Fabrication and electrical resistivity of the monodisperse poly(methyl methacrylate)/silver hybrid particles

2012年 2月

仁荷大學校 大學院
化學工學科
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단분산 PMMA/Ag 하이브리드 입자의 제조와 입자 크기에 따른 전기 저항의 크기 변화

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Fabrication and electrical resistivity of the monodisperse poly(methyl methacrylate)/silver hybrid particles

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Abstract

The monodisperse poly(methylmethacrylate)(PMMA) particles having 5.05 μm size were synthesized by the dispersion polymerization. These particles were used as core particles for PMMA/Ag hybrid particles. For the fabrication of perfect core/shell type of PMMA/Ag hybrid particles, optimum conditions for the electroless silver plating were studied. The variables on the conditions of electroless silver plating were characterized; such as the concentration of silver nitrate solution, concentration of palladium dichloride solution, plating temperature and time. As a result, the optimum condition of preparing conductive hybrid particle with soft surface morphology is as following; activation with 0.1mM PdCl₂ solution followed by 1hr electroless plating under room temperature with 0.1M plating solution.

Various sizes of PMMA/Ag hybrid particles with various silver contents were prepared to understand the electrical resistivity dependency on the particle size and silver content. In addition, resistivity of the hybrid particles was compared to that of the simple mixture of PMMA particles and silver nanoparticles. Three different sizes of PMMA core particles (2.17, 4.36, 7.03 μm) were synthesized via the dispersion polymerization and the silver shell was then plated by the electroless silver plating method using 0.01 ~ 0.2M silver nitrate solution. The characteristics of the PMMA/Ag core/shell hybrid particles were studied by using the field emission scanning electron microscopy (FE-SEM), field emission transmission electron microscopy (FE-TEM), particle size analyzer (PSA), X-ray diffractometer (XRD), thermogravimetric analysis (TGA) and 4-point probe resistivity meter. Based on the FE-SEM and TGA study, each particle size has optimum plating concentration to deposit thick shell with Ag nanoparticles. The lowest electrical resistivity of the hybrid particles with 60 wt% silver was achieved near 10⁻⁴ Ω·cm, whereas that of the simple mixture of PMMA particles and silver nanoparticles reached to 10² Ω·cm, indicating that the resistivity of the hybrid particles was much improved than that of
the simple mixtures. In addition, the percolation threshold was observed at 30 wt% for the hybrid particles, whereas that of simple mixtures was not. In both cases, the particle size barely affected the electrical resistivity upon silver content. Thus, the electrical resistivity value of the hybrid PMMA/Ag particles was acceptable to use in industrial applications.

**Keywords:** electrical conductivity, composite materials, PMMA, silver, electroless plating.
국문요약

입자 크기 또는 Ag 함량과 하이브리드 입자의 전기전도성과의 관계를 연구하고자, 분산중합과 무전해 도금을 이용하여 Core/Shell 형태의 PMMA/Ag 하이브리드 입자를 제조하였다. 먼저, 무전해 Ag 도금의 최적 조건을 알아내기 위하여 분산중합을 통해 5.05 μm의 단분산 PMMA 입자를 제조한 후 무전해 Ag 도금에 영향을 미치는 다양한 변수들을 변화시켜보았다. 변수로는 1) 도금액에 쓰이는 질산은의 농도 변화, 2) PMMA 입자의 활성화 단계에서 쓰이는 PdCl₂의 농도 변화, 3) 도금 온도 변화 및 4) 도금 시간을 변화시켰다. 그 결과, 1.0 mM PdCl₂ 용액으로 PMMA 입자표면을 활성화 시킨 후 0.1M의 AgNO₃ 용액으로 1시간 동안 상온에서 무전해 도금을 실시했을 때 가장 좋은 표면형태를 갖는 PMMA/Ag 하이브리드 입자가 제조되었다.

다음으로 입자크기와 Ag 함량이 하이브리드 입자의 전기 전도성에 미치는 영향을 연구하기 위해 분산중합으로 2.17, 4.36, 7.03 μm 크기의 PMMA 입자를 제조하여 0.01M ~ 0.20M의 AgNO₃ 용액으로 무전해 도금을 실시하였다. 또한 하이브리드 입자와 PMMA/Ag 혼합물과의 전기 전도성을 함께 비교하였다. PMMA/Ag 하이브리드 입자의 특성을 분석하기 위해 FE-SEM, FE-TEM, PSA, XRD, TGA 및 4-point probe를 이용하였다. FE-SEM과 TGA 결과, 통해 입자의 크기에 따라 최적의 도금층을 형성하는 도금액 농도가 존재함을 발견하였다. 가장 낮은 전기 저항은 60 wt%의 은층을 함유하는 하이브리드 입자에서 10⁴Ω·cm의 값을 나타내었으나, 혼합물의 경우 10²Ω·cm의 저항값을 나타내었다. 또한 하이브리드 입자에서 은함량이 30wt%일 때 percolation threshold가 나타났지만 혼합물에서는 은함량의 증가에 따라 전기 저항이 선형적으로 감소하였다. 또한 하이브리드 입자와 혼합물 모두 입자 크기는 전기 저항에 큰 영향을 미치지 않는 것으로 나타났다. 이로써, PMMA 입자와 은나노 입자의 혼합물보다는 PMMA/Ag 하이브리드 입자의 전기 전도성이 향상되고, 하이브리드 입자 또한 percolation threshold가 나타난
이후에는 은함량의 증가 또한 전기 전도성 향상에 큰 영향을 미치지 않음이 판명되었다.

**Keyword:** 전기 전도성, 복합물질, PMMA/Ag, 무전해 도금.
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1. Introduction

Polymer/metal composites have been attracting a great attention over the years in numerous fields. Among them, various types of composites were studied, such as monolithic, mononuclear, Janus type, surface coating and so on [1-3].

When polymer and metal were combined together to form hybrid particles, they exhibited desirable properties such as high hardness, wear resistance, high electrical conductivity and low density. Thus, novel hybrid particles were often applied in nonlinear optical devices, conductive composite, electromagnetic interference (EMI) shielding, electromagnetic wave absorption, catalysts, batteries and sensors [4-6].

The metal with the specific characteristics in electrical conductivity can be applied in various industrial areas such as radio frequency interference (RFI) shielding, electrostatic charges dissipation (ESD), electrical conductive adhesives and circuit elements in microelectronics [7-10]. Silver has the highest electrical conductivity among single metals, and its oxide form is also conductive unlike other metals. Furthermore silver exhibits high thermal conductivity and antibacterial property, and is stable in various conditions [11]. Due to these advantages, silver has been primarily used as polymer/silver composite in various applications. However, in order to obtain high electrical conductivity, the volume fraction of silver, which was dispersed in polymer matrix, has to exceed the percolation threshold, which was generally high for typical fillers (about 9 % by volume, ~36 % by weight) [12]. This limit was solved by developing the polymer/metal hybrid particles [13-15]. Various ways of synthesis for core/shell type of polymer/metal hybrid particles have been reported, for example, physical incorporation [16], reduction of polymer-metal ion complexes [17], chemical metal deposition [18,19], electroless plating [20] and so forth. Among numerous methods, electroless plating method was the most widely implemented technique in industrial field.

Electroless plating is the self-catalytic reduction reaction in aqueous solution and one of the simplest, cost-effective and facile alternative methods due to its easy condition for application. Carbon nanotube, polyaniline powders, ceramic powders,
glass microspheres and ZnO particles were the examples of substrates [14,21,22]. In general, a metal salt can be reduced to metal by reducing agent on a substrate surface without the use of an electrical potential and therefore, this method allows the continuous and uniform metal coatings on the conductive or nonconductive substrates [23,24].

Although many researchers developed a variety of polymer/silver composites, most of studies were concentrated on the techniques for the preparation of polymer/silver hybrid particles or on the conductivity measurements of silver particles dispersed in polymer matrix. Kyung-Do Suh et al. [25] made multihollow PMMA/Ag microspheres by W/O/W emulsion polymerization, Z.L. Wang et al. [20] fabricated bimetallic nanoshells on polymer spheres using an improved electroless plating method and Myoung-Seon Gong et al. [26] prepared PMMA/silver beads via the in situ reduction of silver alkylcarbamate complex. Electrical conductivity of silver-filled polymer matrix was studied in terms of the silver particle size, surfactants and heat treatment [27-29]. Electrical conductivity of silicone rubber filled with Ag-coated nanosphere particles [30] was also reported. The electrical resistivity of nano-sized composites increased due to the increased surface contact area [31].

In this paper, the effect of core particle size on the electrical resistivity of PMMA/Ag hybrid particles and the simple mixture between Ag and PMMA particles was studied by using SEM, TEM, XRD, PSA, TGA and etc. In order to do that, various sizes of PMMA spherical particles (2.17~7.03 μm) were synthesized using the dispersion polymerization and the PMMA/Ag hybrid particles were prepared by electroless plating technique using the silver nitrate solution with various concentration.
2. THEORITICAL BACKGROUND

2. 1. Dispersion polymerization

2.1.1. Introduction

Since polymer dispersions in organic liquids have potential advantage over the more conventional aqueous dispersions or organic solution systems for surface coatings, a number of indirect methods have been developed for their preparation. The methods used have all involved the subsequent conversion of the prepared polymer in a variety of ways to a more or less dispersed form. However, in general, the overall properties of the dispersions produced by these methods, such as particle size, dispersion stability and viscosity, have not been sufficiently satisfactory for their widespread application as surface coatings. Ideally, a process analogous to that of emulsion polymerization is required, in which polymer dispersions of controlled particle size can be prepared directly by a heterogeneous process, but in which the continuous phase is organic instead of aqueous.

Two basic types of heterogeneous polymerization process can be distinguished. In some, as in emulsion polymerization, the initial reaction mixture consists of two separate phases and the polymerization continues in heterogeneous manner throughout. In others, as in dispersion polymerization in organic media, the reaction mixture is initially homogeneous but as polymerization proceeds, polymer soon separates out and the reaction then continues in a heterogeneous manner.

The characteristics of the various types of heterogeneous free-radical polymerization processes both in water and organic liquids are summarized in Table Ⅰ. Precipitation polymerization can be carried out in a range of media in water, e.g. aqueous solutions of acrylonitrile [32], or in organic precipitants, e.g. methyl methacrylate in cyclohexane, or in a monomer in which the polymer produced is insoluble, e.g. acrylonitrile or vinyl chloride [33]. An auto-accelerated polymerization is observed
after the separation of polymer since the radical chain termination processes are restricted by the low mobility of the growing polymer radicals in the viscous reaction medium. The polymer produced is in the form of an agglomerate or slurry. Emulsion polymerization in water is also characterized by a high rate of polymerization producing high molecular weight polymer, which in this case originates from the isolation of radicals in the separate growing polymer particles. Here, the polymer produced is in the form of stable lattes of fine particle size.

The polymer particles produced are larger than those obtained by emulsion polymerization in its strictest sense and tend to settle out on further dilution of the aqueous phase. Suspension polymerization, involving the use of monomer droplets in water, is carried out with an initiator soluble in the monomer by an essentially microbulk type of polymerization [33].

In all of the heterogeneous dispersion polymerization processes described so far in which the polymer is formed as a more or less stable dispersion of controlled particle size, an aqueous continuous phase has been used. Dispersion polymerization in organic liquids is a more recent development [34,35]. It usually involves the polymerization of a monomer dissolved in an organic diluent to produce insoluble polymer dispersed in the continuous phase in the presence of an amphipathic graft or block copolymer as the dispersant. Dispersion polymerization can be regarded as a special type of precipitation polymerization in which flocculation is prevented and particle size is controlled [36].

The development of dispersion polymerization has utilized a blend of the disciplines of both polymer science and colloid science. Consequently, some of the terminology used for its description may be unfamiliar to some readers. The term ‘polymer colloids’ is now frequently used to describe polymer dispersions of colloidal dimensions (that is, in the size range 0.01 to 10 μm) in any medium [37].

Polymer colloids can be considered as being of two basic types, lyophobic and lyophilic colloids. The interaction of lyophobic colloids with the continuous phase is so restricted that they are inherently unstable in the thermodynamic sense and the forces of attraction generated between such particles rapidly lead to their aggrega-
tion. However, the interposition of a repulsive barrier having suitable strength and dimensions between the particles can so retard their aggregation that an indefinitely prolonged stability can be achieved for many practical systems. In contrast, lipophilic colloids interact strongly with the continuous phase and are thermodynamically stable. That is, the Gibbs free energy of mixing is negative and the dispersed condition is the preferred lower-energy state.

Table I. Characteristics of free-radical heterogeneous polymerization process [38].

<table>
<thead>
<tr>
<th>Type of polymerization</th>
<th>Continuous phase</th>
<th>Characteristics</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitation</td>
<td>Water, organic liquids</td>
<td>Monomer and initiator soluble in continuous phase; auto-accelerated polymerization due to gel effect</td>
<td>Agglomerated polymer or slurry</td>
</tr>
<tr>
<td>Emulsion</td>
<td>Water</td>
<td>Low monomer solubility, initiator soluble in continuous phase; ionic/non-ionic surfactants; high rates due to radical isolation</td>
<td>Stable latex (0.1-0.3 μm)</td>
</tr>
<tr>
<td>Dispersion</td>
<td>Water</td>
<td>Low monomer solubility, initiator soluble in continuous phase; polymeric surfactants; gel effect</td>
<td>Coarse (0.5-1.0 μm) but stable ‘emulsions’</td>
</tr>
<tr>
<td>Suspension (pearl, bead)</td>
<td>Water</td>
<td>Low monomer solubility, initiator soluble in monomer; low level of ionic surfactant; gel effect</td>
<td>Coarse (&gt;5 μm) suspension in water</td>
</tr>
<tr>
<td>Dispersion</td>
<td>Organic liquids</td>
<td>Monomer and initiator soluble in continuous phase; graft copolymer dispersant; gel effect</td>
<td>Stable latex (0.1-0.3 μm); dispersion up to 5 μm possible</td>
</tr>
</tbody>
</table>
2. 1. 2. History of dispersion polymerization

Dispersion polymerization in organic hydrocarbon media was first developed by Osmond and coworker at ICI [39]. They polymerized acrylic and vinylic monomers in hydrocarbons with oil soluble polymer stabilizers to produce nonaqueous dispersions (NAD) of polymer particles. Later, Almog et al. [40] extended the concept to dispersion polymerization in polar solvents as a method of forming monodisperse polymeric microspheres. Ober et al. [41-43], Tseng et al. [44], Okubo et al. [45], and Paine et al. [46,47], among other authors, studied this technique in order to control particle size and achieve a narrow particle size distribution. A great deal of research has been devoted to dispersion polymerization during past two decades, as reviewed by Croucher and Winnik [48], Guyot and Tauer [49], Cawse [50], Pichot et al. [51], Asua and Schoonbrood [52], and Ito et al. [53-55]. The present article is intended to discuss state-of-the-art design of microspheres obtained by dispersion polymerization, with particular attention paid to the preparation of novel functional particles, the design of microspheres using the macromonomer technique, and to mechanistic aspects for particle size control.

2. 1. 3. Definition of dispersion polymerization

Dispersion polymerization is a technique which permits preparation of polymer particles in the range 1-15 microns in a rapid process with high conversions. In a dispersion polymerization, the continuous phase is chosen to be a solvent for the monomer to be polymerized, and a non-solvent for the resultant polymer. A steric stabilizer is used to produce a colloidally stable dispersion. In the absence of this stabilizer, the polymerization produces macroscopic particles of polymer of an uncontrolled size, and is thus known as precipitation polymerization [56]. Dispersion polymerization is an attractive and promising alternative to other polymerization methods that affords micron-size monodisperse particles in a single batch process. Dispersion polymerization may be defined as a type of precipitation in which one carries out the polymerization of a monomer in the presence of a suitable polymeric
stabilizer soluble in the reaction medium. The solvent selected as the reaction medium is a good solvent for both the monomer and the steric stabilizer polymers, but a non-solvent for the polymer being formed. Dispersion polymerization, therefore, involves a homogeneous solution of monomer(s) with initiator and dispersant, in which sterically stabilized polymer particles are formed by the precipitation of the resulting polymers. As a continuous medium, the properties of the solvent also change with increasing monomer conversion.

2. 1. 4. Essential formulation component

a. Monomers

The monomer must be soluble in the reaction mixture and its polymer insoluble. Many monomer/solvent pairs satisfy these requirements. The number of monomers which have been subjected to detailed research study remains small, however, with styrene and methyl methacrylate (MMA) being studied by far the most common. By contrast, the monomers used in systems of commercial interests are selected from a wide range, including vinyl chloride, vinylidene dichloride [39], hydroxyalkyl acrylates and vinyl esters [57]. A broad range of acrylic monomers has now been utilized for the preparation of dispersions of polymers in organic media. Early work on the dispersion polymerization process employed rubbers which took part in graft copolymer dispersant. The manufacture of dispersions of poly(vinyl acetate) and its copolymers in water by emulsion polymerization is a large, well-established industry having applications in the emulsion paint and adhesives fields. Styrene and its analogues have been the subject of dispersion polymerization by ionic mechanisms but relatively little has been reported for the corresponding free radical process.

b. Solvents

Both polar and non-polar solvents may be used for dispersion polymerization. Whilst the earlier work on dispersion polymerization involved the use of petroleum distillates and other aliphatic hydrocarbons, most of the recent studies have used
polar solvents such as ethanol and methanol [58,59]. There are few examples of true, radically initiated dispersion polymerizations in which water is the sole solvent. In many cases using alcohol solvents, water is added in order to fine tune the solvency, and thus manipulate the particle size, and size distribution, of the product. Some of the earlier reports on “dispersion” polymerization in aqueous media were strictly suspension polymerizations. In one of the few true examples of an aqueous system, Margel and Wiesel [60] polymerized acrolein in water in the presence of a polyglutaraldehyde stabilizer, using either base catalysis or free-radical initiation by gamma rays to give highly monodisperse polyacrolein microspheres of up to 8 μm diameter. A solvent of growing interest for many industrial processes is supercritical carbon dioxide, but CO₂ is incompatible with many common monomers and all polymers except silicones and fluoropolymers. DeDimone et al. [61] prepared a novel fluorinated stabilizer, PFOA, with a molar mass of 2x10⁵ gmol⁻¹:

![PFOA structure](image)

The 1,1-dihyroperfluorooctylacrylate side chain is “CO₂-philic” and the acrylate backbone forms the “anchor” segment. A dispersion polymerization of MMA in supercritical CO₂ using PFOA was effective in producing monodisperse PMMA microspheres with diameters around 2 μm. Table II summarizes some of the systems which have seen studied by dispersion polymerization.
c. Stabilizers

In dispersion polymerization, the polymeric dispersant is normally employed at concentrations which do not exceed a few per cent by weight. It will be apparent that under these conditions the dispersant will tend to exist as loose aggregates in equilibrium with monomers. Dilute solutions of polymeric dispersants do in fact exhibit light scattering effects characteristic of micellar dispersions. In dispersion polymerization, during or immediately following the precipitation of the insoluble dispersed phase polymer, the dispersant becomes adsorbed on the polymer surface. It is clear that a careful balance between the insoluble and the soluble components is necessary if the dispersant is to function efficiently. When the insoluble (or anchor) group is either too small or does not have some specific interaction with the particle.

<table>
<thead>
<tr>
<th>monomer</th>
<th>Stabilizer</th>
<th>Solvent(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrolein</td>
<td>Poly(glutaraldehyde)</td>
<td>Water</td>
</tr>
<tr>
<td>Divinyl benzene</td>
<td>Poly(vinyl pyrrolidone)(PVP)</td>
<td>Acrylonitrile</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Methanol/water</td>
</tr>
<tr>
<td>MMA</td>
<td>PVP</td>
<td>Methanol</td>
</tr>
<tr>
<td></td>
<td>Poly(1,1-dihydro perfluoro-octyl acrylate)</td>
<td>Supercritical CO₂</td>
</tr>
<tr>
<td></td>
<td>Poly(hydroxystearic acid)</td>
<td>Hydrocarbon</td>
</tr>
<tr>
<td></td>
<td>Poly(2-ethyl-2-oxazoline)(PEOX)</td>
<td>Methanol, ethanol</td>
</tr>
<tr>
<td></td>
<td>Polystyrene-b-poly(ethane-co-propene)</td>
<td>n-Heptane</td>
</tr>
<tr>
<td></td>
<td>Polystyrene-b-poly(vinyl alcohol)</td>
<td>Dioxane/water</td>
</tr>
<tr>
<td></td>
<td>Poly(vinylalcohol-co-vinyl acetate)</td>
<td>Methanol</td>
</tr>
<tr>
<td>Styrene</td>
<td>Poly(acrylic acid)(PAA)</td>
<td>Alcohols</td>
</tr>
<tr>
<td></td>
<td>PVP</td>
<td>Ethanol</td>
</tr>
<tr>
<td></td>
<td>PEOX</td>
<td>Alcohols</td>
</tr>
<tr>
<td></td>
<td>Hydroxypropyl cellulose(HPC)</td>
<td>Ethanol</td>
</tr>
<tr>
<td></td>
<td>Poly(acrylamide)</td>
<td>Methoxyethanol</td>
</tr>
<tr>
<td></td>
<td>Polystyrene-b-poly(ethylene oxide)</td>
<td>Methanol</td>
</tr>
<tr>
<td></td>
<td>Polystyrene-b-poly(vinyl alcohol)</td>
<td>Dioxane/water</td>
</tr>
<tr>
<td>Vinyl acetate</td>
<td>Polystyrene-b-poly(ethane-co-propene)</td>
<td>Heptane</td>
</tr>
<tr>
<td></td>
<td>Poly(ethylhexyl methacrylate)-g-Poly(vinyl acetate)</td>
<td>Isooctane</td>
</tr>
</tbody>
</table>
There obvious links between the anchor/soluble balance concept and the hydrophile/lipophile balance (HLB) system for emulsifiers. Obviously the majority of the dispersants employed in non-aqueous dispersion polymerization would have a low HLB value, but such as the minimum anchor size, prevent the straightforward application of the simple HLB system.

As the solvents employed are normally of low dielectric constant, the usual electrostatic stabilization mechanisms do not apply in dispersion polymerization, and steric stabilizers are therefore used. For a material to be an effective stabilizer it must be amphipathic – i.e. contain both “anchor” segment, with an affinity for the final polymer particle surface, and a solvent soluble segment. The types of amphipathic stabilizers which have been used fall into three classes: (1) homopolymers, (2) block and graft copolymers and (3) macromonomers. Compounds from groups (2) and (3) are immediately effective as stabilizers. This is because block and graft polymers already possess the two chemically distinct segments. Homopolymers can be excellent stabilizers, because during the reaction a graft forms via chain transfer from the growing oligomer to the initially present homopolymer stabilizer, thereby producing a graft copolymer [63]. Many of the fundamental studies now being reported use homopolymer stabilizers which are more readily obtainable. Special graft copolymers may be synthesized for dispersion polymerization in non-polar solvents [39]. The macromonomers are able to copolymerize with the principal monomer to rapidly generate graft copolymer species.

2. 1. 5. Procedures

A typical formulation for the preparation of 2 \( \mu \text{m} \) diameter PMMA microspheres using poly(N-vinyl pyrrolidone) (PVP) as the homopolymer stabilizer and sodium dioctyl sulphosuccinate (Aerosol OT100) as co-stabilizer. This formulation uses non-polar solvents [39,64].
Two main types of procedure have been evolved for dispersion polymerization in organic diluents. The first, a single stage or ‘one-shot’ process, utilizes an initially homogeneous solution of reactants in an organic liquid which is polymerized to completion in a single stage. The second, a feed process, involves an initial ‘seed-stage’, in which polymer dispersion at low solids is produced by a ‘one-shot’ process and polymerization is completed by the further addition of reactants to the ‘seed-stage’.

The solvents, stabilizers and surfactants are heated to 70°C under nitrogen with slow mechanical stirring: suitable stirring rates are in the range 10-50 m min⁻¹ at the agitator tip. The initiator and monomer are each added to the reaction vessel in one portion. It is important to establish thermal equilibrium as soon as possible if monodisperse microspheres are to be formed. After 5 min, opalescence begins to develop in the mixture, and after a further 5 min this turns to milkiness as the polymer particles form. The opalescence corresponds with particle nucleation [63]. The reaction is typically continued for 4-24 h to achieve high conversion. Dispersion polymerization continues at a fast rate until the monomer concentration (initially at 50 %) in the continuous phase has fallen to a low level (c. 2-3 %). The work-up procedure depends on the intended use. Coagulum is not generally present but can be filtered off, and distillation may be necessary to remove residual monomer. The particles may be isolated by sedimentation, centrifugation or spray drying.

2. 1. 6. Properties of dispersion

2. 1. 6. 1. General appearance

If left in the dispersion medium, particles exceeding 0.5 μm diameter will typically settle, but on stirring will readily redisperse, notably if the particles are monosized when they have less tendency to pack tightly. The viscosities of such dispersions are naturally affected by the amount of stabilizer, but the viscosity decrease as the proportion of grafted stabilizer increases [65]. The particles formed are almost invariably true spheres, although there are some reports of anomalous shapes [66]:
for example, Winnik has reported [67] raisin-shaped particles from multistage dispersion polymerizations, when crosslinking monomers were used in an earlier stage.

2. 1. 6. 2. Molecular weights of dispersion polymers

The molecular weight of polymers formed in dispersion polymerizations show a number of unusual features. The molecular weight increases with conversion due to a continuous Tromsdorff effect that starts soon after particle nucleation [59]. For preparation of polystyrene in polar solvents such as ethanol systems where a sharp increase in molecular weight during the course of the reaction was observed [59]. This sudden increase in polymerization rate and molecular weight, known as the Tromsdorff effect, is often observed toward the end of a heterogeneous polymerization reaction: In less polar media, monomer preferentially partitions into the solvent leading to the lower molecular weight more characteristic of solution polymerization [68]. For homologous series of alcohol solvents, the molecular weight of polystyrene reaches a minimum at an alcohol chain length of four carbon atoms [69] and the molecular weight.

2. 1. 6. 3. Effect of reaction variables on particle size

The ability to control particle size and size distribution is one of the most distinctive features of dispersion polymerization [70] and has received a great deal of attention. Monodisperse microspheres are of special interest and are very readily made by this process; but for example in the formulation of surface coatings, a broad or bimodal distribution may be desirable in order to achieve high solids contents or particular rheological behavior. The following sections describe the main factors which influence particle size.

a. stabilizer type

Homopolymers are the most thoroughly studied stabilizers. Statistical copolymers have received less attention, partly because of the need for a “blocky” structure in the actual stabilizing species in order to exploit such copolymers as effective stabi-
lizers. Omi et al. [71] prepared styrene-acrylic acid statistical copolymers which were shown to have a bimodal composition distribution, suggesting “blockness”, and these were capable of stabilizing polystyrene microspheres in ethanol/toluene mixtures. Copolymers of greater homogeneity gave more polydisperse particle size distributions. This seems to emphasize the need for separate solubilizing and anchoring blocks on the stabilizer molecule, although polyacrylic acid itself has also been used successfully to prepare near-monodisperse polystyrene particles [58,72].

Homopolymers vary considerably in their stabilizing efficiency, and low efficiency may be linked to low rates of grafting, which sometimes result in over 90% of the original stabilizer being recoverable in an unchanged state after completion of the reaction. Paine estimated that about 1 in 200 polystyrene chains grafts to hydroxypropyl cellulose (HPC) stabilizer [73]. Exceptionally high stabilizer concentrations (at least equal in weight to the polymer produced) have been used in the formation of conductive polyaniline and polypyrrole dispersions [74-76] initiated by redox systems, though even at these levels, long-term colloidal stability is not always achieved.

Certain block copolymers, for example poly(ethylene oxide)-polystyrene triblock copolymers, can form micelles in the suspension medium and this may hinder the production of large particles, since nucleation may occur within the micelle. However, the use of shorter diblocks of the same composition enables micron-sized particles to be prepared [77].

K. Cao et al. [78] used PAA and PVP to stabilize MMA particles. The suitable concentration range is broader than that of PVP because PAA acts as both a dispersant and a surfactant in situ and PVP only as a dispersant. The particle size decreases and the size distribution becomes more monodisperse with dispersant hydrophobicity increasing or if the dispersant has an ion-group.

b. Concentration and molecular weight of stabilizer

El-Aasser et al. [79] obtained the resulting particle sizes increased with decreasing PVP molecular weight at a given concentration. The particle size also increased with decreasing PVP concentration for a given PVP molecular weight. In most cas-
es, the particles prepared with the three types of PVP stabilizers were uniform and the size decreased with increasing molecular weight and concentration of the stabilizer and the viscosity of the continuous phase. Increasing the PVP concentration increase both the rate of adsorption of the stabilizer and the viscosity of the continuous phase resulting in smaller particles. On the other hand, the solution viscosity increases significantly with increasing molecular weight of the stabilizer, leading to smaller particles.

In emulsion polymerization, the effect of increasing the concentration of micelle forming agents is to produce smaller final latex particles. Although the non-aqueous nature of the medium in a dispersion polymerization normally precludes stabilizer micelles forming, an increase in the amount of steric stabilizer nevertheless generally produces smaller particles. Higher concentrations of true stabilizer will enable a larger surface area to be stabilized, and this leads to a larger number of smaller particles: for poly(hydroxystearic acid)-stabilized systems, the true stabilizer is initially present at high concentration with the result that it is usual for small particles to be formed.

For homopolymer stabilizers adsorption as well as chemical anchoring may be important [80]. Paine [81] derived two stabilization models which assumed either a full or partial adsorption of graft polymer, and these both predict an exponent of -0.5 for the power law dependence of particle size on stabilizer concentration. Adsorption alone would give rise to an exponent of -1 [39,81]. The inference for most of these systems is that adsorption is not sole stabilization mechanism. An exception to the general rule of particle size decreasing with increased stabilizer concentration is the polymerization of styrene in aqueous ethanol [58] stabilized by poly(acrylic acid) (PAA), where the particle size passed through a distinct maximum at 4 % PAA (there were similar indications in the work of Tuncel et al. [72]). This system was also unusual in showing no effect of initiator concentration on particle size.

In the case of macromonomomer systems the majority of the stabilizer will be irreversibly bound, providing the reactivity ratios with the principal monomer are favorable. Macromonomers of quite low molar mass (1000-2000 g mol⁻¹), for ex-
ample I, are effective stabilizers [82,83], and can produce stable particles at concentrations as low as 0.2 wt% (relative to monomers) compared to at least 5 wt% for a homopolymer bearing the same repeat unit. By contrast, the 2,3-butadiene central unit in the oxazolin macromonomer II [84], which contains an unsaturated site of low reactivity, is rather inefficient and this compound need to be used at 2-5 wt% to monomer in order to produce a narrow particle size distribution.

$$\text{(I)} \quad \text{H}_2\text{C}=\text{CH}-\bigg[\text{CH}_2\bigg(\text{NCH}_2\text{CH}_2\bigg)^n\bigg]_{\text{C}=\text{O}}^\text{R}$$

$$\text{(II)} \quad \text{HO}^{-}\bigg[\text{CH}_2\text{CH}_2\text{N}^{-}\bigg[\text{CH}_2\bigg(\text{NCH}_2\text{CH}_2\bigg)^n\bigg]_{\text{C}=\text{O}}^\text{R}^{-}\bigg]^{-}\text{OH}$$

Figure I show the effect of the concentration of an oxazolin macromonomer (I with R=Me and molar mass of 1200 g mol\(^{-1}\)) on the diameter of polystyrene particles formed in ethanol/water mixtures. Two points are notable: the macromonomer is effective at low concentrations; and the more hydrophobic the solvent, the smaller are the resultant particles.

The effects of stabilizer molar mass have not often been studied. For the use of PEOX to stabilize particles [85], a molar mass of 500 kg mol\(^{-1}\) PEOX was. For stabilization of polystyrene particles by HPC [83], it was the low viscosity (i.e. low molar mass) grade which gave the more stable dispersions. The predictions of Paine’s grafting models were that the power law dependence of particle size on stabilizer molar mass would lie between the bounds \(-b\) and \((1-2b)/2\), where \(b\) is the exponent relating the radius of gyration to molar mass. For PVP in methanol, \(b\) is 0.32 [81] and the predicted bounds are -0.32 to +0.18. Figure II, for PVP stabiliza-
tion of PMMA particles in methanol [80], shows exponents of -0.25, -0.19 and -0.14 at 2, 4 and 6% PVP which are closer to a Paine’s “full adsorption” model.

Figure 1. Effect of macromonomer concentration on the diameter of polystyrene particles. Macromonomer I (R=CH₃) copolymerized with styrene in ethanol/water mixtures with the following weight ratios of ethanol to water: (●) 90:10; (■) 80:20; (▲) 70:30; [86].
Figure II. Effect of PVP stabilizer molar mass on the diameter of PMMA particles. The initial PVP concentrations were: (●) 2%; (■) 4%; (▲) 6% by weight of total formulation. concentration [80].

c. Co-stabilizers

In El-Aasser’s investigation [66], the influence of the co-stabilizer was stronger for the lower concentrations of PVP. At a PVP K-30 concentration lower than 2 wt%, monodisperse particles could not be obtained without co-stabilizer. The addition of Aliquat 336 not only decreased the particle size, but also improved the monodispersity. On the other hand, with a PVP K-30 concentration of 4 wt%, monodisperse particles could be obtained without co-stabilizer, and the addition of Aliquat 336 only reduced the particle size slightly.

There are several instances in the literature on dispersion polymerization of so-called co-stabilizers being used in addition to the vital polymeric stabilizer [59,66,79,87]. These are low molar mass compounds, often cationic or anionic surfactants, but sometimes comonomers such as 1-vinyl-1-methyl-sila-14-crown-5 [88]. They have been claimed to be necessary for the formation of monodisperse micro-
spheres in some systems. Used alone, they are incapable of generating colloidally stable dispersions. Their mode of action remains obscure and some workers have found them to have no effect: surface analysis of polystyrene particles formed in the presence of PVP and Aerosol OT100 (AOT), an anionic sulphosuccinate, failed to detect any residues of the AOT [86]. Methyl tricapryl ammonium chloride has been used as a cationic co-stabilizer for PMMA and can apparently have no value when the concentration of true stabilizer is low, e.g. at PVP concentrations of less than 2% of the total mixture [66]. Monodisperse particles may then be formed in conditions normally leading to polydispersity. Almog [59] suggested that, in media of high dielectric constant, such as methanol, the limited amount of ionization of the co-stabilizer may be enough to impart electrostatic repulsion during the nucleation phase, thereby limiting aggregation. Later in the reaction, the high molar mass steric stabilizer will tend to displace the low molar mass co-stabilizer, thus accounting for the inability to detect the latter in the final particle surface.

In the styrene/ethanol system, where the use of AOT and other co-stabilizers had also been reported [88], it is clear that monodisperse spheres can be produced without a co-stabilizer and that factor such as the solubility parameter of the medium are more important for determining particle size distribution [72]. More work needs to be done to elucidate the role of co-stabilizers in solvents of varying polarity and in the presence of different types of steric stabilizer.

There are two possible effects if the co-stabilizer: (1) a specific interaction between stabilizer and co-stabilizer which would change the stabilization efficiency of the adsorbed stabilizer, the viscosity of the continuous phase, and the rate of adsorption and the amount adsorbed; and (2) a colloidal stabilization effect brought about by adsorbed co-stabilizer on the surfaces of the nuclei and aggregates. The co-stabilizer may act to stabilize both the nuclei and the mature particles. The co-stabilizer alone was not able to stabilize the particles, and its function was only to reduce the aggregation rate, thereby reducing the resulting particle size [89].

d. Effect of monomer concentration
The initial monomer concentration is important because the particle number is determined very early in the reaction [90]. Increasing the monomer concentration increases the solubility of polymer particle and thus the critical chain length. It also increases the polymerization rate and thus the precipitation rate of the oligomer chains [87].

The final size obtained in a dispersion polymerization normally increases with increasing monomer concentration. This is found to be the case in both hydrocarbon solvents [91] and in polar media [83,92]. In most cases, monomer is a good solvent for its own polymer, and higher molar mass polymer is therefore formed at higher monomer concentrations. More nuclei will form as a result of the faster rate of polymerization and these will be able to grow larger in the presence of the higher monomer levels. The role of monomer is complicated by its co-solvent action, and the solvent phase in a dispersion polymerization must be considered to consist of the added solvent and the unreacted monomer. This leads to a clear difference from emulsion polymerization: the nature of the dispersion medium changes during the course of the reaction. Very significant shifts in polarity may therefore occur, and this can affect both the nucleation of particles and the efficiency of the stabilizer. Some systems exhibit a region of solvent or monomer composition over which coagulation and flocculation occur. On either side of this region, stable suspensions are obtainable. MMA polymerized in aqueous methanol shows an unstable region at 40-60% methanol [85], and MMA also shows anomalous behavior at moderate monomer concentrations in hydrocarbon solvents [63]. Unusually, PMMA polymerized in methanol with PVP K-30 stabilizer shows a minimum particle size at 10 wt% MMA [66]. This seems to be the result of competition between an increased rate of grafting at higher monomer concentrations, which would lead to more efficient stabilization and smaller particle size, and the increased solvency of MMA for its polymer, leading to a larger critical chain length and hence larger particles.

e. Initiator concentration and type
With increasing initiator concentration, the radical concentration increase and thus the concentration of precipitated oligomer chains. Because of this and the slow adsorption of the stabilizer, the aggregation process is enhanced, resulting in larger particles. Moreover, the larger particles are less likely to capture nuclei or oligomer-radicals from the continuous phase simply due to their reduced total surface area and number density. Therefore, particle formation continues and this stage in the polymerization is extended. When this extension exceeds a certain period, the particle size distribution will be significantly broadened. Therefore, it is expected that there exists a maximum concentration of initiator for producing monodisperse particles under given conditions. Furthermore, a higher stabilizer concentration can increase both the adsorption rate of stabilizer and the viscosity of the continuous phase. These would reduce the extent of aggregation, resulting in smaller particles and a shorter particle formation stage. Therefore, the maximum initiator concentration which is able to produce monodisperse particles would increase with increasing stabilizer concentration [66].

The following changes are caused by an increase of initiator concentration: (1) the number of free radicals and thus the concentration of the precipitated oligomeric chains increases; (2) the solubility of graft-stabilizer with shorter PMMA segment in media increase. Meanwhile, an increase of graft-stabilizer level will lead to the formation of smaller particles. The influence of initiator type is that the more active the initiator, the larger the particle size becomes and the narrower the size distribution tends to be. Hattori et al. [93] found that the surface of the particles was not smooth using ammonium persulfate as initiator and did not understand the reason for this. A reason can be shown that the initiator fragments including sulfate and hydroxyl radical may be trapped within the graft-stabilizer chains may be hydrophilic PVP and sulfate radical or hydroxy, respectively. Thus, the graft-copolymer has weaker stabilization because of greater hydrophilicity. On the other hand, hydrogen bonds may be formed between chains of PVP and the hydroxy group, and a network structure (bridging) among the graft-stabilizers may be formed [78].
f. Effects of temperature and reactor geometry

The particle size increases with increasing temperature. An increase in temperature causes an increase in the solubility of the oligomer chains, the rate constant for initiator decomposition ($k_d$), and the rate constant for propagation ($k_p$). These in turn result in the following changes: (1) an increase in the critical chain length; (2) an increase in the concentration of precipitated chains; (3) a decrease in the rates of both physical and anchoring adsorption due to the increase in the solubility of PVP and the decrease in the length of PMMA segments in the PVP-g-PMMA; (4) a decrease in the viscosity of the continuous phase; and (5) an increase in the rate of growth of the existing particles. Therefore, a decrease in the length of the polymer segments with increasing temperature is expected [87].

Because higher temperature leads to a reduced molar mass, this in turn leads to a sustained nucleation period, and hence larger particles, but with a broader particle size distribution [83]. To avoid the troublesome exothermic effects which can be encountered during scale-up [83], it may therefore be necessary to use a stepwise increase in reaction temperature [94].

Dispersion polymerization, unlike emulsion and suspension polymerizations, is generally found to be free effects due to stirring rate and reactor geometry. This is because the ultimate particle size is a product of a solubility controlled nucleation and growth process. It is quite possible for stirred and unstirred reactions alike to give similar particle sizes [91]. However, magnetic stirring appears to give unreliable results [77,94].

2.1.7. Mechanism of particle formation

Figure III is a simplified scheme showing the main steps occurring in a dispersion polymerization. The reaction begins with all components in homogeneous solution. Once polymerization starts, oligomers appear and grow to a critical value of chain length, at which they precipitate from solution to form the particle nuclei. In the polystyrene/methoxyethanol/HPC system, the critical oligomer molar mass lies
between 9 and 35 kg mol\(^{-1}\) [63]. Nuclei have been detected in the MMA/methanol system by dynamic light scattering and have diameters in the region of 25 nm, which corresponds to approximately 200 oligomer chains [80]. The period over which nucleation occurs is known to be short: plots of particle volume versus conversion [65,86] are virtually continuous through the origin. Both self- and aggregative-nucleation may be occurring. Various growth mechanisms have been proposed, each of which may be favored to a greater or lesser degree depending on the formulation. Pain [63] suggests that for small particles, growth proceeds via capture of oligomers with termination in the particle; for large particles, initiation and growth both occur in the solvent phase leading to particle growth by the aggregation of dead polymer. The latter mechanism is prevalent in the dispersion polymerization of some monomers, for example vinylchloride [39].
Figure III. Schematic of particle growth in dispersion polymerization. (a) Homogeneous solution of monomer, initiator and stabilizer. Initiator decomposes to give (b) oligomeric radicals which begin to precipitate once they reach the critical chain length, and grafting with the stabilizer begins. (c) Self-nucleation and aggregation of nascent polymer species. (d) Particle growth by monomer swelling and further polymerization within particles; stabilization via grafted and adsorbed stabilizer. (e) Continued growth may occur by aggregation of dead polymer to give final particles \[39\].
2. 1. 7. 1. The nature of stabilizer grafting

Paine [63] has emphasized the crucial nature of stabilizer in determining the progress of a dispersion polymerization. Using a pyrene-labelled HPC stabilizer in the preparation of polystyrene microspheres, the formation of a graft copolymer was proved by size exclusion chromatography of the HPC retrieved after the reaction. An increase of 55 kg mol\(^{-1}\) in the molar mass of the HPC had occurred, very similar to the molar mass of the polystyrene in the particles (61 kg mol\(^{-1}\)). The HPC could only with difficulty be washed off the particle surface: only those solvents which had solubility parameters close to that of polystyrene (such as ethoxyethanol) were effective in removing the stabilizer without at the same time dissolving the polystyrene particles completely. In this way, about 78% of the labelled stabilizer could be recovered. Good solvents for the HPC moiety (water and polar alcohols) removed less than 5% of the grafted stabilizer. Further proof that the stabilizer was irreversibly grafted came from the fact that when the stabilized particles were dissolved in dioxane (a good solvent for all the components), the addition of methanol (a non-solvent for polystyrene) produced stable polystyrene particles once more. In comparison, when simple mixtures of polystyrene and HPC were treated in this way, coalescence occurred.

The implication of the discussion so far has been that the stabilizer is attached only to the particle surface, but in reality this model does not describe all the cases. For PMMA formed in the presence of a poly(isobutylene-co-isoprene) (PIB) stabilizer, Winnik and co-workers [95] found the PIB to be distributed within the particles. He proposed that an interpenetrating network of PMMA and rubber had formed, leading to micro-domains within the particle. This may be a typical situation where, due to the presence of unsaturation along the stabilizer backbone, branching and further crosslinking of the true stabilizer may continue within the particle. Perhaps representing the more general case, analysis of polystyrene particles indicates that most of the stabilizer, whether PVP [87] or HPC [73], is on the surface. Electron spectroscopy (ESCA or XPS), which probes a depth of about 7.5 nm into the surface, has proved valuable in determining the fraction of the dry par-
ticle surface covered by stabilizer. For polystyrene particles stabilized with PVP [87], the ratio of N$_{1s}$ to O$_{1s}$ peaks was constant, indicating a surface consisting only of polystyrene and PVP; the molar ratio of the vinyl pyrrolidone and styrene repeat units was calculated to be 0.31. This is similar to the values found in XPS studies of the oxazoling macromonomers on polystyrene [86] and PMMA [82,96]. Thus the surface is incompletely covered with the stabilizers. The levels of stabilizer existing within the particle, estimated by first grinding the particles to expose the core, are found to be slow as to suggest that the soluble moiety must continuously be rejected to the surface as the article grows. A further suggestion by Paine was that as the particle grows, new surface area is created and then, together with the unfavourable Gibbs energy of mixing of the underlying and deposited polymers, may lead to a patchy distribution of stabilizer. For PVP, the domains of stabilizer seem to be about 4 nm in depth, and separated by 7-10 nm on the surface.

The relationship between the polymer conversion and the volume of the particles in the dispersion polymerization, the volume was increased linearly with the particle conversion. These indicate that the number of particles is constant from an early stage of the polymerization, and therefore nucleation takes place in this early stage, followed by growth of the nuclei without formation of new particles. The resulting particle size increases gradually, and the size distribution tends to become more monodisperse during the polymerization process. The reason is due to the higher adsorption ability of smaller particles in the particle growth stage. Therefore, monodispersity is only obtained when the initiation and nucleation stage is very short compared with overall time for condensation.

As shown in figure IV, Kawaguchi et al. [97] had stated that the schematic model for the particle nucleation and growth in dispersion polymerization as follows:

1. Before polymerization, the reaction mixture dissolves completely into the continuous phase.

2. When the reaction mixture is heated, free radicals are formed by initiator decomposition and grow in the continuous phase to produce linear oligomer, polymers, and/or graft copolymers. The solubility of these polymers is a function of their mo-
lecular weight and the composition of the graft copolymers. Polymers with a molecular weight larger than a certain critical value precipitate and begin to coagulate to form unstable particles.

3. These particles coagulate on contact, and the coagulation among them continues until sterically-stabilized particles form.

4. This point is referred to as the critical point, and it occurs when all of the particle contain sufficient stabilizer polymer chains in the surface to provide colloidal stability.

5. After this point, no new nuclei or particles are formed and the particles may grow both by the diffusive capture of oligomers and the coagulation of very small unstable particles (nuclei, precursors) produced in the continuous phase and by the polymerization of the monomer included within the particles until all of the monomer is consumed. The total number of such sterically-stabilized particles remains constant so that their size is only a function of the amount of polymer produced.

Figure IV. Schematic model for the particle nucleation and growth of sterically-stabilized particles in dispersion polymerization [97].
2. 1. 8. Kinetics

Once polymer particles have been formed from the initially-homogeneous reaction mixture, they absorb monomer from the diluent phase and polymerization subsequently proceeds within the particles according to the laws of bulk polymerization kinetics. The high viscosity of the monomer-swollen polymer particles greatly hinders radical termination processes and the resulting increase in radical concentration due to the gel effect accelerates the rate of polymerization. The reduction in termination rate also allows the coexistence of many radicals within a single polymer particle. Any polymer radicals initiated in the diluent phase are rapidly swept up by existing particles before they have had time to grow to more than a very few monomer units in length. Consequently, initiation can be considered as taking place as though all the initiator were confined within the particles, even though the types of initiator used are known to be distributed between the polymer particles and the diluent.

A kinetic equation corresponding to this model for dispersion polymerization has been developed in the following manner [98]. If the polymer particles at a given time occupy a volume fraction $V$ of the whole dispersion, and the rate of initiation in the whole dispersion is $R_i$, then the effective initiation rate in the particles will be given by

$$R_{ip} = R_i / V$$

If the monomer concentration in the particles is $c_{mp}$, the overall polymerization rate in the particles, $R_{pp}$, will be equivalent to the usual expression for bulk or solution kinetics in the form

$$R_{pp} = c_{mp} k_p (R_i / k_t)^{1/2} = c_{mp} k_p (R_i / k_t V)^{1/2}$$

Since essentially all polymerization takes place within the particles in the volume fraction $V$, the overall rate in the whole dispersion is

$$R_p = V R_{pp} = c_{mp} k_p (V R_i / k_t)^{1/2}$$
In emulsion polymerization, the concentration of monomer in the polymer particles is usually taken as constant up to the stage in the polymerization where the monomer droplets disappear [99]. In dispersion polymerization, since the monomer is completely miscible with the hydrocarbon diluent, the concentration of monomer in the polymer particles depends on its partition coefficient, $\alpha$, between polymer and diluent. Thus, the overall rate of dispersion polymerization, where $c_{md}$ is the monomer concentration in the diluent, is given by

$$R_p = \alpha c_{md} k_p (V R_i / k_i)^{1/2}$$

(4)

This is the general equation for dispersion polymerization and it takes into account the principal features of the kinetics which have been established [98], such as the proportionality of the polymerization rate to the square root of initiator concentration, the acceleration in rate which follows the increase in the total volume of the polymer particles and the correlation of rate with that in the bulk polymerization of the monomer. It is important to note that the value of $k_p / k_i^{1/2}$ in this expression is not to be taken as constant but varies as the concentration of monomer in the polymer particles changes, in exactly the same manner as in bulk polymerization at high conversions. In principle, the partition coefficient $\alpha$ may also vary with monomer concentration, but the variation is usually not great constant value is a sufficiently good approximation for use in most of the kinetic experiments.

Since direct analytical procedures, such as a measure of monomer consumed or polymer formed, are experimentally complicated to apply to heterogeneous polymerizations, the bulk of the kinetic studies has been carried out with a micro-calorimetric technique developed for following both homogeneous [100] and heterogeneous polymerization processes [98,101].

2.1.9. Applications

Micron-size monodisperse polymeric microspheres are used in a wide variety of applications, such as toners, instrument calibration standards, column packing materials for chromatography, spacers for liquid crystal displays, and bio-medical and...
biochemical analysis. Because of the commercial and scientific interest in these particles, research into their preparation has been active for the past two decades.

Among the main uses for dispersion polymers are surface coatings for metal panels, particularly in the automotive industry [64]. Crosslinked particles made by dispersion polymerization have been suggested as chromatographic media for separating polystyrene molecules with molar masses in the range $10^3$-$10^7$ g mol$^{-1}$ [94], and as spacers for liquid crystal display panels [102]. Dispersion polymerized particles are also used as anti-blocking and slip agents, for instance in photographic films, where stringent image quality requirement make their narrow size distribution and lack of a large particle size “tail” invaluable. Electrophotographic toners are also commonly referred to in patents: improved uniformity of the toner pigment is claimed when the dispersion polymerization is carried out in the presence of the pigment.

2.2. Electroless plating

2.2.1. Introduction

The large volume production of the many varieties of plastics in the last few decades has been accompanied by increased efforts to coat them with metals. This has included the development of techniques for chemical action, vacuum deposition and spray applications. Major markets have arisen for plated products in the mechanical goods industries, and particularly in the auto industry. Efforts to improve gas mileage have compelled replacement of many metal parts with lighter metal-plated plastic counterparts.

The adoption of plated plastics for the data processing and sound recording fields has accompanied a surge in demand for printed circuits, magnetic tapes and similar parts in these industries.

Surface treatments are important in metal deposition on conductive and nonconductive substrates. Technology developed since the mid-sixties has brought about
improved methods for preparing substrate surfaces for deposition, has enhanced chemical bonding of metal film, and has improved the bright finish of the plated article. Chemical conditioning agents that have been introduced since then have made possible the use of a wide spectrum of plastic substrates.

The patent literature presents some sophisticated organic and inorganic materials and techniques for surface treatments, conditioning agents, sensitizers, stabilizers, activators, catalysts and plating bath compositions. Metals involved in the processes include all the usual base metals as well as the noble metals.[103]

Electroless coatings can be divided into three main categories like (i) alloy coatings, (ii) composite coatings and (iii) metallic coatings. Electroless coating technology is credited mainly to Brenner & Riddell (1946) [104]. By the controlled chemical reduction reaction, the electroless coating chemistry has emerged as one of the leading growth areas in surface engineering, metal finishing etc. and is estimated to grow at a rate of beyond fifteen percent per annum, certainly no other chemistry is growing at this rate. Electroless coating has unique physicochemical and mechanical properties for which they are being used increasingly. Some of the properties which render them usable are:
- Uniformity ($\pm$ 2.5)
- Excellent corrosion resistance
- Wear and abrasion resistance
- Solderability
- High hardness
- Amorphous, microcrystalline deposit
- Low coefficient of friction
- High reflectivity
- Resistivity
- Magnetic properties

Most applications of the electroless coating are based on their wear and corrosion resistance. However, the characteristic like luminescence has a great potential in defence and aerospace applications.
2.2.2 Metallizing pretreatments

2.2.2.1 Sensitizing with acid solution of arsenic group metal [103]

G. Bernhardt; U.S. Patent 3,764,488; October 9, 1973; assigned to Dynamit Nobel AG, Germany describes a process whereby plastic articles are sensitized with an acid solution of a trivalent metal of the fifth main group of the Periodic Table, e.g., arsenic, and are thereafter subjected to an electrolytic metalizing step. This process is particularly valuable in the metalizing of metallizable polyvinyl plastics and in metalizing processes in which one conductor layer is to be deposited by reduction from nickel salt solutions while the support electrodes remain free of metal.

Other suitable plastics are chlorinated polyethylene, mixtures of chlorinated polyethylene and polyvinyl chloride, mixtures of polyethylene and chlorinated polyvinyl chlorides, copolymers of vinyl chloride with ethylene as well as graft polymers of vinyl chloride on vinyl chloride copolymers, and also polyolefins, such as polypropylene or poly-4-methyl-pentene-(1), polyester, etc.

As indicated, the procedure is not limited to the plastics particularly referred to but, generally speaking is applicable to metallizable plastics, including such as ABS polymers, i.e., copolymers and graft polymers of the acrylonitrile, butadiene and styrene, containing as a rule 10 to 30% by weight acrylonitrile, 50 to 70% by weight styrene and 8 to 25% by weight butadiene, metallizable polypropylene types consisting for instance of isotactic polypropylene containing relatively large amounts of an ionogenic, conductive filler material such as zinc sulfide, titanium dioxide, barium sulfate, etc., polysulfones, polyacetals, polyesters, polyamides, and others, as well as mixtures of the plastics mentioned.

Mixtures of the above ABS types and polypropylene types with PVC, post-chlorinated PVC, chlorinated polyethylene, chlorinated polypropylene and others are metallizable in this manner. Polyvinyl chloride, modified polyvinyl chloride, or other plastics resistant to chromosulfuric acid can be used as electrode insulating material. In this way coating of the electrode with metal during a travel-through process can be prevented.
The sensitizing solution can contain 0.5 to 40 g/l, preferably 1 to 10 g/l of compounds of the trivalent arsenic, computed on a chemically equivalent basis as $\text{As}_2\text{O}_3$, and possibly additional amounts of 2 to 200 g/l, preferably 4 to 30 g/l of compounds of the tetravalent tin, computed on a chemical equivalency basis as $\text{SnCl}_4$, and 10 to 300 g/l, preferably 50 to 150 g/l of halides and/or nitrates of the ammonium and/or alkali metals and/or alkaline earth metals, preferably ammonium chloride and/or ammonium nitrate. Other Group V metals can replace arsenic in chemically equivalent amounts.

These sensitizing solutions are immediately ready for use, can be applied at room temperature, and remain stable, clear, colorless and free from deposits for weeks. They, therefore, practically do not require any maintenance.

The metalized plastics manufactured by means of this sensitizing solution exhibit a perfectly smooth surface and a good adhesion of the metal coating onto the plastic surface. Percentages denote percent by weight, unless otherwise indicated. Preparation of sensitizing solutions suitable for the travel-through process is described in Examples 1 through 3.

Example 1: These are mixed in the sequence (b) + (c) + (a) and filled with water to 1 liter.
(a) 2.5 g arsenic(III) oxide are dissolved in 20 cc concentrated HCl.
(b) 30 g $\text{SnCl}_4$ are hydrolyzed in 200 cc water.
(c) 60 g $\text{NH}_4\text{Cl}$ are dissolved in 200 cc water.

Example 2: These are added in the sequence (b) + (c) + (a) and filled with water to a volume of 1 liter.
(a) 4 g arsenic(III) oxide are dissolved in 30 cc concentrated HCl.
(b) 15 g $\text{SnCl}_4$ are hydrolyzed in 200 cc water.
(c) 120 g ammonium nitrate are dissolved in 200 cc water.
Example 3: Following mixing in the sequence (b) + (c) + (a), the solution is filled with water to 1 liter.

(a) 15 g arsenic(Ⅲ) oxide are dissolved in 50 cc concentrated HCl.

(b) 15 g SnCl₄ are hydrolyzed in 200 cc water.

(c) 60 g ammonium chloride and 60 g CaCl₂ are dissolved in 200 cc water.

In Examples 1 through 3 one obtains clear, colorless solutions that remain for weeks free from any deposits.

Example 4: As metallizable polyvinyl chloride types one can use the following copolymers of vinyl chloride.

(a) 92% by weight VC, 8% by weight fumaric acid dicetyl ester or 8% by weight maleic acid dicetyl ester.

(b) 89% by weight VC, 11% by weight maleic acid distearyl ester.

(c) 92% by weight VC, 8% by weight acrylic acid stearyl ester.

(d) 86% by weight VC, 14% by weight lauryl vinyl ether.

(e) 96% by weight VC, 4% by weight ethylene (Cl content 50% by weight).

A pressed sheet made of any one of the materials and having the dimensions 4.0” x 9.0” x 0.4” is treated by the travel-through process as follows. It is pickled in chromosulfuric acid (8 g CrO₃ dissolved in 1 liter 60% sulfuric acid) for 10 minutes at 60°C. Following rinsing with water, the plate is dipped into an arsenic-containing sensitizing bath (prepared discretionally according to Examples 1, 2 or 3) for 2 to 5 minutes at 25°C. Following another rinsing with water, the plate is dipped into hydrochloric acid or sulfuric acid-containing palladium salt solution for a period of 2 to 5 minutes (e.g., 0.1 to 0.25 PdCl₂ dissolved in 10 cc concentrated HCl and filled with water to 4 liters) at 25°C.

Following another rinsing, the plate is dipped into a chemical nickel bath contain-
ing 30 g/l NiSO₄·7H₂O and 30 g/l NaH₂PO₄·H₂O at 60°C. Within 3 minutes it becomes completely coated with metallic nickel; the support electrode remains free from metal. The galvanic reinforcing of the metal coating can then be, alternatively, a per se known dull finish plating, high luster copper depositing, high luster nickel depositing or chromium plating. In this example, the sheet is plated with high luster copper plating by a solution containing 255 g/l CuSO₄·5H₂O; 120 g/l H₂SO₄ concentrate and 8 g/l HCl.

The adhesive strength of the metal coating applied in this manner onto the plastic amounts, according to DIN 40,802, to between 6 and 8 kp. Following removal of the galvanized item, the support electrode is dipped briefly into chromosulfuric acid or nitric acid and can then be reused.

2.2.2.2 Thermoplastic Organic polymer [103]

R.A. Cross, A.J. Testa and R.N. Thompson; U.S. Patent 3,775,176; November 27, 1973; assigned to Amicon Corporation describe a process which concerns rendering nonconductive substrates electroplatable by firmly bonding and uniting thereto an electroplate-receptive coating comprising a film-forming thermo-plastic organic polymer and electrically conductive metallic particles having a largest dimension in the range of 0.02 to 50 microns. The solid portion of the coating comprises at least 20% by volume of a film-forming polymer and at least 25% by volume of metallic particles, the coating further having a microporous structure to a depth of at least 1 micron from the exposed surface. This microporous structure has about 40 to 90% open space, with the major portion of the open space being provided by pores with a largest dimension between 0.1 to 15 microns, and with the metallic particles exposed in this microporous structure.

The coating may be applied in any total thickness, so long as it has the microporous structure described at its exposed surfaces. Such coatings are generally applied in thicknesses ranging from 0.1 to 20 mils. Among the useful film-forming water-insoluble thermo-plastic organic polymers forming the coatings are polyvinyl ace-
tate, polyvinyl butyral, polyvinyl alcohols (e.g., high molecular weight or cross-linked), polyvinyl methyl ether, polyvinylidene chloride, polyvinylidene fluoride, water-insoluble divalent salts of carboxy-methylcellulose, polyurethanes, polyacrylonitrile, polysulfones, polyaryl sulfones, polymethyl methacrylate, cellulose acetate and the like.

Other such polymers include various copolymers such as polyvinyl chloride-polyvinyl acetate, polyvinyl chloride-polyacrylonitrile copolymers and the like. For preparing mist of the nonconductive substrates for electroplating, the relatively polar film-forming organic polymers known to the art are entirely satisfactory and indeed advantageously utilized because of the wide selection of solvents in which they can be suitably dissolved.

Among the electrically conductive metallic particles that are useful in the coating are those formed of the metals copper, tin, nickel, silver, iron, lead, cadmium, chrome, zinc, and mixtures and alloys of these with each other, and the like. These electrically conductive particles are characterized by having a ratio of exposed surface area to weight, prior to being incorporated into the coating, of about 500 to 1,500 or more $cm^2/g$, many times the surface area to weight ratio of a spherical particle of equal weight. Preferably the major portions by weight of such particles in the coating have a largest dimension of about 1 to 5 microns.

Preferred methods for providing a microporous coating include evaporation and leaching. According to the evaporation method, a liquid composition is prepared comprising a solution of the film-forming polymer in a suitable solvent (preferably, about 9 to 25% polymer by volume), and metallic particles admixed with the solution. The relative proportions of polymer and metal particles are preferably about 20 to 50 parts (by volume) polymer to about 80 to 50 parts (by volume) particles, based on the total volume of polymer and metal particles.

In accordance with the evaporation process, this liquid composition is applied to the substrate, and the solvent is evaporated at a temperature below its boiling temperature, yet at a rate sufficient to provide a blushed surface on the coating, to a
depth of at least 1 micron. Low boiling solvents (below about 80°C) with substantial vapor pressures (100mm or more) below about 50°C are particularly useful. Although the choice of solvents depends largely, of course, upon the polymer to be dissolved, useful solvents for polar polymers include acetone, methyl acetate, ethyl acetate, tetrahydrofuran, methylene chloride, chloroform, methanol, ethylene dichloride and the like. The above list makes it apparent that a broad spectrum of solvents can be utilized.

In most circumstances the surfaces of the nonconductive materials to be prepared for electroplating will adhere readily to the microporous precoat comprising the conductive fillers. This adherence will in some cases be primarily mechanical, as for example when a rough cement or ceramic substrate is coated. In some situations, however, a chemical or mechanical treatment of the nonconductive surface will assure an optimum bond between the surface and microporous coating applied thereto. In one such case, the pretreatment with chlorosulfonic acid and sulfuric acid of an article of wood-flour-filled phenolic resin substrate sold as BM-5000 (Union Carbide), resulted in increased bonding strength of electroplates, applied according to the procedure by about 20%.

Examples of the substrate materials receptive to such coatings are polystyrene, polymethyl methacrylate, acrylonitrile-butadiene-styrene copolymers, phenolic resins, and polydiallyl phthalate. Moreover, for higher temperature applications, such heterocyclic, nitrogen-containing polymers as polyimides, polyamide copolymers, polyimidazolines, polyimidazoles and polyimidazolones are useful nonconductive polymeric substrates.

2.2.3 Electroless plating pretreatments

2.2.3.1 Catalytic metal applications [103]

A process described by N. Feldstein; U.S. Patent 4,048,354; September 13, 1977 relates to a method for the formation of colloidal catalytic electroless plating com-
positions that comprises admixing a highly stable nonactive colloidal dispersion with an activity modifier. The mixture so formed is used in electroless plating processes wherein a precleaned substrate is contacted with the colloidal catalytic composition, rinsed, contacted with a reducing or activating solution and then contacted with an electroless plating solution.

The process is applicable to the metallic plating of dielectric substrates by autocatalytic or as more commonly known, electroless plating. Such a process produces a wide variety of products varying from printed circuitry arrays, decorative plated plastics parts and magnetic tapes to metalized fibers.

The term hydrous oxide as used herein is intended to encompass the insoluble oxides and insoluble hydroxides of metals. The preferable hydrous oxides are selected from the group consisting of oxides and hydroxides of cobalt, nickel and copper and mixtures. Other suitable hydrous oxides include oxides and hydroxides of precious metals such as palladium, silver and others.

The term stabilizer is intended to encompass substances which alter the characteristics of the colloid so as to prevent, delay or minimize their coagulation and precipitation. It is believed that these stabilizers are adsorbed onto the surface of the colloids thereby altering the surface charge and hence their stability. Stabilizers may include secondary colloids (gelatin), surfactants, sugars and polyalcohols (glycerol).

The term surfactant (or surface active agent) generally refers to substances which are capable of lowering the surface tension of a liquid or the interfacial tension between two liquids. All useful surfactants possess the common feature of a water-soluble (hydrophilic) group attached to an organic (hydrophobic) chain. Surfactants are also intended to encompass detergents and emulsifying agents.

The term reactivity modifier(s) generally refers to substances which while alone are generally inert in the plating process, their presence promotes activation of the otherwise stable colloids in the plating process. Such modifiers may be of organic or inorganic nature as well as combinations thereof.

In general, the electroless plating process comprises the steps of (1) priming a dielectric substrate by contacting the substrate (preferably one which was previously
cleaned and etched to promote adhesion) with an activated colloidal catalytic solution; (2) rinsing the primed substrate and then (3) developing or activating the substrate further by contacting the substrate with a reducing agent (or activating agent) to form a discontinuous layer of the metal either in a reduced oxidation state or in a more activated state, thus forming the catalytic nuclei active for the initiation of the electroless plating and (4) contacting the substrate with a compatible electroless plating bath.

2.2.3.2 Colloidal Tin-Palladium Catalyst [103]

In R.L. Cohen and R.L. Meek; U.S. Patent 4,008,343; February 15, 1977; assigned to Bell Telephone Laboratories Incorporated, a process is described for the electroless deposition of metals on nonmetallic surfaces. The process involves pretreatment of the nonmetallic surface so as to obtain a surface finish suitable for deposition of colloidal sensitizers which catalyze electroless metallic deposition. The nonmetallic surface is then exposed to a colloidal catalyst solution (typically SnCl₂/PdCl₂) followed by an acid rinse. On completion of this surface activation procedure, the surface is exposed to a bath for the electroless deposition of metal. This procedure, which differs from that traditionally used, insures more reliable catalysis for electroless deposition of metals with shorter initiation times and is simpler in procedure and lower in cost. This procedure, for convenience, can be divided into a sequence of parts as follows:
(a) Physical and chemical preconditioning of the surface so as to permit good adhesion of the catalyst and metal plating to the surface;
(b) Application of the colloidal catalyst solution to the prepared surface;
(c) Acid rinse of the surface;
(d) Water rinse to remove the acid rinse; and
(e) Electroless deposition of copper or nickel on the catalytically prepared surface.

A particular procedure for an epoxy surface will serve to illustrate this part of the electroless deposition process. This type of procedure is usually called a swell-etch procedure. Here, a solvent, which is highly absorbed by the surface (e.g., methyl
ethyl ketone, furan), is used to swell the surface. After swelling, an acid-etch solution (e.g., chromium trioxide and sulfuric acid) is used to etch the surface. Generally, the etching step is carried out at elevated temperatures (50 to 100°C) and a water rinse is used between swelling and etching steps and after the etching step.

Electroless metal plating is often used in the fabrication of electronic circuits to electrically connect two conducting paths on opposite surfaces of the circuit board through a hole in the circuit board. Under these circumstances, the preconditioning procedure is usually somewhat different from that used to prepare a nonconducting surface. Where electrical connection is to be effected, the nonconducting surface should be preconditioned and metal surface cleaned to effect good electrical contact with deposited metal. A typical preconditioning procedure used in this instance is outlined below:

(a) The surface to be plated is dipped into a detergent solution such as alkaline buffered phosphate or neutral pH cleaner to remove the oxide on the metal (generally copper) already on the circuit board. The time in which the surface is exposed to the detergent solution may vary over large limits but a time of 2 to 4 minutes is preferred because the benefits of the detergent solution are fully obtained in this time and longer exposure would be wasteful of time. Similar reasons obtain for the preferred times given below. The surface is then washed with water to remove the detergent.

(b) The surface is then exposed to a wetting agent such as alkyl aryl polyether or certain alcohols. This step is often carried out at elevated temperatures, usually between 50 and 100°C. The preferred time of exposure varies between 5 and 15 minutes. The surface is then washed with water to remove the wetting agent.

(c) The surface is then exposed to a solution of ammonium persulfate (generally a concentration of approximately 180 g/l) at a temperature between 25 and 40°C for a time preferably between 1 and 2 minutes. The surface is then washed with water to
remove the ammonium persulfate solution.

(d) The surface is then exposed to a solution of 10% by volume of concentrated sulfuric acid at room temperature for a time preferably between 2 and 4 minutes. The surface is again washed with water.

(e) The surface is then exposed to a solution of 40% by volume of concentrated hydrochloric acid for a time preferably between 2 and 4 minutes. The surface at this point is not washed with water but is directly exposed to the catalyst solution.

After pretreatment of the surface, the surface to be plated is immersed in a colloidal palladium catalyst solution. This catalyst solution may be prepared in a variety of ways, such as in U.S. Patents 3,011,920 and 3,532,518. A particular example of catalyst solution preparation is as follows: 2 g of palladium chloride are dissolved in 200 ml of concentrated hydrochloric acid and 400 ml of pre water. On complete dissolution of the palladium chloride, 4 g of anhydrous stannous chloride are added to the solution. After mixing this first solution, it is added to a second solution containing 96 g of anhydrous stannous chloride, 14 g of sodium stannate and 400 ml of concentrated sulfuric acid. The catalytic properties of this solution may be increased by heating it to 120 to 150°F for about 3 hours.

Particularly important is that the surface exposed to catalytic solution as described above is next washed with an acid solution with pH less than 1.5. Exposure of the treated surface to an aqueous solution (or water) with pH greater than 1.5 should be avoided until after the acid rinse. Various acid solutions may be used, including hydrochloric acid, perchloric acid and nitric acid. A pH of less than 1.0 is preferred because of greater catalytic activity exhibited under these circumstances. Also, hydrochloric acid is generally preferred for a variety of reasons. This acid is used in other solutions used in the process and, therefore, will minimize outside contamination. On evaporation, no residue remains, which minimizes surface contamination. It is low in cost. It maintains the chloride complexing of the tin ions, which probably facilitates their removal. Chloride salts are usually used in this process and use
of a chloride acid minimizes possible complications which might arise from introducing another ion. Rinse times are not especially critical. It is preferred that rinse times be between 1 and 30 minutes. Rinse periods beyond 30 minutes do not usually produce further improvement, and less than 1 minute might leave some areas of the surface with long initiation times for electroless deposition. A time of 3 to 6 minutes has resulted in short, uniform initiation of electroless plating.

It is believed that the beneficial results of this electroless deposition procedure arise from the fact that the postcatalyst acid rinse prevents precipitation of tin compounds which cover the palladium colloidal particles, inhibiting their catalytic effectiveness. These precipitated tin compounds are difficult to remove from the palladium surface.

The surface is exposed to a water rinse to remove soluble and loose substances such as the acid used in the acid rinse. This is done largely to prevent contamination of the electroless metal plating solution. Where contamination might not be a problem, as for example, where the acid used in the rinse is the same as used in the electroless bath, the water rinse might not be required. Typical wash times are 1 to 15 minutes but the times are not critical.

The electroless deposition of copper or nickel is carried out using conventional electroless baths. A typical electroless copper solution contains a copper salt such as copper sulfate, a complexing agent such as disodium ethylenediaminetetracetate, a reducing agent such as formaldehyde, and sufficient base such as alkali-metal hydroxide to obtain a pH of at least 11. Typical concentrations used are: between 0.002 to 0.15 M for the copper salt; from 0.003 to 1 M for the complexing agent; and from 0.02 to 2 M for the reducing agent.

The time that the surface should be exposed to the electroless plating solution may vary over large limits depending generally on plating conditions and thickness desired. Plating times as short as 10 seconds are often sufficient to obtain the required thickness so that electrolytic copper deposition may be used to increase thickness. Times exceeding 1 hour are usually not profitable because the increase in plating obtained in this time range is usually not particularly profitable. Nickel electroless
plating could also be carried out in any conventional manner. Generally, nickel electroless baths contain a nickel solution such as nickel chloride, a reducing agent such as sodium hypophosphite, and citrate ion combined with the nickel.

### 2.2.4 Electrochemistry of electroless plating

#### 2.2.4.1 Electrochemical behavior- Mixed-potential theory [105]

Electroless plating can be explained by a combination of the cathodic deposition of metal and the anodic oxidation of the reductant at the immersion potential $E_{im}$. The partial reactions are written as follows: the cathodic reaction is

$$\text{ML}_{m}^{n+1} + ne^- \rightarrow M + mL \quad (5)$$

and the anodic reaction is

$$\text{Red} \rightarrow \text{Ox} + ne^- \quad (6)$$

where $L$ indicates a ligand, Red a reductant and Ox an oxidant and $n$ is the number of electrons concerned.

A quantitative description of the electroless system is possible on the basis of the current-potential curves for the overall and partial reactions, which are shown in Fig. V. Curve 1 in the figure shows the current-potential curve for the overall reaction.
Figure V. Schematic current-potential curves for a mixed-potential electrode: curve 1, net current; curve 2, partial anodic current; curve 3, partial cathodic current.

The potential where the net current is zero is designated as the mixed potential $E_{pl}$. Curves 2 and 3 show the current-potential curves for the partial anodic ($i_a$) and the partial cathodic ($i_c$) reactions respectively. According to the mixed-potential theory, the net current $i$ is the result of the superposition of the current of the two partial processes:

$$i_n = i_a + i_c$$  \hspace{1cm} (7)

At the mixed potential, $i_a$ equals $i_c$, which corresponds to the rate $i_{pl}$ of electroless plating; thus

$$i_{pl} = i_a = i_c$$  \hspace{1cm} (8)

2.2.4.2 Catalytic aspects in electroless deposition [106]

Electroless deposition proceeds in different ways depending on the nature of sub-
strate in the initial period. In the case of the plating of nonactive metal or plastics, the substrates are activated by depositing palladium particles prior to electroless deposition. On a palladium-activated non-active metal, electroless metal deposition occurs mainly on the substrate in the vicinity of palladium nuclei on the surface in the initial period, where palladium nuclei function as the sites for anodic oxidation of reductants. On the contrary, the electroless deposition on the palladium-activated non-metal substrate takes place on the edge and in the vicinity of palladium nuclei in the initial period. The deposition occurs on the entire surface of non-activated active metal from the initial period, where the entire surface functions as anodic as well as cathodic sites. Besides the nature of the substrate mentioned above, the initial activity of the substrate for electroless deposition depends on many factors, e.g. the size and distribution of palladium nuclei, smudges, impurities, inclusions, grain boundaries, scratches and other surface defects. In all cases, the deposit grows laterally at the edge of the deposit. Since the entire surface of the substrate is covered with depositing metal in any event, the depositing metal itself should have a catalytic activity so that electroless deposition takes place continuously. The mechanism of electroless deposition has always been discussed in connection with the catalytic effect of the depositing metal, since there are many phenomena that suggest a catalytic effect.

1. Electroless deposition occurs selectively on an active surface.
2. A catalysing procedure is necessary for electroless deposition to take place on a nonactive surface such as plastics and ceramics.
3. There is an induction period before the deposition takes place.
4. A limited variety of hydrogen-containing reductants are used in the electroless process, e.g. hypophosphite, formaldehyde, borohydride, dialkylamine borane and hydrazine.
5. A specific combination of metal and reductant is necessary for electroless plating to take place.
6. Electroless deposition usually accompanies hydrogen evolution, the rate of which is not directly related to that of metal deposition. The hydrogen evolved ori-
ginates mainly from the reductant molecule \([107,108]\).

(7) Poisons for hydrogenation catalysts such as thiourea and mercaptobenzothiazole function as stabilizers in an electroless process \([109,110]\). Thus, it seems that all the phenomena are associated with a catalytic process in the anodic oxidation of the reductants. Palladium is frequently used as an activator, of a non-active substrate for electroless plating. However, this does not mean that palladium is a universally active catalyst for anodic oxidation of the reductants. For example, palladium is not so active for the anodic oxidation of formaldehyde in electroless copper deposition. Therefore the rate of electroless copper deposition is very slow in the initial period. Since copper is a very active catalyst for anodic oxidation of formaldehyde, the deposition rate increases with increase in the surface coverage of copper deposited. The catalytic activity of metals can be quantitatively estimated by electrochemical polarization measurements.

2.2.4.3 Method for determination of electroless deposition rate \([111]\)

The method for determination of the rate of electroless plating has been of great interest in connection with the automatic control of the electroless plating bath.

The rate of electroless plating is usually determined by weight gain measurements which are unsuitable for on-line monitoring. Shippey et al.\([112]\) and Dumesic et al.\([113]\) have attempted to make continuous measurements of electroless plating rates by a resistance probe method and an optical absorption method respectively. Recently, Ricco and Martin\([114]\) have presented a new method by using acoustic waves for monitoring the rate of electroless plating. These three methods utilize the changes in physicochemical properties of the respective probes.

According to the electrochemical mechanism of electroless plating \([115-119]\), it should be possible to estimate the deposition rate by an electrochemical polarization measurement such as the Tafel extrapolation or the polarization resistance method. Gabrielli and Raulin\([120]\) suggested that the polarization resistance was related to the rate of electroless nickel deposition. Ohno and coworkers\([121-125]\) have shown that the instantaneous rates of electroless plating of copper, nickel and cobalt can be
estimated by the polarization resistance method.

2.2.4.3.1. Polarization resistance method [121]

The partial anodic and the partial cathodic currents are written in a generalized form as functions of the potential E:

\[ i_a = f(E) \quad (9) \]
\[ i_c = g(E) \quad (10) \]

where E represents the electrode potential, and \( i_a \) and \( i_c \) are partial anodic and cathodic currents respectively.

In the stationary state, the electrode spontaneously exhibits a mixed potential \( E_{mix} \), i.e. the electroless plating potential \( E_{pl} \) such that \( i_a \) is equal to \( i_c \):

\[ f(E_{pl}) = g(E_{pl}) = i_{pl} \quad (11) \]

where \( i_{pl} \) is the rate of electroless deposition. When the electrode is polarized by an external electric source the net current \( i \) is expressed by

\[ i = f(E) - g(E) \quad (12) \]

the expansion of eqn. (12) for a small potential perturbation in the vicinity of the plating potential \( E_{pl} \) yields

\[ \Delta i = \{ f(E_{pl}) + \Delta \eta f'(E_{pl}) + \frac{1}{2} \Delta \eta^2 f'(E_{pl}) + \cdots \} \]
\[ - \{ g(E_{pl}) + \Delta \eta g'(E_{pl}) + \frac{1}{2} \Delta \eta^2 g'(E_{pl}) + \cdots \} \]

\[ (13) \]

where the prime and double prime indicate the first and second derivatives of the functions respectively, and \( \Delta i \) is the net current caused by the polarization due to \( \Delta \eta \). When terms higher than second order are neglected, eqn. (13) reduces to

\[ \Delta i = f(E_{pl}) \left\{ 1 + \Delta \eta \frac{f'(E_{pl})}{f'(E_{pl})} \right\} - g(E_{pl}) \left\{ 1 + \Delta \eta \frac{g'(E_{pl})}{g'(E_{pl})} \right\} \quad (14) \]

Therefore

\[ \frac{1}{R_p} = \left( \frac{\Delta i}{\Delta \eta} \right)_{E=E_{pl}} = i_{pl} \left( \frac{\partial (\ln f(E))}{\partial E} \right)_{E=E_{pl}} - \left( \frac{\partial (\ln g(E))}{\partial E} \right)_{E=E_{pl}} \quad (15) \]

which can be written as
\[
\frac{1}{R_p} = \frac{i_{p1}}{K}
\]  

where \(R_p\) is the polarization resistance at the electroless plating potential and \(K\) is a constant. The terms in square brackets in eqn. (15) are the slopes of the partial polarization curves on a semilogarithmic graph at the electroless plating potential. Equations (15) and (16) give a generalized relation between the polarization resistance and electroless deposition rate and are fundamentally similar to the Stern-Geary \[126\] relation for the corrosion rate. If the slopes of the partial polarization curves are known, it is possible to estimate the rate of electroless deposition from the polarization resistance using eqn. (16). Although true partial polarization curves are not generally obtained in simple polarization experiments, they can be simulated by the polarization curves obtained in electroless plating baths in the absence of either metal ions or reductants under the assumption that the effects of the metal ions and of the reductants are not interdependent as stated in the preceding section.

In eqn. (16), \(K\) should vary depending on the kinetic parameters of the partial electrode reactions. However, as will be seen later, \(K\) is approximately constant for a given plating bath. Therefore it should be possible to estimate the rate of electroless plating from the measurements of polarization resistance.
Fig. VI. Current density-potential relations for low polarizations in electroless cobalt-plating baths (bath composition, 0.10 mol CoSO₄ l⁻¹, 0.20 mol citrate l⁻¹, 0.50 mol H₃BO₃ 3 l⁻¹, with various DEAB concentrations; pH 7.0; 353 K): line a, 0.105 mol DEAB l⁻¹, \( E_{\text{pl}} = -0.834 \) V(SCE); line b, 0.025 mol DEAB l⁻¹, \( E_{\text{pl}} = -0.790 \) V(SCE); line c, 0.013 mol DEAB l⁻¹, \( E_{\text{pl}} = -0.754 \) V (SCE); line d, 0.063 mol DEAB l⁻¹, \( E_{\text{pl}} = -0.714 \) V (SCE).

Figure VI shows, as an example, the polarization curves of cobalt at low applied potentials in an electroless cobalt plating bath of various concentration of reductant. These curves exhibit a linear relation in the potential region of ±8 mV around the immersion potentials. The slope, i.e. the polarization resistance, decreases with increasing concentration of reductant.

Several devices to measure the polarization resistance have been developed and are commercially available for the measurement of the corrosion rate. Some devices work semiautomatically. The coulostatic method adopted by Suzuki et al. [127] is a relaxation method. This method consists of measuring the potential decay after the double layer has been charged at a few coulombs. If diffusion is not involved, the
potential decay obeys the

$$\log \eta_t = \log \eta_0 - \frac{t}{2.3} C_d R_p$$  \hspace{1cm} (17)

where

$$C_d = \frac{q}{\eta_0}$$  \hspace{1cm} (18)

The polarization resistance is obtained from the slope of the log r/, vs. t graph. The solution resistance is automatically eliminated in this measurement. In electroless plating, however, the net log r/, vs. t curve does not follow a linear relation in many cases and the measurement of polarization resistance by this technique is sometimes difficult.
3. EXPERIMENTAL

3.1. Materials

Methyl methacrylate (Junsei Chemical Co. Ltd, Japan), the monomer for polymer core material, was used after purifying it with an inhibitor removal column (Aldrich, USA). 2, 2’-azobis(isobutyronitrile: AIBN) (Aldrich, USA) as an initiator and polyvinylpyrrolidone (PVP K-90) (Canto chemical, Japan) as a stabilizer were used as received. Methanol (99 %; Samchun Chemical, Korea) was used as the media. Tin(II) chloride (SnCl2)(98 %; Aldrich, USA) and palladium(II) chloride (PdCl2)(99.9+ %; Aldrich, USA) were used as the sensitizing and activating materials, respectively. Hydrochloric acid (35 wt. %; Duksan Chemical, Korea) was used without further purification. Silver plating solution was made up of silver nitrate (AgNO3)(Aldrich, USA), sodium hydroxide (NaOH)(Duksan Chemical, Korea), and ammonium hydroxide(NH4OH)(30 %; Junsei Chemical Co. Ltd, Japan). Glucose (Aldrich, USA), L(+)-tartaric acid (Aldrich, USA) and ethyl alcohol (Duksan Chemical, Korea) were used as the reducing agents. In all preparations, distillated and deionized water was used.

3.2. Synthesis of PMMA/Ag hybrid particles

3.2.1. Preparation of PMMA spherical particles

Monodispersed PMMA spherical core particles were synthesized by the dispersion polymerization using a 250ml round bottom flask with a mechanical stirring at 200rpm under nitrogen atmosphere at 60°C [128]. The particle size was controlled by varying the amount of initiator, stabilizer and water [129]. The recipe of the dispersion polymerization of MMA is given in Table 1. The resultant was repeatedly
rinsed off with methanol and DDI water for removing the non-reacted materials.

3.2.2. Chemical treatment of surface of PMMA particles

Silver was coated onto PMMA spheres by electroless silver plating. In order to proceed a plating, the PMMA polymer particles were at first sensitized using an acid SnCl$_2$ solution (0.1 M SnCl$_2$/0.1M HCl) ultrasonically for 60 min. This resulted in the adsorption of Sn$^{2+}$ ions onto all of surface of the parent spheres. Then, the mixture was washed with DDI water and the supernatant was discarded centrifugally. After removal of the excess of Sn$^{2+}$ ions from the solution through cleaning, the Sn$^{2+}$ ion sensitized particles were then immersed into a palladium chloride (PdCl$_2$) hydrochloride acid ($1.0 \times 10^{-3}$ M PdCl$_2$/0.25 M HCl) solution. A surface redox reaction occurred, involving the oxidation of Sn$^{2+}$ to Sn$^{4+}$ and the reduction of the Pd$^{2+}$ to Pd. This step resulted in creating nanoscopic metallic Pd particles as catalytic sites on the surface of PMMA particles. The Pd-modified particles were rinsed again using DDI water and introduced into an electroless plating solution bath.

3.2.3. Synthesis of PMMA/Ag hybrid particles using electroless silver plating

The silver plating process was carried out using the same process as Brashear et al. did [130]. The first ions of silver, which were reduced, aggregate on the polymer surface to form the nuclei. The onset of this process was indicated by the appearance of hydrogen bubbles. The deposition process can continue after the catalytic sites are coated with silver because it is also a catalyst for the reaction. Subsequently, silver deposition continues automatically. Finally, the product was separated by centrifugation and washed twice with de-ionized water.
3.2.3.1 Optimum condition for the electroless silver plating on PMMA particles

In order to obtain the best condition for electroless Ag plating, the effects of the variables such as 1) plating solution concentration, 2) activation condition, 3) reaction time, 4) reaction temperature were studied. The variables are given in Table 2.

3.2.3.2 Electrical resistivity of the monodisperse PMMA/Ag hybrid particles

In order to investigate the relationship between the silver content or particle size and electrical resistivity, various sizes of PMMA (2.17, 4.36, 7.03 μm) were prepared by using dispersion polymerization. Then, the silver coating onto the PMMA particles was carried out using the same electroless silver plating procedures as did in the previous section.

3.3. Characterizations

Study of the surface morphology of PMMA/Ag hybrid particles was performed by the field emission scanning electron microscopy (FE-SEM, Hitach S-4300). Particle size analyzer (PSA, Beckman Coulter LS230) was used to measure the weight-average diameter (Dw) and distribution of the particles size. Cross-sectional morphology of PMMA/Ag hybrid particles was observed by using the field emission transmission electron microscopy (FE-TEM, Jeol JEM 2100F). The sample was prepared by cutting to a width of approximately 70 nm using ultramicrotome (UTM, MTX) on the copper grid. The structure of the hybrid particles was analyzed using an X-ray diffractometer (XRD, RIGAKU). The content of silver in the PMMA/Ag hybrid particles and the simple mechanical mixtures of PMMA/Ag were measured using a thermogravimetric analysis (TGA, TA Q50) at a heating rate of 20°C/min from 0 to 700°C under nitrogen atmosphere. The resistivity of the hybrid particles
was measured by 4-point probe resistivity meter (Mitsubishi chemical) and high resistivity meter (Mitsubishi chemical). The dried hybrid particles were flattened as a form of 1mm film for resistivity measurement. The specimens were prepared using a hot press at 110°C for 5 minutes under pressure of 100kgf.
Table 1. Recipe used in the dispersion polymerization

<table>
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<th></th>
<th>MMA (wt %)</th>
<th>Initiator AIBN (wt %)</th>
<th>Stabilizer PVP (K-90) (wt %)</th>
<th>Medium (wt %)</th>
<th>RPM</th>
<th>Temperature (°C)</th>
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Table 2. The variables for Ag electroless plating

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<th>Plating temperature (°C)</th>
<th>Plating time (minutes)</th>
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<tr>
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<tr>
<td></td>
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<td>60</td>
</tr>
<tr>
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</tr>
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4. Results and discussion

4.1 Optimum condition for the electroless silver plating on PMMA particles

4.1.1. Preparation of monodisperse PMMA spherical particles using dispersion polymerization

Monodisperse PMMA spherical particles were prepared using the method described in the experimental section and the FE-SEM photograph and PSA data were drawn in Figure 1. As seen in this figure, the particle sizes were monodisperse and the average particle size was 5.05 μm. Size distribution (Cv) was 6.7 %, which was fairly monodisperse. These particles were used for the Ag electroless plating as prepared.

4.1.2. The effect of the plating solution concentration

In order to verify the effect of the quantity of silver ions on the formation of PMMA/Ag composites, AgNO$_3$ concentration were varied in the order of 0.01, 0.03, 0.05, 0.07, 0.10 and 0.15M. In this case, 1g of 5.05 μm PMMA particles were used and reaction was carried out at 25°C during 1hour. Figure 2 showed the FE-SEM images indicating the effect of the AgNO$_3$ concentration. It was obvious that the silver nanoparticles were proportionally deposited on the PMMA surface. However, the silver coating was not smooth or evenly thin, but rough when low concentration of AgNO$_3$ solution was used, resulting in forming island-type silver layer on PMMA surface. Thus, the higher the AgNO$_3$ concentration up to 0.1M, the thicker the uninformed silver layer was obtained. It has been demonstrated that solution concentration was crucial for the formation of continuous silver shell.
FE-TEM images of the above PMMA/Ag hybrid particles were shown in Figure 3, representing the island-type or core/shell type of the composite was prepared.

The reduced silver content was analyzed using TGA in Figure 4(a). In this figure, the silver content increased from 7.96 to 39.92 wt% with the concentration of AgNO\(_3\) solutions from 0.01 to 0.15M, respectively. The higher the AgNO\(_3\) concentration, the higher the resultant silver content was obtained. Thus, silver loading on the PMMA particles increased proportionally to the concentration of plating solution. However the silver content data observed from TGA did not exactly indicate the plated content, because as seen in Figure 2(d) or 2(f), some of silver were left on the coated surface as agglomerate.

4.1.3. **The effect of the activation condition**

The PdCl\(_2\) concentration was varied when the activation step was carried out using the PMMA particles. Figure 5 is the FE-SEM images indicating the effect of the activation condition of (a) 0.5mM, (b) 1.0mM and (c) 1.5mM. The electroless plating was carried out using the same experimental conditions as did in the previous part. As seen in Figure 5, the silver ions were successfully reduced on the PMMA particles when the 0.10mM of PdCl\(_2\) solution was used. The reduction reaction of Ag ions did not properly conducted under the concentration of 0.1mM PdCl\(_2\), and over that concentration, metallic silver particles were roughly coated around the PMMA particles. This can be explained that some silver ions cannot be reduced on the PMMA particle if the lack of palladium on the PMMA surface which the reduction site of silver ion. On the other hand, if there is too much palladium on the PMMA particles, silver shell will be roughly formed because of the dense site of the initial reduction.

FE-TEM images of the above PMMA/Ag hybrid particles were shown in Figure 6. It indicated the same results as did in the above FE-SEM images in Figure 3.
The TGA measurement was performed in order to obtain silver content and the result was shown as a function of PdCl$_2$ concentration in Figure 7. Silver content of PMMA/Ag hybrid particles slightly increased from 33.57 to 38.34 wt% with the concentration of PdCl$_2$ solution from 0.5 to 1.5mM, respectively.

4.1.4. The effect of the reaction temperature

The effects of the reaction temperature of the electroless silver plating were studied. Figure 8 represents the FE-SEM images of PMMA particles plated at (a) 0°C, (b) 20°C and (c) 50°C, respectively. Most of PMMA particles are fully covered with silver shell irrespective of reaction temperature. However, the surfaces of PMMA/Ag hybrid particles plated at 50°C were rough and some particles were not plated because of fast reduction rate.

Figure 9 is the FE-TEM images showing the effects of reaction temperature. The FE-TEM images seemed to be similar among (a) to (c). However, the shell of hybrid particles plated at 50°C (Figure 9(c)) was a little rough and thick. Nonetheless, TGA data drawn in Figure 10 show the lowest silver content of the hybrid particles plated at 50°C. It may seem that some of PMMA particles were not plated with silver and some were plated thick and roughly. Thus, The PMMA/Ag hybrid particles had the highest silver loading when the reaction was implemented at 20°C.

4.1.5. The effect of the reaction time

In order to study the influence of reaction time on the electroless silver plating, plating was carried out for various durations. Figure 11 represents the FE-SEM images of PMMA/Ag hybrid particles plated upon various plating times; (a) 30min, (b) 60min, (c) 120min and (d) 720minutes, respectively. In this figure, the electroless silver plating was not implemented properly, except the Figure 11(b). Only the hybrid particles plated for 60minutes were fully covered with silver, the others were partially plated or not. The core/shell structures of the PMMA/Ag hybrid particles
using FE-TEM images were shown in Figure 12. It also showed that the best reaction time for fabricating the hybrid particles covered with uniform silver shell was for 60 minutes.

The silver content of the hybrid particles upon plating duration was plotted in Figure 13. Silver content was increased until 38.63 wt% during 60 minutes and then, slightly decreased to 35.37 wt%. It is because that the reduction of Ag ions on the surface of PMMA particles continuously progress until 60 minutes and after that, metallic silver particles were detached from the surface of PMMA particles because of the strong alkaline condition.
Figure 1. (a) FE-SEM photograph of the PMMA spherical particles synthesized using the dispersion polymerization used as the core particles; 5.05 μm. (b) PSA data of the synthesized PMMA particles corresponding to (a).
Figure 2. FE-SEM images of 5.05 μm PMMA/Ag hybrid particles plated upon various AgNO₃ concentrations; (a) 0.01, (b) 0.03, (c) 0.05, (d) 0.07, (e) 0.10, (f) 0.15 M, respectively.
Figure 3. FE-TEM images of 5.05 μm PMMA/Ag hybrid particles plated upon various AgNO$_3$ concentrations; (a) 0.01, (b) 0.03, (c) 0.05, (d) 0.07, (e) 0.10, (f) 0.15 M, respectively.
Figure 4(a) TGA curve indicating a weight loss of the PMMA/Ag hybrid particles according to the plating solution concentrations; line a to line f corresponding to the samples a to h shown in Figure 2, respectively. (b) Silver content of PMMA/Ag hybrid particles according to the plating solution concentrations. Error bar means the experimental data.
Figure 5. FE-SEM images of 5.05 μm PMMA/Ag hybrid particles pretreated upon various activation conditions; (a) 0.5, (b) 1.0, (c) 1.5mM of PdCl₂ acid solution, respectively.
Figure 6. FE-TEM images of 5.05 μm PMMA/Ag hybrid particles pretreated upon various activation conditions; (a) 0.5, (b) 1.0, (c) 1.5mM of PdCl₂ acid solution, respectively.
Figure 7. Silver content of PMMA/Ag hybrid particles according to the PdCl$_2$ concentrations.
Figure 8. FE-SEM images of 5.05 μm PMMA/Ag hybrid particles plated upon various plating temperature; (a) 0°C, (b) 20°C, (c) 50°C, respectively.
Figure 9. FE-TEM images of 5.05 μm PMMA/Ag hybrid particles plated upon various plating temperature; (a) 0°C, (b) 20°C, (c) 50°C, respectively.
Figure 10. Silver content of PMMA/Ag hybrid particles according to the plating temperature.
Figure 11. FE-SEM images of 5.05 μm PMMA/Ag hybrid particles plated upon various plating times; (a) 30, (b) 60, (c) 120, (d) 720 minutes, respectively.
Figure 12. FE-TEM images of 5.05 μm PMMA/Ag hybrid particles plated upon various plating times; (a) 30, (b) 60, (c) 120, (d) 720 minutes, respectively.
Figure 13. Silver content of PMMA/Ag hybrid particles according to the plating time.
4.2 electrical resistivity of the monodisperse PMMA/Ag hybrid particles

4.2.1. Preparation of various sizes of monodispersed PMMA particles using dispersion polymerization

Figures 14(a), 14(b) and 14(c) represent the FE-SEM images of the various sizes of PMMA spheres synthesized using the dispersion polymerization. The PSA data shown in Figures 14(a’), 14(b’) and 14(c’) indicated that the particle sizes were monodisperse and the average particle sizes were 2.17, 4.36, 7.03 μm, respectively. Size distribution (Cv) of each particle was 8.1, 6.4 and 8.5 %, which was fairly monodisperse. The weight-average molecular weight was 127,000 g/mol, 193,000 g/mol and 139,000 g/mol and the molecular weight distribution (PDI) was 2.7, 3.1 and 2.9, respectively.

4.2.2. Synthesis of PMMA/Ag hybrid particles

2.2 μm of PMMA particles were used as cores and shown in Figure 15(a). Figures 15(b)–15(h) represent the FE-SEM images of the hybrid particles prepared from the monodisperse 2.2 μm PMMA spheres and various concentrations of AgNO₃ solution listed in Table 3. It was obvious that the silver nanoparticles were proportionally deposited on the PMMA surface to the concentration of AgNO₃ solution. The same behavior was observed for 4.4 μm PMMA particles in Figures 15(a’) ~ 15(h’) and 7.0 μm PMMA particles in Figures 15(a”’) ~ 15(h”’), respectively. It is clear that the silver coating on the surface of 4.4 and 7.0 μm PMMA particles was successfully conducted. However, the silver coating was not smooth or evenly thin, but rough when low concentration of AgNO₃ solution was used, resulting in forming island-type silver layer on PMMA surface. Thus, the higher the AgNO₃ concentra-
tion, the thicker the uniformed silver layer was obtained. In addition, for a given concentration of plating solution and amount of PMMA particles, the larger the PMMA particle size, the better and smoother silver coating was obtained due to the smaller total surface area.

XRD analysis provided further information about the structure of hybrid particles as seen in Figure 16. In the pattern, four diffraction peaks at $2\theta = 38.26^\circ$, $44.47^\circ$, $64.71^\circ$ and $77.74^\circ$ represent the (111), (200), (220) and (311) planes of the face-centered-cubic structure of metallic silver, respectively. It indicated that silver nanoparticles were successfully attached on the surface of the PMMA particles. No diffraction peak characteristics of Ag$_2$O or AgO was observed in the prepared sample, which suggests that the amount of silver oxide in the sample be essentially negligible and hence that the synthesized silver nanoparticles be stable in air.

In order to analyze the formation of silver shell on PMMA particles, TEM measurements were performed and the representative FE-TEM images were shown in Figures 17(a), 17(b) and 17(c) for 2.2, 4.4, and 7.0 $\mu$m cross section morphology of the Ag-coated PMMA particles, respectively. It was reported that the electroless plating of the metal would occur primarily by the autocatalysis of palladium existing on the particle surfaces [2]. Because the Pd particles exist sparsely on core surfaces, silver particles initially do not fully cover the particle surfaces. However, small metal particles grow and coalesce with one another upon the increased concentration of silver ions, resulting in thick deposition of the metal shell.

The thermal stability and the contents of silver loading on the surface of the hybrid particles were measured using the various sizes of PMMA/Ag hybrid particles coated with various concentrations of AgNO$_3$ solution under nitrogen atmosphere. The analysis was performed using the TGA weight loss curves and remainder content at 700°C in each specimen was shown in Figure 18. The results showed similar trend; the higher the concentration of plating solution, the higher loading of silver was observed, and the increased silver loading lead to the relatively good thermal stability and reduced decomposition. However, silver content was not greatly differ-
ent upon the core size. Silver loading on the 2.17 μm particles increased proportionally to the concentration of plating solution, but it did not apply to the larger particles, 4.4 and 7.0 μm. It can be explained that more Ag ions were reduced on the core particles because the surface of small particles still exist lots of spots for coating. However, the surface of large particles was already filled with metallic silver at the same plating condition. Thus, the larger the particle size, the lower the concentration of the plating solution was required for the dense coating on the PMMA surface. Therefore, each particle size has optimum or minimum plating concentration in order to have proper thickness of shell with Ag nanoparticles, and reduction efficiency of Ag ions on the PMMA surfaces was worse above this concentration.

4.2.3. Comparison of electrical conductivity

The electrical resistance of the synthesized PMMA/Ag hybrid particles was plotted as a function of silver content obtained from TGA measurements in Figures 19. For the comparison of the resistance of the hybrid particles upon silver content, that of a simple mixture of PMMA particles and Ag nanoparticles was also measured. In the case of a simple mixture shown as a dotted line, the electrical resistivity (1.53e5 Ω·cm) of the simple mixture of 40 wt% 2.2 μm PMMA and 60 wt% silver was not effectively improved compared to that of pure silver (1.6e-6 Ω·cm) [131]. Furthermore, for 4.4 or 7.0 μm PMMA particles, no significant difference in resistance at low content of silver (15 wt%) was obtained, but the noticeable decrease in resistance (297.25Ω·cm, 117.71 Ω·cm) at 60 wt% silver was obtained, respectively. Moreover, formulation of the simple mixture with more than 60 wt% silver was not easy because the viscosity was dramatically increased due to the large surface area of silver nanoparticles.
On the other hand, the resistance of hybrid particles (solid line) showed different manner from that of the simple mixtures (dotted line in Figure 19). It showed a very high resistance $10^{13} \sim 10^{14} \, \Omega \cdot \text{cm}$ at 5 wt% silver due to the lack of silver to be coated on the PMMA surface and $10^7 \sim 10^{10} \, \Omega \cdot \text{cm}$ at 10~20 wt% silver content. Whereas, the resistance was drastically dropped to $10^{-1} \, \Omega \cdot \text{cm}$ with at 25 wt% silver content. Moreover, the electrical resistivity of hybrid particles reduced from $10^{-1}$ to $10^{-4} \, \Omega \cdot \text{cm}$ between 30 and 60 wt% silver content regardless of the particle size. This might be the percolation threshold effect, which predicts that no conduction occurs until one complete conductive path of particles is created across the sample [132].

The effect of the core size on the electrical resistivity was also studied in hybrid particles. Moreover, the larger the core size, the lower the electrical resistivity was obtained at lower content of silver, but the difference in the electrical resistivity between the polymer particle sizes was trivial over the threshold (30wt%). Jing et al. reported that the smaller the conductive particle size, the lower the threshold was obtained in the polymer matrix filled with conductive particles, [27].

Figure 20 proposed the schematic representation of two different models, simple mixtures of PMMA spheres and silver nanoparticles, and PMMA/Ag hybrid particles, with same silver content. As seen in Figure 20(a), it was difficult to design complete conductive pathway in the simple mixtures since the silver nanoparticles were randomly and heterogeneously dispersed in the PMMA particle matrix. As a result, the resistivity of silver particles did not influence that of the polymer matrix, showing a relatively high value of the resistivity. In contrast to the simple mixtures, PMMA/Ag hybrid particles, closely contacted and continuously connected each other due to the core/shell type, resulted in the formation of conductive pathway at certain content of silver. In this study, the electrical resistivity dramatically decreased with relatively small content of silver at 30 wt%, which is the percolation threshold.
The electrons influencing the electrical resistivity migrate through the silver shell and the size of silver nanoparticles that forms silver shell of the hybrid particle is almost constant irrespective of the core size. As a result, since electrons only migrate through the silver shell, the core particle size does not affect the resistivity.
Table 3 condition of electroless silver plating bath for each size of PMMA particle

<table>
<thead>
<tr>
<th>Samples</th>
<th>Concentration of plating solution (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0\textsuperscript{a}</td>
</tr>
<tr>
<td>b</td>
<td>0.01</td>
</tr>
<tr>
<td>c</td>
<td>0.03</td>
</tr>
<tr>
<td>d</td>
<td>0.05</td>
</tr>
<tr>
<td>e</td>
<td>0.07</td>
</tr>
<tr>
<td>f</td>
<td>0.1</td>
</tr>
<tr>
<td>g</td>
<td>0.15</td>
</tr>
<tr>
<td>h</td>
<td>0.2</td>
</tr>
</tbody>
</table>

\textsuperscript{a} bare PMMA particles
\textsuperscript{b} other plating condition were same for each sample.
Figure 14. FE-SEM photographs of the PMMA spherical particles synthesized using the dispersion polymerization used as the core particles; (a) 2.17 (b) 4.36 (c) 7.03 μm. (a’), (b’) and (c’) are the PSA data of the synthesized PMMA particles corresponding to (a), (b) and (c), respectively.
Fig. 15. FE-SEM image of (a) 2.17, (a’) 4.36, and (a”) 7.03 μm PMMA particles and PMMA/Ag hybrid particles plated upon various AgNO3 concentrations; (b), (b’) and (b’’) 0.01, (c), (c’) and (c’’) 0.03, (d), (d’) and (d’’) 0.05, (e), (e’) and (e’’) 0.07, (f), (f’) and (f’’) 0.10, (g), (g’) and (g’’) 0.15, (h), (h’) and (h’’) 0.20 M, respectively.
Figure 16. XRD patterns of PMMA particles taken after deposition of silver. The peaks correspond to Ag peaks.
Figure 17. Representative of FE-TEM images of PMMA/Ag hybrid particles; (a) 2.2 μm, (b) 4.4 μm, (c) 7.0 μm.
Figure 18. Silver content of PMMA/Ag hybrid particles according to the plating solution concentrations: 2.2 μm (■), 4.4 μm (▲), 7.0 μm (●).
Figure 19. Resistivity of PMMA/Ag hybrid particles as function of silver content (solid line) and random mixture of PMMA particles and Ag nanoparticles (dash line); 2.2 μm (■), 4.4 μm (▲), 7.0 μm (●).
Figure 20. Schematic representative of (a) simple mixtures of PMMA spheres and silver nanoparticles, (b) PMMA/Ag hybrid particles with contents of silver.
5. CONCLUSION

In Chapter I, for the fabrication of poly(methyl methacrylate)/silver hybrid particles, optimum conditions for the electroless silver plating were studied. The thickness of the silver shell was proportional to the concentration of plating solution. However, when 0.15M of silver nitrate solution was used, overdose of silver particle with rough surface was obtained. Concentration of palladium dichloride had an important effect on the plating; particles with the softest surface were obtained when 0.1mM of PdCl$_2$ solution was used. Reaction temperature had little effect on surface morphology, but the highest electric conductivity was achieved under room temperature. Since room temperature does not require additional heating or cooling process, it is the most appropriate reaction temperature. The plating process was complete after about 1hr, and if it kept longer, low plating efficiency was observed. Overall, the optimum condition of preparing conductive hybrid particle with soft surface morphology is as following; activation with 0.1mM PdCl$_2$ solution followed by 1hr electroless plating under room temperature with 0.1M plating solution.

In Chapter II, monodispersed PMMA core particles with sizes of 2.17-7.03 $\mu$m were prepared by the dispersion polymerization, and PMMA/silver hybrid particles were prepared by adding 5 ~ 60 wt% silver using the electroless plating technique. Then, the electrical resistivity of the PMMA/Ag hybrid particles and the simple mixtures of PMMA spheres and silver nanoparticles were measured using 4-point probe resistivity meter. From 0 to 30 wt% silver content, the electrical resistivity of hybrid particles drastically dropped to $10^{-1}$ $\Omega \cdot cm$. With more than 30wt% silver content, the electrical resistivity gradually reduced to $10^{-4}$ $\Omega \cdot cm$, and the PMMA particle size barely influenced the resistivity. Thus, the percolation threshold was observed at 30 wt% silver content. On the other hand, the electrical resistivity of the simple mixtures linearly decreased with increasing silver content, resulting in no percolation threshold was observed.
6. REFERENCES

[64] D. J. Walbridge in ref. 1, Vol. 4, Ch. 15, pp 243-260.