Chem. Mater. **1992**, *4*, 545–555

Controlled Double-Jet Precipitation of Sparingly Soluble Salts. A Method for the Preparation of High Added Value Materials

Jiří Stâvek

Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Majakovskêho 24,
160 00 Prague, Czechoslovakia

Milan Šípek

Department of Physical Chemistry, Prague Institute of Chemical Technology, Technickâ 5,
166 28 Prague, Czechoslovakia

Izumi Hirasawa and Ken Toyokura

Department of Applied Chemistry, Waseda University, Shinjuku-ku, Tokyo 169, Japan

Received July 9, 1991. Revised Manuscript Received January 30, 1992

In recent years considerable attention is given to the development of methods for the preparation of microcrystals with a narrow crystal size distribution (CSD). One promising technique, been developed for the preparation of silver halides crystals, is controlled double-jet precipitation (CDJP). In the CDJP the cation and anion solutions are added simultaneously through separate input lines to a stirred solution of a lyophilic polymer. The formation and growth of monodisperse microcrystals in the bulk of crystallizer and the nucleation of unstable nuclei or primary particles formed near jets occur simultaneously during the whole run. The monodisperse particles are prepared if these unstable nuclei or primary particles continuously disappear from the system by controlled Ostwald ripening or controlled agglomeration, and the matter serves as a source for the growth of constant number of stable particles. The objective of this contribution is to survey this unique precipitation technique while the concept of CDJP can be used in general for the precipitation of various sparingly soluble salts.

1. Introduction

Recently, chemical engineers in the field of industrial crystallization are more often asked to give their attention not only to the crystal size distribution but also to other aspects of the crystal's physical form such as its morphology, its purity, or its internal structure while the average size of crystals should be kept at scales from several nanometers to several micrometers. The chemical composition, phase composition, composition gradient, average crystal size, crystal size distribution, and other factors contribute to the actual properties and performance of desired materials. To fulfill these considerations, some new initiatives and directions are needed in order for research in industrial crystallization to retain its relevance.[1]

Thus, the increasing involvement of chemists and chemical engineers in the field of the crystallization by precipitation from solutions should overcome a traditional characterization of precipitation from solutions as a rather mysterious unit operation[2] and open the door for controlling of processes occurring during precipitation: nucleation, crystal growth, Ostwald ripening, recrystallization, coagulation, and agglomeration. One of the promising techniques to control the processes during the precipitation of sparingly soluble salts from solutions is controlled double-jet precipitation (CDJP), which has been developed for the preparation of monodisperse silver halide crystals.

The main idea of this technique is the formation of constant number of particles in the begin of the precipitation while reactants added later during the run form colloidally unstable particles which serve as a source for the growth of stable particles. The observable nucleation of stable particles is rapidly over as predicted by the LaMer model[3] of the formation of uniform particles. But the LaMer model does not describe the steady-state formation of colloidally unstable particles as it is observed in the CDJP technique. The change of reaction conditions during the CDJP run gives new possibilities for modifying properties of particles during their growth. The purpose of this contribution is to introduce this method as a hopeful technique for the preparation of microcrystals with desired properties: narrow crystal size distribution, well-developed habit, internal structure, and epitaxy.

2. Brief Survey of Precipitation Techniques Related to CDJP

The key to the preparation of uniform and monodisperse systems is the controlled generation of the reacting species which should result in the formation and growth of uniform particles. Great effort has been devoted to the problems regarding the preparation of well-defined colloidal particles over the past several decades. In general, particles with narrow size distribution can be prepared in closed systems (an all-monomer reservoir is built in the form of solute, and no addition of other reactants is needed) or open systems (the monomer reservoir has to be created by mixing of reactants). Many review articles are published,[4-10] and therefore only the precipitation techniques related to the CDJP will be briefly mentioned here. Specifically, the controlled homogeneous precipitation (CHP) in closed systems developed by Matijević and

---

(1) Davey, R. J. *The Chemical Engineer* 1987, *Dec*, 24–26.
(2) Mersmann, A.; Kind, M. *Chem. Eng. Technol.* 1988, *11*, 264–276.
(3) LaMer, V. K.; Dinegar, R. H. *J. Am. Chem. Soc.* **1950**, *72*, 4847–4854.
(4) Overbeek, J. T. G. *Adv. Colloid Interface Sci.* **1982**, *15*, 252–277.
(5) Matijević, E. *Annu. Rev. Mater. Sci.* **1985**, *15*, 483–516.
(6) Haruta, M.; Delmon, B. *J. Chim. Phys.* **1986**, *83*, 859–868.
(7) Sugimoto, T. *Adv. Colloid Interface Sci.* **1987**, *28*, 65–108.
(8) Matijević, E. *Proc. R. Inst.* **1990**, *62*, 161–182.
(9) Brinker, C. J.; Scherer, G. W. *Sol–Gel Science*; Academic Press: London, 1990, Chapter 4.
(10) *MRS Bull.*, Dec 1989 and Jan 1990, two special issues on the preparation of the monodisperse particles.

0897-4756/92/2804-0545$03.00/0

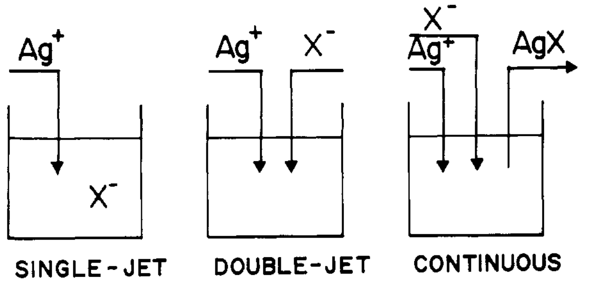

Figure 1. Schematic diagram of mixing of reactants in open systems.

co-workers,[11] the controlled alkoxides hydrolysis in closed systems (CAH) introduced by Stöber et al.,[12] and several other techniques used for the preparation of well-defined particles in open systems.

Matijević and co-workers have demonstrated that an enormous variety of materials can be grown from solutions by controlled homogeneous precipitation and various mechanisms can be evolved: redox reactions, forced hydrolysis, thermal decomposition of complexes, and decomposition of compounds. However, the CHP requires dilute solutions (usually $\sim 10^{-3}$–10^{-2} M), and moreover it is very difficult to scale up this technique. One important conclusion follows from their studies: if a precursor can be placed in solution, the material can be precipitated as a uniform solid when the convenient reaction conditions are found. It seems there are no chemical limitations to produce suspensions with narrow particle size distribution.

Stöber et al.[12] prepared by the controlled alkoxide hydrolysis (CAH) technique in closed systems uniform spherical silica particles by hydrolysis of tetraalkyl silicates and subsequent condensation of silicic acid in alcoholic solutions containing water and ammonia. This method has been extended to other compositions.[9] Although the solutions used in the CAH processes are more concentrated (usually $\sim 10^{-1}$M) than those used in the CHP processes, they are still too dilute for production of commercial amounts of materials. Three ways to increase the rate of production of monodispersed particles via the CAH technique are now known. In the first, the alkoxide and water solutions are mixed in a plug flow reactor[13] and the formation of primary particles and their controlled agglomeration occur simultaneously during the flow of the suspension through the motionless mixer reactor. In second, the concentration of solutions can be increased if the controlled hydrolysis of alkoxides in closed systems is done in the presence of (hydroxypropyl)cellulose, which acts as a steric stabilizer, as was demonstrated by Jean and Ring[14,15]) or in the presence of long-chain carboxylic acids.[16] Bogush and Zukoski[17] prepared the seeds of silica, and during careful very slow addition of another reactants in portions, the seeds grew by controlled agglomeration. By this way they prepared monodisperse secondary particles of silica with large mass fractions in final suspensions and moreover they significantly contributed to the explanation of processes occurring during the growth of monodisperse secondary particles[18–20] in this open precipitation system.

There are three common methods to mix reactants in open systems (Figure 1). In the single-jet method, the cation solution is introduced at a carefully controlled rate over a period of time (or in the case of diluted solutions rapidly) into a stirred solution containing the anions, or vice versa. In the double-jet method the cation and anion solutions are added simultaneously through separate input lines into the crystallizer. The addition rates of the two reactants solutions are balanced to maintain the desired reaction conditions in the crystallizer. In addition to these batch operations, precipitation can be carried out by a continuous method. Continuous streams of reactants are fed to a crystallizer while product is simultaneously removed to maintain a constant reaction volume. If the reactions conditions are carefully controlled, following a transient time period a steady state is reached after which the size distribution and shape of particles remain unchanged. However, the continuous precipitation method in open systems yields particles with polydisperse size distribution.[21,22]

In the single-jet precipitation mode it is possible to prepare monodisperse particles by slow mixing of diluted solutions, e.g., Herak et al.[23] prepared lanthanum and lead iodates, or by rapid mixing of diluted solutions, e.g., Perez and Nancollas[24] prepared calcium fluoride, but it was very difficult to continue their growth because of agglomeration and observable formation of new particles. The monodisperse particles can be grown by the single-jet precipitation if there is formed a solid precursor different from the final product which prevents agglomeration among the isolated secondary particles. This gel-transformation method is applicable mostly to iron oxides and the mechanism was studied by Sugimoto and Matijević.[25]

The main idea of the double-jet precipitation technique is to mix two reactant solutions in a well-stirred crystallizer while the reaction conditions are controlled. Rathje[26] prepared pure hydroxylapatite by simultaneous additions of calcium chloride and potassium dihydrogen phosphate in small portions to boiling water, followed by additions of sodium hydroxide solution to keep the suspension neutral to indicator phenolphthalein. This constant pH precipitation technique (CPHP) was later developed by Nancollas et al.[27] by using an automatic titrator and by Severens and de Bruyn,[28] who controlled pH automatically with the feedback control system. Recently, Ebrahimpour et al.[29] introduced the dual constant composition precipitation (DCCP) technique, in which they control the values of pH and pCa independently. Both the CPHP and DCCP techniques enable preparation of a well-defined single-crystalline phase, but the crystals are agglomerated with wide size distribution. The monodisperse crystals can be prepared if the two solutions are added simultaneously

---

(11) Matijević, E. *Pure Appl. Chem.* **1988**, *60*, 1479–1491.

(12) Stöber, V.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62–69.

(13) Ring, T. A. *MRS Bull.* **1987**, *12*, 34–38.

(14) Jean, J. H.; Ring, T. A. *Langmuir* **1986**, *2*, 251–255.

(15) Jean, J. H.; Ring, T. A. In *Better Ceramic Through Chemistry II*. MRS Symp. Proc. 73; Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; Materials Research Society: Pittsburg, PA, 1986; pp 85–92.

(16) Legrand, F.; de Bruycker, P. *J. Mater. Sci.* **1991**, *26*, 2353–2358.

(17) Bogush, G. H.; Tracy, M. A.; Zukoski, C. F. *J. Non-Cryst. Solids* **1988**, *104*, 95–106.

(18) Look, J. L.; Bogush, G. H.; Zukoski, C. F. *Faraday Discuss. Chem. Soc.* **1990**, *90*, 345–357.

(19) Zukoski, C. F. *Faraday Discuss. Chem. Soc.* **1990**, *90*, 377–383.

(20) Bogush, G. H.; Zukoski, C. F. *J. Colloid Interface Sci.* **1991**, *142*, 19–34.

(21) Wey, J. S.; Terwilliger, J. P.; Gingello, A. D. *AIChE Symp. Ser.* **1980**, *76*, 34–42.

(22) Wey, J. S.; Leubner, I. H.; Terwilliger, J. P. *Photogr. Sci. Eng.* **1983**, *27*, 35–39.

(23) Herak, M. J.; Kratohvil, J.; Herak, M. M.; Wrischer, M. *Croat. Chem. Acta* **1958**, *30*, 221–230.

(24) Perez, L. A.; Nancollas, G. H. *Colloids Surf.* **1991**, *52*, 231–240.

(25) Sugimoto, T.; Matijević, E. *J. Colloid Interface Sci.* **1980**, *74*, 227–243.

(26) Rathje, W. *Ber. Dtsch. Chem. Ges.* **1941**, *74B*, 342–349.

(27) Koutsoukos, P.; Amjad, Z.; Tomson, M. B.; Nancollas, G. H. *J. Am. Chem. Soc.* **1980**, *102*, 1553–1557.

(28) Severens, M. J.; de Bruyn, P. L. *Colloids Surf.* **1986**, *29*, 17–36.

(29) Ebrahimpour, A.; Zhang, J.; Nancollas, G. H. *J. Cryst. Growth* **1991**, *113*, 83–91.

through separate input lines to a crystallizer with a stirred solution of a lyophilic polymer and well-defined reaction conditions, especially pH, excess of cations or anions, type and concentration of solvents, growth inhibitors, growth modifiers, etc. This process is very well-known in photographic industry as the balanced double-jet precipitation or the controlled double-jet precipitation (CDJP)[30-34] for the preparation of silver halide emulsions. [In photographic chemistry, the term emulsion is used to designate a dispersion of photosensitive, solid microcrystals in a protective layer. This differs from the use of the term in colloid chemistry, where it designates a heterogeneous mixture of two or more liquids that do not dissolve in each other but form a relatively permanent dispersion.]

The photographic industry has more than a 100-year-long experience with the precipitation of silver halides in the presence of gelatin,[35] which is until now the best-known protective colloid for this technique and has several important functions during the production of photographic materials. The properties of silver halide crystals play a significant role in the photosensitive materials, and that is why the precipitation process was very intensively studied. The existence of several stages in the precipitation of silver halides (nucleation, growth, Ostwald ripening, agglomeration, recrystallization) was already confirmed by Trivelli and Sheppard,[36] Chibisoff,[37] and Ipatov[38] and intensively studied to control the single-jet precipitation of silver halides.

Loveland and Trivelli[39] measured size distributions of silver halide crystals obtained by mixing of two reactants streams and pointed out on the influence of the mixing way. Arens[40] was first who studied in detail the influence of bromide excess in the crystallizer on the habit of formed silver bromide crystals. He observed formation of various shapes of silver bromide by Ostwald ripening and coagulation of Lippmann emulsions (=silver halide suspensions with particle size smaller than 50 nm prepared for the first time by Lippmann[41]). Zharkov and Dobroserdova[42] mixed solutions of silver nitrate and potassium chloride or bromide in various proportions and observed formation of cubic silver chloride or cubic and octahedral silver bromide crystals at equlibrium ratios of solutions. This effect of double-jet mixing was confirmed by Berry and Marino,[43] who noted formation of cubic silver bromide crystals. When later the pAg value was potentiometrically measured and kept constant during the whole run, monodisperse well-developed silver halide crystals were obtained.[44,45] Claes and Berendsen[46] controlled pAg and pH automatically with two feedback control systems because the pH value plays also a significant role during the nucleation and growth of silver halides. During the past 30 years the CDJP of silver halides was intensively studied and now is used in the photographic industry to make precisely defined silver halide crystals with narrow crystal size distribution as well as developed habit, internal composition, and epitaxy with the rate of production of such materials as ~1 mol AgX dm^{-3} h^{-1}, and this batch process can be scaled up to ~10^3 dm^3.

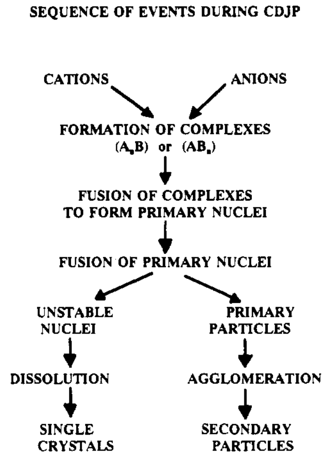

Figure 2. Sequence of events during the CDJ precipitation.

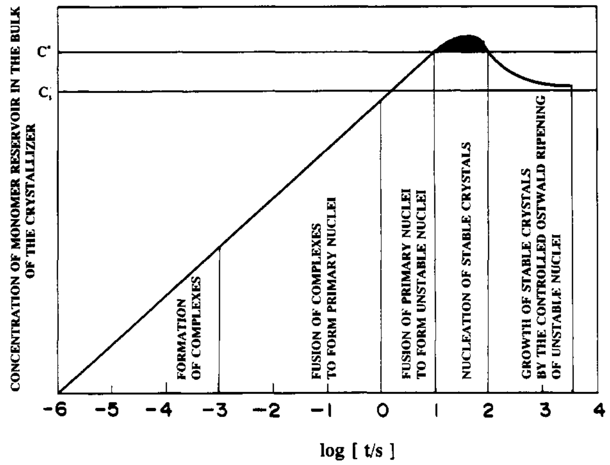

Figure 3. LaMer model of the CDJ precipitation for the growth of monodisperse crystals by the mechanism of the controlled Ostwald ripening.

Recently, it has been found that the CDJP technique can be employed to generate various other sparingly soluble salts with narrow particle size distribution, including oxalates and sulfates,[47,48] and is not limited to the substitution chemical reactions but hydrolytic reactions[49] in aqueous and organic media (controlled double-jet hydrolysis, CDJH) or redox reactions[50] may be utilized to

---

(30) Berry, C. R. In *The Theory of the Photographic Process*, 4th ed.; James, T. H., Ed.; Macmillan Publishing Co.: New York, 1977; pp 88–104.

(31) Wey, J. S. In *Preparation and Properties of Solid State Materials*; Wilcox, W. R., Marcell Dekker: New York, 1981; Vol 6, pp 67–117.

(32) Kharitonova, A. I. *Zh. Nauch. Priklad. Fotogr. Kinematograf.* **1983**, *28*, 226–239.

(33) Szucs, *J. Signalaufzeichnungsmaterialen* **1984**, *12*, 149–162.

(34) Stávek, J.; Sipek; Nývlt, J. In *Proceedings of International Symposium on Preparation of Functional Materials and Industrial Crystallization*; Osaka, Japan, Aug 18–19, 1989; pp 17–23.

(35) Eder, J. M. *History of Photography*, Dover Publications: New York, 1978; pp 421–449.

(36) Trivelli, A. P. H.; Sheppard, S. E. *The Silver Bromide Grain of Photographic Emulsions*; Monograph No. 1 on The Theory of Photography; Eastman Kodak Company: Rochester, NY, 1921.

(37) Chibisoff, K. V. *Untersuchung über die Synthese photographischer Emulsionen.* Ber VIII, Intern, Kongr. Phot., J. A. Barth, Leipzig, 1923; p 208.

(38) Ipatov, P. F. *Usp. Nauchn. Fotogr.* **1955**, *1*, 39.

(39) Loveland, R. P.; Trivelli, A. P. H. *J. Phys. Colloid Chem.* **1947**, *51*, 1004–1027.

(40) Arens, H. *Z. Wiss. Phot.* **1948**, *43*, 120–138.

(41) Lüppo-Cramer, H.; Eder, J. M. *Eder's Handbuch*, 3 Aufl., 1927; Band II, Teil 1:7.

(42) Zharkov, V. N.; Dobroserdova, E. P. *Zh. Nauchn. Priklad. Fotogr. Kinematograf.* **1956**, *1*, 170–173, 250–253, 337–341.

(43) Berry, C. R.; Marino, S. J. *J. Phys. Chem.* **1958**, *62*, 881–881.

(44) Berry, C. R.; Marino, S. J., Oster, C. F. *Photogr. Sci. Eng.* **1961**, *5*, 332–336.

(45) Moisar, E.; Klein, E. *Ber. Bunsen-Ges. Phys. Chem.* **1963**, *67*, 949–957.

(46) Claes, F.; Berendsen, R. *Photogr. Korresp.* **1965**, *101*, 37–42.

(47) Stávek, J.; Hanslík, T.; Zapletal, V. *Mater. Lett.* **1990**, *9*, 90–95.

(48) Stávek, J.; Muraoka, K.; Toyokura, K. In *Proceedings of Bremer International Workshop for Industrial Crystallization*; Bremen, Germany, Sept 12–13, 1990; pp 82–89.

(49) Stávek, J.; Šipek, M. *Czech. Pat. Appl.* 1824–91 (June 14, 1991).

(50) Stávek, J.; Sipek, M. *Czech. Pat. Appl.* 1849–91 (June 17, 1991).

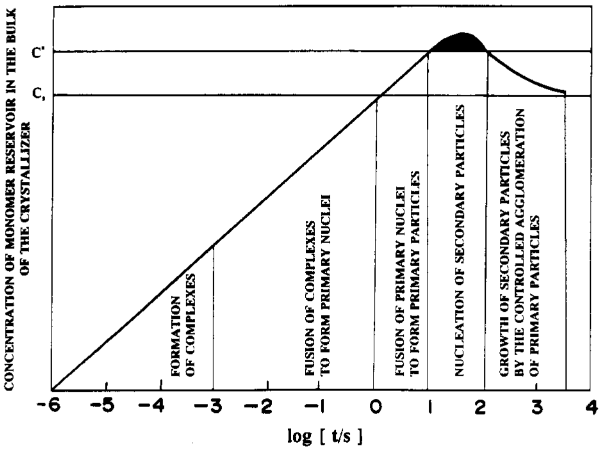

Figure 4. LaMer model of the CDJ precipitation for the growth of monodisperse secondary particles by the mechanism of the controlled agglomeration.

form precipitates with narrow particle size distribution. The unique character of the CDJP technique consists in the formation of a constant number density of colloidally stable particles in the beginning of the reaction while the material added later forms colloidally unstable particles which serve as a source for the growth of those stable particles.

3. Concept of Controlled Double-Jet Precipitation

In the concept of the CDJP technique the formation and growth of monodisperse microcrystals and the nucleation of unstable nuclei or formation of primary particles occur simultaneously during the whole run. However, monodisperse particles may be prepared if these unstable nuclei will disappear from the system via their dissolution and diffusion of the matter to the surface of growing monodisperse microcrystals (mechanism of controlled Ostwald ripening) or via controlled agglomeration of primary particles to form uniform secondary particles (mechanism of controlled agglomeration). In both models of CDJ precipitation the monodiperse microcrystals are formed if the growing crystals or secondary particles are stable against agglomeration and their Ostwald ripening is suppressed. The sequence of events occurring during the CDJ precipitation is shown in Figure 2. The induction period, which is rapidly over, was followed using sophisticated instruments.[51–54] The transition period, during which constant number of stable particles is formed, ends usually within the first minute of the run.[55,56] The data describing the sequence of events during the CDJP run are given in Figures 3 and 4 to express the LaMer model fitted for the CDJP technique. These two models of formation and growth of monodisperse particles will be discussed in more details.

The nucleation of colloidally unstable particles obeys the predictions of classical nucleation theory, while the formation and growth of stable particles are governed by the reaction conditions in the bulk of crystallizer. The nucleation of unstable particles is an extremely rapid process which is very difficult to describe quantitatively.[57–61] However, in the CDJP technique all these colloidally unstable particles escape from the system and the observable number of stable particles is given by the reaction conditions in the crystallizer. This unique feature of the CDJP technique enables to derive quantitative description of processes (number of stable particles and their growth) as a function of reaction conditions in the crystallizer, which can be controlled and measured.

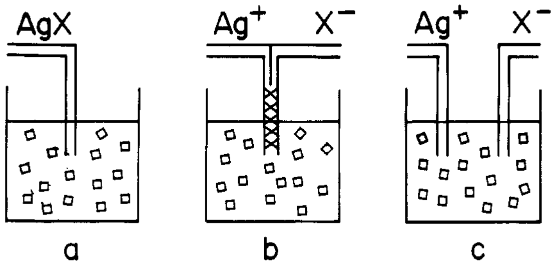

Figure 5. Preparation of monodisperse crystals by the controlled Ostwald ripening of unstable nuclei: (a) addition of a suspension with small crystals; (b) formation of unstable nuclei in a static mixer; (c) formation of unstable nuclei near the jets.

The kinetics of precipitation could be influenced by the reaction conditions (precipitation arrangement, pH, actual concentration of ions which form crystals, type of a lyophilic polymer and its concentration, the presence of growth restrainers or accelerators, reactant addition rate, etc.) and also by hydrodynamic conditions during mixing of ions (mixing of reactants inside or outside of the crystallizer, geometry of crystallizer, type and frequency of revolution of the impeller). Thus, the CDJP technique is governed by reaction and mixing/stirring conditions. If both reaction and mixing/stirring conditions are adjusted to fulfill the desired concept of the CDJ precipitation, then the relative importance of the precipitation processes: nucleation, growth, Ostwald ripening, recrystallization, coagulation and agglomeration may be varied during the precipitation. If observable nucleation is over very rapidly (usually within 1 min), the further addition of reactant solutions results only in growth of the relatively monodisperse crystals already present. Coagulation, agglomeration and contact recrystallization[62] of growing crystals are eliminated by the presence of a lyophilic colloid which is adsorbed on the surfaces of crystals. Ostwald ripening and recrystallization of growing crystals are suppressed by the adjustment of bulk supersaturation to such a value just below the critical supersaturation throughout the precipitation by raising the addition rates of reactants with the particle growth.[63] When the critical bulk supersaturation is exceeded, new stable particles will appear and start to grow.

4. Growth of Monodisperse Microcrystals via Controlled Ostwald Ripening

In the single-jet precipitation of silver halides with wide size distribution, it was observed that larger particles grow at the expense of smaller ones which dissappear from the system because of Ostwald ripening. The idea of the double-jet precipitation is to create constant number of

---

(51) Jagannathan, R.; Wey, J. S. *J. Cryst. Growth* **1985**, *73*, 226–232.

(52) Tanaka, T.; Iwasaki, M. *J. Imaging Sci.* **1986**, *29*, 86–92.

(53) Schmidt, K. H.; Patel, R.; Mersel, D., *J. Am. Chem. Soc.* **1988**, *110*, 4882–4884.

(54) Hon, M. J.; Shah, D. O. In *Interfacial Phenomena in Biotechnology and Materials Processing*; Attia, Y. A., Modigiland, B. M., Chander, S., Eds., Elsevier, Amsterdam, 1988, pp 443–458.

(55) Berry, C. R.; Skillman, D. C. *J. Phys. Chem.* **1964**, *68*, 1138–1143.

(56) Berriman, R. W. *J. Photogr. Sci.* **1964**, *12*, 121–133.

(57) Nielsen, A. E. *Kinetics of Precipitation*; The Macmillan Company: New York, 1964.

(58) Walton, A. G. *The Formation and Properties of Precipitates*; John Willey and Sons: New York, 1967.

(59) Mullin, J. W. *Crystallization*, 2nd ed.; Butterworths: London, 1972.

(60) Nývlt, J.; Söhnel, O.; Matuchová, M.; Broul, M. *The Kinetics of Industrial Crystallization*; Elsevier: Amsterdam, 1985.

(61) Dirksen, J. A.; Ring, T. A. *Chem. Eng. Sci.* **1991**, *46*, 2389–2427.

(62) Sugimoto, T.; Yamaguchi, G. *J. Cryst. Growth.* **1976**, *34*, 253–262.

(63) Wey, J. S.; Strong, R. W. *Photogr. Sci. Eng.* **1977**, *21*, 248–252.

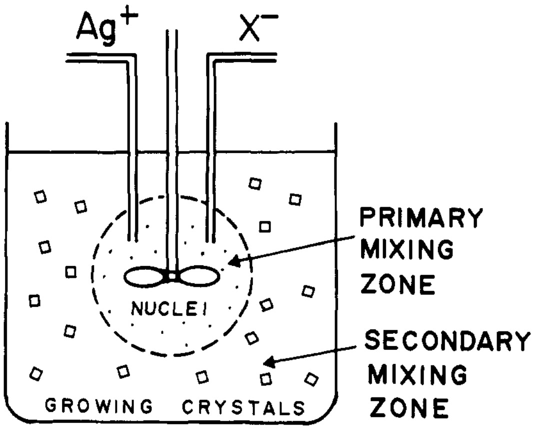

Figure 6. Model of a crystallizer for the CDJP technique.

crystals in as short a burst as possible, and the new added materials will be used for their growth. Markocki and Romer[64] added Lippmann emulsions into the crystallizer, where they became unstable and were dissolved by Ostwald ripening. They observed formation and growth of uniform silver halide crystals. The growth of uniform crystals by the controlled Ostwald ripening of unstable nuclei (Figure 5) can be realized by: dissolution of very small crystals (Figure 5a), mixing of reactants in a static mixer (Figure 5b) or by direct introduction of reactants into the crystallizer (Figure 5c).

The formation and growth of monodisperse microcrystals in the CDJ precipitation via steady-state formation and dissolution of unstable nuclei, which are created in the vicinity of jets, was studied in detail by Berry,[65] Sugimoto,[66] and Wey and Schad.[67] Berry[65] considered that during simultaneous slow introduction of reactants into the crystallizer, the actual supersaturation in the region of jets is typically 10^5–10^8 times the solubility. Gutoff et al.[68] and Berry[65] defined in the crystallizer two regions: the well-mixed bulk of the vessel and a region of extreme supersaturation where the highly concentrated solutions of reactants are introduced. This situation is shown in Figure 6, where two zones are depicted. The primary mixing zone in the vicinity of jets, where are the unstable nuclei formed during the addition of reactants, and the secondary mixing zone, where these unstable nuclei in dependence on the value of supersaturation will survive or redissolve. This influence of supersaturation on the behavior of unstable nuclei in the bulk of the crystallizer is given by Figure 7. If the bulk supersaturation is low enough, the unstable nuclei continuously fed into the secondary mixing zone are dissolved by Ostwald ripening and act as a source of additional matter for the growing crystals (Figure 7a). In this case the uniform crystals can be prepared. To regulate the growth of these monodisperse microcrystals, it is necessary to keep the effective concentration of ions in solution at a value lesser than the solubility of transient nuclei and greater than that of stable growing crystals. Then, there will be a persistent diffusion of matter from the transient nuclei to the solution and from solution to the surface of growing crystals. But if there is a higher value of local supersaturation because of improper reaction or mixing/stirring conditions, some of the transient nuclei will survive and start to grow (Figure 7b). Under such circumstances the monodisperse microcrystals cannot be obtained.

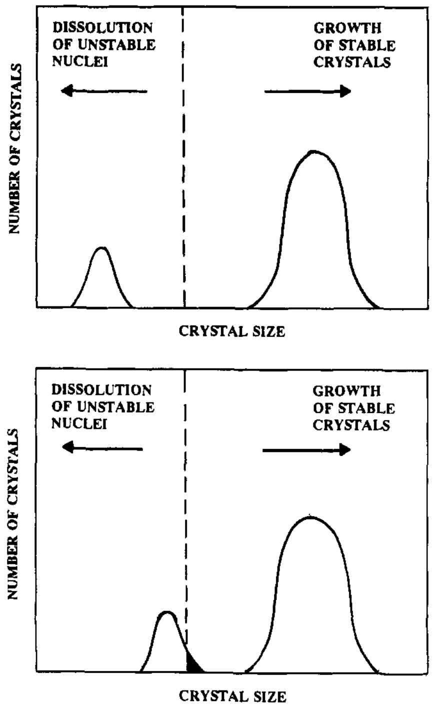

Figure 7. Growth of monodisperse crystals by the controlled Ostwald ripening of unstable nuclei: (a) all unstable nuclei are redissolved and promote the growth of monodisperse crystals; (b) some of unstable nuclei survive in the bulk of the crystallizer, crystals with wide size distribution are formed.

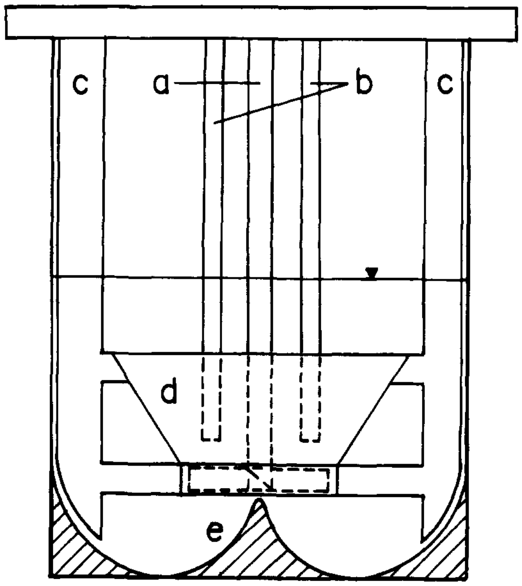

Figure 8. Design of a convenient crystallizer for the CDJP technique (a) axial impeller; (b) jets; (c) baffles; (d) conical draft-tube; (e) profiled bottom.

From these considerations it follows that a convenient design of an apparatus for the CDJP technique, given by the Figure 8, should delimit two regions in the crystallizer[69,70] as shown in Figure 6: (i) A small primary mixing zone-around the feed jets where extreme supersaturation

---

[64] Markocki, W.; Romer, W. *Korpuskularphot. Vortr. Diskuss. Int. Kolloq.* **1962**, *4*, 149–161.

[65] Berry, C. R. *Photogr. Sci. Eng.* **1976**, *20*, 1–4.

[66] Sugimoto, T. *J. Colloid Interface Sci.* **1977**, *62*, 286–294; **1978**, *63*, 16–26; **1978**, *63*, 369–377.

[67] Wey, J. S.; Schad, M. J. *J. Imag. Sci.* **1986**, *30*, 193–197.

[68] Gutoff, E. B.; Cottrell, F. R.; Margolis, G.; Denk, E. G.; Wallace, C. H. *Photogr. Sci. Eng.* **1974**, *18*, 8–11.

[69] Stávek, J.; Fořt, I.; Nývlt, J.; Šípek, M. In *Proceedings of 6th European Conference on Mixing*; Pavia, Italy, May 24–27, 1988; pp 171–176.

[70] Stávek, J.; Vondrák, P.; Fořt, I.; Nývlt, J.; Šípek, M. *J. Cryst. Growth* **1990**, *99*, 1098–1103.

Table I. Behavior of Unstable Nuclei and Stable Crystals during the Controlled Double-Jet Precipitation

precipitation stage	behavior of unstable nuclei	behavior of stable nuclei
nucleation	formed near the jets	are formed within 1 min
crystal growth	dissolved owing to Ostwald ripening	constant number grow
Ostwald ripening	dissolved in the bulk solution	Ostwald ripening has to be suppressed
recrystallization	dissolved in the bulk solution	recrystallization has to be suppressed
coagulation	eliminated by the presence of a convenient lyophilic polymer	
agglomeration	eliminated by the presence of a convenient lyophilic polymer	

is created by the micromixing of reactants continuously introduced from jets. This is the nucleation zone in which the reactants are mixed and unstable nuclei are formed. (ii) A secondary mixing zone—the bulk of the reactor contents in the rest of the vessel which should be well mixed, and where unstable nuclei are dissolved owing to Ostwald ripening, and the matter diffuses through the bulk solution and deposits on the surfaces of the constant number of formerly formed crystals with an equal probability for all crystals.

Thus, in this open system, a primary mixing zone for nucleation and a secondary mixing zone for dissolving of unstable nuclei and growing of crystals coexist in the same solution throughout the precipitation process. In the early stage, the number of stable nuclei increases with the growing supersaturation by the dissolution of the unstable nuclei, and when a sufficient number of the slightly grown stable nuclei have been built up in the bulk phase, they become able to absorb the whole solute provided by the constant dissolution of all unstable nuclei. From this moment, the growing crystals cease to increase in number, whereas the unstable nuclei generated in the primary mixing zone begin to act as a monomer source. Thus, after a short stage of observable nucleation (Figure 3), the only growth of stable crystals occurs in the bulk and that is why the system can produce microcrystals with narrow distribution function. The behavior of unstable nuclei and stable crystals during the CDJ precipitation is schematically given in Table I.

5. Growth of Monodisperse Secondary Particles via Controlled Agglomeration of Primary Particles

We have found that under certain conditions the monodisperse particles can be prepared using the CDJ precipitation technique not only by dissolution of unstable nuclei but even by the mechanism of agglomeration of primary particles to form secondary particles with narrow size distribution composed of many smaller primary particles. The growth of monodisperse particles via controlled agglomeration of much smaller particles can be explained as follows (Figure 4): First, the very fine primary particles begin to form by growth of unstable nuclei. In the early stage, they increase in number, whereas no appreciable growth takes place without agglomeration among them. In the course accumulation of the primary particles, they suddenly start to coagulate (=a special case of agglomeration occurring only for very small particles, where the clusters are held together by physical forces alone) to form clusters as the nuclei of the secondary particles consisting of a limited number of primary particles. After that these secondary particles promptly gather the neighboring particles within the individual attraction fields, and during the CDJ precipitation they continue to incorporate the newly formed primary particles (Figure 9). The present lyophilic polymer does not prevent the agglomeration of primary particles to the surface of constant number of growing secondary particles but prevents successfully the agglomeration among the secondary particles. The agglomeration of primary particles appears to be against the general rules for the formation of monodisperse particles. However, if the clustering of the primary particles is regarded as the nucleation of the secondary particles, this system is still in compliance with the LaMer model (Figure 4). The sequences of formation of monodisperse particles by the mechanism of controlled agglomeration are given in Table II.

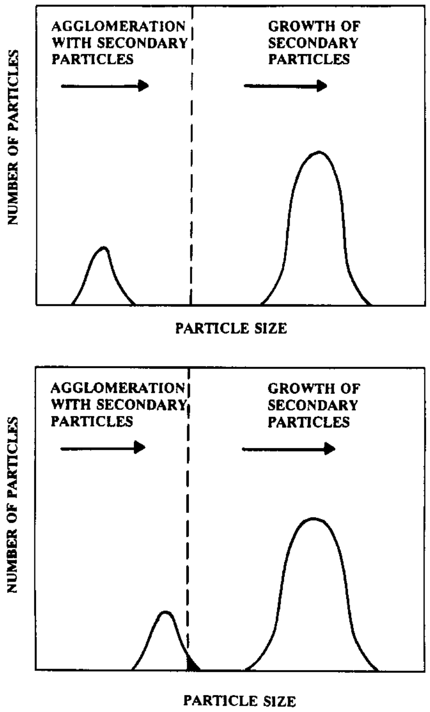

Figure 9. Growth of monodisperse secondary particles by the controlled agglomeration of primary particles: (a) secondary particles scavange all primary particles in the bulk of the crystallizer; (b) some primary particles agglomerate among them and form new stable secondary particles.

The possible explanation of this behavior can be found in the discussion of Zukoski and Overbeek.[19] The large particles can accept primary particles and small aggregates formed during the whole reaction, because the small

Table II. Behavior of Primary and Secondary Particles during the Controlled Double-Jet Precipitation

precipitation stage	behavior of primary particles	behavior of secondary particles
nucleation	formed near the jets	are formed within 1 min
crystal growth	escape via agglomeration in the bulk solution	grow via agglomeration of primary particles
Ostwald ripening		Ostwald ripening has to be suppressed
recrystallization		intracontact recrystallization may occur; intercontact recrystallization eliminated
coagulation		coagulation among secondary particles eliminated
agglomeration		agglomeration of secondary particles eliminated

particle–large particle repulsion barrier remains small enough. Then the small particle–large particle Smoluchowski collision rate allows those small particles to coagulate on the large ones such that their concentration remains so low that they can never become stable in their own right by collision with one another. If the large particles are present in sufficient density, they scavange the suspension for primary particles and the nuclei are not given time to form a large stable floc by agglomeration with one another.

6. Requirement for the Controlled Double-Jet Precipitation

There are two basic requirements to achieve the CDJP concept: only a single burst of stable nuclei may occur, and all colloidally unstable particles have to disappear from the system. To prevent the formation of new stable nuclei during the growing stage, it is very important to keep the value of supersaturation in the bulk of crystallizer lower than critical supersaturation which determines if the continuously formed nuclei in the bulk will survive or will be redissolved. Wey and Strong[71,72] introduced an experimental technique to examine the growth rate of silver halide crystals at the critical supersaturation condition at which the formation of new stable nuclei just begins to occur. Their approach involves changing the reactant addition rate into the crystallizer charged with monodispersed silver halide crystals under carefully controlled conditions. This technique enables to evaluate the critical reactant addition rates and critical growth rates of crystals, while the formation of new stable nuclei could be detected by electron microscope. The critical addition rate is defined as the highest rate of addition of reactants which does not form new observable nuclei. The critical growth rate can be calculated from the critical addition rate, diameter, and amount of seed crystals. Jagannathan and Wey[73,74] and Matsuzaka[75] studied influences of various growth factors on the crystal growth rate such as intercrystal distance (thickness of diffusion layer), crystal size, crystal composition, crystal habit, pH, pAg, temperature. These data are very important to decide if the mechanism of growth is diffusion controlled or surface reaction controlled and to select the flow rates of reactants into the crystallizer to promote growth of monodisperse crystals.

To find the critical growth rates, which depend on the surface properties of growing crystals and reaction conditions in the crystallizer, the growth of seeds has to be measured in a well-stirred crystallizer. Mixing and stirring conditions play a significant role during the precipitation reactions: (i) mixing together reactants on molecular scale; (ii) distribution of supersaturation throughout the reaction space; (iii) mass transfer between already formed particles and regions of supersaturation.

It is important to avoid excessive supersaturation regions in the bulk of crystallizer where the unstable nuclei could survive the effect of Ostwald ripening or primary particles become stable due to their coagulation among them. A convenient design of an apparatus should delimit two regions in the crystallizer (Figure 6): a small primary mixing zone around the feed jets where extreme supersaturation is created by the mixing of continuously introduced reactants from jets, and a secondary mixing zone—the bulk of the reactor contents in the rest of the vessel which should be well mixed to ensure the same growing conditions for all particles present in the crystallizer. An example of such crystallizer for the CDJP technique is shown in Figure 8, where the radial baffles, conical draft tube, profiled bottom, axial flow impeller, and position of jets are combined in order to simulate the model from Figure 6.

7. Advantages of the Controlled Double-Jet Precipitation

The knowledge and control of reaction and mixing/stirring conditions during the CDJ precipitation enables one not only to prepare microcrystals with very narrow size distribution but also to obtain suspensions with predetermined crystal size distributions, to change in certain range the average crystal size, to manipulate the composition of crystals, to modify the habit of growing crystals, to influence epitaxial growth, etc. The CDJ precipitation of silver halides remains until now the most intensively studied system and numerous experimental data were published. A brief summary of this unique precipitation system will be given here.

There were several attempts to correlate the constant number of growing microcrystals in the CDJ precipitation to the reaction conditions.[76–78] Leubner derived[79–81] models for crystal formation under kinetically controlled growth conditions, crystal nucleation in the presence of Ostwald ripening agents, or crystal formation in the presence of growth retrainers. Sugimoto[82] derived formula for the constant number of growing microcrystals for the diffusion-controlled growth, which is very similar to Wagner's formula cited in ref 76:

$$N = \frac{QRT}{5.90\pi D\sigma V_{\rm m}C} \tag{1}$$

where Q is the molar addition rate of monomers into the crystallizer, R is the gas constant, T is the absolute temperature, D is the diffusion coefficient of monomers, σ is the surface energy, $V_{\rm m}$ is the molar volume of solid, and C is the solubility of the solid. The experimental evidences have been obtained to confirm this theoretically derived relation for the description of the nucleation period in the CDJ precipitation of silver bromide and silver chloride.

The size distribution of crystals is largely dependent on the precipitation technique. The double-jet precipitation technique produces suspensions with a narrow size distribution if the Gibbs–Thomson effect is suppressed during the growth of stable crystals. Berry and Skillman[83,84] examined the size distribution of silver halide crystals and observed virtually constant width of the size distribution. Berriman,[56] on the other hand, observed a substantial widening of the size distribution during a silver bromide double-jet precipitation. Hirata and Hohnishi[85] measured the size distribution for two distinct populations of mon-

---

(71) Wey, J. S.; Strong, R. W. *Photogr. Sci. Eng.* **1977**, *21*, 14–18.

(72) Strong, R. W.; Wey, J. S. *Photogr. Sci. Eng.* **1979**, *23*, 344–348.

(73) Jagannathan, R.; Wey, J. S. *J. Cryst. Growth* **1981**, *51*, 601–606.

(74) Jagannathan, R.; Wey, J. S. *Photogr. Sci. Eng.* **1982**, *26*, 61–64.

(75) Matsuzaka, S. In *Proceedings of First East-West Symposium on Photographic Chemistry*; Hawaii, Oct 28–Nov 2, 1984, B22.

(76) Klein, E.; Moisar, E. *Ber. Bunsen-Ges. Phys. Chem.* **1963**, *67* 349–355.

(77) Loginov, V. G.; Denisova, N. B. *Zh. Nauchn. Prikl. Fotogr. Kinematograf.* **1975**, *20*, 231–233.

(78) Leubner, I. H.; Jagannathan, R.; Wey, J. S. *Photogr. Sci. Eng.* **1980**, *24*, 268–272.

(79) Leubner, I. H. *J. Phys. Chem.* **1987**, *91*, 6069–6073.

(80) Leubner, I. H. *J. Cryst. Growth* **1987**, *84*, 496–502.

(81) Leubner, I. H. *J. Imag. Sci.* **1987**, *31*, 145–148.

(82) Sugimoto, T. In *Proceedings of the 11th Symposium on Industrial Crystallization*; Mersmann, A., Ed.; Elsevier: Amsterdam, Sept 18–20, 1990; 435–440.

(83) Berry, C. R.; Skillman, D. C. *Photogr. Sci. Eng.* **1962**, *6*, 159–162.

(84) Berry, C. R.; Skillman, D. C. *J. Phys. Chem.* **1963**, *67*, 1827–1830.

(85) Hirata, A.; Hohnishi, S. *Bull. Soc. Photogr. Jpn.* **1966**, *16*, 1–7.

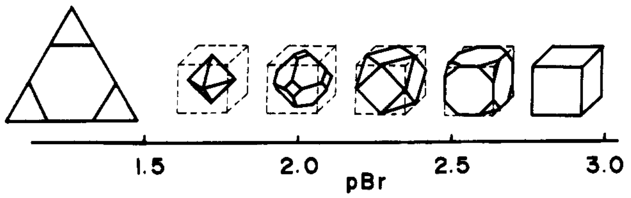

Figure 10. Influence of bromide ion excess in the crystallizer on the habit of growing silver bromide crystals.

odisperse silver bromide cubic crystals and found that the small crystals grew more rapidly than the large ones. These contradictory results were explained by Wey and Strong,[63] who demonstrated the influence of Gibbs–Thomson effect on the growth behavior of two distinct populations of silver bromide crystals growing together under various supersaturation conditions of the double-jet precipitation. Sugimoto[86] described an interesting phenomenon: reversed Ostwald ripening. In this case, smaller monodisperse cubic silver bromide crystals grew at the expense of larger octahedral silver bromide crystals during aging at a low pBr, or small octahedral crystals grew at the expense of larger cubic crystals during aging at a high pBr.

For some applications it would be more advantageous to obtain suspensions with predetermined crystal size distributions. This novel precipitation technique was developed by Wey,[87] who invented the triple-jet technique, in which in addition to two reactant solutions a third solution containing seed silver halide crystals is introduced to the crystallizer charged with seed silver halide crystals. The addition rate of the solution with seed crystals can be changed during the run, and this effect dramatically influences the crystal size distribution.

Silver halide crystals, except those consisting predominately of silver iodide, have a cubic crystal lattice structure belonging to the space group $Fm3m$. These crystals can exist in three unique forms, cube, octahedron, and rhombic dodecahedron, and four families of forms, the icositetrahedra, trisoctahedra, tetrahexahedra, and hexoctahedra. The cubes, tetradecahedra (combination having {100} and {111} faces), and octahedra of silver halides were prepared by the CDJ precipitation at various bromide ion concentrations[88,89] in solution (Figure 10). These results give a clear evidence that even a slight change in the concentration of ions involved in the precipitation reaction causes an observable modification of crystal habit. The theory describing the dynamic nature of the equilibrium form and the steady form defined as a growth form in the steady state of these crystals was developed by Sugimoto.[90] Wyrsch[91] and Claes et al.[92] prepared monodisperse rhombic dodecahedra of silver chloride in the presence of a growth modifier. Maskasky published an enormous study[93] detailing the preparation of additional growth of cubic or octahedral seed crystals in the presence of organic compounds (growth modifiers) the four new crystal forms of silver bromide crystals. The seven different forms of silver bromide crystals are shown in Figure 11. If twinning occurs during the nucleation, the tabular silver halide crystals can be prepared (T-grain emulsion technology[94] introduced by Eastman Kodak). A significant amount of research has been given to the explanation of nucleation and growth of tabular silver halide crystals.[95-101]

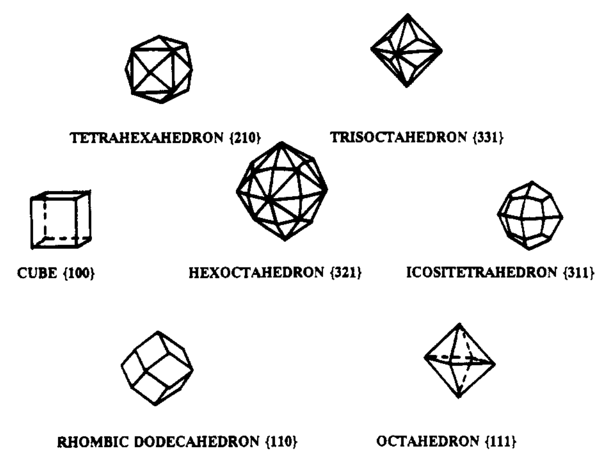

Figure 11. Seven different forms of silver bromide crystals prepared by the CDJ precipitation.[93]

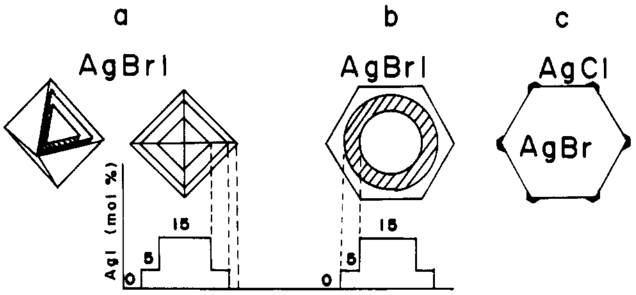

Figure 12. Multistructured silver halide crystals: (a) AgBrI octahedral crystal;[103] (b) tabular AgBrI crystal;[94] (c) selective epitaxial growth of AgCl on the tabular AgBr crystal.[104,105]

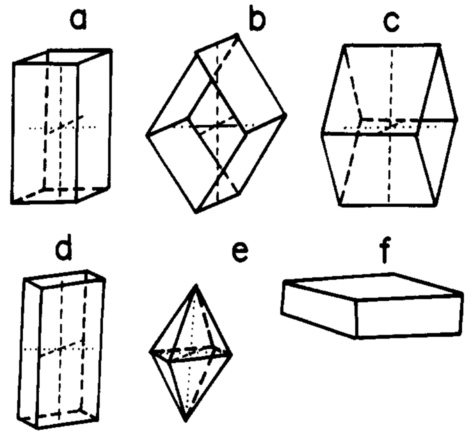

Figure 13. Commonly developed forms and form combinations in $2/m2/m2/m$: (a) pinacoid; (b) rhombic prism {011} and pinacoid {100}; (c) prism {101} and pinacoid {010}; (d) prism Z {110} and pinacoid {001}; (e) rhombic dipyramid; (f) barite crystal.

During the growth of seed crystals with a narrow crystal size distribution, it is possible to vary the composition of growing crystals and/or to incorporate some dopants into

---

[86] Sugimoto, T. *Nippon Shashin Gakkaishi* **1983**, *46*, 306–312.
[87] Wey, J. S. *J. Imag. Sci.* **1990**, *34*, 202–206.
[88] Hirata, A.; Hohnishi, S. *Nippon Shashin Gakkaishi* **1973**, *36*, 359–365.
[89] Markocki, W.; Zaleski, A. *Photogr. Sci. Eng.* **1973**, *17*, 289–294.
[90] Sugimoto, T. *J. Colloid Interface Sci.* **1983**, *91*, 51–68; **1983**, *93*, 461–473.
[91] Wyrsch, D. In *Proceedings of International Congress of Photographic Science*; Rochester, NY, Aug 20–26, 1978; p 122.
[92] Claes, F.; Libeer, J.; Vanassche, W. *J. Photogr. Sci.* **1973**, *21*, 39–44.
[93] Maskasky, J. *J. Imag. Sci.* **1986**, *30*, 247–254.
[94] Anonymous; *Res. Discl.* **1983**, *225*, 20–58.
[95] Berriman, R. W.; Herz, R. H. *Nature* **1957**, *180*, 293–294.
[96] Sugimoto, T. *Photogr. Sci. Eng.* **1984**, *28*, 137–145.
[97] Breslav, Yu. A.; Peisakhov, V. V.; Kaplun, L. Ya. *Usp. Nauchn. Fotogr.* **1986**, *24*, 5–46.
[98] Maskasky, J. E. *J. Imag. Sci.* **1987**, *31*, 15–26.
[99] Karpinski, P. H.; Wey, J. S. *J. Imag. Sci.* **1988**, *32*, 34–39.
[100] Sugimoto, T. *J. Imag. Sci.* **1989**, *33*, 203–205.
[101] Jagannathan, R. *J. Imag. Sci.* **1991**, *35*, 104–112.

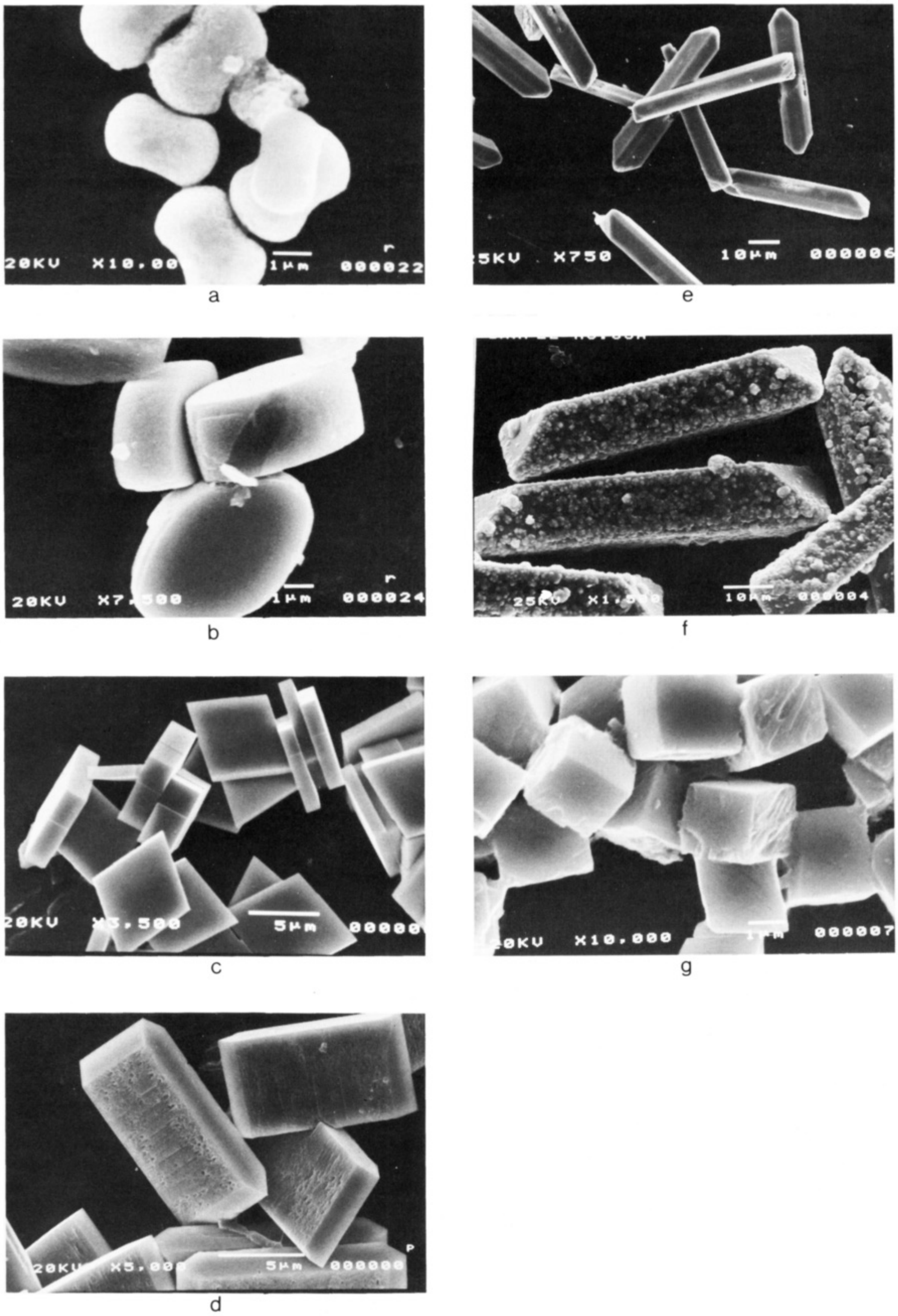

Figure 14. Influence of reaction conditions on the habit of lead sulfate crystals prepared by the CDJ precipitation:[107] 1.0 M solutions of ($Pb(NO_3)_2$ and Na_2SO_4 were added by flow rate 10 $cm^3\ min^{-1}$ into the crystallizer: V_0 = 1000 cm^3 2% inert gelatin, t = 60 °C, pPb = 2.0, four baffled crystallizer equipped by the four pitched blade axial impeller 500 rpm, run 10 min: (a) pH = 5.0 (adjusted by acetic acid); (b) pH = 3.5 (adjusted by acetic acid); (c) pH = 2.0 (adjusted by acetic acid); (d) pH = 1.0 (adjusted to pH = 2.0 by acetic acid then by hydrochloric acid); (e) pH = 1.0 (presence of 0.1 M tartaric acid and adjusted by nitric acid) run 30 min; (f) continue of run *d* at pH = 3.5 (adjusted by ammonia) for 10 min; (g) 0.1 M solutions of (barium 1:9 lead) acetates and sulfuric acid pH = 1.0 (adjusted by hydrochloric acid), pBa = 2.0.

the volume of growing crystals and thus manipulate the internal structure of crystals.[102] The ability to control the composition gradient of the growing crystals leads to the formation of the so-called double-structure or multistructure crystals or to the preparation of epitaxial crystals. Matsuzaka[103] developed the CDJP technique to obtain multistructure octahedral crystals (Figure 12a). In Figure 12b is given an example of a multistructure tabular silver halide crystal.[94] Maskasky[104,105] introduced a technique to precipitate overgrowth deposits onto the corners and edges of silver bromide tabular crystals (Figure 12c). This technique involves adding of a compound—site director—to seed tabular crystals before the overgrowth deposition. Numerous other possibilities to modify habit, internal composition, and epitaxy of silver halides are now known and well described in the patent literature. Breslav and Peisakhov[106] reviewed methods for the preparation of photographic emulsions with various core-shell and epitaxial silver halide crystals.

8. Influence of Growth Mechanism on the Particles Formed by the CDJP Technique

The two different growth mechanisms employed in the CDJP technique, which were discussed in previous sections, result in the formation of particles with different properties. The potentiality of the CDJ precipitation will be briefly demonstrated on the growth of lead sulfate crystals[107,108] and calcium carbonate particles.

The lead sulfate crystals have an orthorhombic crystal lattice belonging to the space group $F2/m2/m2/m$. Such crystals can exist in three types of forms: pinacoids, prisms, and dipyramids (Figure 13). It is known that orthorhombic crystals consist of a combination of two or more forms. Moreover, the relative development of various forms of an orthorhombic crystals changes significantly its habit. This is true for the case of lead sulfate crystals precipitated by the CDJ precipitation. There were prepared various types of crystal habit: acicular, columnar, bladed, tabular, and lamellar. The change in the reaction conditions (pH value, presence of a growth modifier and its concentration, influence of other ions etc.) modifies the resulting habit of crystals.

At pH > 4.5, the elongated secondary particles of lead sulfate grew by agglomeration of small primary particles (Figure 14a). Some of these secondary particles were broken during centrifuging at 10000 rpm. In the pH region 2.5–4.0 we observed the growth on monodisperse particles with a transition shape between that of an elongated one and that of well-developed crystal faces (Figure 14b). At pH < 2.5, a well-developed habit of lead sulfate crystals was formed. The tabular crystals of lead sulfate surrounded by {001} and {110} faces grow at pH = 2.0 in the presence of acetic acid (Figure 14c). If the pH decreased to 1.0, the combination of pinacoid {100} and rhombic prism {101} grew (Figure 14d). The nucleation and growth at pH = 1.0 in the presence of tartaric acid leads to the acicular crystals (Figure 14e) surrounded by faces {102}. If these seed crystals surrounded by {102} and {110} faces were used for their growth in the higher pH region, the surface was covered by epitaxial growth (Figure 14f). The monodisperse pinacoids were prepared by the precipitation with isomorphous barium cations (Figure 14g). Various similar effects were observed also for the case of the CDJ precipitation of calcium carbonate particles. For example, the monodisperse secondary particles grew at the reaction conditions given in Figure 11. The secondary particles obtained under these reaction conditions were not broken during centrifuging at 10000 rpm.

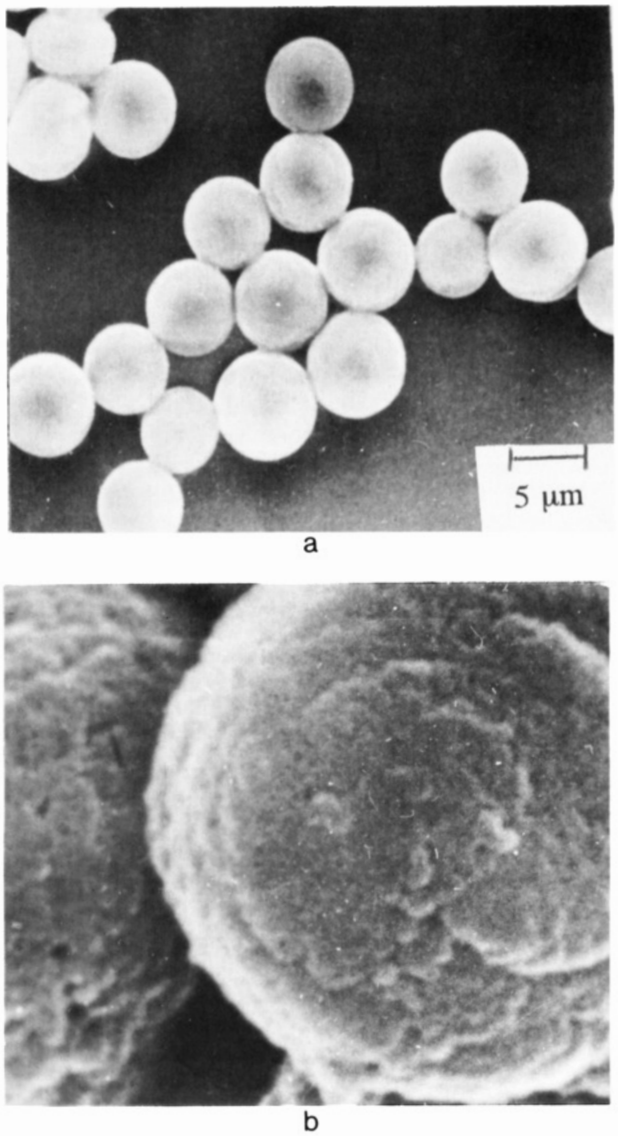

Figure 15. Formation of monodisperse calcium carbonate secondary particles by the CDJ precipitation 1.0 M solutions of $Ca(NO_3)_2$ and Na_2CO_3 were added by the flow rate 10 cm^3 min^{-1} into the crystallizer: V_0 = 1000 cm^3 2% inert gelatin, t = 50 °C, pH = 10.0 (adjusted by ammonia), pCa = 2.0, axial impeller 500 rpm.

9. Conclusions

In the controlled double-jet precipitation the formation and growth of monodisperse crystals or secondary particles and the nucleation of unstable nuclei or formation of primary particles occur simultaneously during the addition of reactants into the crystallizer. However, the monodisperse crystals may be prepared if unstable nuclei will disappear from the system by their dissolution and diffusion of the matter to the surface of growing crystals (mechanism of controlled Ostwald ripening) or by ag-

---

(102) Moisar, E.; Wagner, S. *Ber. Bunsen-Ges. Phys. Chem.* **1963**, *67*, 356–359.

(103) Matsuzaka, S. In *Proceedings of Second East-West Symposium on Photographic Chemistry*; Hawaii, Nov 1988; p 160.

(104) Maskasky, J. E. *J. Imag. Sci.* **1987**, *31*, 93–99.

(105) Maskasky, J. E. *J. Imag. Sci.* **1988**, *32*, 160–177.

(106) Breslav, Yu. A.; Peisakhov, V. V. *Zh. Nauchn. Prikl. Fotogr. Kinematograf.* **1985**, *30*, 150–157; **1985**, *30*, 228–236.

(107) Stávek, J.; Hirasawa, I.; Muraoka, K.; Toyokura, K. In *Proceedings of Fourth World Congress of Chemical Engineering*; Karlsruhe, Germany, June 16–21, 1991; pp 10.6.6.

(108) Stávek, J.; Hirasawa, I.; Muraoka, K.; Toyokura, K. *J. Cryst. Growth*, accepted.

glomeration of primary particles to promote the growth of uniform secondary particles (mechanism of controlled agglomeration). The presence of a convenient lyophilic polymer prevents the intercontact recrystallization and agglomeration among growing crystals or secondary particles, respectively.

The formation and growth of stable crystals or secondary particles are governed by the reaction conditions in the bulk of well-stirred crystallizer. The selection of reaction conditions enables one to modify the properties of formed crystals or secondary particles: size distribution, average size, habit, internal composition, and epitaxy.

Second-Order Nonlinear Optical Properties of Poled Polymers of Vinyl Chromophore Monomers: Styrene, Methacrylate, and Vinyl Benzoate Derivatives Having One-Aromatic-Ring Push–Pull Chromophores

Akio Hayashi,* Yoshitaka Goto, and Masaharu Nakayama

Tsukuba Research Laboratory, Nippon Oil and Fats Co., Ltd., Tsukuba, Ibaraki 300-26, Japan

Krzysztof Kaluzynski

Department of Chemistry, Polish Academy of Sciences, Lodz, Sienkiewicza 112, Poland

Hisaya Sato, Kazuaki Kato, Katsuhito Kondo, Toshiyuki Watanabe, and Seizo Miyata

Department of Material Systems Engineering, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan

Received July 22, 1991. Revised Manuscript Received February 7, 1992

Vinyl monomers having a nonlinear optical one-aromatic-ring chromophore were synthesized and polymerized with a radical initiator. The polymers (S-1 and M-1a,b) having nitro and amino groups showed high second harmonic generation (SHG) of d_{33} coefficients over 22–30 pm/V and d_{31} of 7.0–8.8 pm/V, after corona poling, respectively. These values gradually decreased over a period of a few weeks. The d_{33} of S-1 reached a level of about 65% of the initial value of $d_{33} = 14$ pm/V after about 2500 h and stayed constant after that, to the end of our observation after 14 months at room temperature. The chromophore copolymer of S-1 with M-1 had a lower T_g than those of the each homopolymer; therefore, the SH wave intensity of the copolymer showed larger temporal decay than those of the homopolymers. The chromophore copolymers (CS-75, -86) with a bifunctional chromophore monomer (S-9) showed lower decay of SH wave intensity than that of the homopolymer. Poly(vinyl (dimethylamino)benzoate) showed $d_{33} = 2.2$ pm/V and has an excellent low absorption cutoff wavelength of $\lambda_{\mathrm{cutoff}} = 360$ nm.

Introduction

In recent years interest in nonlinear optical properties of organic materials has rapidly increased in the fields of telecommunication technologies and integrated optics. Nonlinear optics is expected to be a novel key technology in these fields. It is already known that organic compounds essentially have much larger nonlinear optical coefficients and faster response times than inorganic ones. There have been many investigations to estimate molecular hyperpolarizability, β, using various molecular orbital calculations. It has become possible to predict β values accurately for given molecular structures. However, for the potential application to optical devices, e.g., the frequency doubler, all optical signal switching, and so on, it is necessary to further examine properties of the aggregation state of these molecules.

Many types of molecular aggregation systems have been investigated as possible nonlinear optical organic materials, e.g., single crystals,[1-4] L–B films,[5] ferroelectric polymers such as PVDF–TrFe[6] and PVDCN-VAc,[7] polymer blend systems,[8] and polymers possessing chromophores as pen-

---

(1) (a) *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: New York, 1987; Vol. 1. (b) Zyss, J.; Chemla, D. S.; Nicoud, J. F. *J. Chem. Phys.* **1981**, *74*, 4800–4811.

(2) (a) Fichou, D.; Watanabe, T.; Takeda, T.; Miyata, S.; Goto, Y.; Nakayama, M. *Jpn. J. Appl. Phys.* **1988**, *27*, 38–38. (b) Zhang, G. J.; Kinoshita, T.; Sasaki, K.; Goto, Y.; Nakayama, M. *Proc. SPIE* **1989**, *1147*, 116–123. (c) Zhang, G.; Kinoshita, T.; Sasaki, K.; Goto, Y.; Nakayama, M. *J. Cryst. Growth* **1990**, *100*, 411–416. (d) Kitaoka, Y.; Sasaki, T.; Nakai, S.; Yokotani, A.; Goto, Y.; Nakayama, M. *Appl. Phys. Lett.* **1990**, *56*, 2074–2076. (e) Zhang, G. J.; Kinoshita, T.; Sasaki, K.; Goto, Y.; Nakayama, M. *Appl. Phys. Lett.* **1990**, *57*, 221–223.

(3) (a) Hosomi, T.; Suzuki, T.; Yamamoto, H.; Watanabe, T.; Sato, H.; Miyata, S. *Proc. SPIE* **1989**, *1147*, 124–128.

(4) (a) Oliver, S. N.; Pantelis, P.; Dunn, P. L. *Appl. Phys. Lett.* **1990**, *56*, 307–309. (b) Wakita, K.; Sonoda, N.; Shimizu, T.; Kaida, S. *J. Appl. Phys.* **1991**, *69*, 545–547.

(5) (a) Decher, G.; Tieke, B.; Bosshard, C.; Gunter, P. *Ferroelectrics* **1989**, *91*, 193–207. (b) Li, D.; Ratner, M. A.; Marks, T. J.; Zhang, C.; Yang, J.; Wong, G. K. *J. Am. Chem. Soc.* **1990**, *112*, 7389–7390.