



Chapter IV

Results and Discussion

4.1 Effect of Mechanical Homogenizing Speed on

4.1.1 The Particle Size and Size Distribution

In this research, a typical mechanical homogenizer is used to mix and disperse all ingredients for suspension polymerization to generate small, uniform, and well controlled monomer droplets. In this study, the mechanical homogenizer speeds investigated were 3000, 7000, 8000, 9000, 10000, and 12000 rpm. Table 4.1 illustrates the effect of mechanical homogenizer speed on some characteristics of the copolymer. It was found that the desirable size of the resulting particles can be effectively controlled by adjusting the speed of mechanical homogenizer. The influence of mechanical homogenizing speed or mixing rate on the mechanism of the formation and stability of the monomer dispersion is rather complex. Generally, increasing the mixing rate corresponds to increase the shear force leading to a decrease of the average size of monomer droplets. However, after the polymerization the coalescence of polymer particles is irreversible even more vigorous mixing rate is given. On exceeding a certain rate of mixing, no further increase in the number of

Table 4.1 Effects of the mechanical homogenizing speed on particle size distribution and molecular weight in suspension copolymerization of styrene and n-butyl acrylate

Sample	Mechanical homogenizing speed (rpm)	\bar{D}_n (μm) ^{a,f}	\bar{D}_w (μm) ^{a,b}	PDI ^c	σ ^d	CV (%) ^e	\bar{M}_n ($\times 10^{-4}$)	\bar{M}_w ($\times 10^{-4}$)	\bar{M}_w / \bar{M}_n
H1	3000	15.2	17.0	1.1	3.28	21.55	0.73	3.18	4.35
H2	7000	5.2	5.9	1.1	1.16	22.34	1.98	7.14	3.60
H3	8000	4.0	5.5	1.4	1.18	29.40	2.41	7.18	2.98
H4	9000	3.8	5.3	1.4	1.65	43.44	3.36	8.81	2.62
H5	10000	2.6	3.5	1.3	0.92	35.48	3.25	9.59	2.96
H6	12000	3.7	4.0	1.3	1.34	36.27	3.57	8.75	2.45

a = Calculated diameter

b = Determined by scanning electron microscopy

c = Polydispersity index

d = Standard deviation

e = Coefficient of variation

monomer droplets is observed, but the association of the polymer particles is initiated, which causes an increase in particle size. Under these conditions, a larger number of small particles with much greater surface area are produced, a higher concentration of stabilizer is needed to stabilize them. If the system does not contain the required amount of stabilizer, the particles coagulate and a dispersion is formed with a larger particle size.⁴³ It could be described that the stabilizer acts like a spacer or matrix between particles that inhibit coalescence. These stabilizer would exist on the surface of particles, preventing particle contact. As mechanical homogenizing speed increased means a mixing rate increased, a higher power of mixing was generated, the space become smaller due to the system being more dynamic. As a result, the smaller particles will be generated.⁴⁴

The relation between the particle size and mechanical homogenizing speed was shown in Figure 4.1. It presents that the particle size decreased rapidly with an increase in the mechanical homogenizing speed from 3000 to 7000 rpm, and the largest particle size of 15.2 μm was obtained at a mixing speed of 3000 rpm. However, above a rate of 10000 rpm, any increase in mechanical force does not contribute to much reduction in particle size, but an increase in a broader particle size distribution was observed as shown in Figure 4.2. It could be described that the mixing or shearing force to disperse all ingredients for the suspension polymerization in producing the polymeric particles with a narrow size distribution was limited to a critical value.

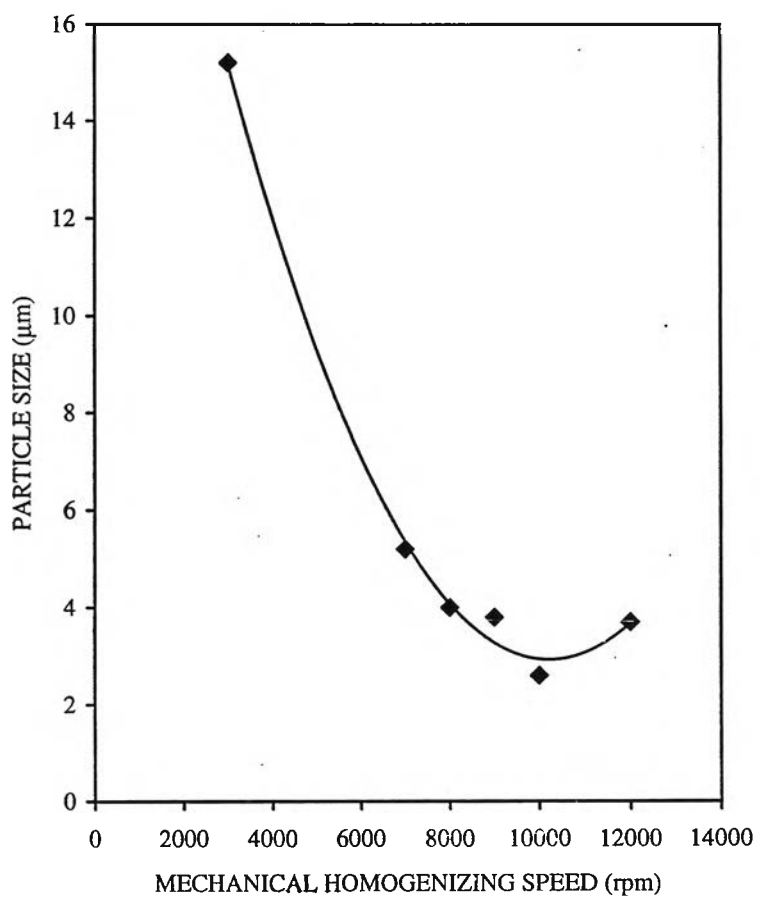
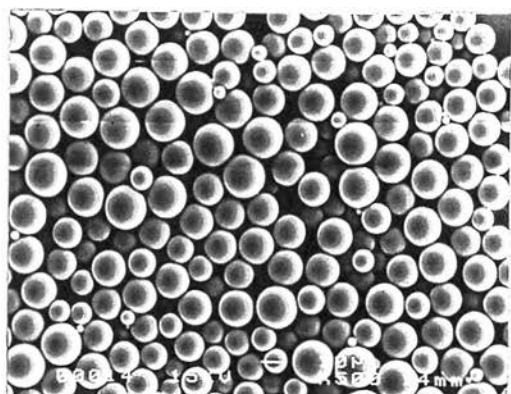
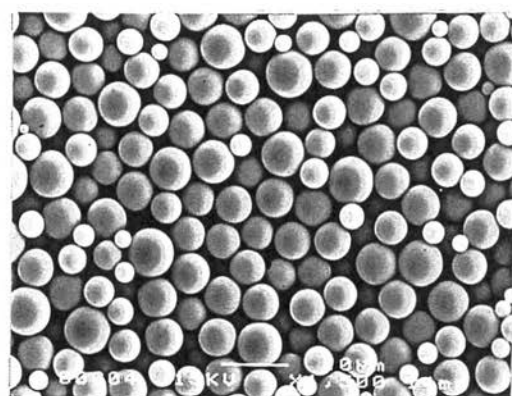


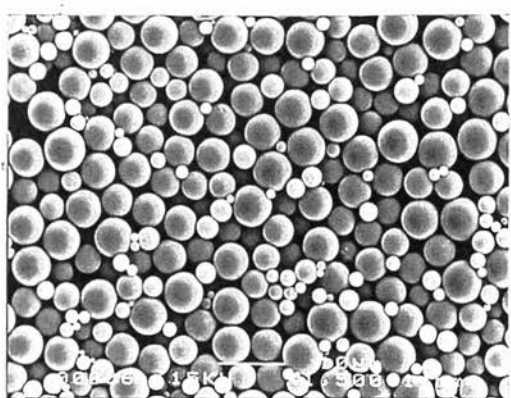
Figure 4.1 Effect of the mechanical homogenizing speed on particle size of the copolymer



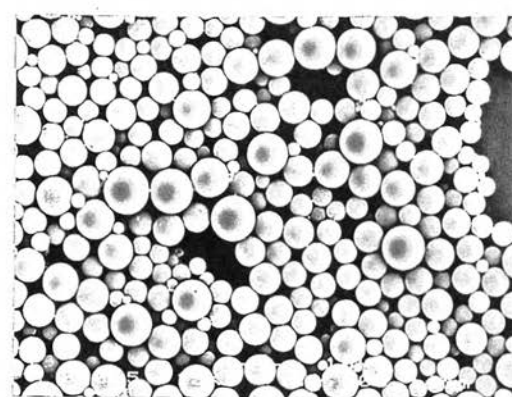
(a) sample H1



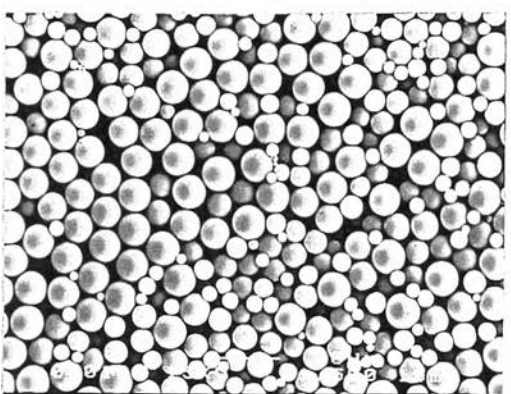
(b) sample H2



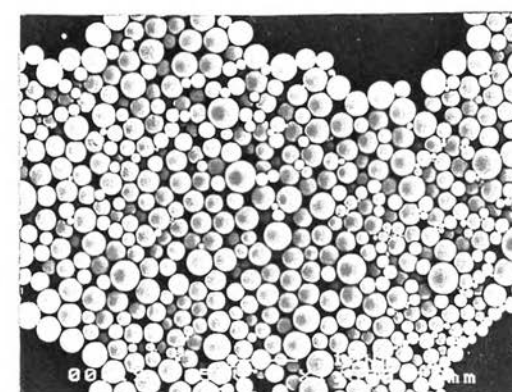
(c) sample H3



(d) sample H4



(e) sample H5



(f) sample H6

Figure 4.2 SEM photographs of the copolymers prepared at various mechanical homogenizing speeds: (a) H1, 3000 rpm (b) H2, 7000 rpm (c) H3, 8000 rpm (d) H4, 9000 rpm (e) H5, 10000 rpm (f) H6, 12000 rpm

4.1.2 The Average Molecular Weights and Molecular Weight Distribution

The relation between mechanical homogenizing speed and average molecular weights is presented in Figure 4.3. The most important practice in suspension polymerization is how to control the particle size and the narrow size distribution of the final polymer beads. It is imperative to produce polymer particles of the desired and uniform size. This aim could be achieved by forming monomer droplets of uniform diameter at the beginning of the polymerization through the use of the mechanical homogenizer. The small and uniform of monomer droplets were obtained but the dispersed droplets are not fairly monodispersed by this technique. At a lower mechanical homogenizing speed of 3000 rpm larger particles were generated and tended to associate. Additionally, an undesirable stabilizer concentration brings in coalescence beads to form a large particle size with the smaller surface areas. This resulted may be discussed by the assumption that, in the suspension polymerization system, the large particles grow by capture of dead polymers of low molecular weights from the solution.

Nevertheless, when the mechanical homogenizing speed increase from 7000 to 10000 rpm, a decrease of particle sizes and the smaller particles were obtained. This phenomenon can be discussed as follows. In the suspension polymerization system, the smaller particles with their greater surface areas can grow by efficiently capturing the oligomeric radicals before they reach to critical molecular weight and terminate in the continuous phase, leading to proceed the polymerization within the particles.

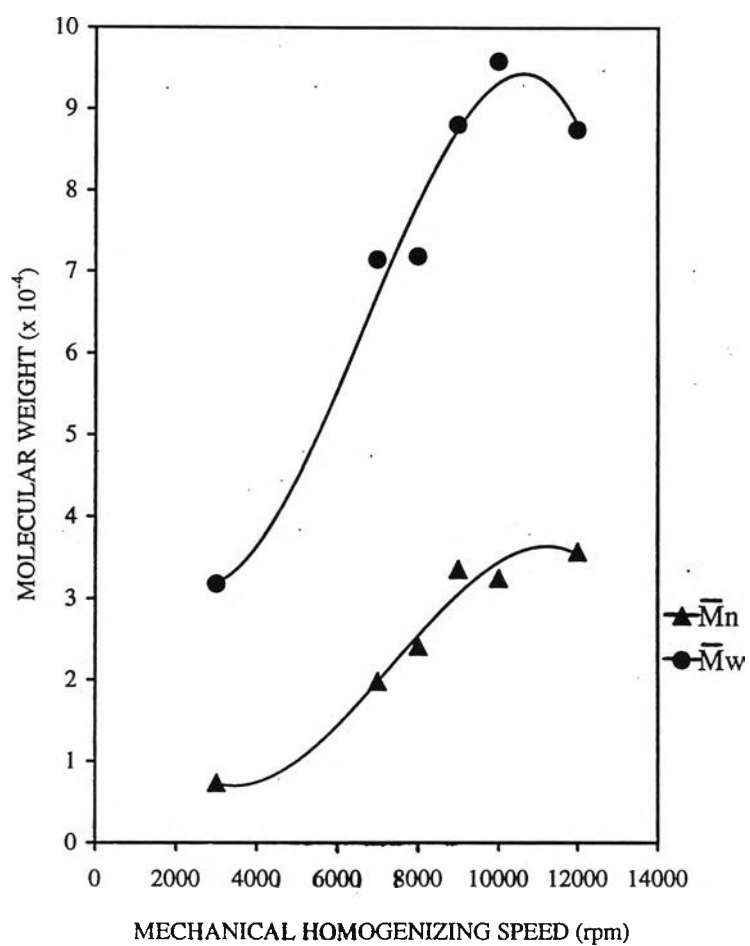


Figure 4.3 Effect of the mechanical homogenizing speed on average molecular weights of the copolymer

Therefore, it usually exhibits the high molecular weights, which is typical for the suspension polymerization. This technique is normally used for preparing polymer dispersions with larger particles. At a higher mechanical homogenizing speed of 12000 rpm, many monomer droplets were generated until a certain critical rate of mixing, no further increase in the number of monomer droplets is observed. When they are polymerized, the association of the particles has occurred, which causes an increase in particle size. A higher concentration of stabilizer is needed to stabilize the growing particles. Applying a high concentration of stabilizer produces more stable monomer suspension, but the quality of the resulting copolymer is reduced. If a lower stabilizer concentration is used, a higher degree of particle coalescence is observed, which is consumed to make bigger monomer droplets and eventually larger particles are resulted in as described previously.⁴⁵

4.2 Effect of the Agitation Rate

4.2.1 The Particle Size and Size Distribution

It is noted that among various factors influencing particle size, stirring rate provides a relatively convenient means of particle size control for most practical purposes. To mix and disperse all ingredients through by, the use of mechanical homogenizer is one of the best machines for this purpose. Good agitation was required to ensure a complete mixing of the reaction mixture and to prevent them from sedimentation to the bottom. Through the shearing action from the agitation and local turbulence, together with surface tension forces, the monomer assumes a more or less stable spherical form. In this study, the agitation rates investigated were 140, 180, 240, and 300 rpm. The effect of agitation rate on some characteristic of the copolymer is given in Table 4.2. It was found that the size of the resulting particle can be effectively controlled by adjusting the agitation rate. Generally, particle size decreases with increasing rate of agitation in a given system. Lower stirring rates may not be sufficient to establish a steady state droplet size distribution, whereas too vigorous stirring may exceed the shear tolerance of the reactor system. Since the distribution of shearing action in an agitated reactor can be very nonuniform, an equilibrium condition is only possible if all the particles move through a zone of maximum shear.

In such suspension systems, the dispersed monomer droplets tend to associate. Mechanical agitation exerts the monomeric substance to a viscous drag causing elongation to a threadlike form with subsequent degeneration into drops.

Table 4.2 Effects of the agitation rate on particle size, size distribution, and molecular weight in suspension copolymerization of styrene and n-butyl acrylate

Sample	Agitation rate (rpm)	$\bar{D}_n (\mu\text{m})^{a,b}$	$\bar{D}_w (\mu\text{m})^{a,b}$	PDI ^c	σ^d	CV (%) ^e	$\bar{M}_n (\times 10^{-4})$	$\bar{M}_w (\times 10^{-4})$	\bar{M}_w / \bar{M}_n
A1	140	5.8	6.4	1.1	1.25	21.55	1.59	6.26	3.93
A2	180	5.4	5.9	1.1	1.21	22.34	2.79	7.88	2.82
A3	240	5.0	7.0	1.4	1.47	29.40	3.55	8.32	2.35
A4	300	4.7	6.6	1.4	2.04	43.44	3.50	8.98	2.57

a = Calculated diameter

b = Determined by scanning electron microscopy

c = Polydispersity index

d = Standard deviation

e = Coefficient of variation

Simultaneously, through the reverse process of coalescence, the drops tend to revert to the original monomeric mass. In other words, after the completion of stirring, the particles (in the absence of the stabilizer) rapidly associate into a separating oil phase. Clusters of globules, held together by weak residual forces, but not fused, tend to disperse under the disruptive stress of an agitated system. Addition of the stabilizer suppresses association of the particles and lowers the rate of the coalescence. With the onset of polymerization and the accompanying increase in viscosity there is greater resistance to distribution of droplets due to viscous drag but, unfortunately, a greater tendency toward aggregation through collisions with neighboring globules. The latter phenomenon is minimized when using the stabilizers which are selectively adsorbed at the interface forming a protective film of molecular proportions. According to these, the viscosity in the phase boundary layers is much higher in presence of adding stabilizers.⁴⁶ As agitation rate increased, the stabilizer which acts like a spacer or matrix (or more generally, the protective colloid) become smaller due to the system being more dynamic. As a result, the smaller particle will be generated. Figure 4.4 illustrates schematically the enlarged droplet of monomer supported by an adsorbed film of poly(vinyl alcohol).

Figure 4.5 shows the relation between the particle size and rate of agitation. It presents that the particle size decreased slightly with an increase of agitation rate from 140, 180, 240 to 300 rpm, and their distribution shifts towards the small particle size as shown in Figure 4.6. It can be described that an increase in agitation rate leads to an increase in shearing force, which can disperse the oil phase to form the small droplet sizes.

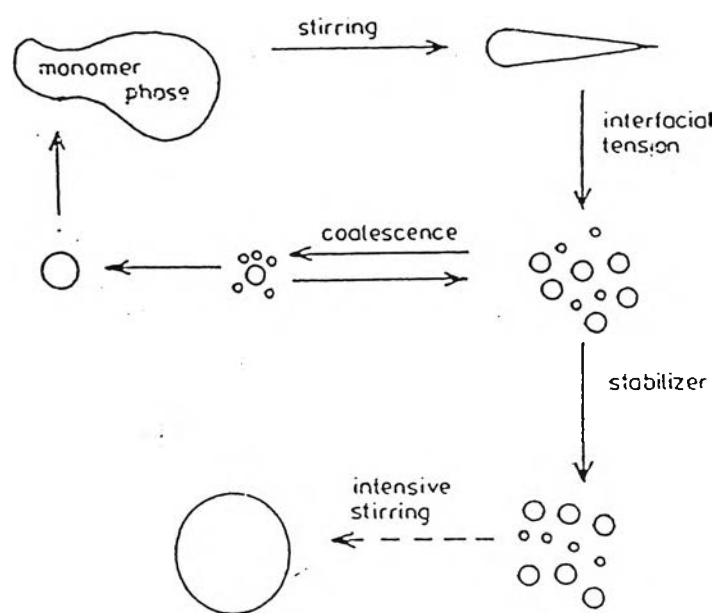


Figure 4.4 Schematic diagram of states of dispersion in suspension polymerization of divinylbenzene.⁴⁷

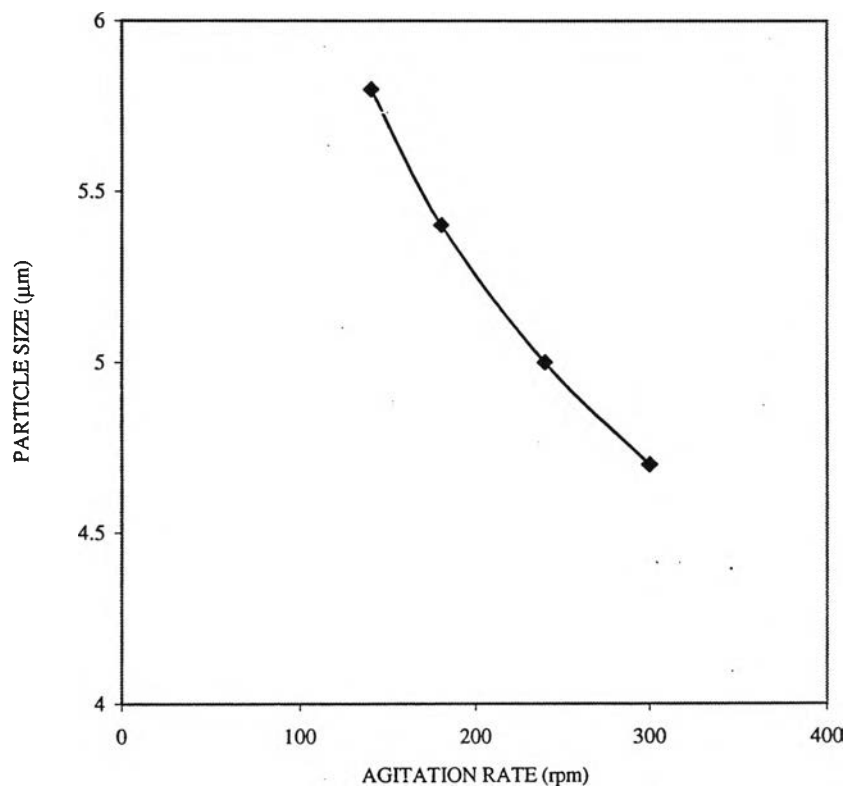
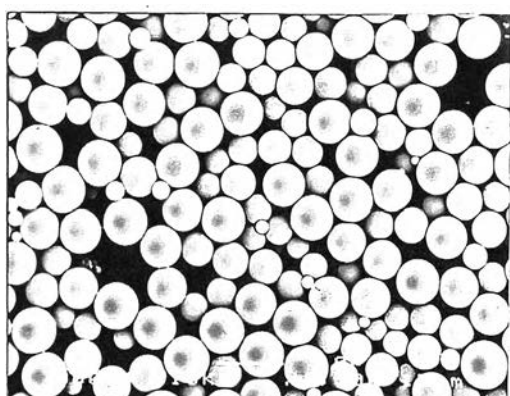
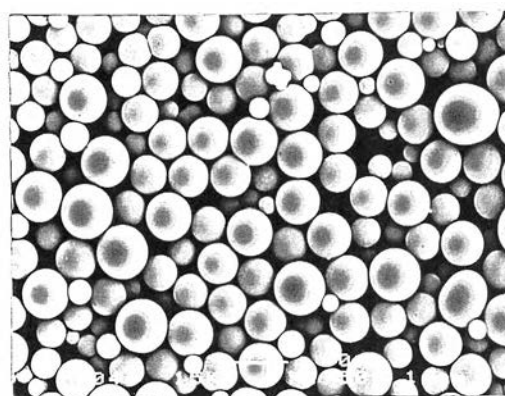


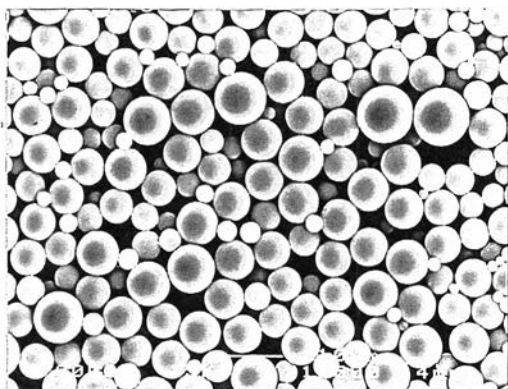
Figure 4.5 Effect of the agitation rate on particle size of the copolymer



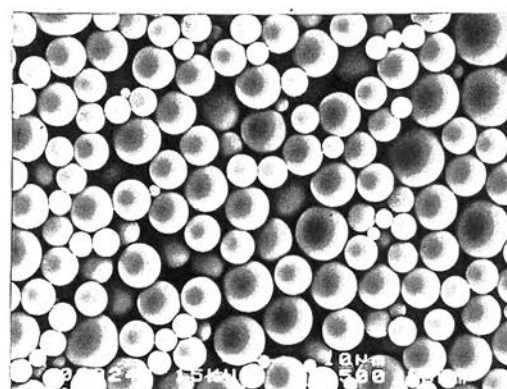
(a) sample A1



(b) sample A2



(c) sample A3



(d) sample A4

Figure 4.6 SEM photographs of the copolymers prepared at various agitation rates:

(a) A1, 140 rpm (b) A2, 180 rpm (c) A3, 240 rpm (d) A4, 300 rpm

4.2.2 The Average Molecular Weights and Molecular Weight Distribution

The relation between agitation rate and average molecular weights is presented in Figure 4.7. The results indicated that at lower stirring rates of 140 rpm, it provided the relatively low molecular weight copolymer. This result could be explained by the assumption that large particle can capture oligomeric radicals in solution for further polymerization less efficiently due to the smaller surface, leading to low molecular weights. Increasing the agitation rate from 180, 240, to 300 rpm, slightly higher average molecular weight was obtained. An increase in the intensity of stirring usually leads to a decrease of the average size of the polymer particles. Because under these conditions, the shearing force is very large and generate smaller particles with a much greater surface area. The smaller particles can grow by efficiently capturing the oligomeric radicals, which are terminated in the continuous phase, leading to the polymerization within the particles. As such, the resulting copolymer has a high molecular weight.

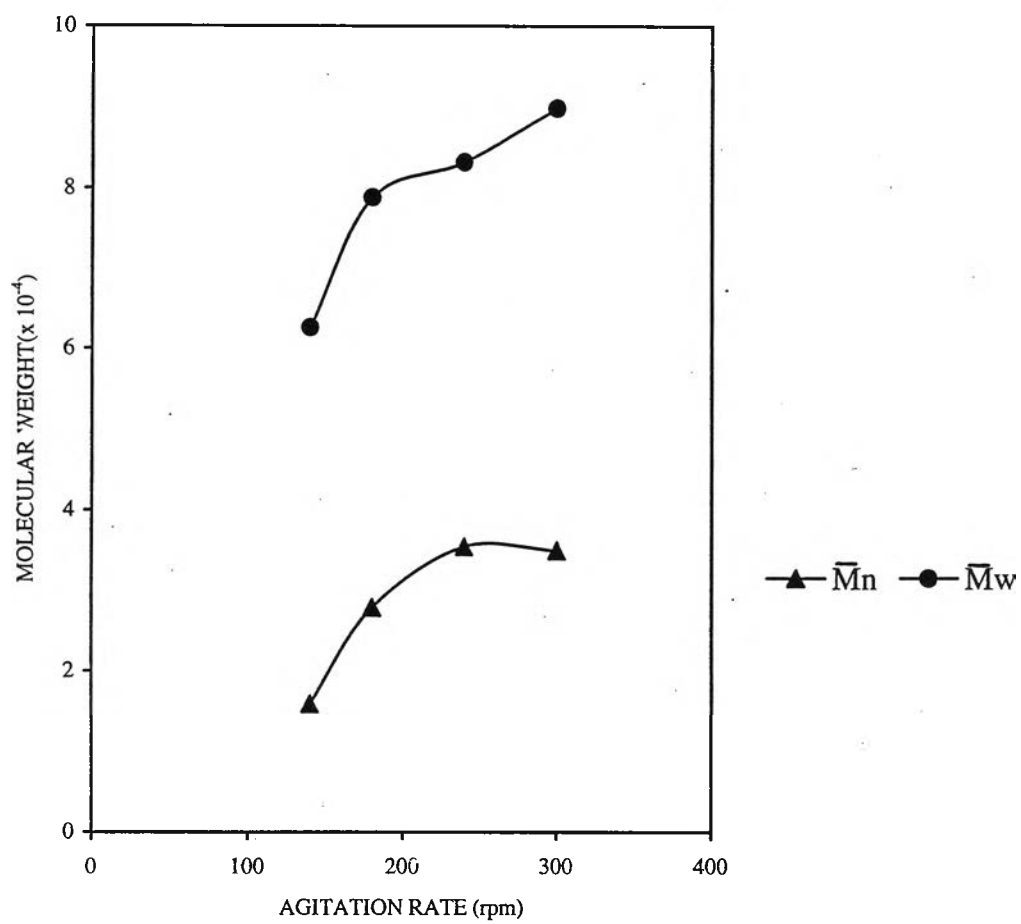


Figure 4.7 Effect of the agitation rate on average molecular weights of the copolymer

4.3 Effect of the Dispersant Concentration

4.3.1 The Particle Size and Size Distribution

Poly(vinyl alcohol) (PVA) was used as a stabilizer in the preparation of the micron-sized styrene and normal butyl acrylate copolymer beads by suspension polymerization. The effects of stabilizer concentration on the particle size, size distribution, average molecular weights and molecular weight distribution were investigated by varying the stabilizer concentrations of 1, 3, and 5 % wt based on the monomer weight.

Suspension polymerization is a reaction which proceeds in the disperse medium. When using a stabilizer in suspension polymerization, the monomer is emulsified by vigorous stirring in the aqueous phase. The polymerization starts, as with a homogeneous polymerization, where an oil-soluble initiator decomposes into initiating radicals. Initiation, propagation, and termination proceed in monomer droplets. The stabilizer is a decisive factor, affecting the dispersion of monomer in water, particle formation and the stability of the polymer suspension. The stabilizer plays a particular role in the system by being adsorbed on the surface of the monomer droplets, and it suppresses coalescence of the monomer and polymer particles.⁴⁸

Poly(vinyl alcohol) is a copolymer of vinyl alcohol and vinyl acetate moiety. A partially saponified poly(vinyl acetate) is a classical representative of a group of the stabilizer formed by water-soluble polymers. It has been established that the stabilizing properties are dependent on the concentration, the degree of hydrolysis,

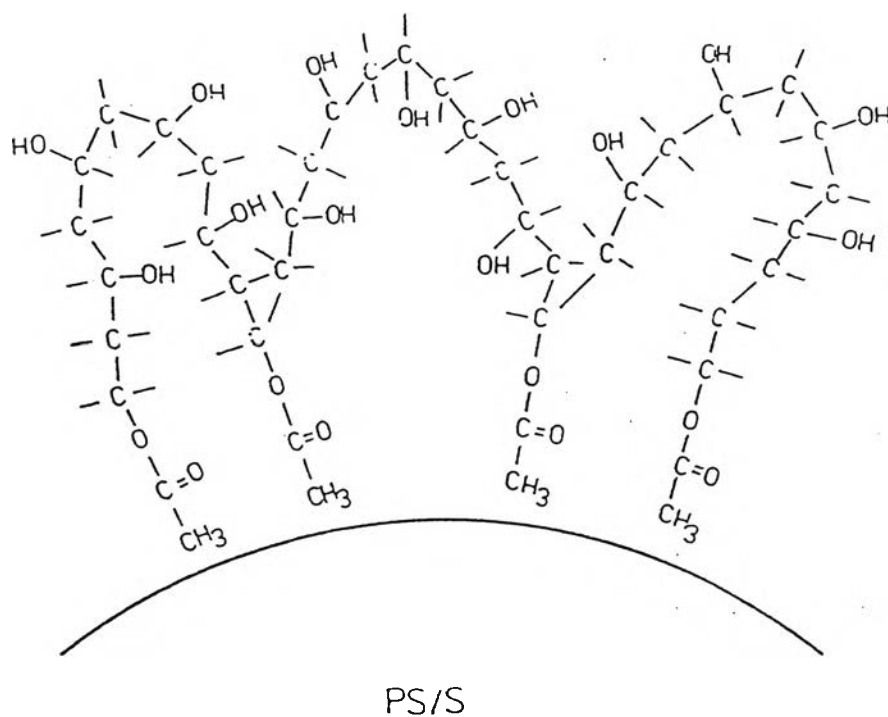


Figure 4.8 Mechanism for stabilizing polymer dispersion (poly(styrene)/styrene) by poly(vinyl acetate) or poly(vinyl alcohol) with residual acetate groups

and the molecular weight of the stabilizer. The stabilizing properties are also dependent on the stage of the polymerization when the poly(vinyl alcohol) is added. After dispersing the monomer phase in water, the partially hydrolysed poly(vinyl acetate) is adsorbed onto the monomer particle surface, and the particles then change gradually into polymer particles. It is localized on the surface such that the terminal acetate groups contact the surface of the oil or polymer phase, while the hydroxyl groups are oriented outwards from the interphase into the water as shown in Figure 4.8. The coalescence occurs due to the collisions of particle droplets in a turbulent flow, most of the collisions results in coalescence. The stabilizer, being spread over the particle surface, creates a protective membrane which prevents coalescence of the particles during collision. In this situation, the polymer particles do not coalesce if the repulsive forces prevail over the attractive ones. Collisions of these stable particles are accompanied only by overlap of their surface layers in the zone of mutual overlap, the osmotic pressure increases owing to the flow of water into these regions, which gradually separates the particles one from another. The rate of separation of the suspension particles, whose surface layers mutually overlap after collision, is not only a function of the osmotic pressure but also of the forces of mutual interaction of the stabilizer molecules and of interactions between the stabilizer molecules and polymer or monomer.

As shown in Table 4.3 and Figure 4.9, the particle size generally decreases with increasing the stabilizer concentration. The average particle sizes decrease from 5.5 to 4.8 μm with an increase in the stabilizer concentrations from 1 to 5 wt %. It can be explained that the mutual interactions of the particles (or their surface layers) cause an increase in the viscosity of the polymer dispersion. Increasing in the

Table 4.3 Effects of the poly(vinyl alcohol) dispersant concentration on particle size, size distribution, and molecular weight in the suspension copolymerization of styrene and n-butyl acrylate

Sample	Dispersant concentration (wt %)	$\bar{D}_n (\mu\text{m})^{a,b}$	$\bar{D}_w (\mu\text{m})^{a,b}$	PDI ^c	σ^d	CV (%) ^e	$\bar{M}_n (\times 10^{-4})$	$\bar{M}_w (\times 10^{-4})$	\bar{M}_w / \bar{M}_n
D1	1	5.5	6.4	1.1	1.25	21.55	6.58	16.84	2.56
D2	3	5.2	5.9	1.1	1.21	22.34	6.32	21.04	3.33
D3	5	4.8	7.0	1.4	1.47	29.40	1.28	24.25	18.97

a = Calculated diameter

b = Determined by scanning electron microscopy

c = Polydispersity index

d = Standard deviation

e = Coefficient of variation

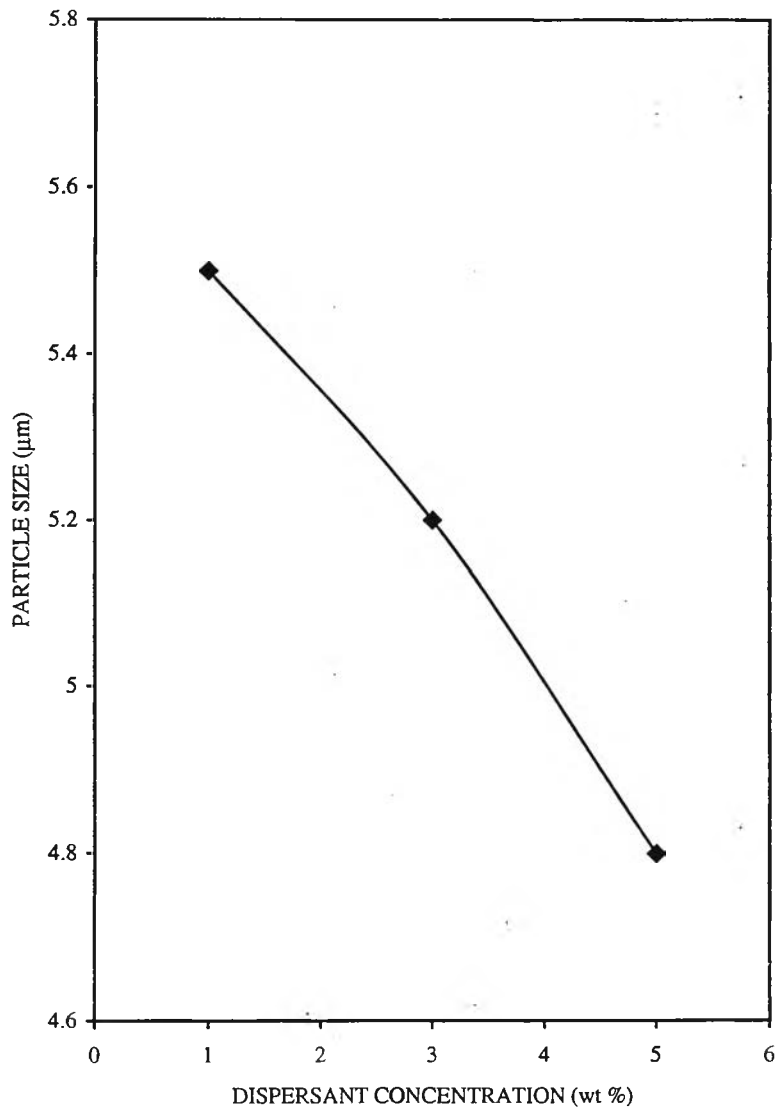
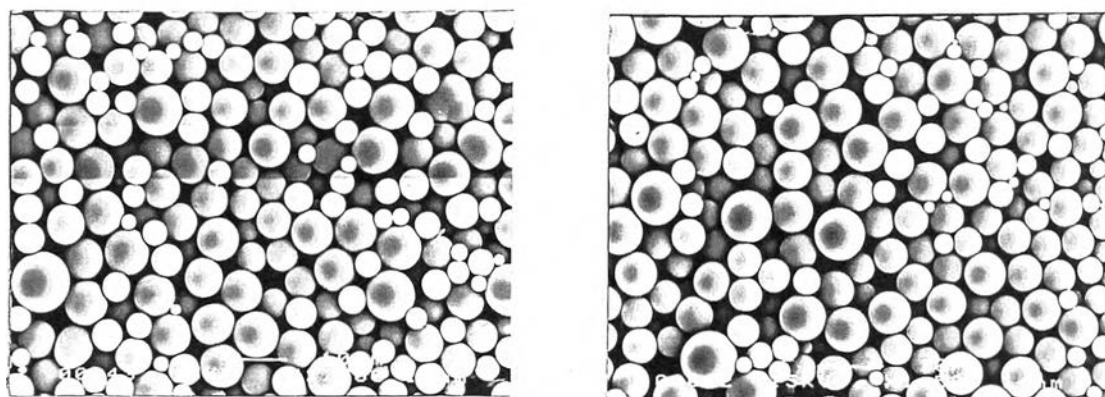


Figure 4.9 Effect of the dispersant concentration on particle size of the copolymer

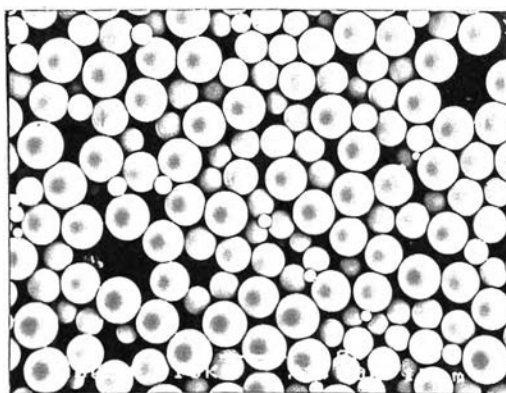
concentration of the stabilizer produces an increase in the viscosity of the reaction medium and the rate of PVA adsorption on the particle surface. The stability of polymer particles in the suspension system is also increased. The increase in stability follows the formation of an efficient protective layer on the particle surface and thus reduces the particle size of the resulting polymer.

Figure 4.10 shows SEM photographs of particles prepared with different concentrations of PVA. At a low concentration of PVA, the particles coalesce and cannot sufficiently cover the surface of particles. The number of particles would decrease, the average diameter increased, and the undesirably wide distribution was obtained as a general characteristic of suspension polymerization. Increasing in the concentration of PVA increases the viscosity of the system, the tendency for polymer particles to coalesce decreases, and the stability of the particles in the suspension increases. The stability of the particles is effective when the stabilizer is present on the surface layers between the water and the monomer droplets. Collisions of droplets separated by water layers containing such the stabilizer less seldom result in coalescence than collisions in the absence of the stabilizer or the protective agents. Accordingly, the viscosity in the phase boundary layers is much higher in presence of the added stabilizer. The soluble suspending agent may form a gel-like protective layer that keeps monomer droplets separated and hinders coalescence. The smaller particles and desirable size distribution is obtained.



(a) sample D1

(b) sample D2



(c) sample D3

Figure 4.10 SEM photographs of the copolymers prepared at various dispersant concentrations: (a) D1, 1 wt % (b) D2, 3 wt % (c) D3, 5 wt %

4.3.2 The Average Molecular weights and Molecular Weight Distribution

The average molecular weights of the copolymer prepared with different PVA concentrations are shown in Table 4.3. The value of $\overline{M}_w/\overline{M}_n$ was in the range of 3.03 to 3.33. In most cases, the higher molecular weight was observed when the concentration of PVA was increased. It could be described that the average molecular weights were inversely related to particle sizes. In other word, the average molecular weights of the resulting copolymer are directly related to the surface areas. Higher concentration of PVA leads to small particles with great surface areas and high molecular weights as well. Suspension polymerization occurs both in the continuous phase and in the monomer droplets. The molecular weights of the copolymer originating from polymerization within the particles are typically higher than those in the continuous phase, because the termination rate is reduced by the viscosity of the monomer/polymer particle medium (the gel effect). The smaller particles with their greater surface areas, a high proportion of the polymerization occurs within the particle because solution-initiated oligomeric radicals are captured more efficiently by these beads before they reach the critical molecular weight and terminate in the continuous phase. On the other hand, the large particles can capture dead polymer molecules in solution and they, therefore, exhibit the lower molecular weights. The relation between average molecular weights and PVA concentration is presented in Figure 4.11.

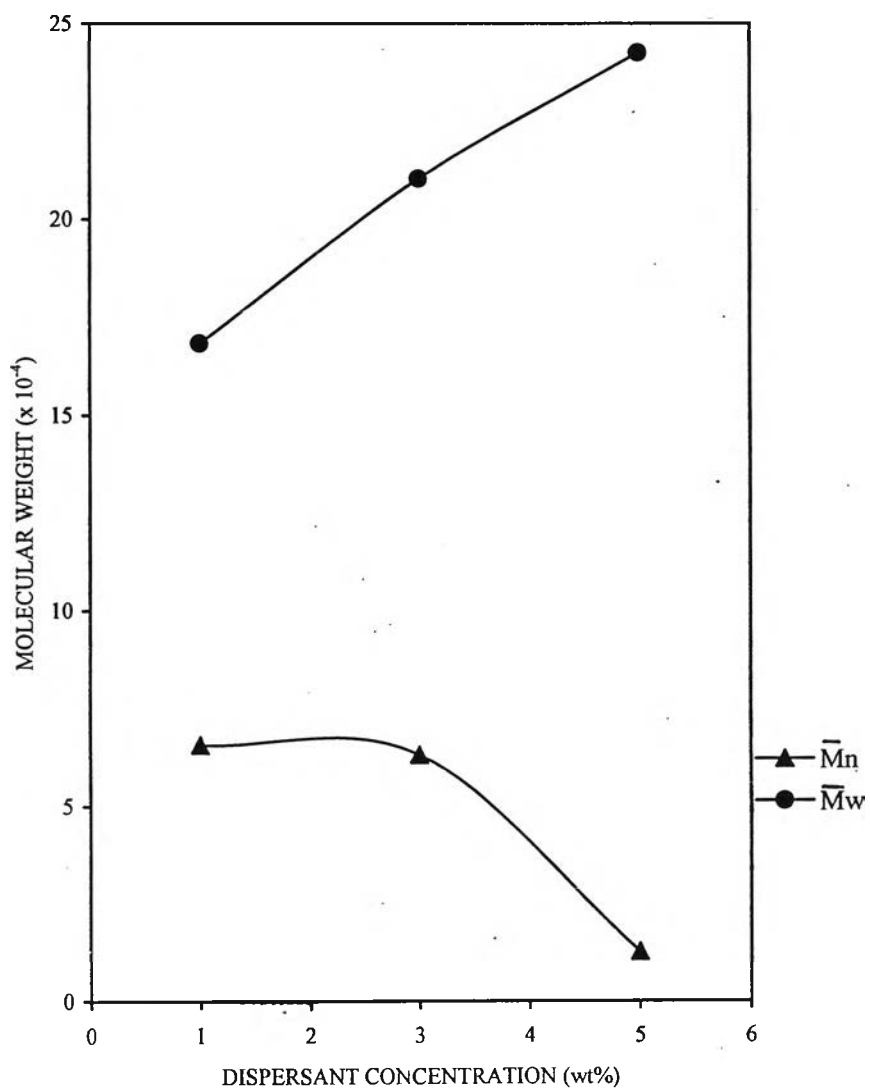


Figure 4.11 Effect of the dispersant concentration on average molecular weights of the copolymer

4.4 Effect of Reaction Time

4.4.1 Particle Growth and Conversion

Generally, the first stage of the suspension polymerization, liquid monomer is dispersed in water in the presence of a stabilizer into a fine dispersion. The polymerization starts with the decomposition of an oil-soluble initiator to produce initiating radicals, which attack the monomer droplets. After the start of polymerization, the polymer precipitates from the emulsified monomer particles as very small particles. They are unstable and associate effectively into larger aggregates called “primary particles”. In the other words, it can be explained that during the growth stage of the reaction, the stabilized particles become so efficient at scavenging unstabilized smaller particles that new nuclei are captured almost immediately, before they have a chance to become stabilized themselves. All the evidence from electron micrographs indicate that very few particles form after the stage of particle formation unless the solvency of the medium is drastically altered or substantial amounts of additional dispersant are added. The number of particles therefore, remains virtually unchanged throughout the remaining course of the polymerization, unless some form of aggregation intervenes, as may happen if the total particle surface formed outruns the amount of dispersant available. The growing particles may also swell with monomer and capture growing oligomer radicals from solution (efficiently if the particle density is high enough), leading to solid phase polymerization of much higher molecular weights that are terminated in solution.⁴⁹

On the conversion aspect, at low conversion (below 1 %), a high concentration of primary particles develops with a low polymer content which undergo brownian motion. The monomer particles are subject to coalescence because their mutual collision leads to the formation of larger particles, the size of which depends on the effect of coagulation. As polymerization proceeds to the medium stage, conversion is characterized by increased stickiness of the polymer particles and their greater tendency to coalesce. The coalescence of these particles is irreversible: neither addition of extra stabilizer nor more vigorous stirring lead to dispersion of the associates. The size of the primary particles and the polymer fraction (gel) in the particle increase. By the association of primary particles, a continuous network is formed with a character depending on the size of the particles, their number and the character of their mutual interaction. The network appears at conversions from 10 to 30 % and its cohesion affects the properties of the polymer gel phase and the porosity of the resulting polymer. If the continuous network is formed at lower conversion, the final product shows high porosity. Stirring leads in this case to a particle distribution according to the sizes and their efficient association. If the conditions for growth of the primary polymer particles as individuals are dominant, in the presence of high inter-particle repulsive forces, the primary particles grow side by side without aggregation. The product being formed shows low porosity as a consequence of the tight packing of the particles accompanied by a considerable contraction of the monomer. As the reaction reaches higher conversions, the polymer particles lose their stickiness and are no longer vulnerable to coalescence. The particle also loses its porous character because the fraction of the polymer phase formed by the primary particles increases. With increasing size of the primary particles and with the

generation of new particles, the space between the particles is filled and the original spherical aggregates are deformed and transform to a continuous polymer phase.

The formation of the primary particles is thus the combined result of four processes that take place inside a monomer droplet:

1. The formation of polymer molecules due to the polymerization reactions.
2. The separation of the polymer phase from the monomer phase with the formation of insoluble polymer particles (basic particles).
3. The aggregation of the particles.
4. The growth of the particle due to polymerization in the polymer phase.

In this research, the particle growth was investigated in terms of the particle size, size distribution, and average molecular weights of the copolymer formed at various reaction times of 6, 8, 10, and 12 hrs, respectively. The effect of reaction time on some characteristics of the copolymer are listed in Table 4.4. The SEM photographs of the particles formed at different reaction times are shown in Figure 4.12. Increasing polymerization times from 6, 8, 10, to 12 hrs, the conversion increases from 56.2, 72.7, 83.5 and 88.4 %, respectively, because the monomer was increasingly converted to the polymer. Figure 4.13 shows the relationship between the percentage of conversion (p) versus the reaction time (t) for this system. The average particle size also increases with increasing the polymerization time. The increased particle size at higher polymerization times due to that the microspheres were aggregated from to form the larger particles.

Table 4.4 Effects of the reaction time on particle growth, conversion, and molecular weight in suspension copolymerization of styrene and n-butyl acrylate

Sample	Reaction time (hrs)	$\bar{D}_n (\mu\text{m})^{a,b}$	$\bar{D}_w (\mu\text{m})^{a,b}$	PDI ^c	σ^d	CV (%) ^e	$\bar{M}_n (\times 10^{-4})$	$\bar{M}_w (\times 10^{-4})$	\bar{M}_w / \bar{M}_n	% Conversion
t1	6	3.8	4.2	1.1	1.35	35.53	3.33	11.52	3.46	56.2
t2	8	5.0	5.5	1.1	1.24	24.80	3.55	14.99	4.22	72.7
t3	10	5.5	7.2	1.3	1.27	23.09	3.65	15.27	4.18	83.5
t4	12	6.4	8.3	1.3	1.42	22.19	6.58	16.84	2.56	88.4

a = Calculated diameter

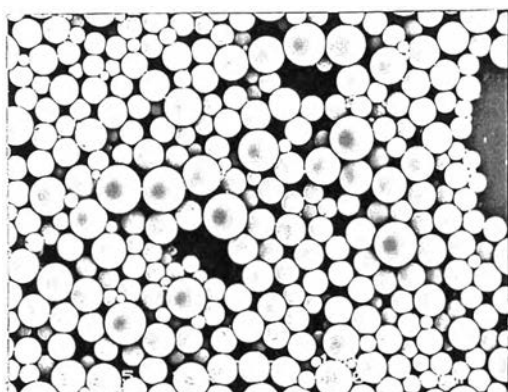
b = Determined by scanning electron microscopy

c = Polydispersity index

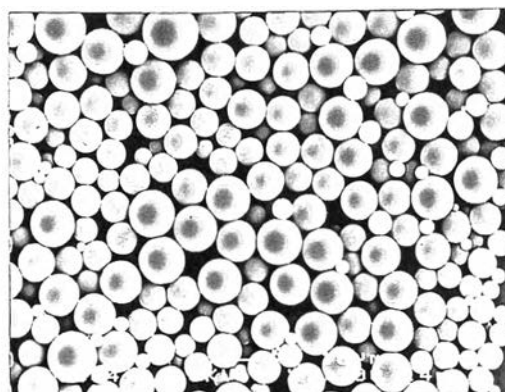
d = Standard deviation

e = Coefficient of variation

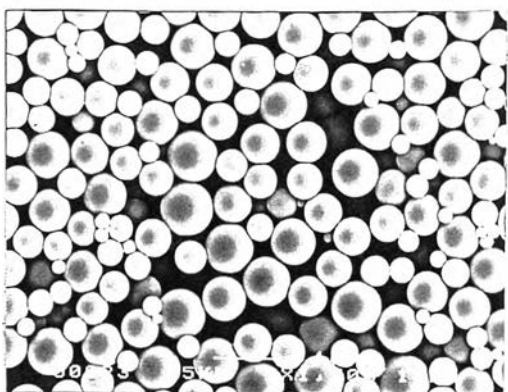
f = Determined by gravimetric method



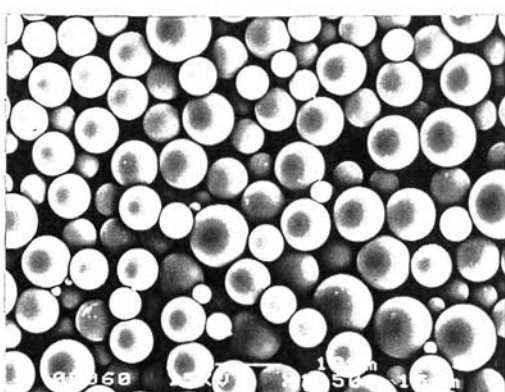
(a) sample t1



(b) sample t2



(c) sample t3



(d) sample t4

Figure 4.12 SEM photographs of the copolymers prepared at various reaction times:

(a) t1, 6 hrs (b) t2, 8 hrs (c) t3, 10 hrs (d) t4, 12 hrs

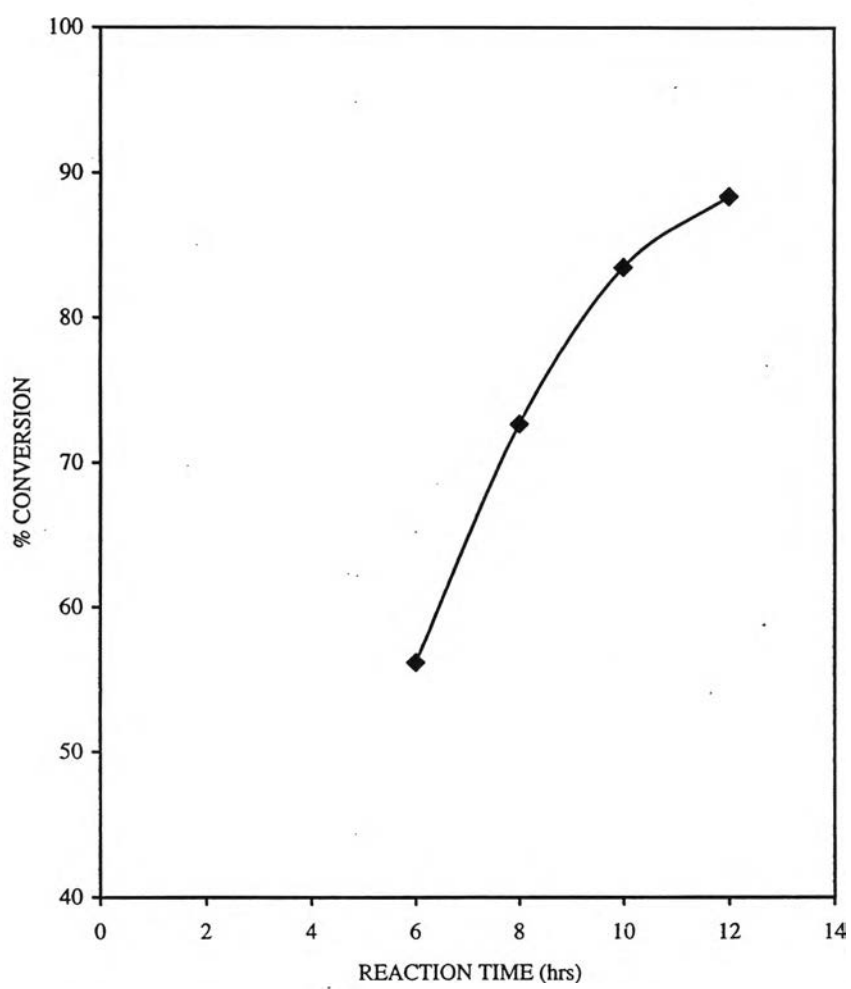


Figure 4.13 Reaction time versus conversion during growth of the copolymer particles

4.4.2 The Average Molecular Weights and Molecular Weight Distribution

The average molecular weights increased as a function of polymerization time. As the polymerization progresses, the critical chain length of oligomer radical is increased and the growth of the copolymer particles is increased as mentioned above. The average molecular weight is gradually increasing, the complete of the polymerization or high conversion gave larger particle sizes with the higher average molecular weights. From the Figure 4.14, we can see that the average molecular weight increased from 115,000 to 168,000 when the polymerization times proceed from 6 to 12 hr.

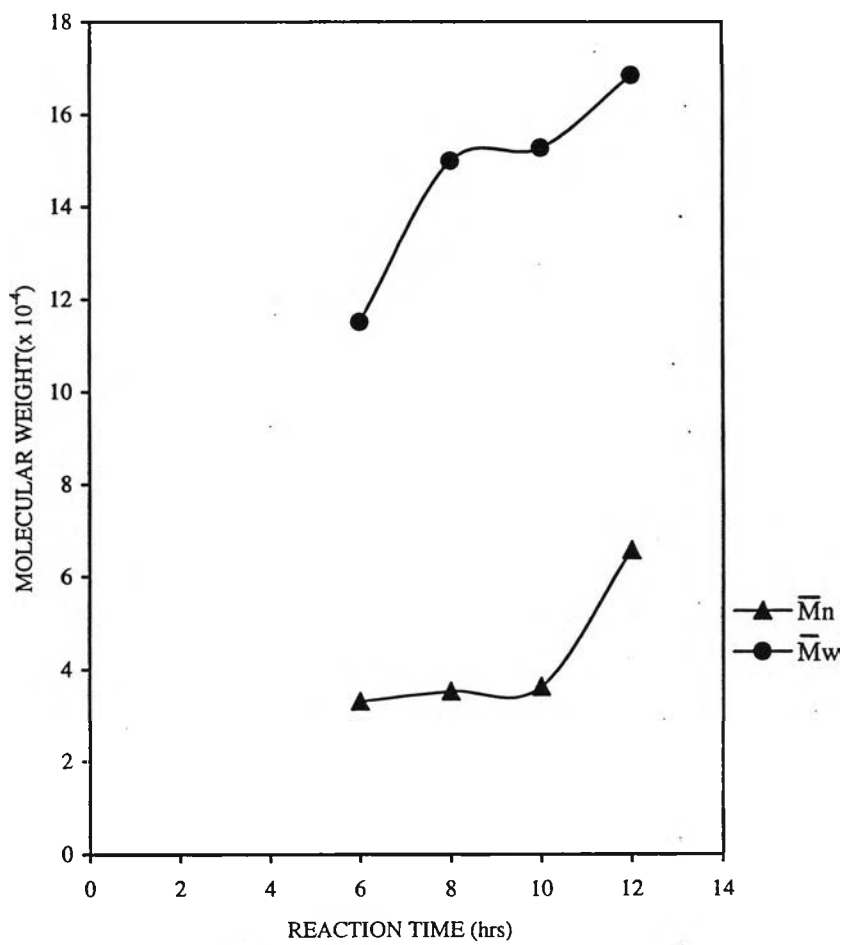


Figure 4.14 Effect of the reaction time on average molecular weights of the copolymer

4.5 Effect of Initiator Concentration on

4.5.1 The Particle Size and Size Distribution

Benzoyl peroxide (BPO) was used as an initiator in the preparation of the micron-sized styrene and normal butyl acrylate copolymer beads by suspension polymerization. The effects of initiator concentration on the particle size, size distribution, average molecular weights and molecular weight distribution were investigated by varying the initiator concentrations of 0.2, 0.6, 1, 1.4, and 2 wt %. Table 4.5 and Figure 4.15 present the effect of initiator concentration on the particle size and size distribution related to benzoyl peroxide concentration. The result indicated that the particle size slightly increased with increasing initiator concentration. The conversion also increases due to more initiating radicals formed in the initiation step.

The average particle size and size distribution of the copolymer beads obtained, as shown in Table 4.5 and Figure 4.15, indicate that the particle size increases from 3.8 to 6.1 μm , when the initiator concentration increases from 0.2 to 2 wt %. The formation of larger particle size with increasing initiator concentration could be as follows: (1) initiation of more polymer chains, (2) the rate at which stabilizer molecules adsorb on the particles, and (3) a higher rate of polymer chain aggregation. The lower molecular weight at higher initiator concentrations represents the formation of more polymer chains. Therefore, the polymer chain density at the onset of nucleation is higher, which causes a higher rate of polymer chain aggregation and increases the number of chains per nucleus. The net increase in polymer chain

Table 4.5 Effects of the initiator concentration on particle size, size distribution, and molecular weight in suspension copolymerization of styrene and n-butyl acrylate

Sample	Initiator concentration (wt %)	\bar{D}_n (μm) ^{a,b}	\bar{D}_w (μm) ^{a,b}	PDI ^c	σ ^d	CV (%) ^e	\bar{M}_n ($\times 10^{-4}$)	\bar{M}_w ($\times 10^{-4}$)	\bar{M}_w / \bar{M}_n
I1	0.2	3.8	4.2	1.1	1.37	36.05	1.07	3.88	3.62
I2	0.6	4.5	5.9	1.3	1.26	28.00	0.48	3.77	7.86
I3	1.0	5.0	5.5	1.1	1.44	28.80	0.94	2.98	3.17
I4	1.4	5.4	7.0	1.3	1.15	21.30	0.38	2.04	5.31
I5	2.0	6.1	6.7	1.1	1.25	20.49	0.32	1.49	4.64

a = Calculated diameter

b = Determined by scanning electron microscopy

c = Polydispersity index

d = Standard deviation

e = Coefficient of variation

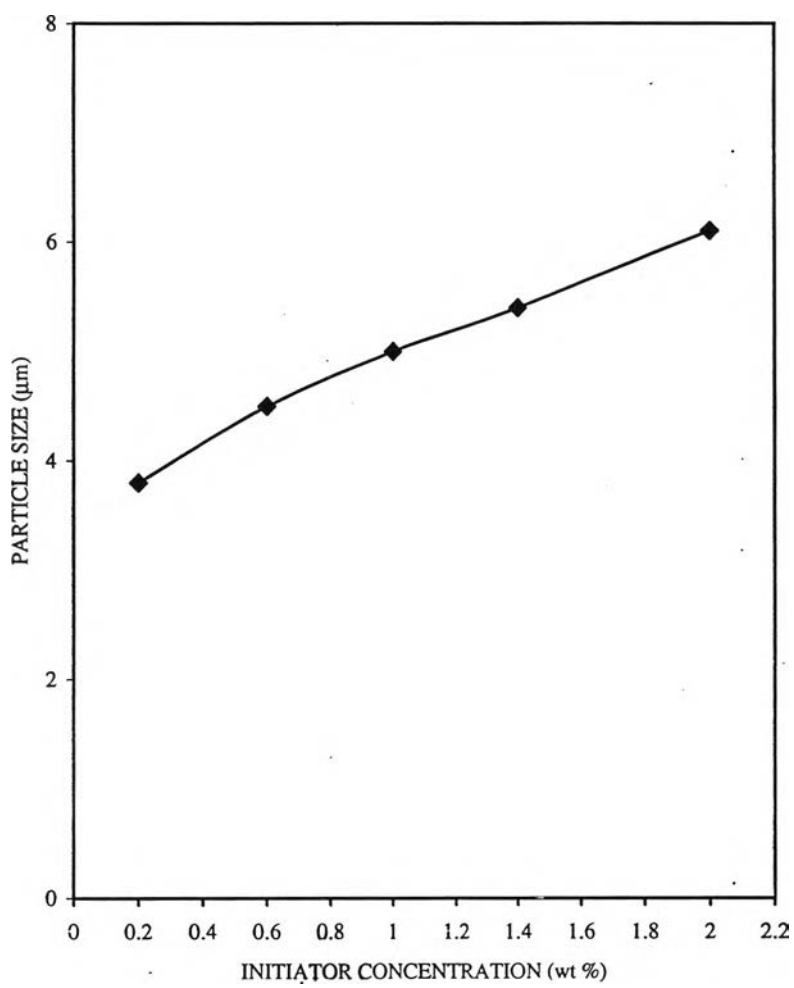
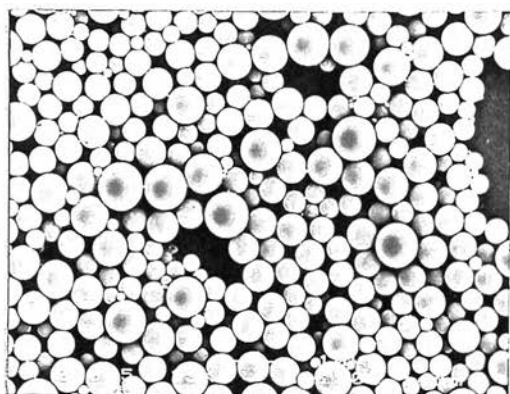
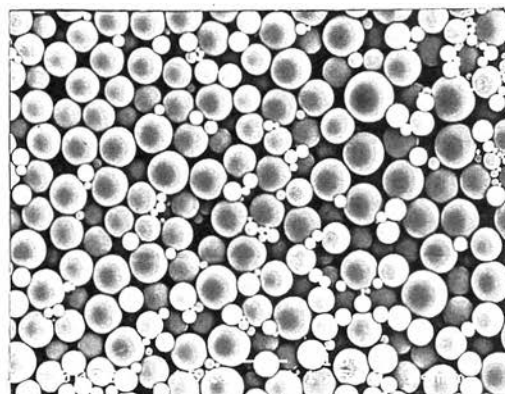


Figure 4.15 Effect of the initiator concentration on particle size of the copolymer

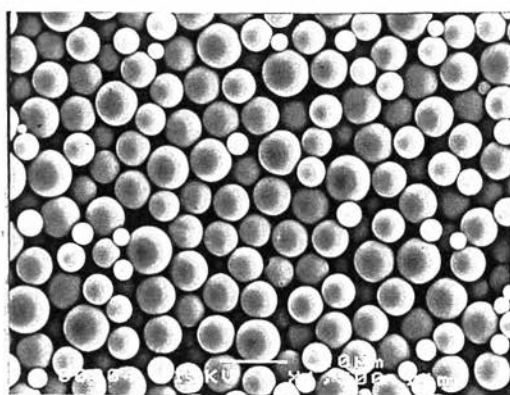
aggregation number is caused by a higher number of polymer chains per unit volume and a faster drop in the solvency of the medium. The rapid change in the medium solvency is expected to take place based on increased polymerization rates at higher initiator concentrations. Therefore, larger particle sizes are nucleated as shown by SEM photographs in Figure 4.16.



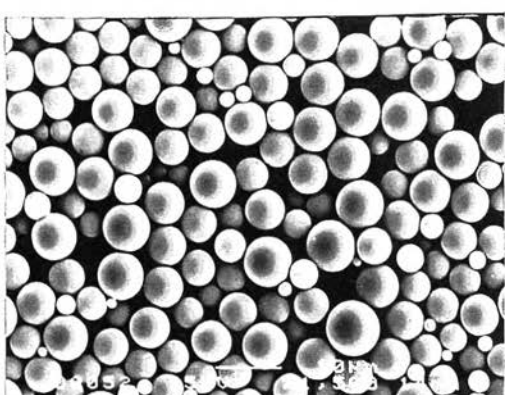
(a) sample I1



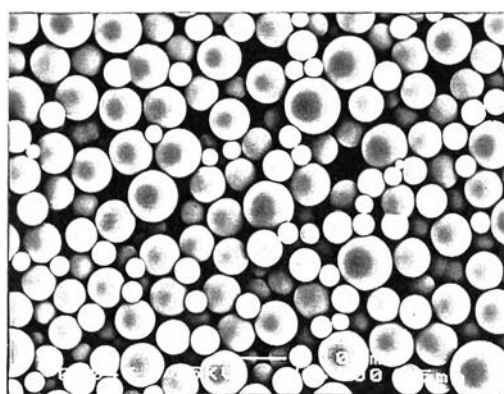
(b) sample I2



(c) sample I3



(d) sample I4



(e) sample I5

Figure 4.16 SEM photographs of the copolymers prepared at various initiator concentrations: (a) I1, 0.2 wt % (b) I2, 0.6 wt % (c) I3, 1.0 wt % (d) I4, 1.4 wt % (e) I5, 2.0 wt %

4.5.2 The Average Molecular Weights and Molecular Weight Distribution

Figure 4.17 shows the relation between the average molecular weights and initiator concentration. The results indicated that, the molecular weight decreased with an increase in the initiator concentration. When increasing initiator concentrations because of more initiating radicals generated in the polymerization system, led to a rapid production of polymers with short kinetic chain length. Kinetic chain length of the polymers is thus governed by the initiator concentration. The average kinetic chain length decreased as the initiator concentration increased. This is entirely reasonable, because increasing the number of growing chains increases the probability of termination. As the result, the final polymeric particles with low molecular weights were obtained. In other words, the gel effect or the Trommsdorff effect or the Norris-Smith effect found at lower initiator concentration was very viscous and reduced the chain mobility. As such, chain-end radicals had a lower probability to be terminated. However, the small monomer molecules could still diffuse to the active chain ends. Even the termination rate decreased, there was a marked increase in the polymerization rate (autoacceleration). The increase in the rate was usually accompanied by an increase in the reaction exotherm, autoacceleration caused processing difficulties, particularly in bulk polymerizations. Higher molecular weights also resulted from the decrease in a termination rate at lower initiator concentrations.

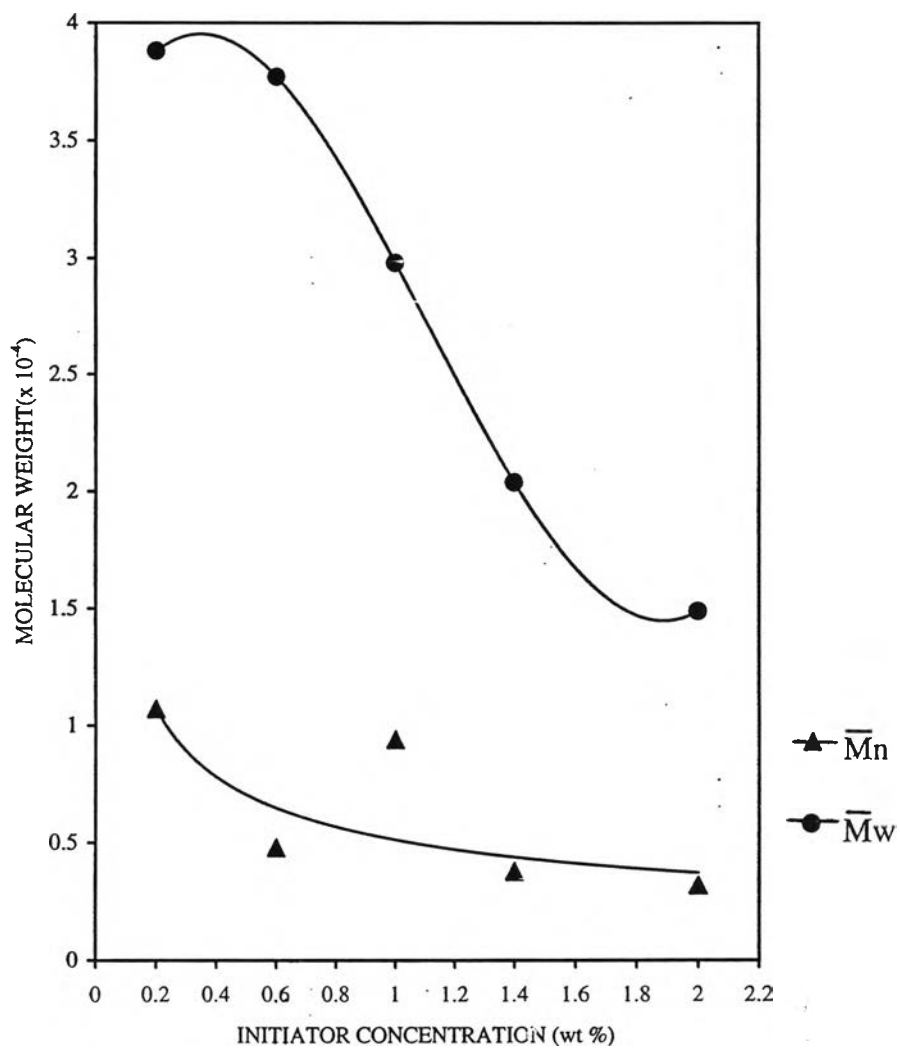


Figure 4.17 Effect of the initiator concentration on average molecular weights of the copolymer

4.6 Effect of Reaction Temperature

4.6.1 The Particle Size and Size Distribution

The effect of reaction temperature on suspension polymerization of styrene and normal butyl acrylate was investigated by varying the reaction temperature of 70, 75, 80, 85°C while the other parameters were kept constant.

Table 4.6 and Figure 4.18 show the effect of reaction temperature on the average particle size and size distribution. The result indicates that when increasing the reaction temperature from 70°C to 85°C, the particle size slightly increased from 5.0 to 5.8 μm , respectively. Basically, the reaction temperature is one of the important parameters to control the formation of particles. Theoretically, the reaction temperature involves both thermodynamic and kinetic aspects of chain polymerization. On the thermodynamic aspect, increasing the temperature increases the magnitudes of ΔH and ΔS , i.e., both are positive as more heat is given. The reaction therefore, spontaneously proceeds and more copolymer will be produced. The latter can be explained that increasing the reaction temperature resulted in an increase in particle size of polymer, because the critical chain length of precipitated oligomer chains was increased due to increase in the solubility of oligomer chains in the continuous phase at the higher reaction temperature. Increase in the concentration of precipitated oligomer chains caused by increases in both the decomposition rate constant of the initiator (k_d) and the propagation rate constant of the monomer (k_p), these could therefore lead to an increase in their aggregates and the resulting larger polymeric particles were obtained as shown by SEM photographs in Figure 4.19.

Table 4.6 Effects of the reaction temperature on particle size, size distribution, and molecular weight in suspension copolymerization of styrene and n-butyl acrylate

Sample	Reaction temperature (°C)	\bar{D}_n (μm) ^{a,b}	\bar{D}_w (μm) ^{a,b}	PDI ^c	σ ^d	CV (%) ^e	\bar{M}_n ($\times 10^{-4}$)	\bar{M}_w ($\times 10^{-4}$)	\bar{M}_w / \bar{M}_n
T1	70	5.0	5.5	1.1	1.57	31.40	5.88	12.30	2.09
T2	75	5.2	6.2	1.2	2.32	44.62	5.29	11.22	2.12
T3	80	5.5	7.2	1.3	2.35	42.73	4.22	10.26	2.43
T4	85	5.8	6.4	1.1	1.28	22.07	3.79	9.98	2.63

a = Calculated diameter

b = Determined by scanning electron microscopy

c = Polydispersity index

d = Standard deviation

e = Coefficient of variation

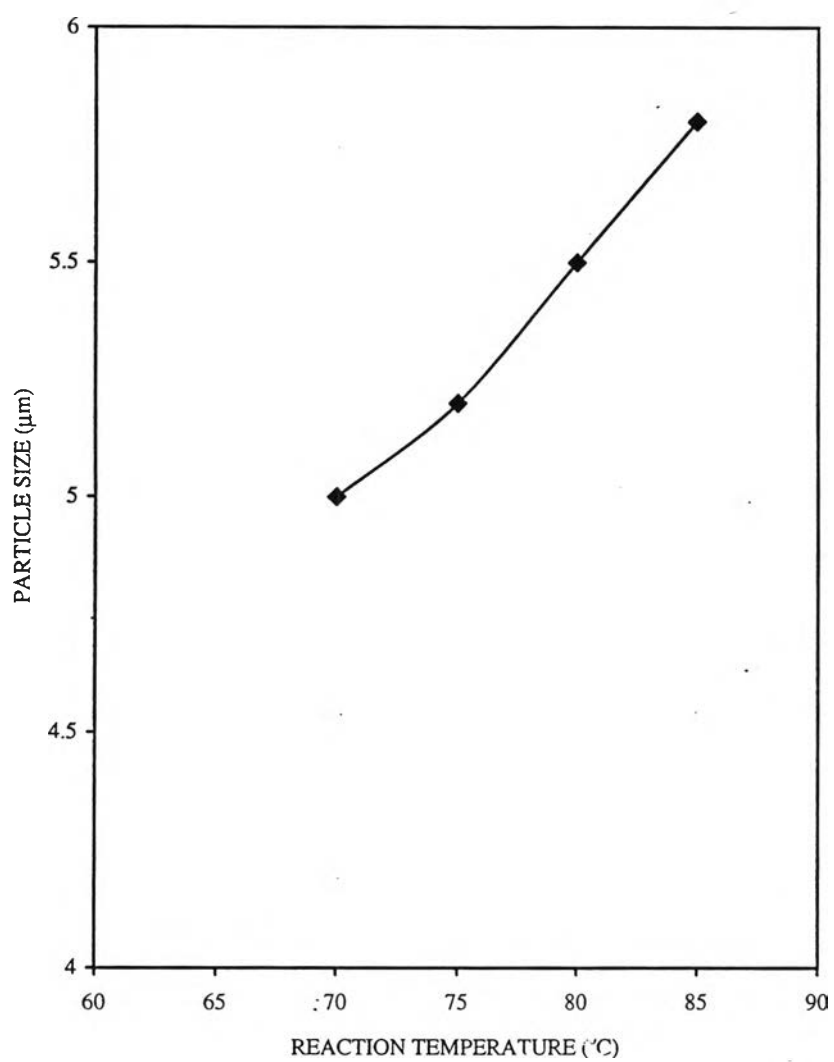
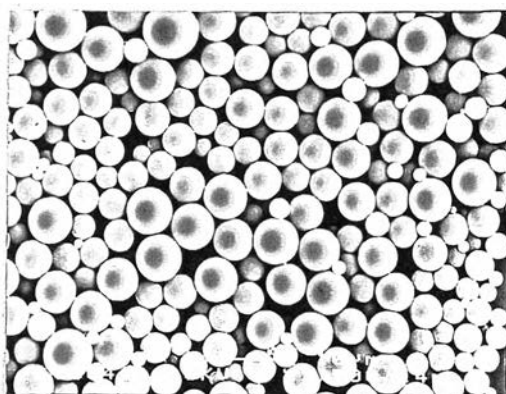
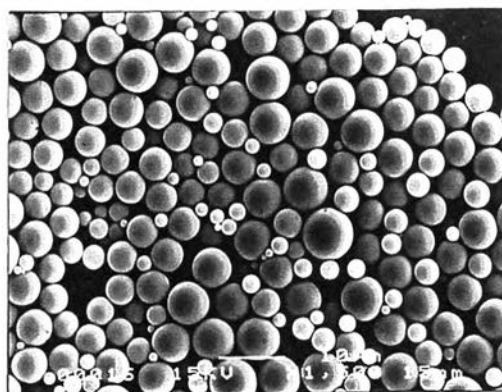


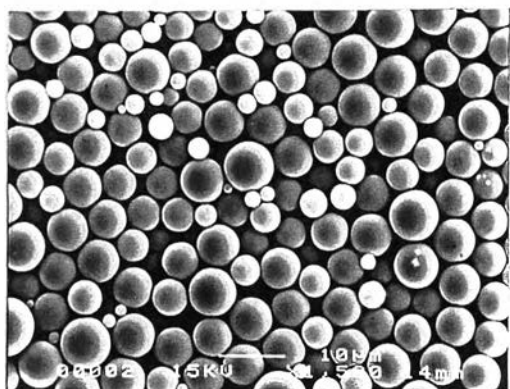
Figure 4.18 Effect of the reaction temperature on particle size of the copolymer



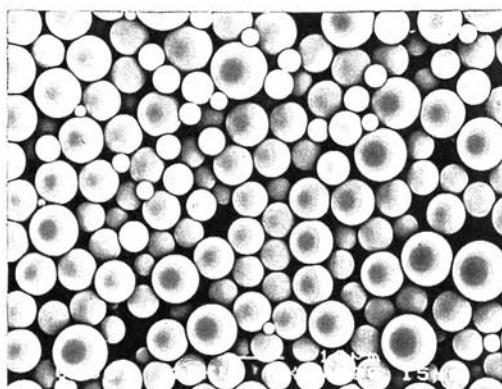
(a) sample T1



(b) sample T2



(c) sample T3



(d) sample T4

Figure 4.19 SEM photographs of the copolymers prepared at various reaction temperatures: (a) T1, 70°C (b) T2, 75°C (c) T3, 80°C (d) T4, 85°C

4.6.2 The Average Molecular Weights and Molecular Weight Distribution

Figure 4.20 shows the relation between the average molecular weights and temperature. The results indicated that, as increasing the reaction temperature, the average molecular weights decreased. Increasing reaction temperature increases the solubility of oligomeric chains and thus the locus of the polymerization shifts to the continuous phase. A majority of the oligomeric radicals terminate in the continuous phase before they are captured by the existing particles, resulting in a lower molecular weight. For other explanations, at low temperatures, more monomers are converted to polymers per initiator per fragment than at high temperatures, where the higher rate of free radical formation will actually enhance the probability of chain termination by initiator.⁵⁰ As a result of these competing effects, the initiator becomes exhausted more quickly at high temperatures, leading to producing short kinetic chain length, the resulting polymeric particles with low molecular weight were obtained. Additionally, high temperatures reduces the viscosity of the polymerization medium which accelerates the polymerization rate because the gel effect is smaller than that of at low temperature.

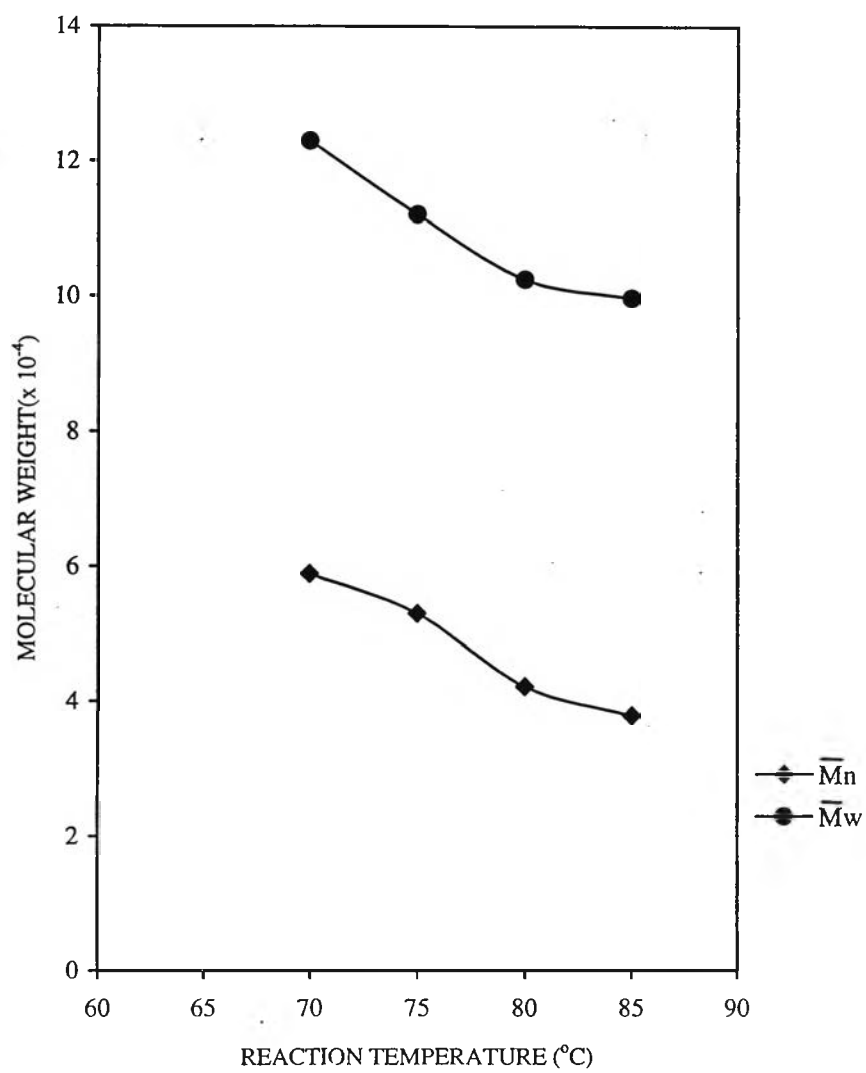


Figure 4.20 Effect of the reaction temperature on average molecular weights of the copolymer

4.7 Effect of Monomer Feed Ratio on

4.7.1 The Particle Size and Size Distribution

In this experiment, the polymerization was performed by varying the ratio between the styrene and normal butyl acrylate at 90/10, 85/15, and 80/20 mol %. The effect of the monomer composition on the particle size and size distribution is showed in Table 4.7 and Figure 4.21. The results were found as shown by SEM photographs in Figure 4.22. Increasing the mole percent of nBA feed from 10 % to 20 %, the particle size slightly increased. The increase was not significant because the amount of nBA used was limited due to its low glass transition temperature (-54°C).⁵¹ The largest particle size was obtained from 20% feed ratio of nBA, while the smallest size was obtained from 10% feed ratio of nBA.

The result can be described by two main reasons: (1) the different interactions between the two monomers and the dispersant^{52,53} and (2) the change in solvency of the reaction medium.⁵⁴ For the first reason, as mentioned above, at the beginning of polymerization, primary radicals were produced by the thermal decomposition of BPO, which in turn react with St and nBA to form the growing oligomer chains with a reactive free radical at the end (this step is an exactly conventional solution polymerization). When the oligomer chains reach their critical chain length, they precipitate to form nuclei either by self or aggregative mechanism.⁵⁵ These nuclei are unstable and will aggregate with each other, they adsorb simultaneously the dispersant and become stable against flocculation when sufficient dispersants are completely adsorbed onto the particle surface. It can be assumed that two types of dispersant may

Table 4.7 Effects of the monomer feed ratios on particle size, size distribution, molecular weight, and glass transition temperature in suspension copolymerization of styrene and n-butyl acrylate

Sample	Monomer Feed ratios of (St/nBA) (mol %)	\bar{D}_n (μm) ^{a,b}	\bar{D}_w (μm) ^{a,b}	PDI ^c	σ ^d	CV (%) ^e	\bar{M}_n ($\times 10^{-4}$)	\bar{M}_w ($\times 10^{-4}$)	\bar{M}_w / \bar{M}_n	T_g ($^{\circ}\text{C}$) ^f
M1	90/10	4.8	5.76	1.2	1.24	25.83	3.73	9.94	2.67	79
M2	85/15	5.2	6.76	1.3	1.36	26.15	3.70	8.74	2.36	71
M3	80/20	5.4	7.02	1.3	1.45	26.85	0.76	7.41	9.82	65

a = Calculated diameter

c = Polydispersity index

e = Coefficient of variation

b = Determined by scanning electron microscopy

d = Standard deviation

f = Determined by differential scanning calorimetry

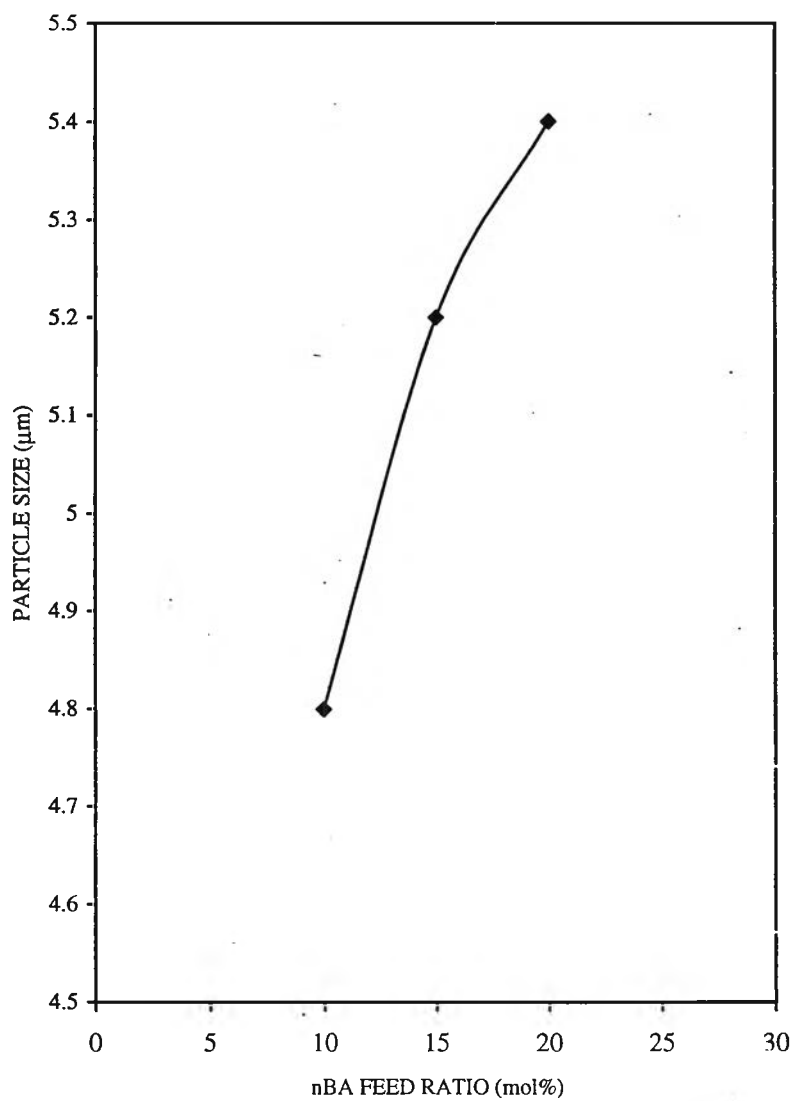
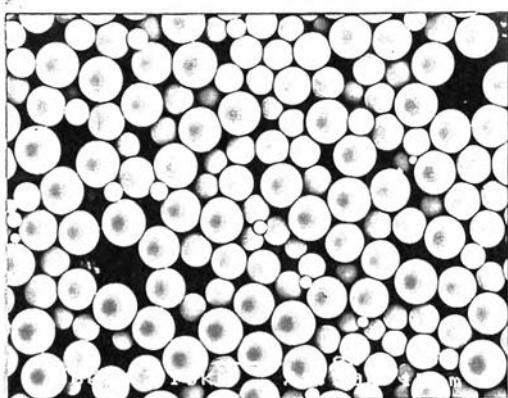
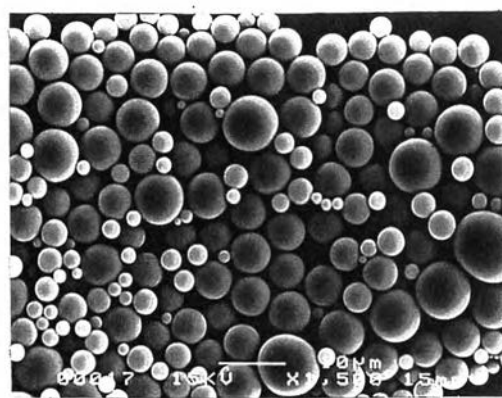


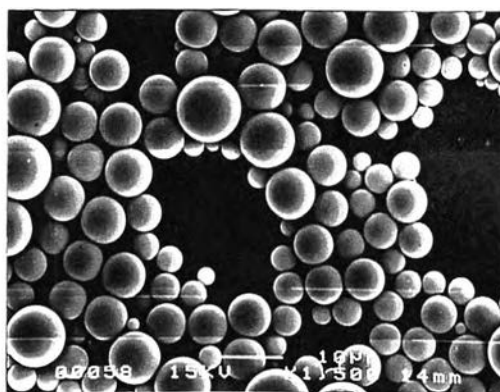
Figure 4.21 Effect of the monomer feed ratios on particle size of the copolymer



(a) sample M1



(b) sample M2



(c) sample M3

Figure 4.22 SEM photographs of the copolymers prepared at various monomer feed ratios (St/nBA): (a) M1, 90/10 mol % (b) M2, 85/15 mol % (c) M3, 80/20 mol %

coexist, the precursor polymer (PVA) and its graft copolymer (PVA-g-P(St-co-nBA) which is created in situ during polymerization. When only the homopolymer of PVA is used as a dispersant, the stabilizing efficiency is rather poor because it is soluble in the medium. However, it is believed that PVA, which possesses an active alpha-hydrogen can generate free radical sites through a hydrogen abstraction, and these sites may then function as a growth center upon an additional polymerization of St and nBA, yielding the graft copolymer. According to the electron donating-electron accepting theory, it was usually observed that the reactivity of an electron-donor radical would be greater with an electron-acceptor than with an electron-donor substrate.⁵⁶ For this explanation, the styrene monomer is adsorbed much stronger on the free radical-PVA molecules than is the normal butyl acrylate, as the styrene monomer is a stronger electron donor for the PVA matrix. This contribution leads to the smallest particles with increasing styrene content.

The latter reason involves the change of the solubility of the copolymer in the reaction medium. Comparing the polarity of styrene and normal butyl acrylate, the latter is more polar and also more soluble in the medium. Increasing the relative amount of nBA in the monomer composition means an increase in the polarity of the reaction medium. Therefore, the copolymer rich in nBA is more soluble in the continuous phase than is the copolymer rich in styrene, resulting in the greater importance of the polymerization in the solution, and thus the larger particle sizes with the low average molecular weight are obtained.

4.7.2 The Average Molecular Weights and Molecular Weight Distribution

Table 4.7 and Figure 4.23 show the average molecular weight of the resulting polymers at various monomer feed ratios. The highest average molecular weight of the polymer formed was obtained from 10 mol % nBA, while the lowest molecular weight was obtained from 20 mol % nBA. It can be explained that there is a trend to decrease the average molecular weight with increasing nBA content. It is similar to most systems that smaller particles with greater surface area can grow by capture of radicals and nuclei in the solution and further polymerization within particles (as bulk polymerization) leading to gel effect, as shown from the result that decrease in the termination rate as the viscosity of the polymerization medium increases. Although the diffusion of monomer is still possible within the increasingly viscous medium, the diffusion of the much larger growing polymer radicals is considerably retarded and makes them much less likely to terminate with each other. Although the polymer growth continuous largely unhindered under these conditions, the termination rate is considerably reduced. Therefore, the high average molecular weights of resulting polymers are obtained from the smaller size particles.

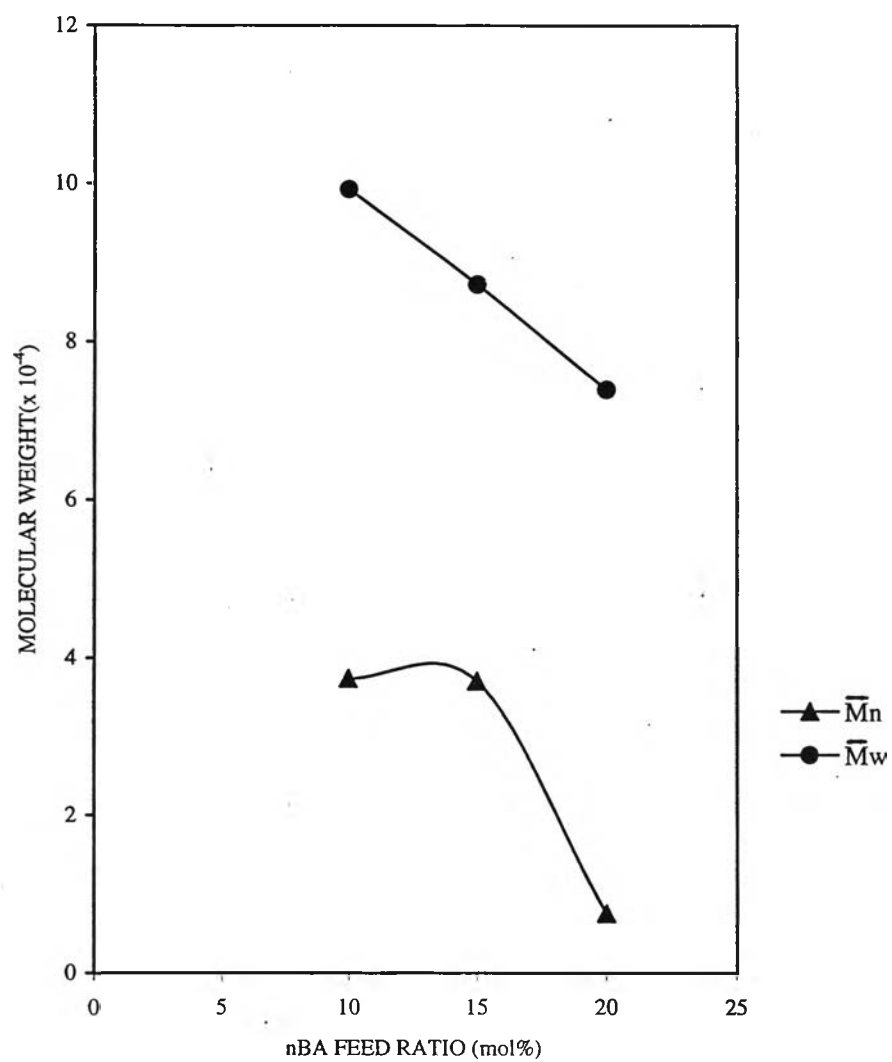


Figure 4.23 Effect of the monomer feed ratios on average molecular weights of the copolymer

4.7.3 Glass Transition Temperature

Glass transition temperature of the copolymer is an important property in characterizing the 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 T_g about 50-70°C.⁵⁷

The copolymer were investigated by DSC to identify the T_g value. The DSC thermograms of the copolymers, synthesized with different St/nBA feed ratios are shown in APPENDIX A. The T_g values was found in the range of 65 to 79°C. It can be noted that varying the feed ratio of the copolymer has a direct impact on glass transition temperature of the resulting copolymers. The relation between T_g and nBA content are presented in Figure 4.24. The T_g of the copolymer decreased as the amount of nBA increased. This effect is due to the lower glass transition temperature of Poly(nBA)(-54°C)⁵⁸, the copolymer rich in nBA possess the lowest T_g at 65°C whereas the copolymer rich in St has the highest T_g at 79°C.

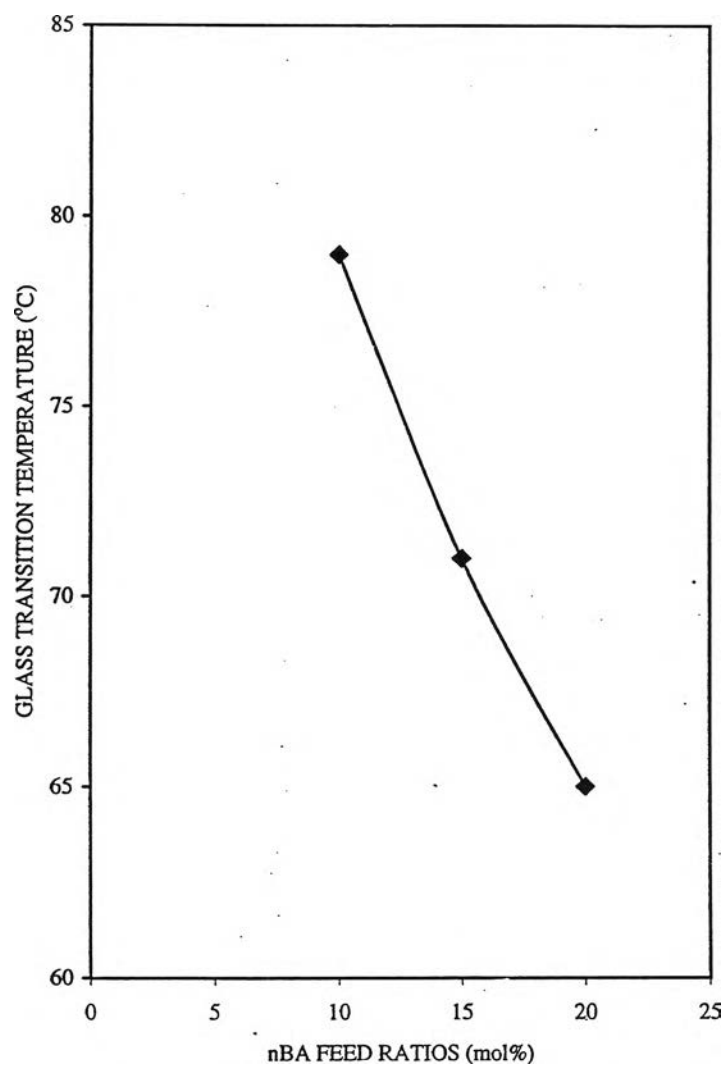


Figure 4.24 Effect of the monomer feed ratios on glass transition temperature of the copolymer

4.8 Effect of Crosslinking agent Concentration

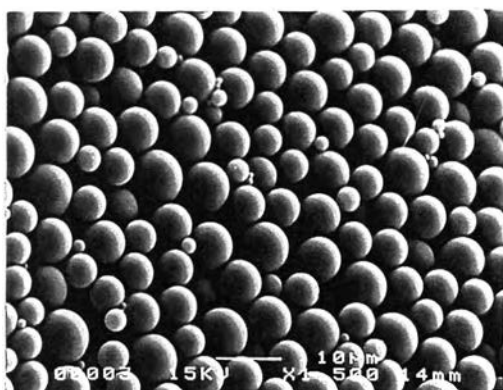
4.8.1 Particle Morphology

In this research, divinylbenzene (DVB) was used as a crosslinking agent. The concentration of DVB was varied at 1, 3, 6, and 8 wt % based on the monomer weight. The results of suspension polymerization in the presence of the crosslinking agent at different concentrations were illustrated in SEM photographs in Figure 4.25. It was found that the concentration range of the crosslinking agent producing spherical particles is limited. As the DVB concentration was increased from 1 to 6 wt %, the average particle size was decreased slightly and the particle uniformity remained unchanged. When 8 wt % of DVB was used, the particles tended to flocculate and a neck-like structure was observed.

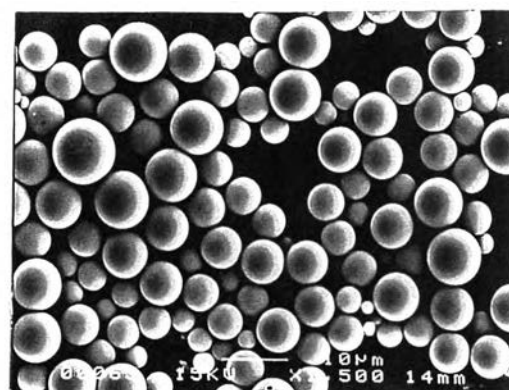
When DVB was incorporated to develop the network within the particles, a pendent vinyl group of DVB can further react with a growing chain in the region of the particle subsurface, making the ability of the adsorbed PVA graft copolymer chains that act as an effective steric stabilizer become compromised, because the reaction irreversibly links the PVA graft copolymer chains to the bulk particle phase. Once the freedom of movement has been restricted in this way, and the grafts can no longer migrate with the advancing surface, it becomes redundant and unless it is replaced by the fresh dispersant from the continuous phase. The particles then begin to be unstable or destabilize.⁵⁹ At the concentration of DVB less than 6 wt %, the effect of destabilization was not observed, although some parts of the particles covered with the adsorbed PVA graft copolymers tied to the particle phase with the DVB

copolymer, the gel was insufficiently crosslinked to render it rigid enough to paralyze the grafts. In other words, it has an elasticity that permits the bound chains of PVA graft copolymers to have an enough freedom of movement to maintain the particle stability.

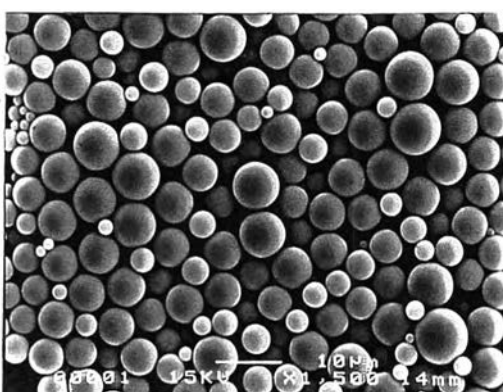
As the level of DVB increased to 8 wt % the deviation from sphericity became apparent. More graft chains at the surface are immobilized, leading to the partial flocculation to commence. To maintain their stability, the particles began to minimize their surface exposure by coalescence with each other. From this phenomenon, the particles forming the neck-like structure were obtained.



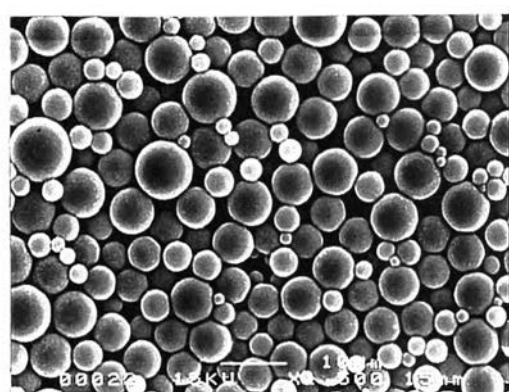
(a) sample C1



(b) sample C2



(c) sample C3



(d) sample C4

Figure 4.25 SEM photographs of the copolymers prepared at various crosslinking agent concentrations: (a) C1, 1 wt % (b) C2, 3 wt % (c) C3, 6 wt % (d) C4, 8 wt %

4.9 Preparation of Micron-Sized Polymerized Toner by Suspension Polymerization

In this study, the micron-sized polymerized toners were prepared by suspension polymerization. The appropriate condition for the synthesis of styrene and normal butyl acrylate copolymer obtained in the Section 3.4.1 was used as the polymeric matrix. For this section, we have explored the possibility of incorporating carbon black into suspension polymerized copolymers. The effects of carbon black on the various properties of polymerized toner were investigated. Then, the resulting polymerized toner were characterized for the following properties: particle size and size distribution by SEM, molecular weight and molecular weight distribution by GPC, thermal properties by DSC, carbon black distribution of the sample bead by TEM, and triboelectric charging properties of the resulting polymerized toners by a Blow-off method.

4.9.1 Effect of carbon black

4.9.1.1 The Particle Size and Size Distribution

In this research, carbon black, with a mean particle size of 21 nm, pH 10, and a surface area of $115 \text{ m}^2\text{g}^{-1}$ was used as a coloring agent in suspension copolymerization of styrene and normal butyl acrylate. The carbon black concentrations were investigated by varying the amounts of carbon black of 1, 3, 5, and 7wt% based on the monomer weight. The appropriate condition for a synthesis of

styrene and normal butyl acrylate copolymer obtained in Section 3.4.1 used as the polymeric matrix were shown as follows:

Initiator concentration :	1 wt%
Dispersant concentration :	5 wt%
Monomer feed ratio :	80/20 mol%
Reaction temperature :	70°C
Reaction time :	8 hrs
Agitation rate :	180 rpm
Mechanical homogenizer speed :	7000 rpm
Crosslinking agent :	6 wt%
Charge controlling agent :	2 wt%
Sodium dodecyl benzene sulfonate :	0.05 wt%

Generally, it has been known for many years that most radical polymerizations are adversely influenced by the presence of carbon black, such that the reaction may be retarded or indeed completely inhibited.⁶⁰ It can be explained that the functional groups on the surfaces of carbon black, which are likely to interact with primary or propagating radicals, hence giving rise to the retarding/inhibiting effects. The propagating radicals reacted with a surface functional group of the carbon black can give rise to a grafting reaction.⁶¹ In other words, when the peroxy compounds are used as an initiator, a primary interaction of the primary radicals with the carbon black takes place, and indeed the carbon black can induce decomposition of the peroxy initiator even at low temperature. The reaction involved is certainly an

oxidation process. Its surface oxidation of the carbon black by strong oxidizing agents including peroxy species occurs.

In addition, it is well-known that carbon blacks act as strong radical scavengers. In suspension polymerization of vinyl monomers in the presence of carbon blacks, peroxides, such as benzoyl peroxide, as an initiator are usually used. At the beginning of polymerization, primary radicals were produced by thermal decomposition of benzoyl peroxide, which in turn reacted with monomer particles to form the growing oligomer chains with a reactively free radical at the end. In the presence of carbon black, these corresponding radicals are bonded onto the surface by an addition 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 polycondensed aromatic rings of carbon black as shown in Figure 4.26.

Consideration in terms of surface functional groups of the carbon black, as functionality increased tend to the inhibitory effect increases. The mechanism of the free radicals formed on the carbon black surface with quinonic oxygen groups two major types of products are obtained quinone and ether formed by reaction at the C and O atoms of a quinone, respectively. Attack of a propagating radical at oxygen yields the aryloxy radical, which can terminate by coupling and/or disproportionation with another propagating radical (or itself) or add monomer. Attack on the ring carbon yields radicals, which can react with another propagating radical to form the quinone. In the case of phenolic are poor retarders even toward highly reactive radicals such as the poly(vinyl acetate) propagating radical.⁶² Phenols with electron-donating groups act as more powerful retarders. The presence of an electron-

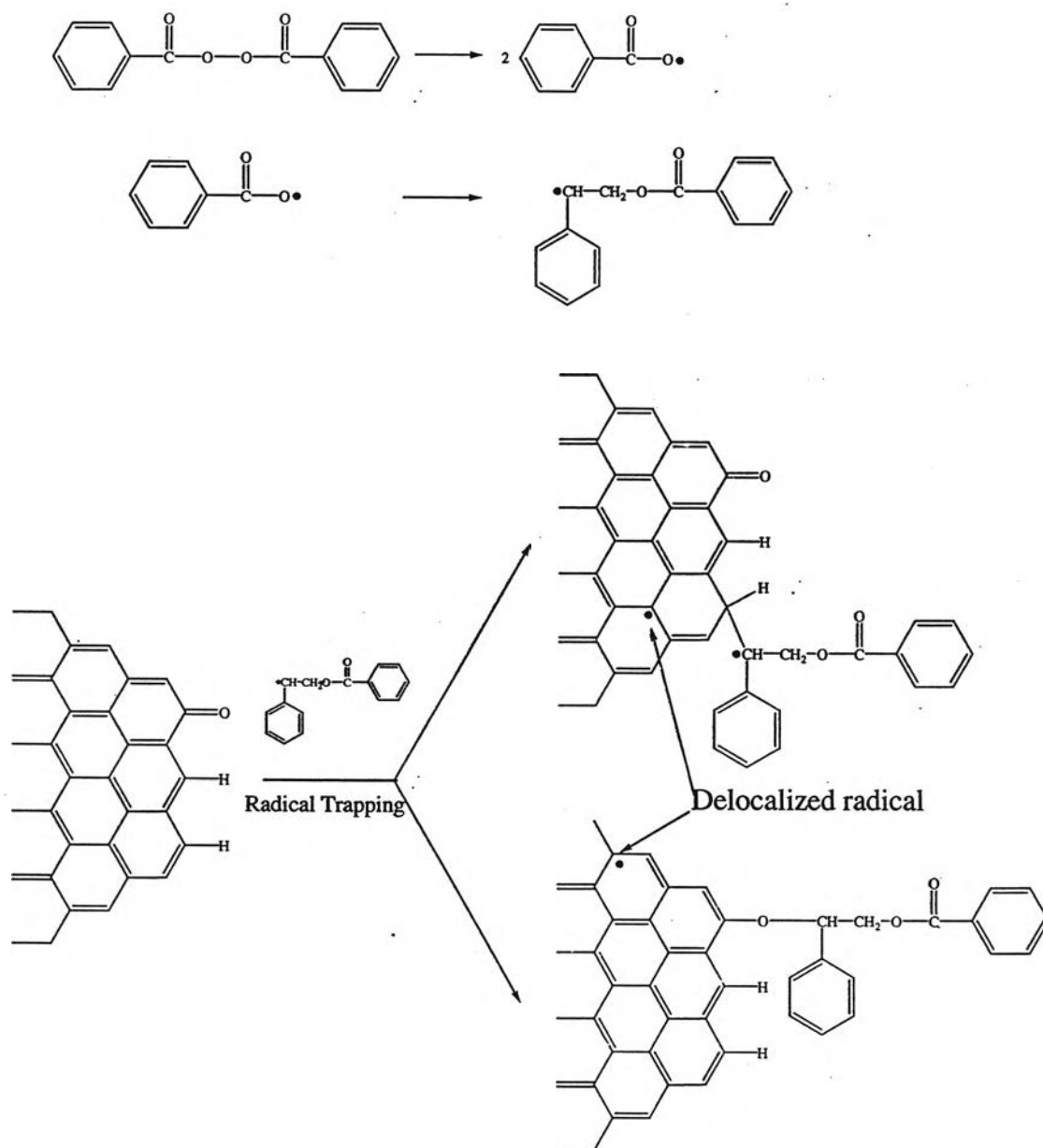


Figure 4.26 Mechanism of the free radicals formed on the carbon black surfaces by the addition of initiator radicals

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.

Table 4.8 and Figure 4.27 show the effect of carbon black feed levels on the average particle size and size distribution, where the first entry is a control reaction in the absence of any carbon black additive. The result indicates 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 carbon black feed levels from 1 wt% to 5 wt%, the particle size slightly increased from 5.2 to 5.8 μm , respectively, as shown in Figure 4.28. The carbon black has a strong inhibitory effect on the radical polymerization, therefore, increases in carbon black feed levels decreased the rate of polymerization. If the excess amount was added, the polymerization could be completely inhibited. It can be noted that the presence of carbon black during the radical chain polymerization, the free-radical process was inhibited because a low radical concentration with a low polymer content was obtained. The non-radical monomer particles are subject to coalescence because of their mutual collision and lead to the formation of larger particle, the size of which depends on the effect of coagulation. In contrast to the polymerization in the absence of carbon black, more radical concentrations were produced the polymerization rate increased to result in smaller-sized polymer molecules. The carbon black feed levels also have a strong effect on the final yield of polymer beads. A typical yield of the control reaction (without carbon black content) is 72.7 %. An addition of 1 wt% carbon black to the

Table 4.8 Effects of the carbon black feed level on particle size, size distribution, molecular weight, glass transition temperature and conversion in suspension copolymerization of styrene and n-butyl acrylate.

Sample	Carbon black feed level (wt %)	$\bar{D}_n (\mu\text{m})^{a,b}$	$\bar{D}_w (\mu\text{m})^{a,b}$	PDI ^c	σ^d	CV (%) ^e	$\bar{M}_n (\times 10^{-4})$	$\bar{M}_w (\times 10^{-4})$	\bar{M}_w / \bar{M}_n	$T_g (\text{°C})^f$	% Conversion ^g
Control	-	5.0	5.5	1.1	1.24	24.80	3.55	14.99	4.22	72	72.7
CB1	1	5.2	6.8	1.3	1.37	26.35	0.64	10.17	15.98	70	65.2
CB2	3	5.4	7.0	1.3	1.25	23.15	0.73	8.26	11.28	69	56.4
CB3	5	5.8	7.5	1.3	1.44	24.83	0.53	3.80	7.23	66	25.6
CB4	7	Irregular shape	-	-	-	-	-	-	-	-	aggregated

a = Calculated diameter

c = Polydispersity index

e = Coefficient of variation g = Determined by gravimetric method

b = Determined by SEM

d = Standard deviation

f = Determined by DSC

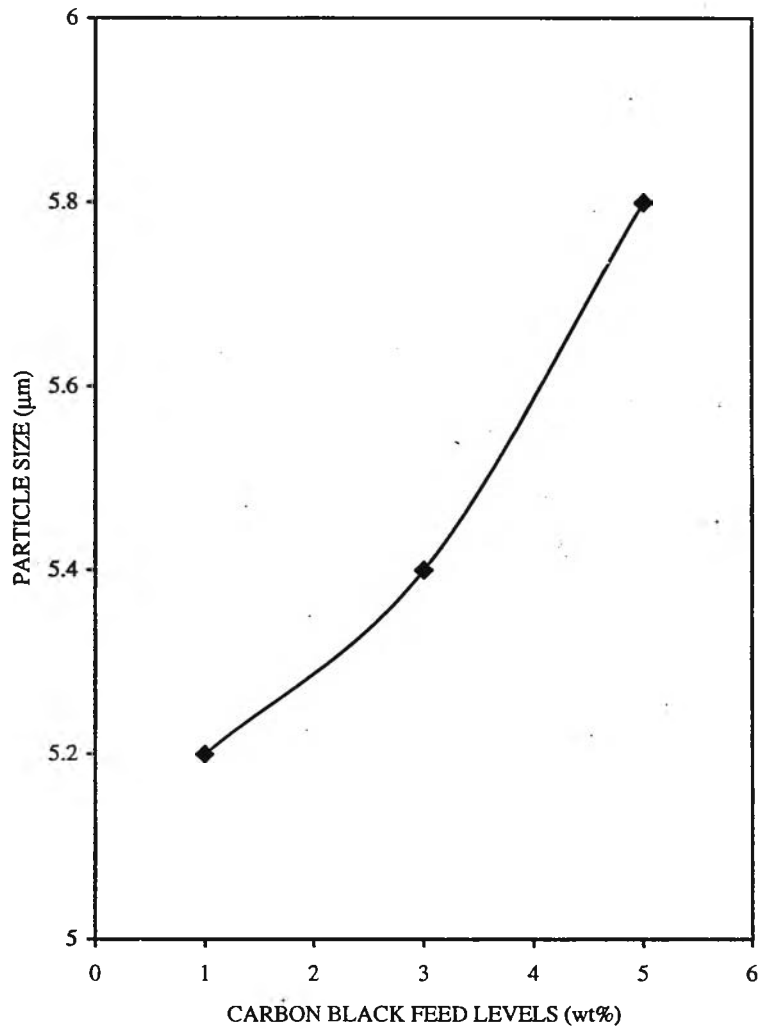
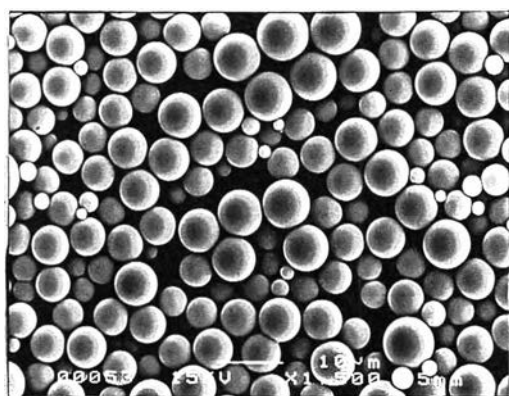
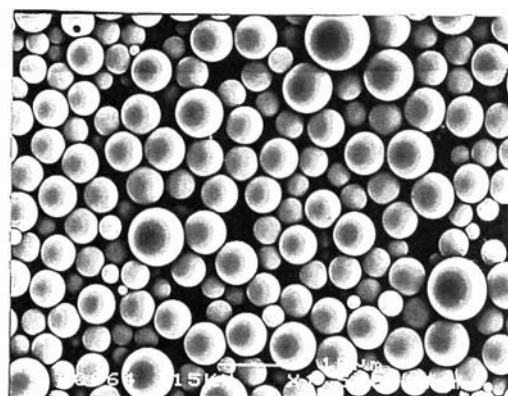


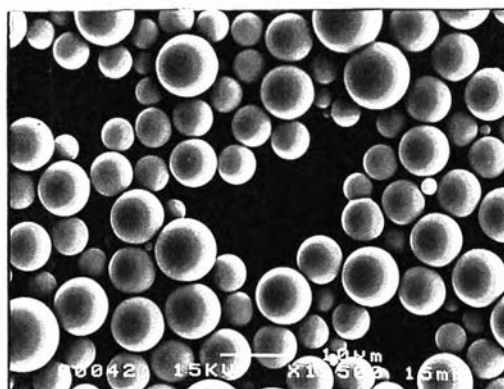
Figure 4.27 Effect of the carbon black feed levels on particle size of the polymerized toner



(a) sample CB1



(b) sample CB2



(c) sample CB3

Figure 4.28 SEM photographs of the polymerized toner prepared at various carbon black feed levels: (a) CB1, 1 wt % (b) CB2, 3 wt % (c) CB3, 5 wt %

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 the high feed levels of carbon black. These results also demonstrate clearly the significant effect of the carbon black levels on the polymerization yield. At low carbon black feed levels, the yield of beads slightly increased, which can be rationalized by the decreased inhibitory effect of the carbon black caused by both increases in the radical concentration and the rate of polymerization. The black color tone of the resulting polymerized toner correlated with both the carbon black feed levels and the particle size, and the percentage of conversion, which was described above as presented in Table 4.9.

4.9.1.2 The average Molecular Weights and Molecular Weight Distribution

These experiments revealed that addition of even a small amount of carbon black into the polymerization mixture inhibits the polymerization reaction or degrades the molecular weight. The average molecular weights decreased as an increased of the amount of the carbon black. As the polymerization progresses in the presence of carbon black, which acts as a strong radical scavenger, increased inhibitory effect due to a low radical concentration, and the rate of polymerization is thus decreased. The critical chain lengths of oligomer radicals are decreased or are completely inhibited (in the case of excess carbon black was added) and the growth of the copolymer particles is decreased. As mentioned above, the polymerization mixture with a low radical concentration (rich in non-radical monomer) tended to coalescence, which led to the larger particle sizes with the lower average molecular weights. This result may be discussed by the assumption that, in the suspension polymerization system, the large particles grow by capture of dead polymers of low molecular weights from the solution. The relationship between the carbon black feed level and average molecular weight is presented in Figure 4.29. One can see that the \bar{M}_n is constant with increases in carbon black content, while the \bar{M}_w is markedly decreased. The number of the small molecule is present all the time. The number of the larger molecules is absent due to radical scavenger.

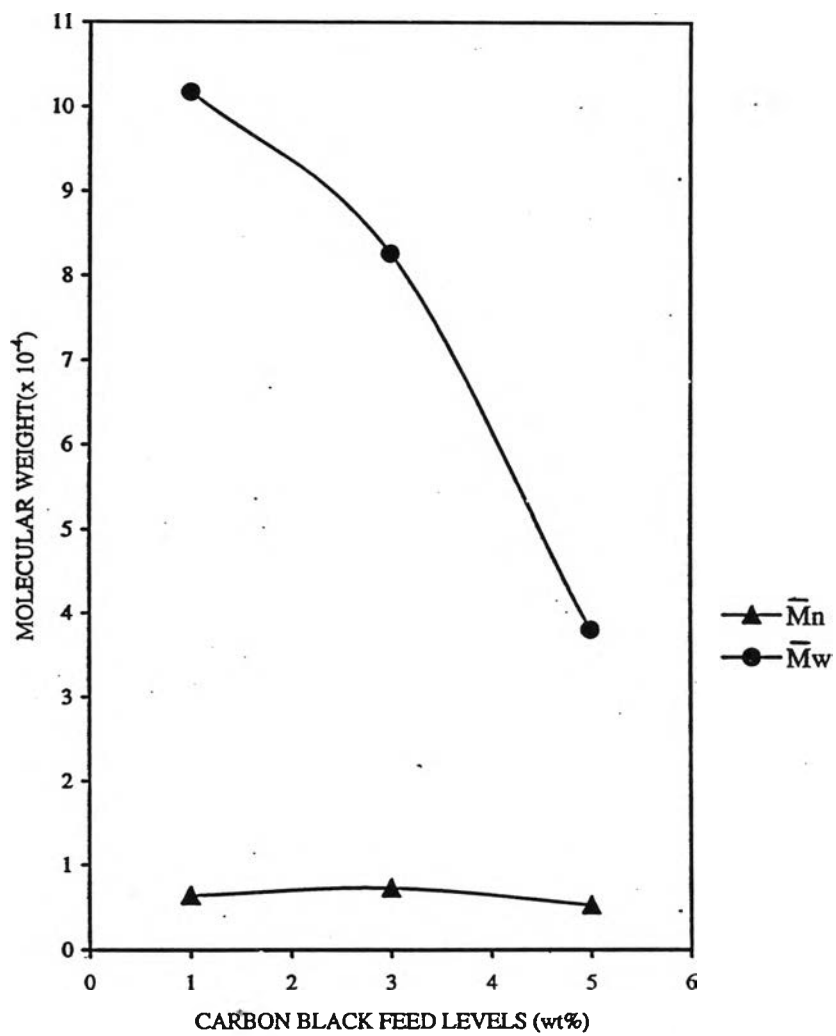


Figure 4.29 Effect of the carbon black feed levels on average molecular weights of the polymerized toner

4.9.1.3 Glass Transition Temperature

Glass transition temperature of the copolymer is an important property in characterizing 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 T_g about 50-70°C.

The resulting polymerized toners were investigated by DSC to identify the T_g value. The DSC thermograms of the polymerized toner, synthesized with different carbon black feed levels are shown in APPENDIX A. 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 relation between T_g and the carbon black feed levels is presented in Figure 4.30. The T_g of the polymerized toner decreased as the carbon black feed levels increased. It can be explained that the radical termination by the carbon black additives gives rise to a small fraction of oligomeric material of sufficiently low molecular weights to act as a plasticizer. The average molecular weight also has a strong, important effect on the T_g value. The resulting copolymer with a high average molecular weight leads to a high T_g value.

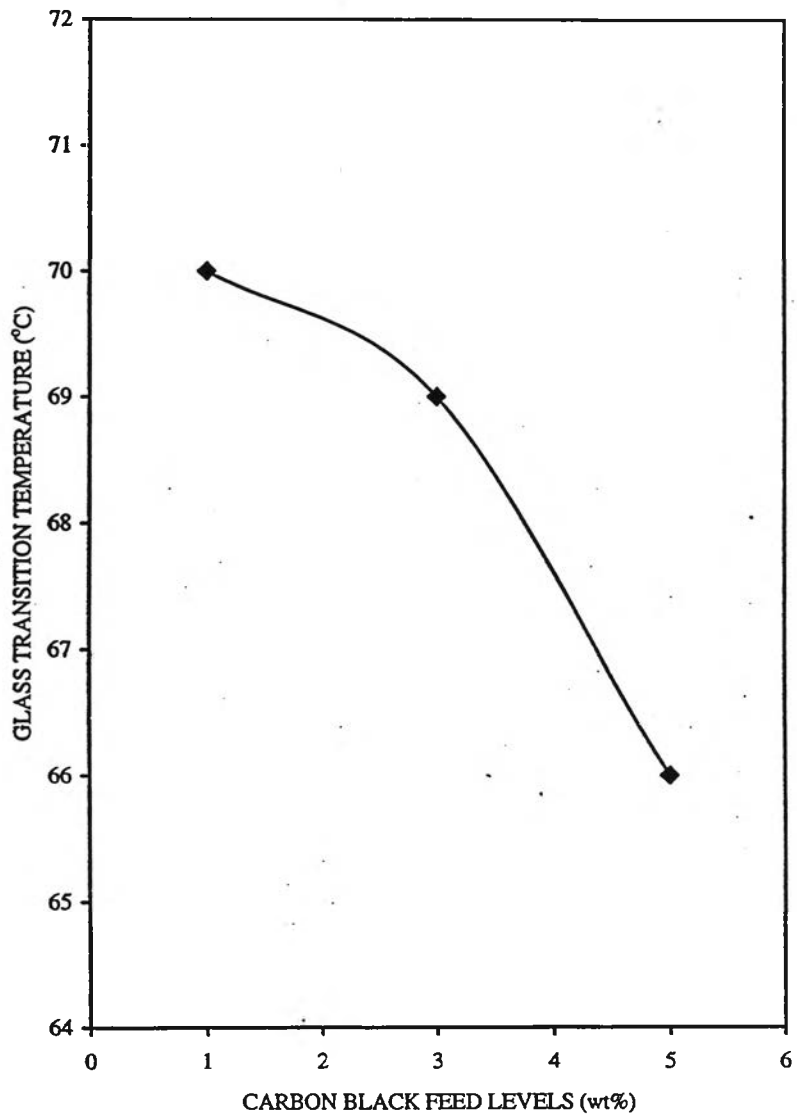


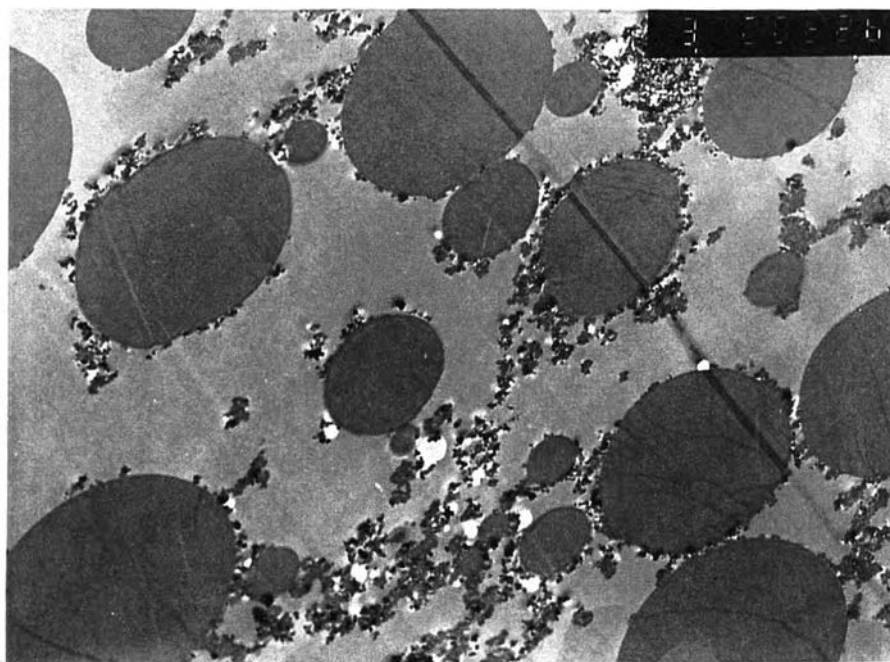
Figure 4.30 Effect of the carbon black feed levels on glass transition temperature of the polymerized toner

Table 4.9 Physical properties of the copolymers of styrene and normal butyl acrylate in the presence of carbon black

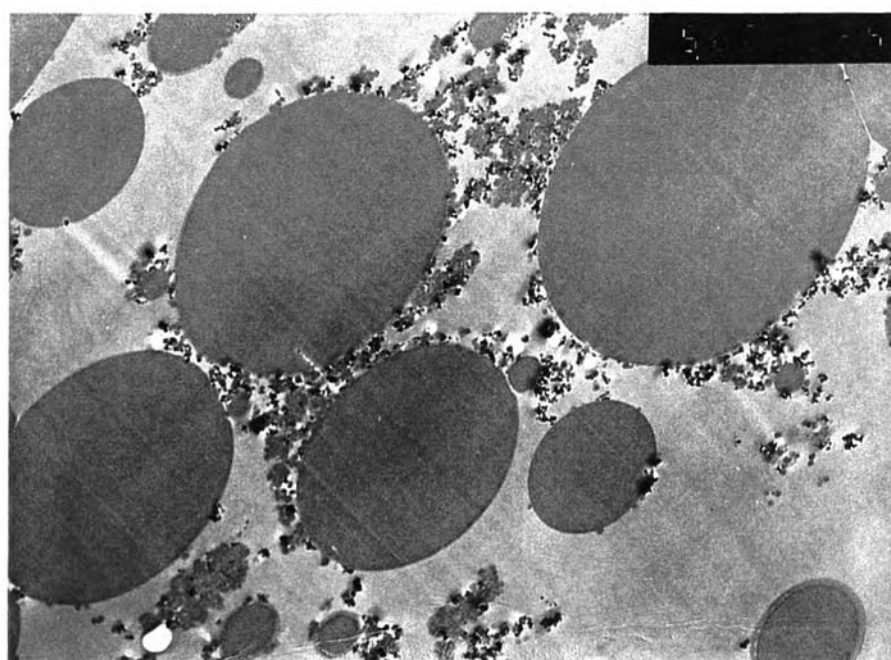
Carbon black (wt%)	Particle size (μm)	Color	Conversion (%)
0	5.0	White	72.7
1	5.2	Slightly gray	65.2
3	5.4	Grayish	56.4
5	5.8	Dark gray	25.6
7	Irregular shape	Black	aggregated

4.9.1.4 The distribution of carbon black on the polymerized toner particles

In this research, the distribution of the carbon black on the beads of beaded polymerized toner was obtained by transmission electron microscopy(TEM). The toner particles were embedded in epoxy resin and then cut into a thin film by an ultramicrotome. The samples were then either partially oxidized or coated with gold to increase their conductivity. The distribution of the carbon black on the toner particles (3 wt%) is shown in Figure 4.31. The electron micrographs presents the distribution of carbon black on the polymer surfaces. This technique tends to produce polymer beads with excess amounts of carbon black on the surface. In addition, toner produced from such a synthesis likely to contain low carbon black contents, which required some dispersion agents to disperse them in liquid phases. However, this technique gives difficulties because the disperse carbon black hardly provides a true reproduction of densities. It was possible to observe a large number of pictures the distributions and also the extent to which dispersion of the carbon black into toner particles or agglomerations of carbon black took place at the surface of toner particles.



Sample CB2 ($\times 5550$)



Sample CB2 ($\times 7500$)

Figure 4.31 TEM photographs of the carbon black distribution on surfaces of the toner particles in the presence of carbon black 3 wt%

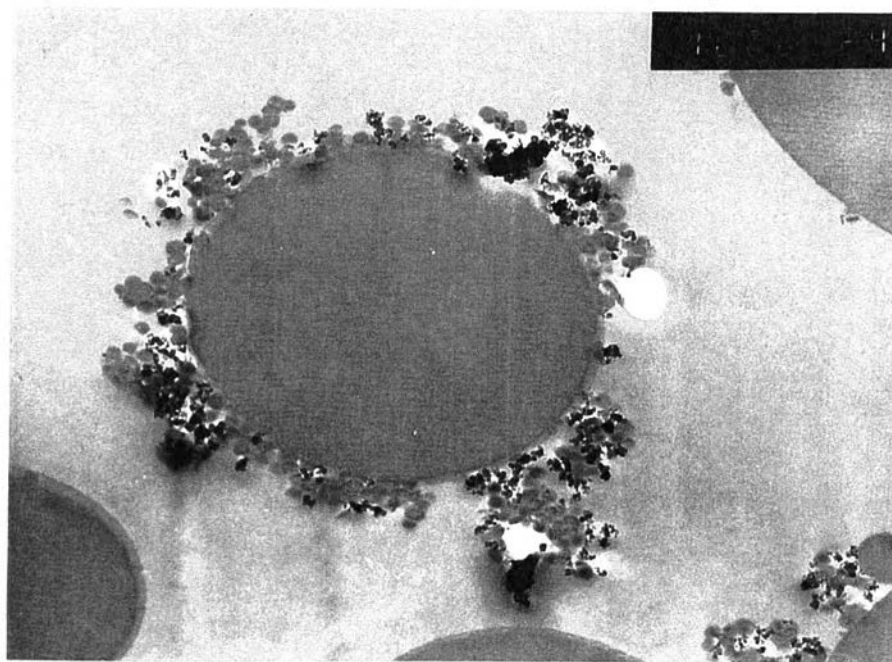
Sample CB2 ($\times 16500$)

Figure 4.31 TEM photographs of the carbon black distribution on surfaces of the toner particles in the presence of carbon black 3 wt%

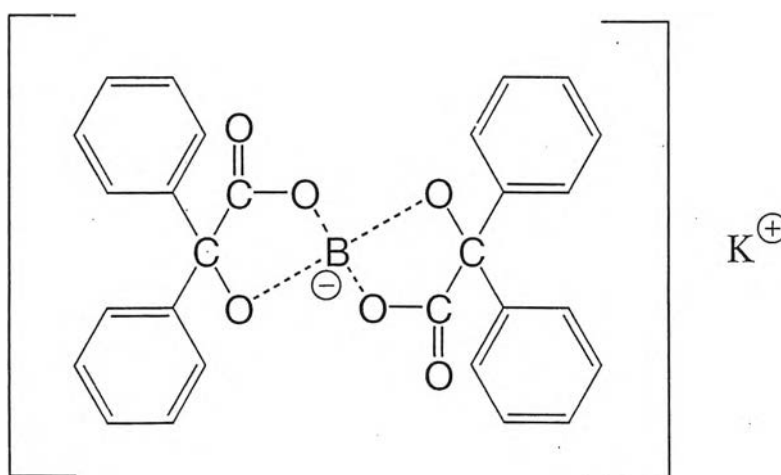


Figure 4.32 Molecular structure of boro bis(1,1 diphenyl-1-oxoacetyl) potassium salt charge control agent.

4.10 The effect of charge control agent concentration

4.10.1 Triboelectric properties

The electrophotographic process involves the charging mechanism of toner particles 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 charged were of the wrong sign, then the toner may develop into the blackground areas which ideally should be free of toner. If the toner is uncharged, or very weakly charged, then machine dusting and contamination can easily occur. However, toner of too high a charge is also undesirable, in terms of low print densities caused by low toner particles detached from the carriers. In addition, the developed toner mass-per-unit-area is inversely proportional to the toner charge-to-mass ratio. It would therefore be highly desirable to be able to measure the charge of each toner particle and to tailor the distribution of toner charges to have an adequate average charge with little uncharged, wrong sign, or very highly charged toner.

Charge control agent, CCA, is added into a toner either on its surface or in bulk to give an adequate charge level or rate of charging. The addition of charge control agent is required both for positive and negative toners. Styrene-acrylate copolymers are tribochargeable both positively and negatively when a suitable CCA is selected.⁶³ The selection of CCA depends on the expected purposes. Recently, constraints of green enact to protect and preserve the environment worldwide forced the toner industry to avoid using heavy metal containing CCAs. Chromium containing charge control agents will be restricted and the other CCAs have been

developed to replace the heavy metal complex charge control agents. Newly non-chromium containing and environmentally friendly CCAs were developed, the CCAs based on boro-bis(1,1-diphenyl-1-oxo-acetyl) with difference counter ions of Li^+ , Na^+ , K^+ and Ca^{++} were used in the study of their charging properties in terms of q/m value. Kiatkamjornwong et al.⁶⁴ compared the mono-valent ionic complex of CCA with the di-valent ionic complex, they found that the latter generate a more charges and gave the higher q/m values, due to its electronic configuration and its high affinity to polarization and ionization.

The effect of the charge control agent concentrations on the triboelectric properties of toner was investigated. The recipe of the toner used in this experiment is as follows: the polymerized toner at the concentrations of carbon black 3 wt% in styrene-normal butyl acrylate copolymer (80/20) matrix with the diameter in the range of 4-10 μm , CCA of boro bis(1,1-diphenyl-1-oxo-acetyl) potassium salt (non-chromium complexes type) of 2 and the carrier, TSV-200 (steel type) with the size of around 50 μm . The structure of the CCA is depicted in Figure 4.32.

Figure 4.33 shows the effect of the charge control agent concentration on triboelectric properties of toners. It was found that the q/m values increased as an increase of charge control agent concentrations. Birkett and Gregory⁶⁵ proposed that the charging process probably involved a transfer of the counter-ions of the charge control agent on the toner surface to the carrier surface upon contact. For the present case, the polymerized toner particles having spherical and a smooth surface charge uniformly. Increase the concentration of charge control agent is to increase the stronger 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 values of q/m .

Developer: PT-702 toner and TSV-200 carrier

Toner concentration: 3 wt%

Rotating speed: 1000 rpm

Table 4.10 The q/m values of developer, PT-702 toner and TSV-200 carrier, at 1000 rpm by MS 1 Minishaker at 65 ± 3 %RH and 25 ± 2 °C evaluated at various times

Rotating time (sec)	μC (volt)	Toner weight (g)	q/m $-\mu\text{C g}^{-1}$
30	0.0264	0.0024	10.99
60	0.0213	0.0019	11.20
90	0.0196	0.0017	11.50
120	0.0303	0.0026	11.66
240	0.0236	0.0019	12.43
360	0.0247	0.0018	13.70
720	0.0272	0.0015	18.10

Developer: N-09S toner and TSV-200 carrier

Toner concentration: 3 wt%

Rotating speed: 1000 rpm

Table 4.11 The q/m values of developer, N-09S toner and TSV-200 carrier, at 1000 rpm by MS 1 Minishaker at 65 ± 3 %RH and 25 ± 2 °C evaluated at various times

Rotating time (sec)	μC (volt)	Toner weight (g)	q/m $-\mu\text{C g}^{-1}$
30	0.0484	0.0026	18.60
60	0.0606	0.0029	20.91
90	0.0668	0.0031	21.54
120	0.0864	0.0034	25.44
240	0.1180	0.0041	28.80
360	0.0864	0.0030	28.80
720	0.0873	0.0029	30.10

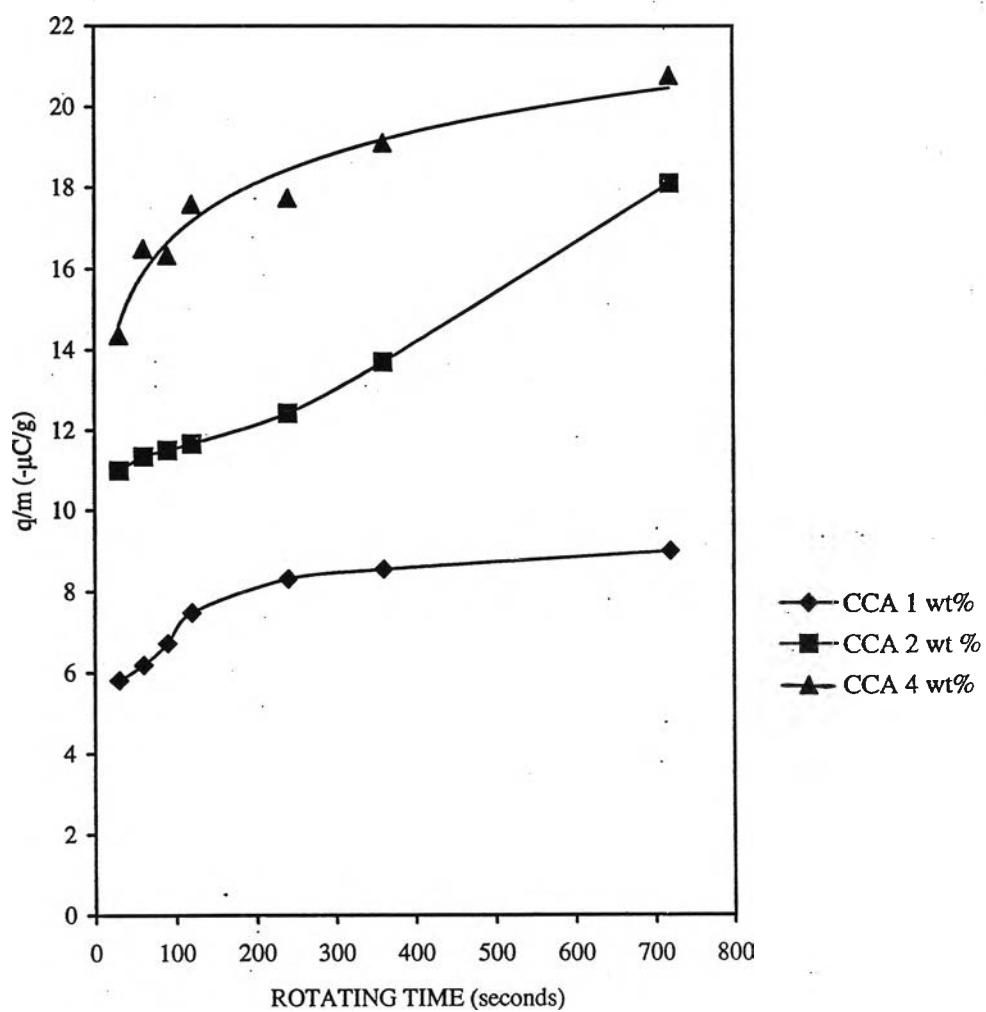


Figure 4.33 Effect of charge control agent concentrations on triboelectric properties of the polymerized toner

4.11 Analysis of Print Quality

The image qualities of the polymerized toners prepared in a laboratory (PT-702) and of a commercial grade toner (N-09S) were printed on the commercially uncoated paper by OKI 400 micro line CL Printer. Ten print-outs were printed for each type of the toners with a test form shown in Figures 4.34 (a) and 4.34 (b), respectively. The solid and background densities of the print-outs were measured by a reflection densitometer (Macbeth). Comparisons of the copy samples show that the solid density values of N-09S toner were higher than those of the PT-702, but the background density values of both toner types were little different as shown in Figures 4.36 and 4.37, respectively. The edge sharpness and edge raggedness of the lines (0.5 points) and the characters of both toner types were illustrated by an image analyzer as shown in Figures 4.38 to 4.40, respectively. We found that the edge sharpness and raggedness produced by N-09S toner were better than our toner, because the former had a stronger ink density.

The N-09S toner produces the better, thin lines and fine dot images with much less raggedness. Both toner types are polymerized toner with a spherical-shape, which have more evenly and uniformly triboelectric charges than that of the irregular-shape toners. Therefore, the higher charged toner could transfer more toner particles to the paper. The difference in the print densities come from the q/m values of the toner charge and the loading of the carbon black on the toner particles. The PT-702 toner gave a background fog and image raggedness. The reason for this could be that the PT-702 toner contains lower charges, most probably resulted from a poor distribution of CCA (See TEM pictures in Figure 4.31). These lowly charged toners

were picked up by the photoconductor, but were not transferred to the paper by the electric field. Consideration of the CCA type and concentration, the main structure of CCA contained in N-09S toner is a negative charge, which contains heavy metal ions like chromium with 2.4 (wt%) as shown in Figure 4.35. The symbol X represents an alkyl-amine functional group and the positives 2 and 4 are the NO₂ groups. The PT-702 toner used boro bis(1,1-diphenyl-1-oxo-acetyl) potassium salt (non chromium complexes type) as a charge control agent with (2 wt%). The structure of latter one are shown in Figure 4.32. Both of the CCA type and concentration affect the q/m values and also influence the image qualities. The results indicated that q/m values of N-09S toner is in a range of 25-30 $\mu\text{C g}^{-1}$, while the q/m values of PT-702 toner is in a range of 11-18 $\mu\text{C g}^{-1}$. This phenomenon could be described that both theoretical and experimental investigations indicated that the q/m values increased by an increase of an amount of the CCA. The N-09S toner contained more amount of the CCA than did the PT-702 toner. Therefore, the N-09S toner gave higher q/m values than the latter one. In addition, CCA contain heavy metal ions like chromium could generate the higher tribo-electric (q/m) values than could the CCA containing non chromium complexes type, therefore the higher q/m values were obtained in the first case. However, the CCA containing heavy metal ions strongly violent the green enact in terms of protection and preservation of the environment worldwide; this CCA will therefore be restricted.

As described above, the q/m values also affects the result image qualities. The PT-702 toner contains lower charges. These lowly charged toner particles were picked up by the photoconductor, but were not transferred to the paper by the electric field. The roles of charge control agents affecting the charge distribution are not fully

understood. However, Birkett and Gregory⁶⁶ have proposed that the charging process probably involves transfer of the counter-ion of the charge control agent on the toner surface to the carrier surface upon contact. The image qualities were thus obtained in the presence of the CCA containing the azochromium metal complex with a higher CCA concentration as described above. Theoretically, chances of toner charging in a monocomponent nonmagnetic development are less than those in a dual-component development. The charging rate of the toner, of course, affects the quality of the print image. Monocomponent toners accept charges mainly from the development roller surface, and the contact time between toners and the development roller surface is very short. Therefore, monocomponent toners are used in the charge rising region, which is unstable in the toner charging process. In terms of the carbon black content, the bulk electrical conductivity of the toner has a significant effect on q/m . The range of carbon black concentration is important because typical black toners are limited. One possible explanation for this is as follows. Even at a low carbon black concentration, localized clusters of the carbon black particles form, which give rise to local regions of higher conductivity that are electrically isolated from one another by the polymer. Thus, the local conductivity of the toner may be high at the point of contact between the toner and the carrier, even though bulk conductivity of the toner is low, and tends to decrease the chargability, and also the image qualities as well.⁶⁷

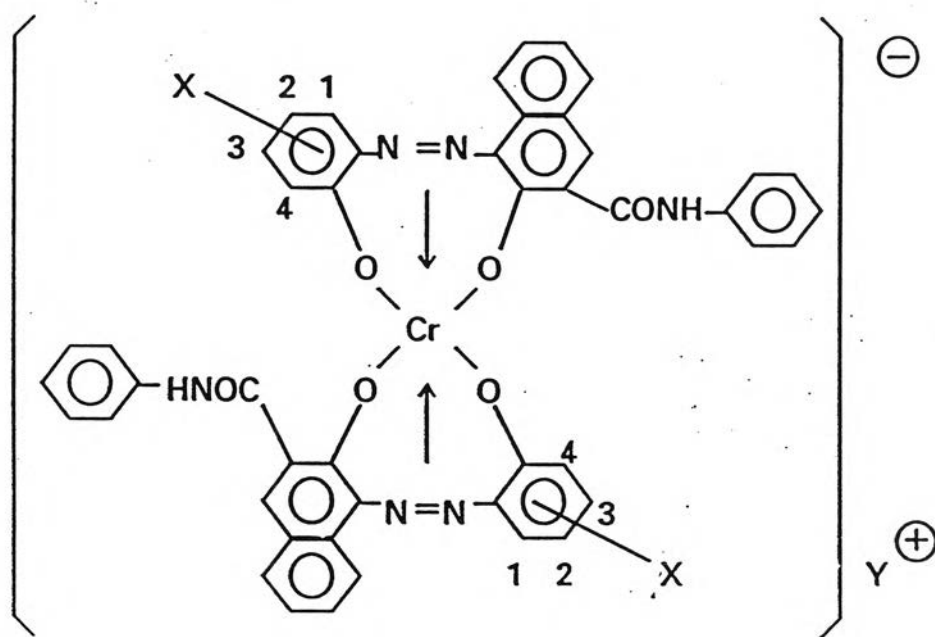


Figure 4.34 Molecular structure of azochromium metal complex charge control agent

This is a test form

This is a test form

This is a test form

A B C D E F G H I J K L M N O P Q R S T U V W X Y Z
a b c d e f g h i j k l m n o p q r s t u v w x y z

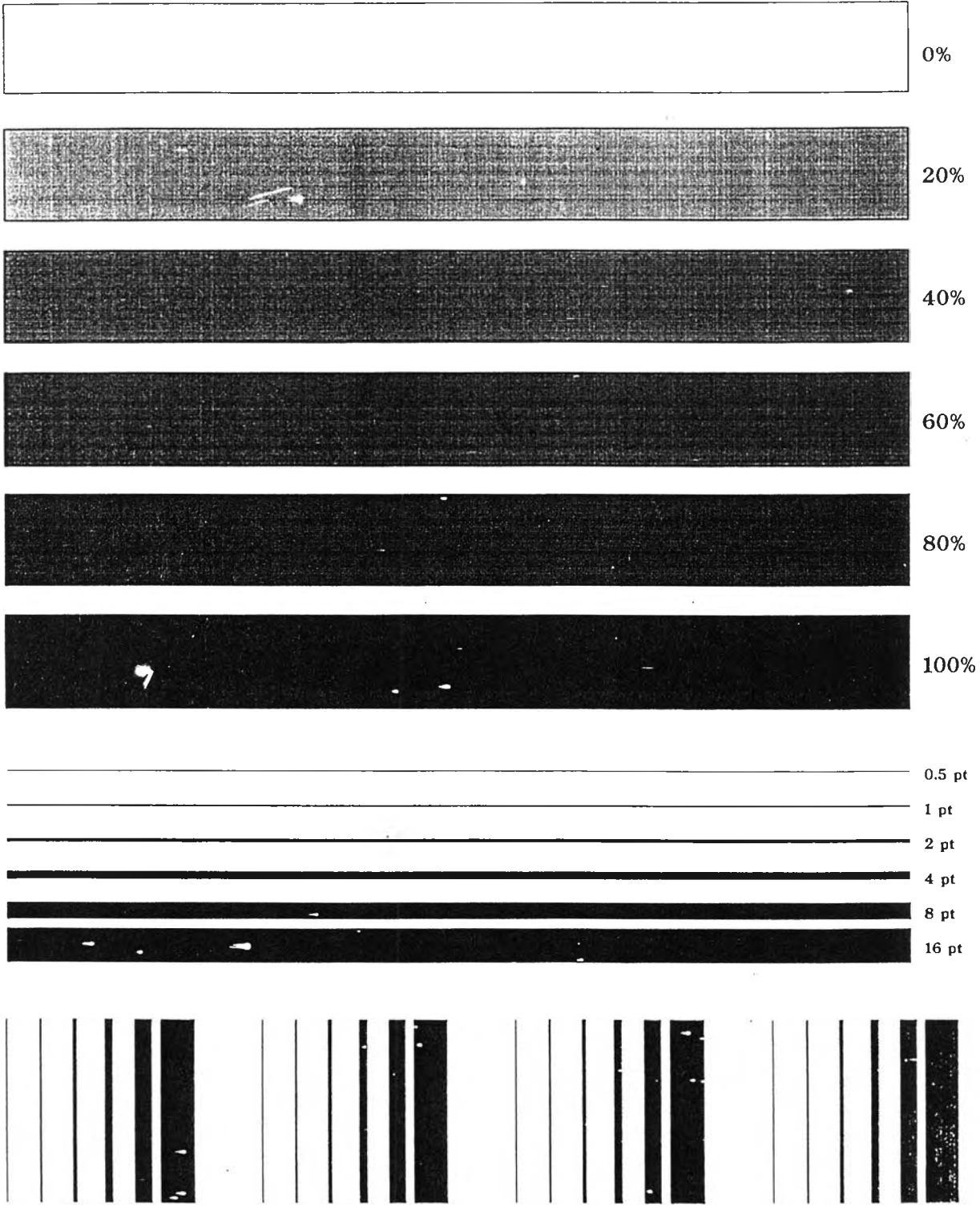


Figure 4.35 (a) A test form printed by N-09S toner

This is test form

This is test form

This is test form

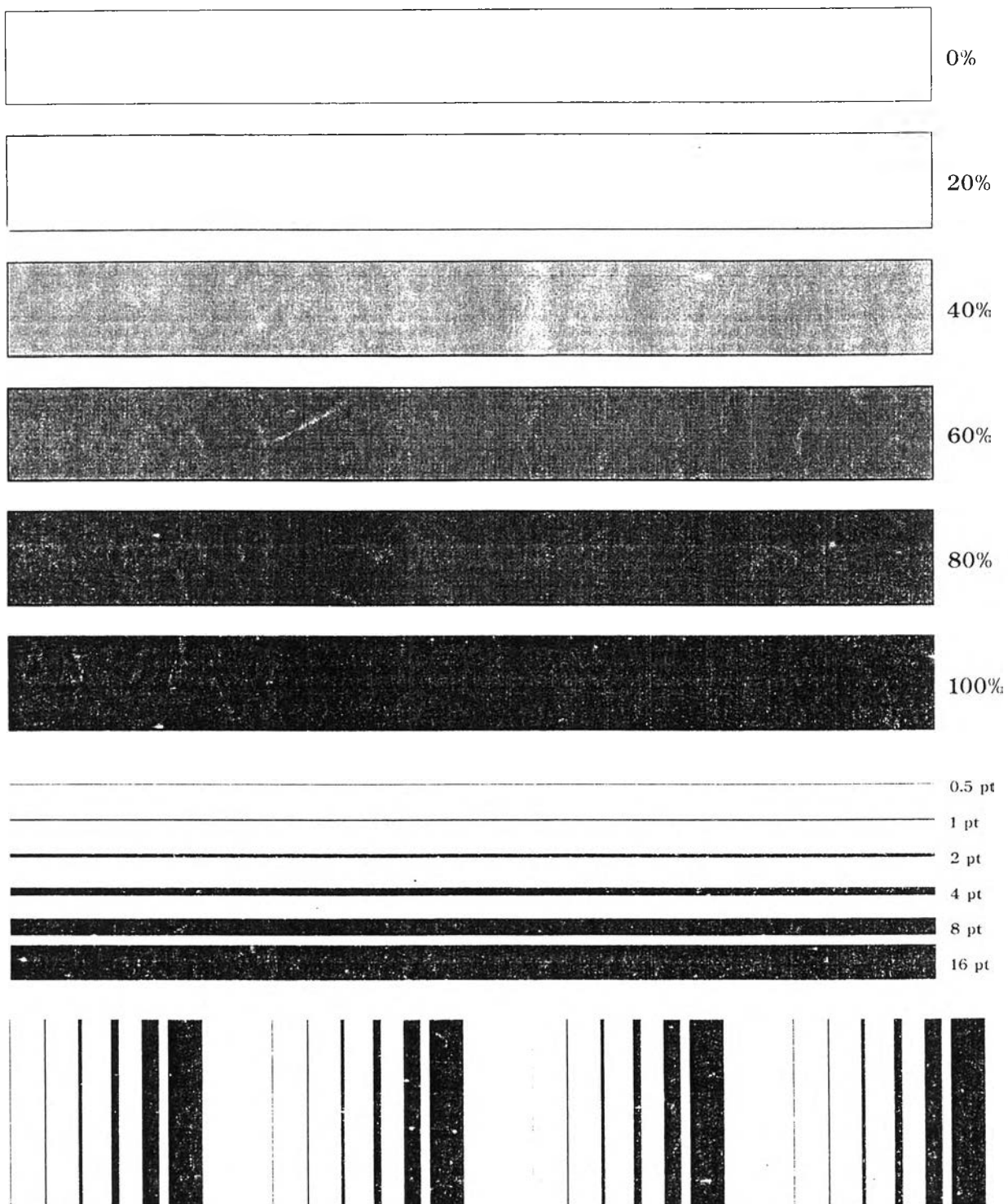


Figure 4.35 (b) A test form printed by PT-702 toner

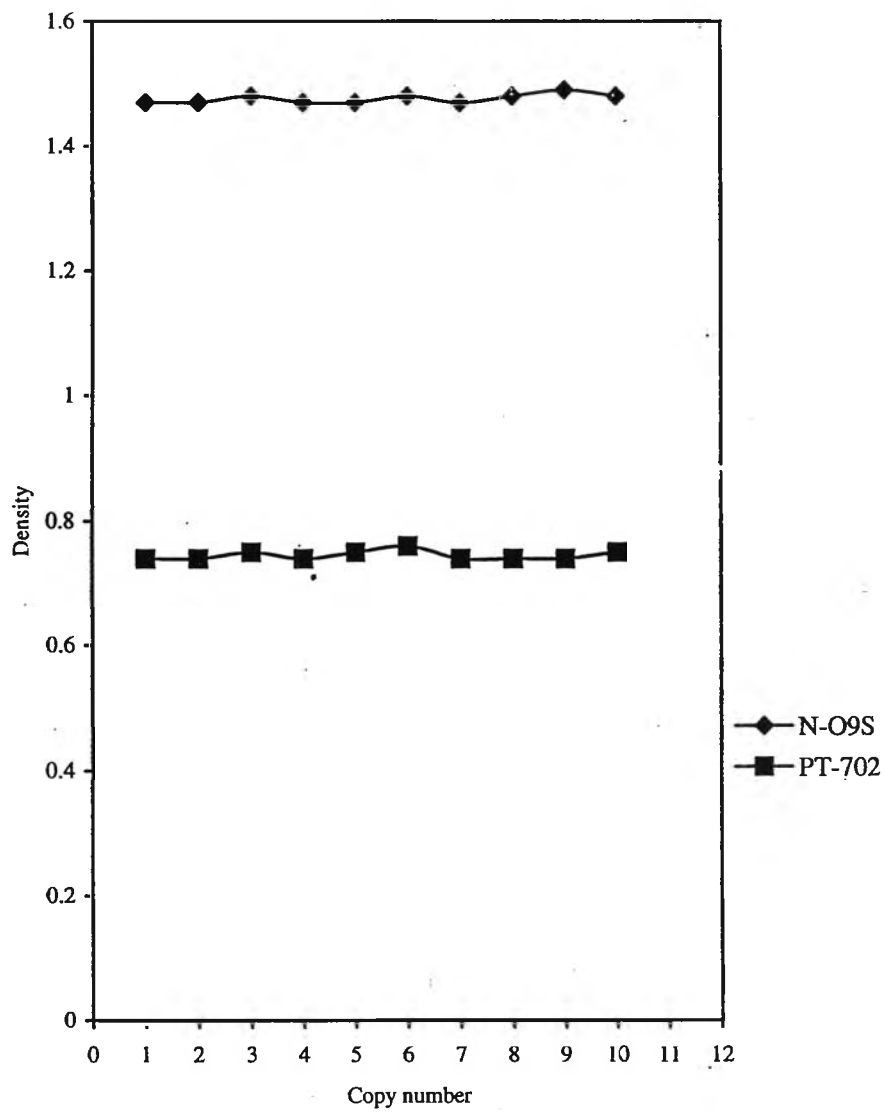


Figure 4.36 Dependence of solid density on copy number for N-09S and PT-702 toner

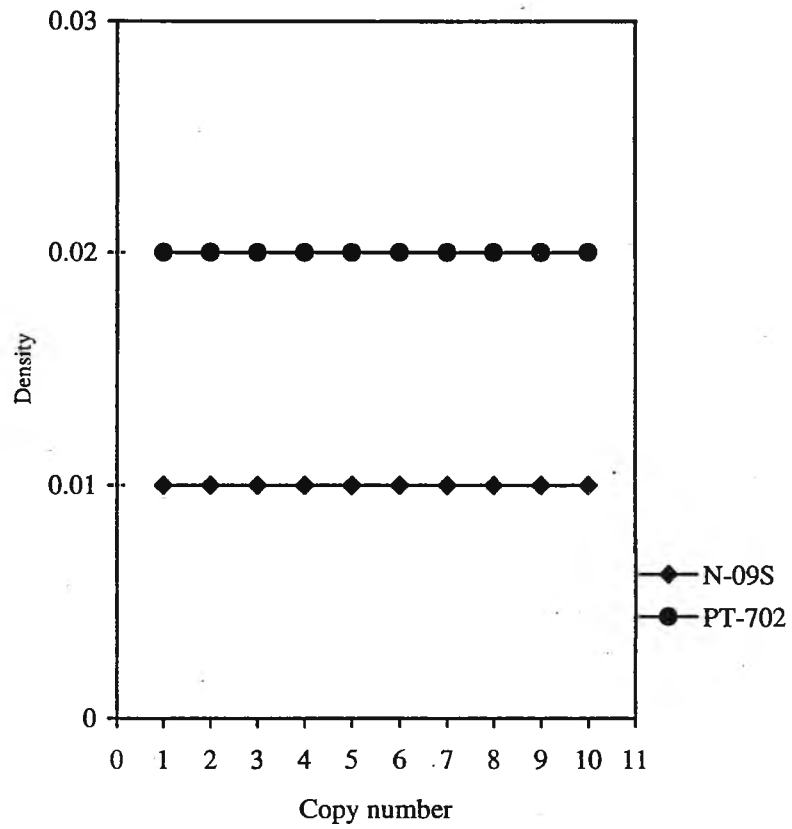


Figure 4.37 Dependence of background density on copy number for N-09S and PT-702 toner



Figure 4.38 The photos of the lines and “a” character by the image analyzer:

(a) N-09S toner and (b) PT-702 toner

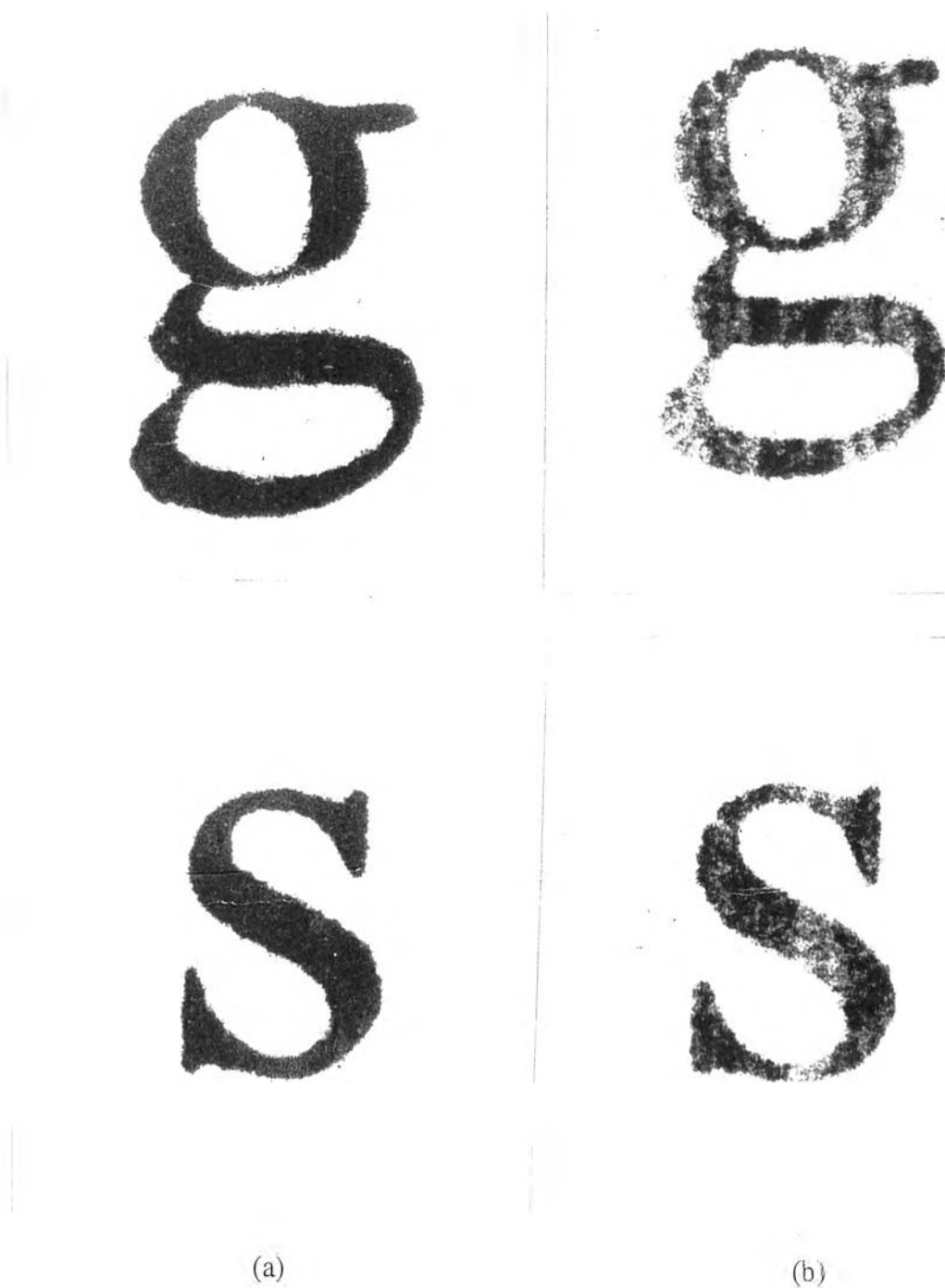


Figure 4.39 The photos of the “g” and “s” character by the image analyzer:

(a) N-09S toner and (b) PT-702 toner

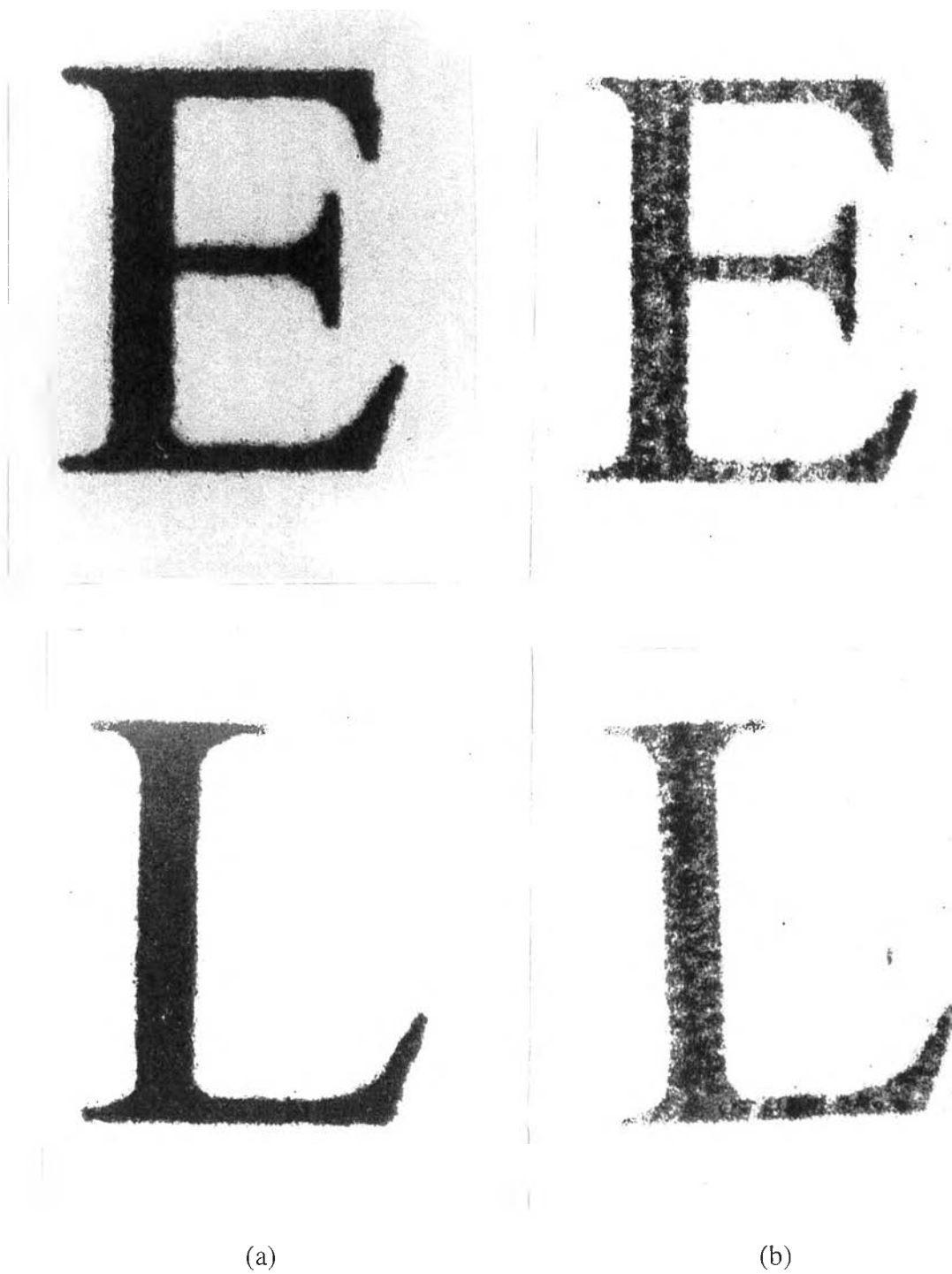


Figure 4.40 The photos of the “E” and “L” character by the image analyzer:

(a) N-09S toner and (b) PT-702 toner