous phase), which is well below 1% of the total solids in the continuous phase (around 2.0 wt % based on medium).

In styrene dispersion polymerizations in ethanol, it was found that the power dependence of particle size on initiator concentration was smaller at higher stabilizer concentrations (i.e., power dependencies were

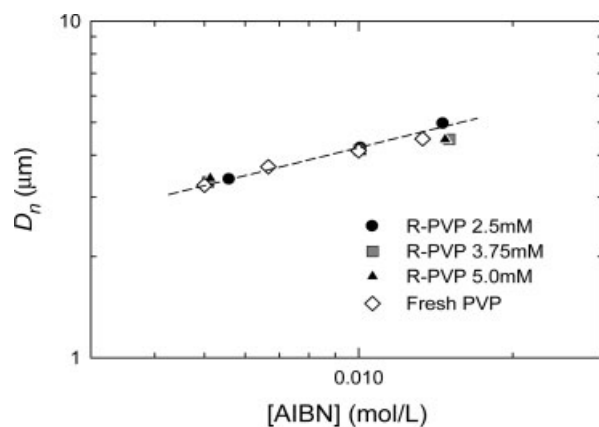


Figure 8 Dependence of PMMA particle size on initiator concentration employing different recycled stabilizers obtained from MMA dispersion polymerizations at different initiator concentrations. "R-PVP 2.5 mM" indicates that the recycled stabilizer is recovered from a MMA dispersion polymerization using 2.5 mM AIBN.

0.4 and 0.2 at PVP K-30 concentrations of 1.9 and 2.5 wt % (based on total), respectively).¹⁶ If recycled PVP stabilizer differs from pure PVP, then the dependence of the particle size on the initiator concentration should differ. Recycled stabilizer was collected from batch MMA dispersion polymerizations employing different initiator concentrations. It was expected that the degree of modification of the PVP structure (grafting) should vary with initiator concentration. The recycled stabilizers were used in subsequent batch MMA dispersion polymerizations with varying initiator concentration.

Besides the possible formation of medium-soluble graft polymer, there are other residues that might affect the results using recycled stabilizer. One is residual initiator left from the previous polymerization. As all bottle polymerizations were run at 70°C for 24 h, one can estimate from the decomposition rate constant of AIBN that only about 3.7% of the initiator should remain in the system. This should have been further reduced during the drying of the serum at 75°C overnight. Therefore, the effect of residual initiator is not considered to be significant. Another component present in the recycled stabilizer is the medium-soluble PMMA. Since these polymers are recovered at the end of a dispersion polymerization (low residual MMA in the medium), they are easily dissolved in the original dispersion polymerization system since MMA is a good solvent for PMMA. The presence of these soluble polymers could possibly affect the nucleation process.

The final particle sizes resulting from the MMA dispersion polymerizations using different recycled stabilizers and initiator concentrations are shown in Figure 8. Results using fresh PVP K-30 are also shown

for comparison. As can be seen, there is no significant effect of the PVP used; the power dependence of particle size on initiator concentration remained unchanged. Therefore, no evidence of any effect of either graft-modified PVP K-30 or medium soluble PMMA was found, indicating that their amounts (if any) are too small to impact the nucleation.

CONCLUSIONS

The kinetics of dispersion polymerizations of MMA were found to be independent of the stabilizer (PVP) concentration, and therefore, independent of the number of particles. This is attributed to the high radical concentration in the micron-size particles (pseudo-bulk kinetics). Comparison between precipitation and dispersion polymerizations revealed that nuclei formation occurs similarly in both polymerizations, contributing significantly to the early polymerization kinetics and the development of the molecular weight distributions. No change was found in the molecular weight distribution of the stabilizer during a dispersion polymerization of MMA, and no differences were found between fresh stabilizer and recycled stabilizer, indicating that no significant modification of the stabilizer present in the continuous phase had occurred.

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