

Synthesis and Characterization of Styrenic-Based Polymerized Toner and Its Composite for Electrophotographic Printing

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ABSTRACT: Suspension polymerization in an aqueous medium was applied to the syntheses of styrenic-based polymerized toner particles. Poly(vinyl alcohol) and benzoyl peroxide were used as a dispersant and an initiator, respectively. The resulting polymerized toners were found to be smooth on their spherical surfaces, and the particle sizes were 4–10 μm with a coefficient of variation of 20–30%. In most cases, a correlation between small particle sizes with high weight-average molecular weights was observed. The glass-transition temperature (T_g) of the polymerized toner could be controlled by the molar ratio of the comonomer between styrene and *n*-butyl acrylate (nBA). T_g decreased when the content of nBA in copolymer increased, due to its rubbery state along with the increasing carbon black feed level, because the surface functional groups of the carbon

black pigment inhibited the rate of polymerization and decreased the molecular weight of the resulting polymerized toners. The T_g 's of the resulting polymerized toners were 66–70°C. Triboelectricity [the charge-to-mass ratio (q/m)] of the resulting polymerized toners was 7–20 μCg^{-1} in the presence of borobis(1,1-diphenyl-1-oxo-acetyl)potassium salt. An analysis of print quality showed high background fog, low maximum density, and a small amount of image raggedness. The print result correlated with the q/m values. This article elucidates the polymerization technique, charging properties, and image qualities. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 238–248, 2003

Key words: polystyrene; composite; polymerized toner; particle size distribution

INTRODUCTION

Polymerized toners have attracted much attention recently because the demand for fine imaging and high resolution with uniformity in electrophotography has increased ever since full-color copiers and printers that use electrophotographic systems were introduced. To achieve high-resolution images in electrophotography, the processes and materials involved in electrophotography must be improved. The enhancement of image quality requires that toners have a very small particle size within a narrow size distribution to produce better print images with higher resolution and less edge roughness. Smaller particle sizes together with uniform size distribution make it possible to impart a much more even charge on the particles, which becomes easier to control within the machine as they are transferred onto the paper. Thus, the particle size and size distribution are important parameters strongly influencing the quality of toners.

Conventionally, most toners are currently produced by a pulverization method in which charge control

agents (CCAs), colorants, modifiers, and other additives are dispersed in a molten toner resin matrix, followed by cooling, crushing, pulverization, and classification of the pulverized material to separate toner particles with the intended particle size. This method results in toners with a relatively wide size distribution. These toner particles are frequently significantly larger or smaller than average and also have an irregular shape. The irregular size and shape of the toner particles make it difficult to put a uniform charge on them. Without a uniform charge, toner particles become very difficult to control in the machine, and dusting can occur. Additionally, low toner yield in either the development or transfer stage can be obtained, which results in void areas during printing. Also, toner particles outside of the size specification must often be discarded, increasing waste and reducing manufacturing yields. The production cost thus has a sharp increase in the energy needed for pulverization and a decrease in collection efficiency during classification. Finally, with this pulverization method, it is extremely difficult to uniformly disperse solid fine particles, such as a magnetic powder or colorant, in a resin. This insufficient dispersion can cause increased fogging, lower image density, lower toner color-mixing characteristics, and lower transparency. A colorant that is uncovered on the cleavage surface of the toner

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may cause variation in the development characteristics of the toner.¹

As a solution for overcoming this problem, the production of toner with a polymerization method is attractive. The selection of the polymerization method depends on the expected performance for the toner particles. With the dispersion polymerization method, it is easy to synthesize particles with an average particle size of 7 μm or less and a narrow particle size distribution, but it is difficult to retain inner additives inside each particle. Toner particles produced through the emulsion polymerization method generally have particle sizes on a submicrometer scale or smaller. In addition, polymer particles from this method must be increased to the actual size of commercially used toner because the emulsion-type particles are in the range of hundreds of nanometers. In the emulsion polymerization method, there are two methods for growing the particles. One is a seed polymerization method, and the other is a coagulation method, both of which are rather complicated and require numerous time-consuming reaction steps and procedures.²

To obtain uniformity of toner particles with a small size, a good pigment and additive dispersion in the binder resin are necessary. Suspension polymerization is a process that overcomes the aforementioned problems because of the simplicity of the reaction process and equipment. With this method, toner particles are directly formed by the polymerization of a monomer droplet in an aqueous medium. The properties of the resulting polymerized toner can be controlled by variation of the monomer types and polymerization conditions.

In this study, the synthesis of a styrenic-based polymerized toner by the suspension polymerization for electrophotographic printing was performed. The physical properties, charging properties, and image quality produced by the polymerized toner were also investigated. The goal of this article is to report the synthesis procedure of styrene (St)/*n*-butyl acrylate (nBA) for the toner binder, which allowed the preparation of the polymerized toners by suspension polymerization, from which desired toner properties could be obtained. The effects of the carbon black level, CCA concentration, and rotating speed on triboelectric charging and in relation to printed images were investigated.

EXPERIMENTAL

Materials

St and nBA (both from Eternal Resin Co., Bangkok, Thailand) were used as monomers without further purification. Benzoyl peroxide (BPO) and divinylbenzene (DVB; Merck, Hohenbrunn, Germany) were used as an initiator and a crosslinking agent, respectively.

TABLE I
Standard Polymerization Recipe for the Synthesis of St and nBA Copolymer Microspheres Used as Binder Resins for the Toner Particles

Phase	Composition (parts)
Dispersion phase	
St monomer	80
nBA monomer	20
BPO	1
DVB	6
Continuous phase	
Water	450
PVA	5
SDS	0.05

^a Polymerization conditions were as follows: polymerization temperature = 70°C, polymerization time = 8 h, agitation rate during the polymerization = 180 rpm, and mechanical homogenizer speed for mixing during the whole polymerization mixture = 7000 rpm.

They were used as received. Poly(vinyl alcohol) (PVA; with a degree of hydrolysis of 86.5–89%, Nippon Synthetic Chemicals Industry, Inc., Osaka, Japan) and sodium dodecyl sulfate (SDS; Kishida Chemical Co., Tokyo, Japan) were used as the suspension stabilizer and costabilizer, respectively. Borobis(1,1-diphenyl-1-oxo-acetyl), a CCA, was provided by Japan Carlit Co. (Tokyo, Japan), and Printex 60, the coloring agent was provided by Degussa (Frankfort, Germany). All chemicals were used as received.

Suspension polymerization

The recipe for the synthesis of St and nBA copolymer microspheres used as a binder resin for toner particles by suspension polymerization and their properties are given in Tables I and II, respectively. This recipe gives the appropriate experimental conditions from which the preparation of the polymerized toners with desired properties was obtained. In this study, the standard recipe and the reaction parameters were kept constant throughout the whole study, whereas the carbon black feed level and the concentration of CCA were varied. A monomer mixture of St and nBA, DVB, and BPO used as the dispersed phase was prepared. The CCA and carbon black were dispersed in the aqueous phase of PVA and SDS as suspension stabilizers by shearing at a speed of 3,000 rpm for 3 min with a mechanical homogenizer (T. K. Robonics, Osaka, Japan). Then, the pigment was added to the mixture of the dispersed phase. The resulting mixture was stirred by the mechanical homogenizer again at a constant speed of 7,000 rpm for 10 min. The homogeneous mixture was transferred into a four-necked glass reactor. This suspension was polymerized at 70°C for 8 h at an agitation speed of 180 rpm (SCR-120, Iuchi Co., Ltd., Ibaraki, Japan) under a slow purging of nitrogen gas for deoxygenation. The reaction was ter-

TABLE II
Effect of Carbon Black Feed Levels on the Suspension Copolymerization of St and nBA

Sample	Carbon black feed level (wt %)	d_n (μm) ^{a,b}	d_w (μm) ^{a,b}	PDI	σ	CV (%)	M_n ($\times 10^{-5}$)	M_w ($\times 10^{-4}$)	M_w/M_n	T_g ($^{\circ}\text{C}$) ^c	Conversion (%) ^d
Control	—	5.0	5.5	1.1	1.24	24.8	36	15	4.2	72	72.7
CB1	1	5.2	6.8	1.3	1.37	26.4	6.4	10.2	16	70	65.2
CB2	3	5.4	7.0	1.3	1.25	23.2	7.3	8.3	11.3	69	56.4
CB3	5	5.8	7.5	1.3	1.44	24.8	5.3	3.8	7.2	66	25.6
CB4	7	Irregular shape	—	—	—	—	—	—	—	—	Aggregated form

^a Calculated diameter.

^b Determined by SEM.

^c Determined by DSC.

^d Determined by the gravimetric method.

minated by cooling to room temperature. The resulting polymeric microspheres were dispersed in the deionized water, and the dispersion was sonicated for about 5 min in an ultrasonic bath. The polymer particles were isolated from the mixture by centrifugation. The supernatant was decanted, and the remaining polymer was washed with deionized water and centrifuged again by repetition of the previous washing step until the supernatant was clear. Then, it was dried at room temperature for 24 h. Finally, the product was dried in a vacuum oven at 30°C for 24 h to remove the residual water.

Characterization

The average molecular weight and molecular-weight distributions were measured with a gel permeation chromatograph (Shimadzu, Kyoto, Japan). The measurements were made with an ultraviolet-visible detector and a pair of Showa Denko columns, Kyoto, Japan (Shodex GPC K-806 M; 300 \times 8 mm internal diameter, packed with St/DVB gel with 17,000 theoretical plates) at 25°C. High-performance liquid chromatography (HPLC)-grade chloroform was used as the eluent at a flow rate of 1.0 cm³ s⁻¹. The molecular weights of the polymers were obtained by calculation from the calibration lines with the polystyrene standard supplied by Showa Denko (S-66.0).

The thermal behavior of the copolymer was measured with a differential scanning calorimeter (DSC7, PerkinElmer, Norwalk, CT) to obtain the glass-transition temperature (T_g). Then, 10–20 mg of the sample was put in an aluminum pan and sealed with a covering lid. Measurements were carried out over a temperature range of 0–150°C at a heating rate of 20°C min⁻¹ under a nitrogen atmosphere.

The particle sizes and size distribution of polymer particles were measured with scanning electron microscopy (SEM; Jeol, JSM-6400, Tokyo, Japan). The particles from a diluted aqueous dispersion were deposited onto a glass cover slip glued to an aluminum

stub. They were dried under vacuum and sputter-coated with 15 nm of gold at an intensity of 15.0 kV under various magnifications. The number-average diameter (d_n) and weight-average diameter (d_w) of the polymer particles were determined by calculation of the diameters (d_i 's) of 50–100 particles (N) on the electron micrograph from the following equations:

$$d_n = \frac{\sum_{i=1}^N d_i}{N} \quad (1)$$

$$d_w = \frac{\sum_{i=1}^N d_i^4}{\sum_{i=1}^N d_i^3} \quad (2)$$

The polydispersity index (PDI), the coefficient of variation (CV), and the standard deviation (σ) are defined as

$$\text{PDI} = \frac{d_w}{d_n} \quad (3)$$

$$\text{CV} = \frac{\left[\frac{\sum_{i=1}^N (d_i - d_n)^2}{N - 1} \right]^{1/2}}{d_n} \times 100 \quad (4)$$

$$\sigma = \frac{\text{CV} d_n}{100} \quad (5)$$

The percentage monomer conversion was measured gravimetrically. The polymer was precipitated by deionized water from the serum, separated by centrif-

ugation, and dried in a vacuum, and then, the dry weight was measured.

The distribution of the carbon black on the polymerized toner was obtained by transmission electron microscopy (TEM; JEM-200CX, Tokyo, Japan). The toner particles were embedded in epoxy resin, set, and then cut into thin films by an ultramicrotoming technique. The samples were then either partially oxidized or coated with gold to increase their conductivity.

Triboelectrification measurements

The triboelectric charge of the developer mixture was measured by the blow-off method. A shaker (IKA MS 1 Mini-shaker, Wilmington, DE) was used to mix the polymerized toner and carrier. The carrier was made from steel, and the size of the steel ball was around 50 μm . The shaker rotated a mixing cell with an eccentric radius of 2.5 mm. The rotation speed was set at 1000 rpm. The toner concentration was 3 wt % in a glass mixing cell with an inside diameter 24 mm. The charge-to-mass ratio (q/m) measurements were carried out in an approximately 0.12 g of sample, and the results were taken from the developer at 30, 60, 90, 120, 240, 360, and 720 s. The toner charge was measured by the blow-off method as follows. The mixture of the toner and carrier was thinly layered on #500 metal mesh (500 apertures/in.), which was locked in a cylindrical Faraday cage. A vacuum cleaner was used to suck the carrier from the back of the mesh. The toner was removed from the carrier and forced to exit the cage. The carrier was retained in the cage by the screen. The mass lost and the resultant charge on the Faraday cage were measured, and thus, the average q/m of the mixture was calculated.

Effect of the CCA on triboelectric charging

The effect of the CCA concentration on the triboelectric properties of the toner was investigated. The recipe of the toner used in this experiment was as follows: polymerized toner at a 3 wt % concentration of carbon black in St/nBA copolymer (80/20) particles with a diameter of 4–10 μm ; borobis(1,1-diphenyl-1-oxo-acetyl)potassium salt (nonchromium-complex-type CCA) of 1, 2, and 4 wt %; and 96 wt % of the carrier, which was made from steel and coded as TSV-200. The carrier had an average size of around 50 μm .

Effect of the rotation time on triboelectric charging

The rotation time for the different concentrations of the borobis(1,1-diphenyl-1-oxo-acetyl)potassium salt CCA in the toner was varied from 100 to 700 s at an increment of 100 s. q/m values were measured by the previously mentioned technique.

Evaluations of print quality

The resulting polymerized toner (PT-702) was poured into a developing unit of the OKI 400 microline CL printer. One type of plain-paper sheet was printed at the appropriate toner conditions with a test form, which was produced by the Aldus PageMaker 5.0. Ten plain-paper sheets were printed with the same toner. Each sheet consisted of A to Z characters; different percentage halftones of 0, 20, 40, 60, 80, and 100%; and 0.5-, 1-, 2-, 4-, 8-, and 16-point lines (1 point = $\frac{1}{72}$ in.). The printouts were measured for solid density and background density. The densities were measured by a reflection densitometer (Macbeth, Zurich, Switzerland), which was calibrated with black and white tiles, and the background density was measured by the null density mode of the reflection densitometer, which was calibrated to be zero on the same type of paper surface. We also used a commercial grade toner (N-09S) to print in a similar manner as that of the synthesized toner (PT-072) to compare the print qualities.

RESULTS AND DISCUSSION

Effect of carbon black concentration on particle size and conversion

Table I shows the standard polymerization recipe for the synthesis of St and nBA copolymer microspheres used as a binder resin in the toner particle. This standard recipe produced the copolymer microspheres under the conditions mentioned in Tables I and II, giving the characteristics of the microspheres and a percentage conversion of 72.7%. When carbon black was included in the polymerizing recipe, the percentage conversion decreased steadily, as shown in Table II. It has been known for many years that most types of radical polymerization are adversely influenced by the presence of carbon black, such that the reaction may be retarded or, indeed, completely inhibited as a strong radical scavenger.³ This can be explained by the fact that the functional groups on the surfaces of carbon black are likely to interact with primary or propagating radicals, giving rise to the retarding/inhibiting effects. In the presence of carbon black, these radicals are bonded onto the surface by an additional reaction with polycondensed aromatic rings and quinonic oxygen groups on the surface. The free radicals, formed on the carbon black surface by the addition of initiator radicals, were stabilized by delocalization through the polycondensed aromatic rings of carbon black, as shown in Figure 1. In addition, the propagating radicals reacting with a surface functional group of the carbon black can give rise to a grafting reaction.⁴ In other words, when the peroxy compounds are used as initiators, primary interaction of the primary radicals with the carbon black takes place, and indeed, the carbon black can induce the decomposition of the

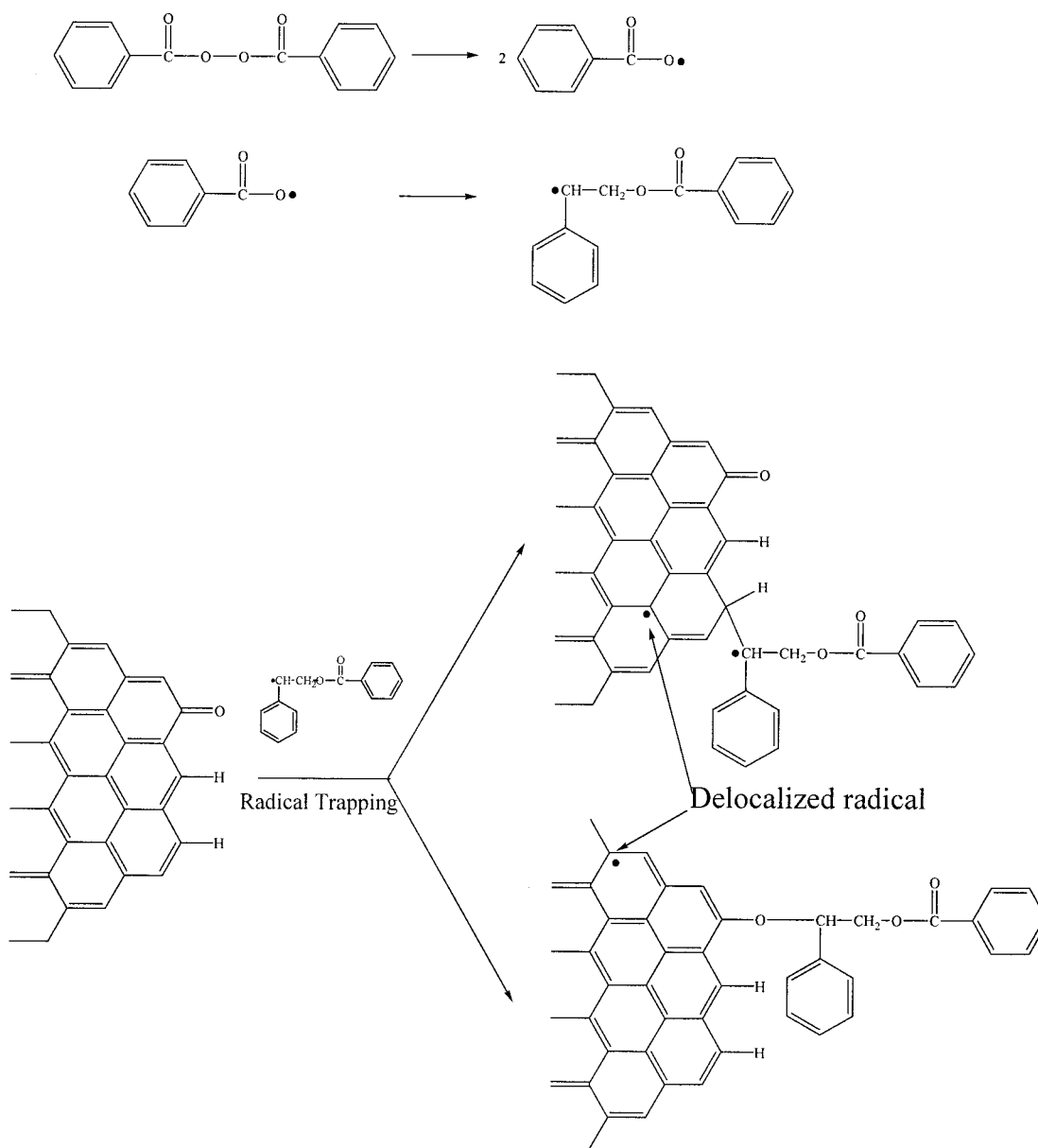


Figure 1 Mechanism of free-radical formation on carbon black surfaces by the addition of initiator radicals.

peroxy initiator even at a low temperature. The reaction involved is certainly an oxidation process. Surface oxidation of the carbon black takes place by strong oxidizing agents, including peroxy species.

When the surface functional groups of the carbon black are considered, an increase in the number of functionalities also increases the inhibitory effect. As shown in Figure 1, the mechanistic reaction of the free radicals formed on the carbon black surface with quinonic oxygen groups yields two major types of products, obtained as quinone and ether, formed by the reaction at the C and O atoms of a quinone, respectively. The attack of a propagating radical at the oxygen atoms yields aryloxy radicals, which can be terminated by a coupling and/or disproportionation re-

action with another propagating radical (or itself) or added monomers. Attacking on the ring carbon yields radicals, which can react with other propagating radicals to form quinone. Even the poor-retarder phenolic compounds react with highly reactive radicals, such as the poly(vinyl acetate)-propagating radical.⁵ Phenols with electron-donating groups act as more powerful retarders. The presence of an electron-withdrawing group on the phenol ring decreases its activity as an inhibitor. Most phenols are active, or much more active, only in the presence of oxygen. The mechanism for inhibition by phenols has been attributed to hydrogen transfer to the propagating radical, adding to the ring or abstracting hydrogen from a substituent group on the ring.

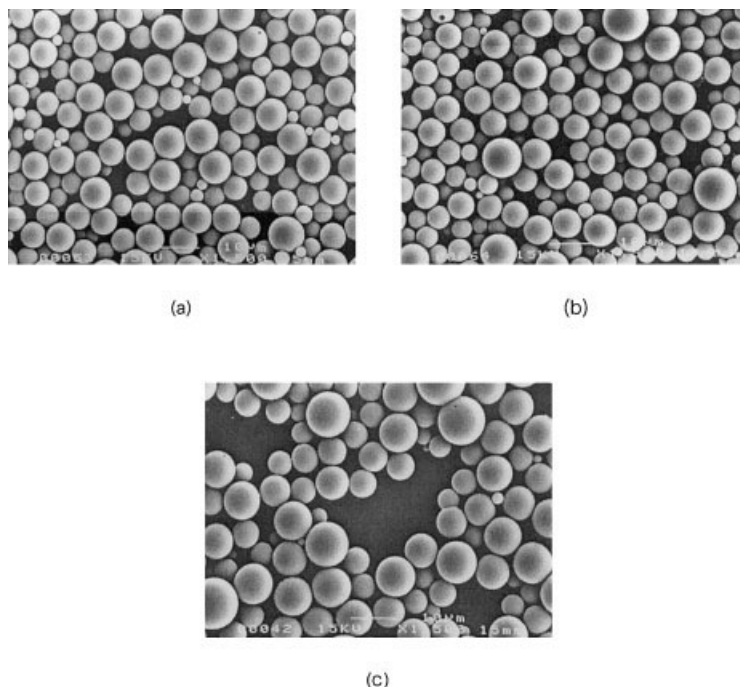


Figure 2 SEM photographs of the polymerized toner prepared at various carbon black feed levels: (a) 1 wt % (CB1), (b) 3 wt % (CB2), and (c) 5 wt % (CB3).

Table II shows the effect of the carbon black feed level on the average particle size and size distribution, where the first entry is the control reaction in the absence of any carbon black additive.⁶ The results indicated that the incorporation of the carbon black in the polymerization mixture did not have a significant effect on the particle size. With further increases in the carbon black feed levels from 1 to 5 wt %, the particle size slightly increased from 5.2 to 5.8 μm , as shown in Figure 2. Carbon black had a strong inhibitory effect on the radical polymerization; therefore, the increases in carbon black feed level decreased percentage conversion. When the carbon black loading was about 7%, an irregular particle shape (aggregated form) was obtained, and the percentage conversion could not be precisely determined. If an excess amount was added (higher than 7%), the polymerization could be completely inhibited. In the presence of carbon black, the free-radical process was somewhat inhibited because low polymer contents, due to lower radical concentration, were obtained. The particles were coalesced because of their mutual collision, which led to the formation of larger particles, the size of which depended on the extent of coagulation. In contrast, in the absence of carbon black, a greater radical concentration was produced, and the polymerization rate increased, resulting in smaller sized polymer molecules.

The carbon black feed levels also had a strong effect on the final yield of polymer beads. A typical yield of the control reaction (without carbon black content) was 72.7%. An addition of 1 wt % carbon black to the

polymerization mixture decreased the yield to about 65.2 wt %, with further decreases to 56.4 and 25.6% when the feed levels of carbon black were increased to 3 and 5 wt %, respectively. A tar-like product was often formed at the bottom of the reactor at high feed levels of carbon black. These results also clearly demonstrated the significant effect of the carbon black feed level on the polymerization yield. At low carbon black feed levels, the yield of polymer particles slightly decreased, which could be rationalized by the increased inhibitory effect of the carbon black caused by decreases in both the radical concentration and conversion. The hue of the carbon black pigment in the resulting polymerized toners correlated well with both the carbon black feed level and the particle size, as shown in Table III.

TABLE III
Physical Properties of the Copolymers of St and nBA in the Presence of Carbon Black

Carbon black (wt %)	Particle size (μm)	Hue of the polymerized toner
0	5.0	White
1	5.2	Slightly grayish white
3	5.4	Gray
5	5.8	Dark gray
7	Irregular shape	Black

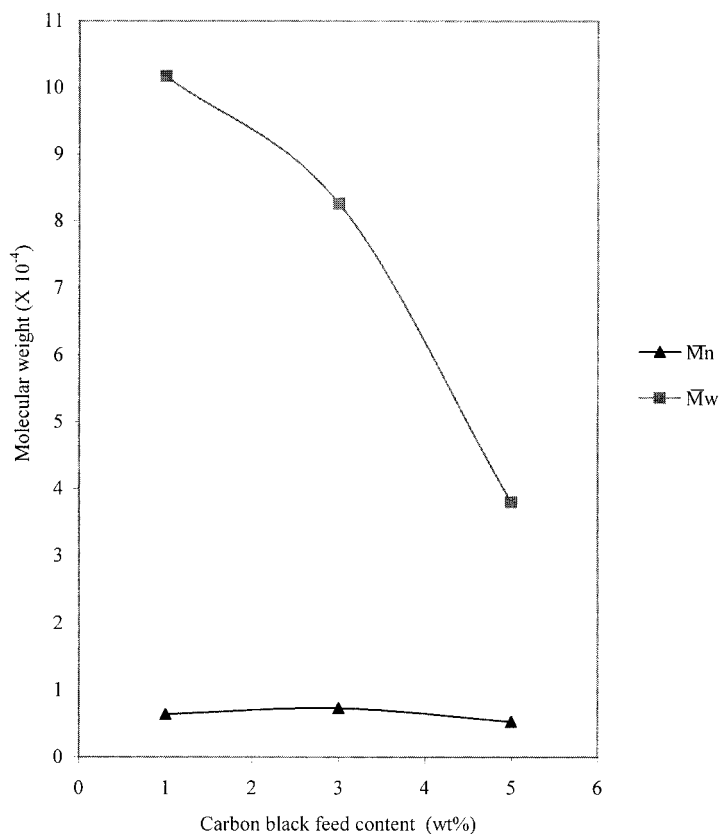


Figure 3 Effect of the carbon black feed level on the average molecular weight of the polymer toner.

Effect of carbon black concentration on molecular weight and weight distribution

The average molecular weights decreased with increasing amounts of carbon black. As the polymerization progressed in the presence of carbon black, which acted as a strong radical scavenger, there was an increased inhibitory effect because of a low radical concentration, and the rate of polymerization was thus decreased. The critical chain lengths of oligomer radicals were decreased or were even completely inhibited (in the case of excess carbon black concentration), and the growth of the copolymer particles was decreased. As mentioned previously, the polymerization mixture with a low radical concentration (rich in non-radical monomers or oligomers) tended to coalescence, which led to larger particle sizes with lower average molecular weights. This result can be explained as follows: In the suspension polymerization system, the large particles grew by the capture of dead polymers of low molecular weight from the solution. The relationship between the carbon black feed level and average molecular weight is presented in Figure 3. One can see that the number-average molecular weight (\bar{M}_n) was relatively constant with increases in the carbon black content, whereas the weight-average molecular weight (\bar{M}_w) decreased markedly. A number of the small molecules were present all the time.

Larger molecules were absent because of radical scavengers.

The T_g of the copolymer is another important property in the characterization of a toner resin for xerography because it corresponds to an acceptable blocking temperature, the temperature at which the toners flow into the paper. For adequate blocking, toners generally should have a T_g of about 50–70°C. The resulting polymerized toners were investigated by differential scanning calorimetry to identify the T_g value. The T_g is often marked by a change in the conductivity of the polymer matrix, found in the range of 66–70°C. The T_g value decreased as the carbon black feed level was increased. This could be explained by the fact that the radical termination by the carbon black additives gave rise to a small fraction of oligomeric material of sufficiently low molecular weight to act as a plasticizer. The average molecular weight also had a strong, important effect on the T_g value. The resulting copolymer with a high average molecular weight yielded high T_g values.

The distribution of the carbon black on the toner particles is shown in Figure 4. The transmission electron micrographs illustrate the distribution of carbon black on the polymer surfaces. This technique tends to produce polymer particles with excess amounts of carbon black on the surface. In addition, toner pro-

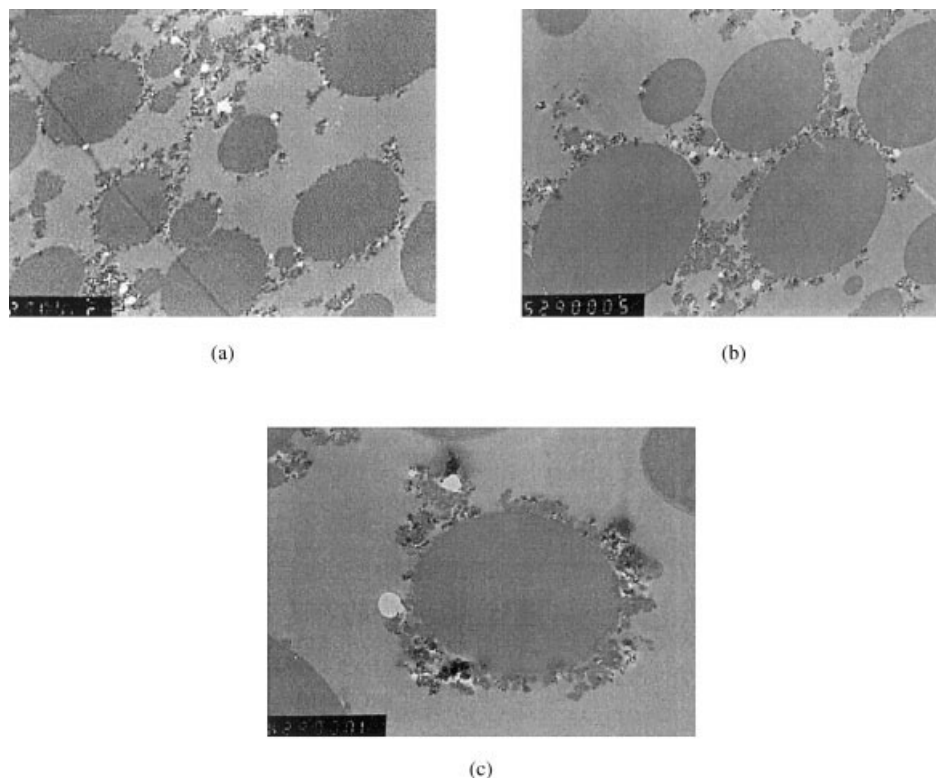


Figure 4 TEM photographs of the carbon black distribution on the surfaces of the toner particles in the presence of carbon black (sample CB2): (a) 5550 \times , (b) 7500 \times , and (c) 16500 \times .

duced from such a synthesis technique is likely to contain a low carbon black content. In other words, they indeed require some dispersion agents to disperse themselves in liquid phases. However, such a dispersing agent introduces difficulties because the dispersed carbon black hardly provides true tone reproduction (density). We observed a large amount of carbon black distributions on the toner particles or agglomerations of carbon black on the surface of the toner particles.

In most cases in the experimental results, an inverse correlation between particle size and molecular weight was obtained. As the particle size decreased, the average molecular weight increased. This rationale depended mainly on the locus of the polymerization, which involved both solution and monomer-swollen particle phases. The molecular weights from particle-phase polymerization were usually higher than those in the solution polymerization because the termination rate was reduced because of the gel effect. For small particles, a higher proportion of the polymerization occurred in the particle phase because the oligomeric radicals initiated in solution were captured more efficiently by the smaller particles because of their greater surface area. In contrast, the large particles could grow by the capture of dead polymer molecules already in the solution, thus exhibiting the low molecular weight.

Effects of CCA concentration and rotation time on q/m values

A CCA is added to a toner either on its surface or in bulk to give an adequate charge level or rate of charging. The addition of a CCA is required both for positive and negative toners. St/acrylate copolymers are tribochargeable, both positively and negatively, when a suitable CCA is selected.⁷ The selection of the CCA depends on the expected applications. Recently, "green laws" enacted to protect and preserve the environment worldwide forced the toner industry to ban the use of toxic, metal-containing CCAs, which are harmful to humans and animals. Chromium-containing CCAs are thus restricted, and other CCAs have been developed to replace the toxic, metal-complex CCAs. Non-chromium-containing and environmentally friendly CCAs have been recently developed, and CCAs based on borobis(1,1-diphenyl-1-oxo-acetyl) with different counter ions of Li^+ , Na^+ , K^+ and Ca^{2+} were used in a study of their charging properties in terms of the q/m value by Kiatkamjornwong et al.⁸ The authors compared the monovalent ionic complex of the CCA with the divalent ionic complex and found that the latter generated more charge and higher q/m values because of its electronic configuration and its high affinity to polarization and ionization. The structure of the CCA used here, borobis(1,1-diphenyl-1-oxo-acetyl)potassium salt, is depicted in Figure 5.

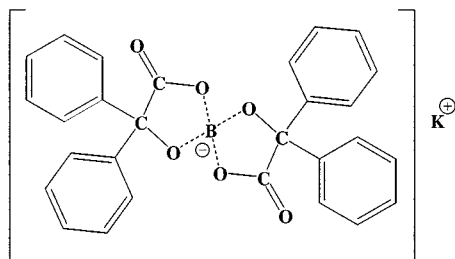


Figure 5 Molecular structure of borobis(1,1-diphenyl-1-oxo-acetyl)potassium salt CCA.

Figure 6 shows the effect of the CCA concentration on the triboelectric properties of the toners. The q/m values increased along with an increase in CCA concentration. Birkett and Gregory⁹ proposed that the charging process probably involves a transfer of the counterions of the CCA on the toner surface to the carrier surface on contact. The polymerized toner particles for this study were spherical with a uniformly smooth surface (Fig. 2). An increase in the concentration of CCA can increase the number of effective charging sites of the toner, which should result in a reduction in the charging time for a saturated charge to develop and increase the value of q/m . However, the toner containing the lower CCA concentration (1 wt %) produced relatively stable charges when the toner mixture was rotated for 200 s. The toners containing higher CCA content needed a longer rotation time to reach a stable charge. Nonetheless, the q/m values obtained from 1% CCA addition were too low for printing applications. The charging rates of the

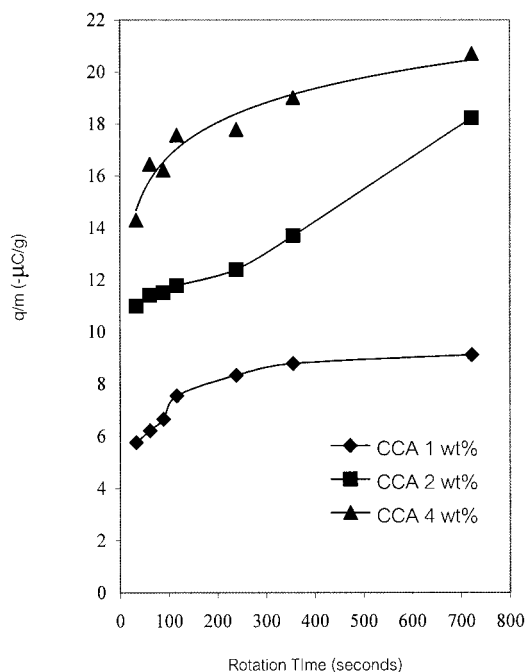


Figure 6 Effect of CCA concentration on the triboelectric properties of the polymerized toner.

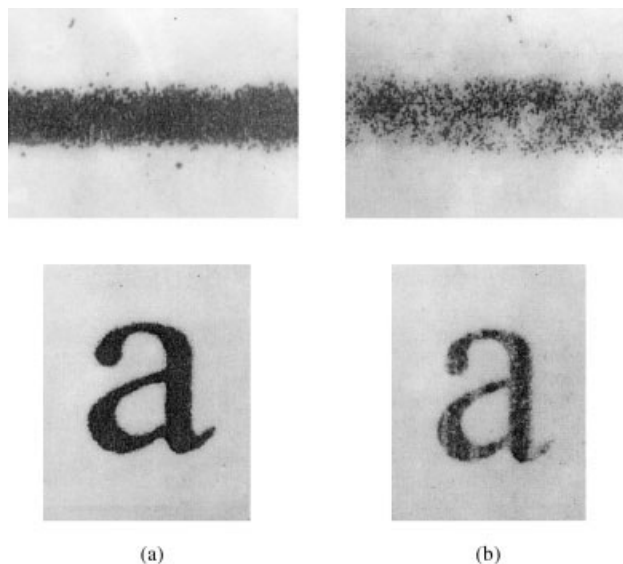


Figure 7 Photographs of lines and *a* characters by the image analyzer for (a) N-09S toner and (b) PT-702 toner.

three toners were different. The higher the CCA concentration was, the greater the increase in q/m was. The electrophotographic process involves the charging mechanism of toner particles and transfer onto the photoreceptor by electric fields. It is, therefore, of primary importance that the toner particles have the correct electrostatic charge. If the toner particles were charged to the wrong sign, the toner might be transferred into the background areas, which ideally, should be free of toner. If the toner is uncharged or very weakly charged, machine dusting and contamination can easily occur. However, toner of too high a charge is also undesirable, in terms of low print densities because too few toner particles detach from the carriers. In addition, the developed toner mass per unit area is inversely proportional to the toner q/m . It would, therefore, be highly desirable to be able to measure the charge of each toner particle and to assign the distribution of toner charges to have an adequate average charge with few uncharged, wrong sign, or very highly charged toner particles.

Analyses of print quality

Comparisons of the print samples (produced by N-09S and PT-702 toners) showed that the solid density values from the former toner were higher than those from latter toner, but the background density values of both toner types were slightly different. The edge sharpness and edge raggedness of the lines (0.5 points) and the characteristics given by both toner types were illustrated by an image analyzer, as shown in Figure 7. We found that the edge sharpness and raggedness produced by the N-09S toner were better than those

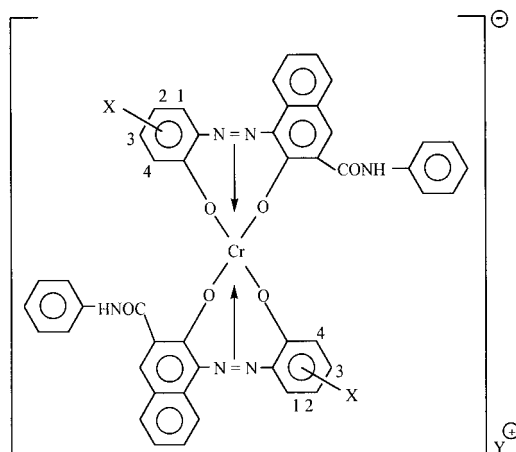


Figure 8 Molecular structure of the azochromium metal complex CCA.

from our PT-702 toner because the former had a uniform and stronger ink density.

The N-09S toner produced better thin lines and fine-dot images with much less raggedness. Both toners were spherically shaped, polymerized toners, which have even and more uniform triboelectric charges than irregularly shaped toners. Therefore, the more highly charged toner could transfer more toner particles to the paper. The difference in the print densities came from the q/m values of the toner charge and the loading of carbon black on the toner particles. The PT-702 toner gave a little background fog and image raggedness. The reason for this could have been that the PT-702 toner contained lower charges, most probably resulting from a poor distribution of CCA. A smaller amount of charged toner was picked up by the photoconductor but could not be transferred to the paper by the electric field. With regard to the CCA type and concentration, the CCA used for the N-09S toner was negatively charged, containing some heavy metal ions, such as 2.4 wt % chromium, as shown in Figure 8. The letter X represents an alkyl-amine functional group, and the positions 2 and 4 are the NO_2 groups. The PT-702 toner used 2 wt % borobis(1,1-diphenyl-1-oxo-acetyl)potassium salt (nonchromium complex type) as the CCA (Fig. 5). Both the CCA type and concentration affected the q/m values and greatly influenced the image quality. The results indicated that the q/m values of the N-09S toner were in the range $25\text{--}30 \mu\text{C g}^{-1}$, whereas the q/m values of the PT-702 toner were in the range $7\text{--}20 \mu\text{C g}^{-1}$. This result was investigated with both theoretical and experimental techniques. Both indicated that the q/m values increased with increasing CCA concentration. The N-09S toner contained a higher amount of the CCA than did the PT-702 toner. Therefore, the former gave higher q/m values than the latter. In addition, a CCA containing a heavy metal ion such as chromium

could generate the higher triboelectric (q/m) values than the CCA containing a nonchromium complex. Therefore, the higher q/m values were obtained in the first case. However, CCAs containing heavy metal ions are environmentally destructive, and this CCA will, therefore, be restricted in the near future.

As described previously, the q/m values also affected the resulting image qualities. The PT-702 toner contained a lower charge. These less charged toner particles were picked up by the photoconductor but were not transferred to the paper by the electric field. The roles of CCAs affecting the charge distribution are not fully understood. However, Birkett and Gregory⁹ proposed that the charging process probably involves transfer of the counterion of the CCA on the toner surface to the carrier surface on contact. Better image qualities were thus obtained in the presence of the CCA containing the azochromium metal complex with a higher CCA concentration, as described previously.

In terms of the carbon black content, the bulk electrical conductivity of the toner had a significant effect on q/m . The range of carbon black concentration was important because a small amount of the typical black toners was used. One possible explanation of this is as follows. Even at a low carbon black concentration, localized clusters of the carbon black particles formed, which gave rise to local regions of higher conductivity that were electrically isolated from one another by the polymer. Thus, the local conductivity of the toner may have been high at the point of contact between the toner and the carrier, even though the bulk conductivity of the toner was low and tended to decrease the charging ability and also the image quality.¹⁰

CONCLUSIONS

The amount of carbon black used as a coloring pigment incorporated into the polymerization mixture was limited. With further increases in carbon black feed level from 1 to 5 wt %, the particle size slightly increased. Moreover, a tar-like product with an irregular shape was often formed at the bottom of the reactor. The carbon black feed level also had a strong effect on the final yield of polymer beads. With further increases in carbon black feed level, the final yield tended to decrease. This result could be explained by the fact that the carbon black had a strong inhibitory effect on the radical polymerizations and, therefore, increases in carbon black feed levels decreased the rate of polymerization. The free-radical process was inhibited because both low radical concentrations and low molecular weight polymers were obtained. The resulting polymerized toner with T_g values in the range of $66\text{--}70^\circ\text{C}$ was achieved by adjustment of the proper molar ratio of the comonomer between St and nBA and of the carbon black concentration.

A certain amount of CCA was added to the polymerized toner to give an adequate charge level or rate of charging. The results indicated that the q/m values slightly increased, followed by an increase of the CCA concentration from 1 to 4 wt %. The resulting polymerized toners, with q/m values in the range 7–20 $\mu\text{C g}^{-1}$, were obtained. Increasing the concentration of the CCA increased the number of effective charging sites of the toner, which resulted in a reduction in the charging time for a saturated charge to develop and increased the value of q/m .

Analyses of the print quality from the synthesized toner showed relatively higher background fog, lower maximum density, and a little image raggedness with decreasing q/m . Further development of the carbon loading and the addition of some additive could help us obtain a full density range of the print.

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