CROATICA CHEMICA ACTA
CCACAA, ISSN 0011-1643, e-ISSN 1334-417X
Croat. Chem. Acta **85** (3) (2012) 269–276.
http://dx.doi.org/10.5562/cca1919

Original Scientific Article

Effect of Polyvinylpyrrolidone on the Formation AgBr Grains in Gelatine Media

Marijana Jukić,[a,*] Igor Sviben,[a] Zoran Zorić,[a] and Stjepan Milardović[b]

[a]*Department of Chemistry and Biochemistry, Faculty of Food Technology and Biotechnology, University of Zagreb, Pierottijeva 6, HR-10000 Zagreb, Croatia*
[b]*Department of Chemistry, Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, HR-10000 Zagreb, Croatia*

RECEIVED MAY 16, 2011; REVISED FEBRUARY 2, 2012; ACCEPTED MAY 23, 2012

Abstract. In this study, AgBr nanoparticles were prepared by controlled single jet method in the presence of gelatine and polyvinylpyrrolidone (PVP). In order to obtain better insight about the effect of PVP and its compatibility with gelatine on the formation of AgBr nanoparticles, effects of both components (gelatine, PVP) in the process of physical ripening on grain and grain size distribution were investigated. Several processing variables such as PVP/Ag weight ratio and addition time were investigated. PVP of three different molecular weights (PVP/ K 15, $M_w = 1.0 \cdot 10^4$ g mol^{-1}, PVP/ K 25, $M_w = 2.4 \cdot 10^4$ g mol^{-1}, PVP/ K 30, $M_w = 4.0 \cdot 10^4$ g mol^{-1}) were tested for their ability to act as capping agent.
With increasing PVP molecular mass its inhibiting effect on physical ripening of grain increases and grains with narrow size distribution are obtained (95 % grains size from 0.22 to 0.44 μm). (doi: 10.5562/cca1919)

Keywords: silver bromide, polyvinylpyrrolidone (PVP), physical ripening; nanoparticles, particle size distribution

INTRODUCTION

In the last decade, study of synthesis and characterization of metallic nanostructure materials have received great attention because of their potential applications as modern materials for electronics, optic, phonic, photography, catalysis, pigments and cosmetics.[1–4] Due to their physical and chemical properties which are closely dependent on particle shape, average size and size distribution,[5,6] these materials exhibit new attractive size-related electrical, mechanical, transport, magnetic and optical properties that differ from their bulk counterparts. So special nanostructure with well-defined size and shape was required and therefore, development of synthesis for control over particle morphology and size with high dispersion and narrow distribution is an important goal, which is often difficult to achieve. Generally this is achieved through control of nucleation and growth by varying the synthesis parameters such as reducing agent, stabilizer and pH of the reaction system.[7,8] Type and concentration of precursors, nature and amount of surfactants or protective reagents is also very important for nanoparticle size and shape control.[9]

Previous studies have shown that surfactants or polymers can influence crystallization process in one or several crystallization steps (nucleation, crystal growth, aggregation) and, as a consequence, can control crystal phase formation. That is the reason why surfactants have been used for preparation of specific morphologies, sizes, or new crystal structures of inorganic[10–12] or organic materials.[13,14]

In recent years, polyvinylpyrrolidone (PVP) non-toxic, high molecular weight, water-soluble polymer has been the focus of many studies as a polymeric protective agent for nanoparticles growth.[15,16] PVP acts as stabilizer or capping agent, preventing aggregation of metal particles and retaining uniform colloidal dispersion. Additionally, PVP is used as a shape-controlling agent or ‘‘crystal-habit modifier’’, promoting attachment of metal atoms onto specific crystal faces and leading to anisotropic growth of nuclei into nanostructure. PVP possesses hydrophilic polar groups, that will interact preferentially on the crystal by chemical adsorption, which obviously slows (or prevents) growth and promotes a highly anisotropic crystal growth.[17]

It is proposed that polar groups, such as the C=O groups of PVP chain, can interact with metal ions and

---

[*] Author to whom correspondence should be addressed. (E-mail: mjukic@pbf.hr)

form coordinating complex.[18] It is suggested that electron clouds are strongly partial to oxygen in polar carbonyl group (C=O) and nitrogen atom transfers its electrons to pyrrolidone ring of PVP. Correspondingly, chemical reaction can take place between PVP and metal ions, in which metal ions receive lone pair electrons from the ligands −N and C=O group in pyrrolidone ring and form atomic metal that further grows into particles. From the general field of colloid chemistry, it is known that fast reduction/nucleation relative to growth results in small particle with a narrow size distribution.[19]

PVP has been reported to be effective for dispersion polymerization of pyrrole[20] and aniline[21] in aqueous acidic conditions. Sterically stabilized polyaniline dispersions were also obtained with oxidative polymerization of aniline in the presence of PVP.[22] Murugesan *et al.* has recently reported that PVP plays a multi-faceted role involving the functions of co-doping, polymer support structure enhancement, steric and thermal stabilization and solubilisation towards polyaniline emeraldine salt (PANI).[23]

Cao and co-workers have prepared monodisperse poly (methylmethacrylate) particles in size range 1−5 μm by unseeded dispersion polymerization in methanol-water media using PVP as a steric dispersant.[24]

Wei *et al.* reported that sodium dodecyl sulphate and/ or PVP complex can strongly influence the crystal morphology, texture and polymorphic structure of calcium carbonate crystal growth.[25]

PVP as inert polyamide polymer interacts with many inorganic materials such as metallic salts[26] and metal oxides,[27] affecting crystal habits and morphology. For examples, nanosize dispersions of Pt-group metals with a narrow particle distribution have been synthesized by chemical reduction of selected metal compounds with ethylene glycol in the presence of PVP.[28] Feng and co-workers reported synthesis of Fe_3O_4 single crystal nanorods controlled by PVP.[29]

Among these various nanoparticles, synthesis of nanosized silver colloids has significantly increased due to their wide applications ranging from antimicrobial activity[30] and microelectronics[31] to bio-nanotechnology.[32] In order to keep the silver colloid in nanometre range and uniform shape with very narrow particle size distribution, PVP was used almost exclusively as the protective agent during synthesis that my be carried out in either by polyol process,[33,34] γ-irradiation[35] or reducing agent.[36,37]

Silver halide which have numerous applications and the most notable being major photographic material, may be one of the rare materials with which advantages of monodispersed particles are fully utilized in industry.[38] Silver halide microcrystals have been used as a high quality photosensitive, imaging material for photography.[39,40] Complementary to microcrystal of conventional photographic emulsions used in a number of photon processing materials with size varying in the range from 0.5 to 10 μm, AgX (X = Cl, Br, I) crystals of 10–100 μm in size are utilized only for specific applications such as holography and photographic engineering. Recently, monocrystaline silver halides attract an increasing interest of researchers from the fundamental point of view because of the contribution to energy-level structure and surface states. When their size decreases below 100 nm they exhibit drastic changes of their photo physical properties. This type of behaviours is common for nanocrystallites of several different semiconductors.[41] Silver halides are also very good solid electrolytes with ionic conductivity similar to molten salts.[42] It was also reported to act as a catalyst[43], ion semiconductor[44] and material for silver nanoparticle synthesis.[45]

More recently, synthesis of silver halide nanoparticles has received great attention for antimicrobial materials and separation membranes.[46–49] For example, silver bromide (AgBr)/poly(4-vinyl pyridine) (P4VP) nanocomposites formed good coatings on surfaces and were found to kill both airborne and waterborne bacteria; the primary advantage of this nanocomposite over other silver ion containing antibacterial materials is the ability to tune the release of biocidal Ag^+ ions.[49]

Silver halide salts are sparingly soluble in water and consequently, crystal population is very dense when is prepared in aqueous solution and gelatine must be used to prevent crystal aggregation. In these conditions silver halide crystals reach a small size because gelatine layer covers their surface.[50]

Considerable attention was given to development of methods for the preparation of silver halide crystals in gelatines media with narrow crystal size distribution, because sensitivity and resolving power of silver halide photographic materials depends strongly on size and structure of suspension crystals. Resolving and covering power increases with decreasing of grain size and is inversely proportional to mean grain diameter.[51]

Grain size depends on many factors such as the duration of precipitation, temperature at which precipitation occurs and presence of silver halide solvents during precipitation or during physical ripening. In general, grain size will increase with increase of precipitation time and temperature, and whenever solvents are present.[52]

Growth of crystals from solutions is determined by rates of certain surface reactions and by diffusion processes in solution surrounding the crystals.[53] This is generally considered to involve two processes occurring sequentially: transport of solute material from bulk supersaturated solution to the crystal surface by diffusion and incorporation of solute material into crystal lattice by surface integration. Interparticle effect on crystal growth is related to the diffusion step.[54]

The influence of PVP on the rate of mass-transfer processes in course of Ostwald ripening of AgBr and AgI is determined like the interface process of ionic crystals. Abbasi[55] quantitatively measured these processes by radiochemical technique. His finding was that very low concentration of PVP is very effective when adsorbs on the surface of crystals and reduces the rate of mass-transfer processes.

Significant differences in the case of silver halide crystal growth have been observed during physical ripening depending on the nature of protective colloid present in these systems. The absence of any appreciable growth implies that either Ostwald ripening or coalescence ripening occurs with a particular protective colloid.

The use of PVP as the suspending agent for silver halide grains in photographic emulsions is, like that of polyvinyl alcohol, restricted by its inhibiting effect on physical ripening. Perry[56] concluded that formation of a complex between silver ions of silver halide surface and nitrogen atoms contained in PVP might play an important part in adsorption processes involving this as protective colloid. Improvements in silver halide grains and their surface characteristics of the grains have been associated with the use of polyvinylpyrrolidone. Pueskuelev *et al.*[57] have studied the influence of this polymer on dispersibility of emulsions with high resolving power and concluded that PVP, used with gelatine in 3:4 ratio favours the formation of ultra fine emulsions with a resolving power of 3200 lines/mm and with satisfactory sensitivity and edge sharpness.

The influence of polyvinylpyrrolidone on the properties of silver halide grains is a function of its compatibility with gelatine. Zarnoretchki *et al.*[58] have shown that this compatibility is a function of molecular mass of polyvinylpyrrolidone and it decreases with increase of molecular mass. Perry[56] has also studied the effect of gelatine and PVP compatibility and concludes that these results indicate that gelatine ensures aggregative stability of emulsions, while PVP, which is absorbed on crystal growth activity centres, inhibits Ostwald growth by forming silver gelatines. When PVP is absorbed on all crystal growth activity centres the effect of any further PVP concentration increase is negligible.

Silvertet *et al.*[59] reported that the size and size distribution of silver particles are greatly governed by PVP because the nucleation and growth steps are mainly depend on the reaction rate during the particles formation period. They concluded that amount of both the precursor and the PVP controls the size and size distribution of the silver particles.

Yano *et al.*[60] have used turbidity measurements to determine the effect of various polymers such as polyacrylic acid, polyvinylpyrrolidone, polyvinyl alcohol, polyacrylamide and poly (1-vinyl-2-methylimidazole) on crystal growth in silver chloride solutions. They concluded that, if a polymer, which is strongly adsorbed by silver chloride, is mixed with another polymer which is weakly adsorbed; the latter has little or no effect on physical ripening.

Herz[61] investigated the chemical factors for the control of silver halide recrystallization and growth in aqueous AgCl, AgBr and AgI dispersions. Author concluded that variations of excess lattice ion concentrations and additives such as polymers exert parallel effect on equilibrium solubility and either increase or diminish growth rates.

In the present work, as a continuation of our previous research, silver bromide nanoparticles with small sizes and narrow distributions were synthesized in the presence of polyvinylpyrrolidone (PVP). Factors affecting particle size and distribution were examined. An attempt has been made to study effects of reaction parameters, including, PVP/Ag weight ratio, PVP molecular weight and PVP addition time in the process of physical ripening on the formation of silver bromide nanoparticles in the presence of gelatine. Gelatine played a decisive role in preventing AgBr particle aggregation. On the basis of experimental results, the effects of reaction parameters were discussed. Attempts have been made to obtain uniform silver bromide nanoparticles with a controlled mean size and a narrow distribution.

EXPERIMENTAL SECTION

All experiments were performed with commercially available reagents of analytical purity which were used without further purification.

Silver nitrate ($AgNO_3$) was purchased from Johnson Matthey Silver & Coating Technologies, inert gelatine type 66023 was purchased from *Gelita AG* (Eberbach, Germany), polyvinylpyrrolidone with average molecular weights of (PVP/ K 15, $M_w = 1.0 \cdot 10^4$ g mol^{-1}, PVP/ K 25, $M_w = 2.4 \cdot 10^4$ g mol^{-1}, PVP/ K 30, $M_w = 4.0 \cdot 10^4$ g mol^{-1}), potassium bromide (KBr) and 1-phenyl-1*H*-tetrazole-5-thiol were purchased from Aldrich Chemical Co.

AgBr grains are usually prepared through nucleation, ripening and growth processes. The nucleation process is carried out by the controlled single jet method. Crystals were namely produced by controlled addition of $AgNO_3$ aqueous solutions, which was added to an aqueous gelatine and alkali halide solution while stirring.

Standard conditions for preparing all solutions were: $c(AgNO_3) = 6.6 \cdot 10^{-1}$ mol dm^{-3}, $c(KBr) = 2.5 \cdot 10^{-1}$ mol dm^{-3} and gelatine mass fraction $w = 1.8$ %. A centrally mounted radial-flow turbine provided agitation. Nucleation was performed at 50 °C. The temperature was then raised to 70 °C. During the ageing, for each run pH was adjusted to 5.8 and time to 45 min. The mixture turned yellow as soon as a few drops of silver nitrate was added, implying the formation of AgBr nanoparticles.

Cooling to 25 °C and addition of methanol solution of 1-Phenyl-1*H*-tetrazole-5-thiol stopped the ageing of emulsion samples. Sample was desalted by flocculation and gelatine was separated from crystals by trypsine.

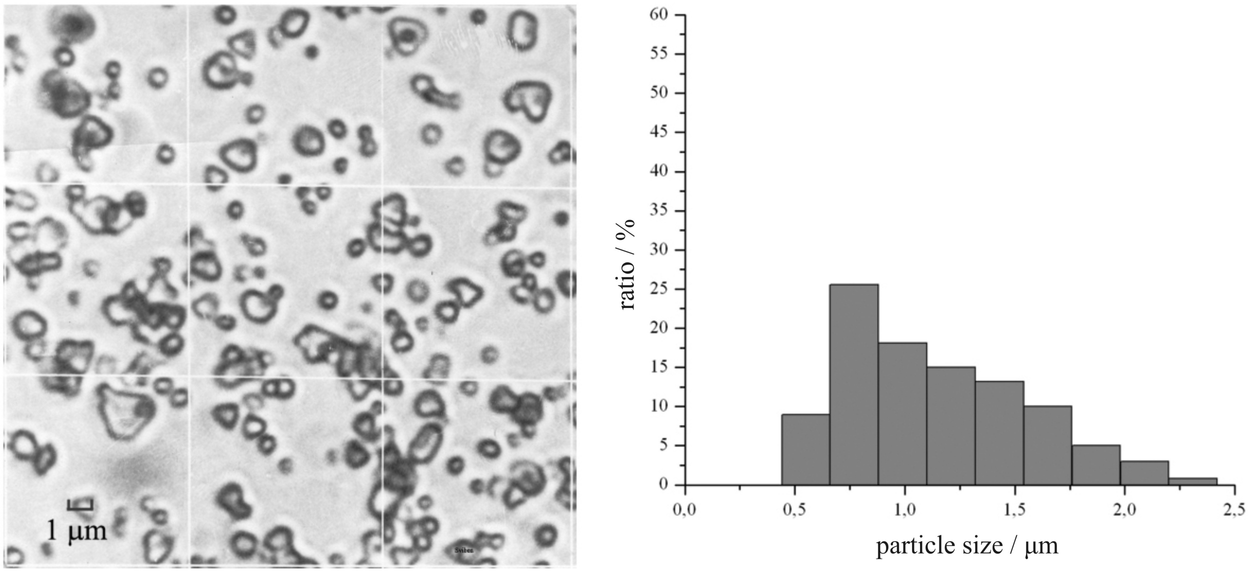

Figure 1. Photomicrograph and corresponding particle size histogram for AgBr control suspension prepared without PVP (run 0, in Table 1).

Sample for observation was prepared by placing a 5 cm^3 of the colloidal dispersion in gelatine solutions (50 cm^3, $w = 0.5$ %) and than coated on a glass plate, followed by evaporating the solvent at an ambient temperature.

Samples were observed by Carl Zeiss Axiostar Plus optical microscopy under the immersion and total magnification of 1000× was achieved. From the microscope photographs of silver-halide grains in prepared emulsions, photographic prints 5000× magnified were made.

From enlarged photomicrographs the size of each crystal was determined by measuring their diameters with a graduated magnifying glass. The counts were then plotted as frequency histograms. Size distribution histograms were obtained on the basis of measurement of about 300 particles. Aggregated particles were not taken into account to calculate size distributions.

The effects of the PVP/Ag weight ratio, PVP addition time and PVP molecular weight in the process of silver bromide physical ripening on the formation of grain size, grain size distribution and grain shape were investigated.

In a series of digestions the effects of the PVP/Ag weight ratio (PVP/ K 25, $M_w = 2.4 \cdot 10^4$ g mol^{-1}) were examined in the ranges from $0.67 \cdot 10^{-3}$ to $3.35 \cdot 10^{-3}$, under otherwise initial conditions.

The effect of PVP addition time in the process of physical ripening of suspension on grain size and grain size distribution was investigated in the concentration of optimal PVP/Ag weight ratio. Aqueous PVP solution was added in 5 min interval since 5 to 30 min after the precipitation start.

The effect of three different molecular weights of PVP (PVP/ K 15, $M_w = 1.0 \cdot 10^4$ g mol^{-1}, PVP/ K 25, $M_w = 2.4 \cdot 10^4$ g mol^{-1}, PVP/ K 30, $M_w = 4.0 \cdot 10^4$ g mol^{-1}) were examined in optimal weight ratio and addition time conditions.

Aqueous PVP solution ($w = 0.1$ %) was prepared by dissolving PVP powder in water/ethanol (2/8) and stirred for 1 h at room temperature.

To avoid photolytic reaction of AgBr, precipitation, ageing of the crystals, preparation of the specimen and mounting in the microscope were done under a red safe light.

RESULTS AND DISCUSSION

In formation of silver halide salts which are sparingly soluble in water and consequently crystal population is very dense, gelatine must be used to prevent crystal aggregation. PVP was used almost exclusively as the protective agent which was adsorbed on the surfaces of particles and as a consequence controlled the formation of crystal. Generally, this was verified in many other reports.

In the present study, a primary purpose of introducing PVP was to protect AgBr nanoparticles from growing. In order to obtain a better insight about the effect of PVP and its compatibility with gelatine on the formation of AgBr nanoparticles, a series of subsequent experimental suspensions were prepared with varying PVP/Ag weight ratios, PVP addition times and molecular weights. Effects of both components (gelatine, PVP) in the process of silver bromide physical ripening on grain formation and grain size distribution were investigated.

Sizes of AgBr particles obtained from photomicrograph of control initial suspension were observed to be in the range of 0.44–2.42 μm as are shown in Figure 1

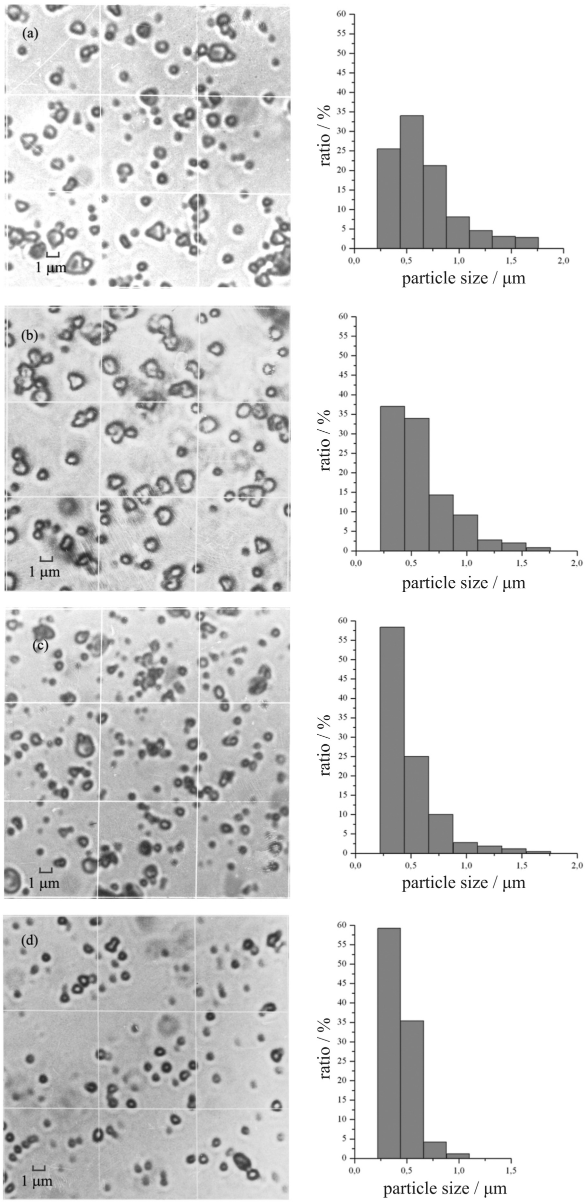

Figure 2. Photomicrographs and corresponding particle size distributions histogram for AgBr particles prepared at 45 min reaction time with PVP/Ag (PVP/ K 25, $M_w = 2.4 \cdot 10^4$ g mol^{-1}) weight ratios: (a) $0.67 \cdot 10^{-3}$; (b) $1.01 \cdot 10^{-3}$; (c) $1.34 \cdot 10^{-3}$; (d) $2.40 \cdot 10^{-3}$ added 10 min after precipitation.

which shows grain and grain size distribution histogram for initial suspensions. Control experiments performed without PVP in the presence of gelatine, and 45 minute physical ripening time induced formation of big and non-uniform silver bromide particles. During this conventional ripening process, the nuclei grow and become large enough to be identified in terms of their morphology. Silver halide crystals can grow with a large variety of shape. From Figure 1, one can observe that population of crystals shows different morphologies, and that the mixture of spherical, triangular and octahedral shaped AgBr crystals were obtained.

The effect of PVP/Ag (PVP/ K 25, $M_w = 2.4 \cdot 10^4$ g mol^{-1}) weight ratio variation from $0.67 \cdot 10^{-3}$ to $3.35 \cdot 10^{-3}$, under otherwise standard conditions are shown in Figure 2. PVP was added 10 minutes after the beginning of precipitation.

From silver bromide particle size distribution histograms obtained at PVP/Ag weight ratios from $0.67 \cdot 10^{-3}$ to $1.01 \cdot 10^{-3}$ (Figure 2(a,b)), disappearance of large grain size from 1.76 µm to 2.42 µm was observed. The size of AgBr particles obtained was in range 0.22–1.76 µm. By increasing the weight ratio from $1.34 \cdot 10^{-3}$ (Figure 2(c)) to $1.60 \cdot 10^{-3}$ small grain size (0.22 µm to 0.44 µm) number has grown making it approximately 60 % of all grains. The mean size of AgBr particle is smaller than the corresponding ones shown in Figure 1 and the distribution is more unimodal. Further increase of PVP/Ag weight ratio from $2.4 \cdot 10^{-3}$ Figure 2(d) to $3.35 \cdot 10^{-3}$ had no significant effect on grain size and grain size distribution. It should be noted that the yield of spherical habit grains increases with increasing PVP concentrations.

These results confirm Perrys[56] hypothesis that gelatine ensures the aggregative stability of suspensions, while PVP inhibits growth in the way that it adsorbs on crystal growth activity centres and limits their increase. Perry concluded that complex formation between silver ions from silver halide crystal surfaces and nitrogen atoms contained in high molecular mass synthetic polymer (PVP) may play an important role in adsorption processes involving it as a protective colloid. When all of crystal growth activity centres are saturated the effect of PVP/Ag weight ratio increase becomes negligible.

The results presented in Figure 2 indicate that PVP/ K 25 in suspensions with an excess of halide ions determinates formation of the small grain at very low PVP/gelatine weight ratio ($2.16 \cdot 10^{-3}$ to $4.32 \cdot 10^{-3}$). Pueskuelev *et al.*[57] reported influence of this polymer on dispersitivity of suspension with excess of silver ions if PVP was used with gelatine in 3:4 ratio. The difference between findings of Pueskuelev and results presented in this work is probably due to the fact that Pueskuelev investigated synthesis of ultra fine suspensions with an excess of silver ions and grain size under 0.05 µm, while this work investigated influence of PVP on suspension with excess of halide ions.

The results obtained with the addition of various controlled amounts of PVP/ K 25 suggest that very low weight ratio of PVP/ Ag ($1.34 \cdot 10^{-3}$) is effective for inhibiting physical ripening and this is in agreement with the work of Abbasi.[55] His finding was that very low PVP concentration is very effective when it adsorbs on crystal surfaces and reduces the rate of mass-transfer processes in suspensions.

Table 1. The effect of PVP addition time (run 1 to 6) and molecular weight (run 1, 7, 8) on AgBr grain size in physical ripening process

Run	m (PVP) / m (Ag)	PVP addition time / min	Grain size diameter / μm D_{min}	D_{max}	Grain size (0.22–0.44 μm) number ratio / %
		$M_w \approx 24000$ g mol^{-1}			
0	–	–	0.44	2.42	0.0
1	$1.34 \cdot 10^{-3}$	5	0.22	1.10	72.8
2	$1.34 \cdot 10^{-3}$	10	0.22	1.76	58.4
3	$1.34 \cdot 10^{-3}$	15	0.22	1.76	19.9
4	$1.34 \cdot 10^{-3}$	20	0.22	1.54	15.5
5	$1.34 \cdot 10^{-3}$	25	0.22	1.98	9.0
6	$1.34 \cdot 10^{-3}$	30	0.44	2.20	0.0
		$M_w \approx 10\,000$ g mol^{-1}			
7	$1.34 \cdot 10^{-3}$	5	0.22	1.32	15.2
		$M_w \approx 40\,000$ g mol^{-1}			
8	$1.34 \cdot 10^{-3}$	5	0.22	0.66	94.6

The effect of changing PVP addition time under optimal PVP/Ag weight ratio ($1.34 \cdot 10^{-3}$) on the process of physical ripening and the grain size and grain size distribution are shown in Table 1 (run 1 to 6). Aqueous PVP solution was added in 5 min interval since 5 to 30 min after the beginning of precipitation. Data in Table 1 confirms that fine crystals formed in region of the jet disappear by physical ripening while the number of large crystals increase (control suspension run 0).

The changes in average AgBr grain size which are formed in the presence of the PVP during the Ostwald-ripening ranged from 5 to 30 min after the precipitation start are indicated in Table 1 (run 1–6). When PVP was added 5 min after the precipitation (run 1) 72.8 % of the resulting AgBr grain size was 0.22 μm to 0.44 μm. The absence of large grains is noticeable which can be explained by adsorption of PVP on the surface of grains. Adsorption of PVP prevents further crystal growth and unavoidability of coalescence into large grains. Later addition of PVP reduces its impact on grains size and distribution as shown in Table 1 (runs 2–6).

The results of experiments carried out with three different PVP molecular weights (PVP/ K 15, $M_w = 1.0 \cdot 10^4$ g mol^{-1}; PVP/ K 25, $M_w = 2.4 \cdot 10^4$ g mol^{-1}; PVP/ K 30, $M_w = 4.0 \cdot 10^4$ g mol^{-1}), which were examined in predetermined optimal PVP/Ag weight ratio ($1.34 \cdot 10^{-3}$) and PVP addition time (5 minutes) after precipitation in process of physical ripening AgBr particles are shown in Figures 3(a–c) respectively.

The short-chain PVP polymer PVP/ K 15 gave particles in range 0.22–1.32 μm having 15.2 % particles from 0.22 μm to 0.44 μm (Figure 3(a)). The longer-chain PVP polymer PVP/ K 25 gave smaller nanoparticles in range 0.22–1.10 μm having 72.8 % particles from 0.22 μm to 0.44 μm (Figure 3(b)). With increasing

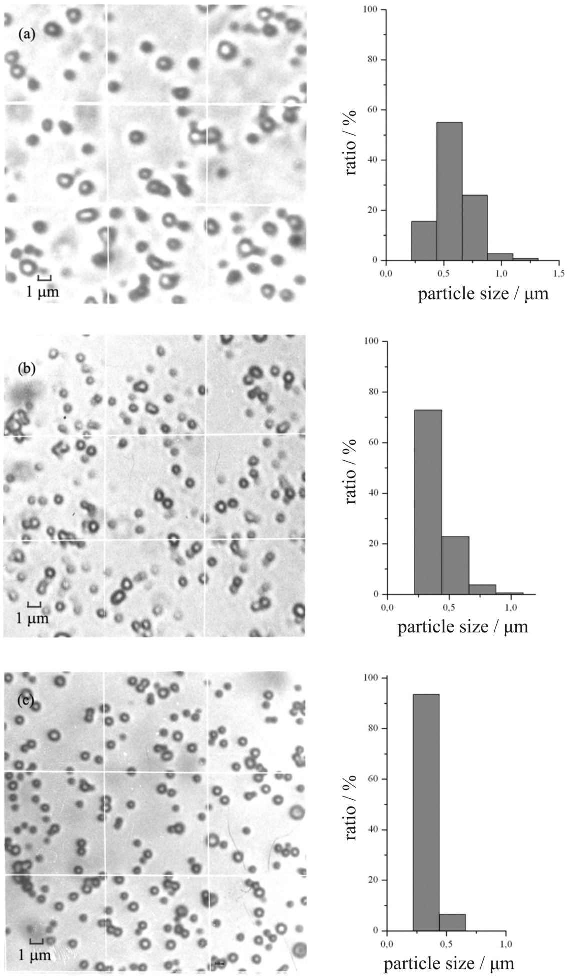

Figure 3. Photomicrographs with particle size distribution histograms as a function of various PVP molecular weights: (**a**) PVP/ K 15, $M_w = 1.0 \cdot 10^4$ g mol^{-1}; (**b**) PVP/ K 25, $M_w = 2.4 \cdot 10^4$ g mol^{-1}; (**c**) PVP/ K 30, $M_w = 4.0 \cdot 10^4$ g mol^{-1}. PVP/Ag weight ratio $1.34 \cdot 10^{-3}$ added 5 min after precipitation.

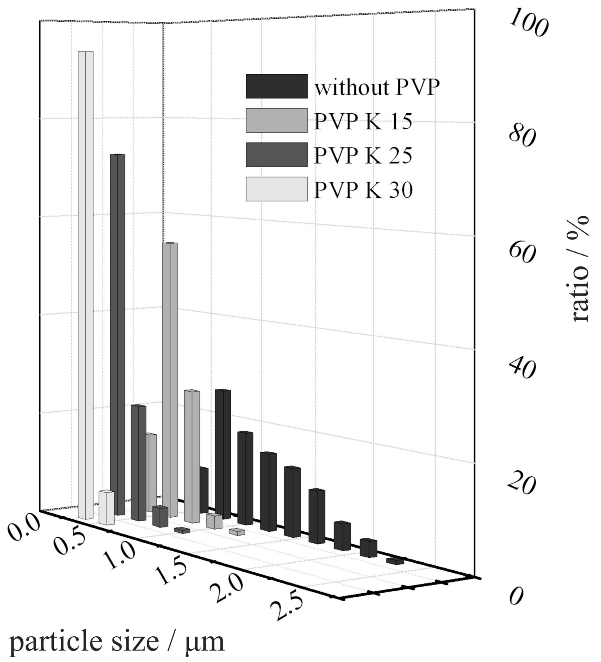

Figure 4. Comparison of particle size distribution histograms of AgBr control suspension from Figure 1 with particle size distribution histograms prepared as a function of various PVP molecular weights shown in Figure 3.

molecular weight of polymer (PVP/ K 30) at constant weight ratio (PVP/Ag) silver bromide particles with uni-modal grain distribution (about 95 % grains from 0.22 to 0.44 μm) were obtained as are shown in Figure 3(c).

It is evident from the photomicrographs (Figure 3(a–c)), that population of crystals shows almost same spherical shapes, and the addition of PVP with three different molecular weights studied in the present investigation have no influence on crystal habit, but the average size of the AgBr nanoparticles was reduced with the increase of PVP molecular weight which is shown in Figure 4.

A similar result was also observed by Kan[17] and Zhang[19] using PVP as stabiliser or capping agent. The absence of any appreciable grain growth shows that neither Ostwald ripening nor coalescence occurs under the above mentioned optimal conditions which imply that PVP acts as a capping agent. Different PVP molecular weights have significant effect on particle size, and are one of decisive factors in determination particle size and their distribution.

CONCLUSION

In this study, AgBr nanoparticles were prepared by controlled single jet method in the presence of gelatine and polyvinyl pyrrolidone (PVP) as a protective agent.

In AgBr suspensions with an excess of halide ions, very low PVP/gelatine weight ratio ($2.16 \cdot 10^{-3}$) was found to control and have significant effect on grain size, grain size distribution and grains morphology. These results confirm Perrys[56] hypothesis that gelatine ensures aggregative stability of suspensions, while PVP inhibits growth in the way that it adsorbs on crystal growth activity centres and thus limits their increase.

By increasing PVP/Ag weight ratio to $1.34 \cdot 10^{-3}$ and $1.60 \cdot 10^{-3}$, mean size of AgBr particles decreases and their distribution is more uni-modal, while further increase of weight ratio had no significant effect on the grains and becomes negligible. Shapes of AgBr crystals were found to be strongly depend on the concentrations of PVP.

With increasing PVP molecular weight its inhibiting effect on physical ripening increase and grains with narrow size distribution are obtained (95 % grains size from 0.22 to 0.44 μm). The absence of any appreciable grain growth shows that neither Ostwald ripening nor coalescence occurs under the above mentioned optimal conditions which imply that PVP acts as a protective colloid. Different molecular weights of PVP have significant effect on particle size and are one of decisive factors in determination particle size and their distribution but not their morphology.

Acknowledgements. Support for this study by the Ministry of Science and Technology of Croatia (project No. 058-2261-2253) is gratefully acknowledged.

REFERENCES

1. D. Chen and L. Gao, *J. Crystal Growth* **264** (2004) 216–222.
2. S. E. J. Bell and N. M. S. Sirimuthu, *J. Am. Chem. Soc.* **128** (2006) 15580–15581.
3. H. Wei, Q. Shen, Y. Zhao, D.J. Wang, and D.F. Xu, *J. Crystal Growth* **250** (2003) 516–524.
4. J. Bai, Y. Li, M. Li, S. Wang, C. Zhang, and Q. Yang, *Appl. Surf. Sci.* **254** (2008) 4520–4523.
5. S. Samanta, S. Pyne, P. Sarkar, G.P. Sahoo, H. Bar, D.Kr. Bhui, and A. Misra, *J. Molecular Liquids* **153** (2010) 170–173.
6. M. Tsuji, N. Miyamae, M. Hashimoto, M. Nishio, S. Hikino, N. Ishigami, and I. Tanaka, *Colloids and Surfaces A: Physicochem. Eng. Aspects* **302** (2007) 587–598.
7. L. Lu, H. Wang, S. Xi, and H. Zhang, *J. Mater. Chem.* **2** (2002) 156–161.
8. Y. Chen, K. Yong Liew, and J. Li, *Materials Letters* **62** (2008) 1018–1021.
9. M. J. Hostetler, J. E. Wingate, C. J. Zhong, J. E. Harris, R. W. Vachet, and M. R. Clark, *Langmuir* **14** (1998) 17–22.
10. L. Jong-Min, J. Young-Doo, K. Dae-Wook, L. Young-Ho, and O. Seong-Geun, *Mater. Chem. Phys.* **114** (2009) 549–555.
11. T. Sugimoto, F. Shiba, T. Sekiguchi, and H. Itoh, *Colloid and Surfaces A: Physicochem. Eng. Aspects* **164** (2000) 183–203.
12. W. Hongshui, Q. Xueliang, C. Jianguo, W. Xiaojian, and D. Shiyuan, *Mater. Chem. Phys.* **94** (2005) 449–453.
13. J. Yano, H. F.uredi-Milhofer, E. Wachtel, and N. Garti, *Langmuir* **16** (2000) 9996–9999.

14. H. Furedi-Milhofer, A. Kamyshny, and N. Garti, *J. Crystal Growth* **198–199** (1999) 1365–1370.
15. K. Chou and Y. Lai, *Mater. Chem. Phys.* **83** (2004) 82–88.
16. T. Tsuji, D.-H. Thang, Y. Okazaki, M. Nakanishi, Y. Tsuboi, and M. Tsuji, *Appl. Surface Sci.* **254** (2008) 5224–5230.
17. C. Kan, C. Wang, J. Zhu, and H. Li, *J. Solid State Chem.* **183** (2010) 858–865.
18. J. Bregado-Gutiéírrez, A. J. Saldívar-García, and H. F. López, *J. Appl. Polymer Sci.* **107** (2008) 45–49.
19. Z. Zhang, B. Zhao, and L. Hu, *J. Solid State Chem.* **121** (1996) 105–110.
20. S. P. Armes and M. J. Aldist, *J. Chem. Soc. Chem. Commun.* (1989) 88–93.
21. P. Ghosh, S. K. Siddhanta, and A. Chakrabarti, *Eur. Polym. J.* **35** (1999) 699–710.
22. P. R. Somani, *Mater. Chem. Phys.* **77** (2002) 81–85.
23. R. Murugesan, G. Anitha, and E. Subramanian, *Mater. Chem. Phys.* **85** (2004) 184–194.
24. K. Cao, J. Yu, B.-G. Li, B.-F. Li, and Z.-R. Pan, *Chem. Eng. J.* **78** (2000) 211–215.
25. H. Wei, Q. Shen, Y. Zhao, D. Wang, and D. Xu, *J. Crystal Growth* **260** (2004) 511–516.
26. M. Liu, X. Yan, H. Liu, and W. Yu, *Reactive Funct. Polym.* **44** (2000) 55–64.
27. M. Zheng, M. Gu, Y.Jin, H. Wang, P. Zu, P. Tao, J. He, *Mater. Sci. Eng. B* **87** (2001) 197–200.
28. F. Bonet, V. Delmas, S. Grugeon, R. Herrera Urbina, P-Y. Silvert, and K. Tekaia- Elhsissen, *NanoStruct. Mater.* **11** (1999) 1277–1284.
29. L. Feng, L. Jiang, Z. Mai, and D. Zhu, *J. Colloid Interface Sci.* **278** (2004) 372–375.
30. S. T. Dubas, P. Kumlangdudsana, and P. Potiyaraj, *Colloids Surf. A* **289** (2006) 105–109.
31. W. A. de Heer, *Rev. Mod. Phys.* **65** (1993) 611–676.
32. W. C. Chan, D. J. Maxwell, X. H. Gao, R. E. Bailey, M. Y. Han, and S. M. Nie, *Curr. Opin. Biotech.* **13** (2002) 40–46.
33. Y. Sun, B. Mayers, T. Herricks, and Y. Xia, *Nano Lett* **3** (2003) 955–960.
34. J.-M. Lee, Y.-D. Jun, D.-W. Kim, Y.-H. Lee, and S.-G. Oh, *Mater. Chem. Phys.* **114** (2009) 549–555.
35. H. S. Shin, H. J. Yang, S. B. Kim, and M. S. Lee, *J. Colloid Interface Sci.* **274** (2004) 89–94.
36. Y. Gao, P. Jiang, L. Song, J. X. Wang, L. F. Liu, D. F. Liu, Y. J. Xiang, Z. X. Zhang, X. W. Zhao, X. Y. Dou, S. D. Luo, W. Y. Zhou, and S. S. Xie, *J. Crystal Growth* **289** (2006) 376–380.
37. Z. Khan, S. A. Al-Tnabaiti, E. H. El-Mossalamy, and A. Y. Obaid, *Colloids and Surfaces A: Physicochem. Eng. Aspects* **352** (2009) 31–37.
38. T. Sugimoto and F. Shiba, *Colloids and Surfaces A: Physicochem. Eng. Aspects* **164** (2000) 205–215.
39. J. E. Makasky, *J. Imaging Sci. Technol*. **40** (1996) 79–84.
40. P. K. de Boer and R. A. de Groot, *J. Phys. Chem. A* **103** (1999) 5113–5115.
41. V. P. Oleshko, A. Van Daele, R. H. Gijbels, and W. A. Jacob, *NanoStruct. Mater.* **10** (1998) 1225–1246.
42. G. S. Nunes, P. B. Allen, and J. L. Martins, *Solid State Commun* **105** (1998) 377–380.
43. N. Kakuta, N. Goto, H. Ohkita, and T. Mizushima, *J. Phys. Chem. B* **103** (1999) 5917–5919.
44. M. I. Freedhoff, A. P. Marchetti, and G. L. Mclendon, *J. Lumin.* **70** (1996) 400–413.
45. S. B. Brichkin, V. F. Razumov, and M. G. Spirin, *Colloid J.* **62** (2000) 8–12.
46. C. Sun, P. Chen, and S. Zhou, *Mater. Lett.* **61** (2007) 1645–1648.
47. J. Shen, X. Zheng, H. Ruan, L. Wu, J. Qiu, and C. Gao, *J. Membr. Sci.* **304** (2007) 118–124.
48. V. Sambhy, M.M. MacBride, B.R. Peterson, and A. Sen, *J. Am. Chem. Soc.* **128** (2006) 9798–9808.
49. J. H. Koh, J. A. Seo, J. T. Park, and J. H. Kim, *J. Colloid Interface Sci.* **338** (2009) 486–490.
50. A. Millan, *J. Crystal Growth* **208** (2000) 592–598.
51. P. Broadhead, *J. Photogr. Sci.* **30** (1982) 165–169.
52. P. Glafkides, *Photographic Chemistry, Vol. 1*, Fountain Press, London 1958.
53. R. Jagannathan and J. S. Wey, *Photogr Sci Eng* **26** (1982) 61–64.
54. J. S. Wey, *Preparation and Properties of Solid State Materials, Vol. 6*, Marcel Dekker, New York, 1981, Ch.2.
55. N. Abbasi and A. Winzer, *J. Chem Soc of Pakistan* **13** (1991) 229–233.
56. E. Perry, *J. Photogr. Sci. Eng.* **5** (1961) 349–356.
57. G. Pueskuelev, O. Zarnorechki, and V. Kabaivanov, *J. Photogr. Sci.* **22** (1974) 235–241.
58. O. Zarnorechki, G. Puskulew, and W. S. Kabaiwanow, *Plaste. Kaut.* **21** (1974) 745–749.
59. P. Y. Silvert, R. Herrera-Urbina, and K. Tekaia-Elhsissen, *J. Mater. Chem.* **7** (1997) 293–299.
60. T. Yano, N. Itoh, and S. Iguchi, *Nippon. Shat.* **29** (1966) 17–24.
61. A. H. Herz, *J. Image Sci. Tech.* **39** (1995) 40–46.