

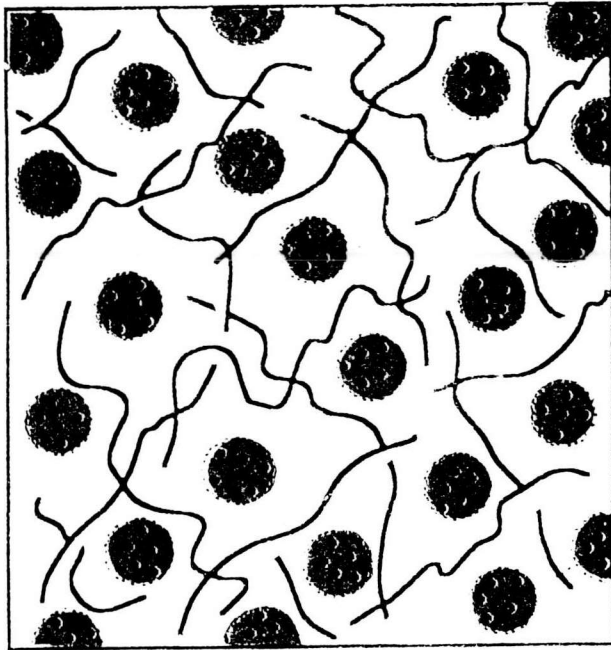
CHAPTER IV

RESULTS AND DISCUSSION

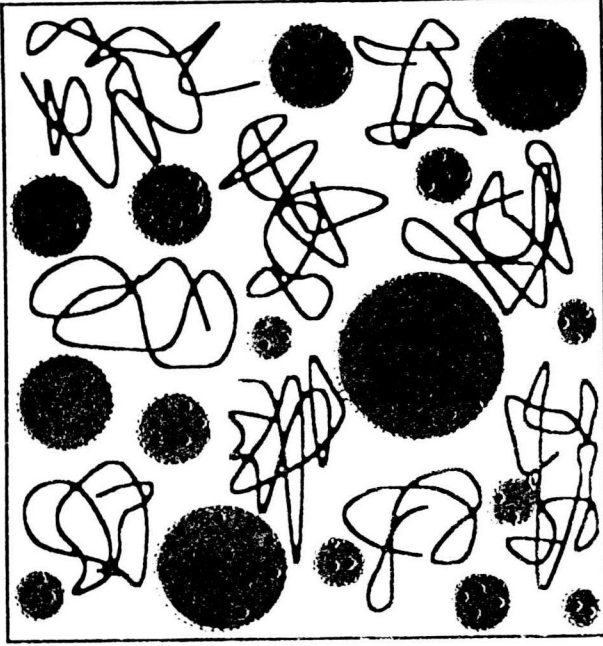
The particle formation mechanism of the dispersion copolymerization was the first parameter studied. It was done by comparing the dispersion copolymer composition with the solution and bulk copolymer compositions. In the dispersion polymerization, the effects of matrix polymer, monomer feed ratio, solvent mixing ratio and reaction temperature were also studied. The dispersion copolymers were characterized for the following properties: average molecular weights, particle size, surface properties and thermal properties.

Referring to the research work of N. Ogata and S. Chujo (6) on the synthesis of polystyrene (PS) super-fine particles by controlling the particle diameter, the synthesis technique utilizes the phenomenon that the free space where the monomer was concentrated changes according to the morphologies of matrix polymer solution. The result obtained from his research was the polymer with a smallest particle size of $0.64 \mu\text{m}$. The method used in their research was the radical polymerization of styrene in poly(methyl vinyl ether) (PMVE) as a matrix polymer, which was dissolved in ethanol and n-hexane solvents, with a solvent ratio of the 80:20 weight% of ethanol/n-hexane. In this system, ethanol was a good solvent and n-hexane was a poor solvent for PMVE matrix polymer. The schematic view of styrene monomer in good and poor solvent which was proposed by the Ogata's group was shown in Figure 4.1.

The idea of the present research work was based upon the above-mentioned research work. In the present work, styrene-co-methyl methacrylate polymer was synthesized by using the dispersion polymerization in the mixed solvent of ethanol and n-hexane; PMVE was used as a matrix polymer. The solution and bulk copolymerizations were also carried in order to find out the particle formation mechanism of the dispersion copolymerization.



Good Solvent : Ethanol



Poor Solvent : n-Hexane



Matrix Polymers : 
 [Poly(methyl vinyl ether)(PMVE); $M_w=46000$, $M_w / M_n=2.92$]
 Monomers : 
 [Styrene]

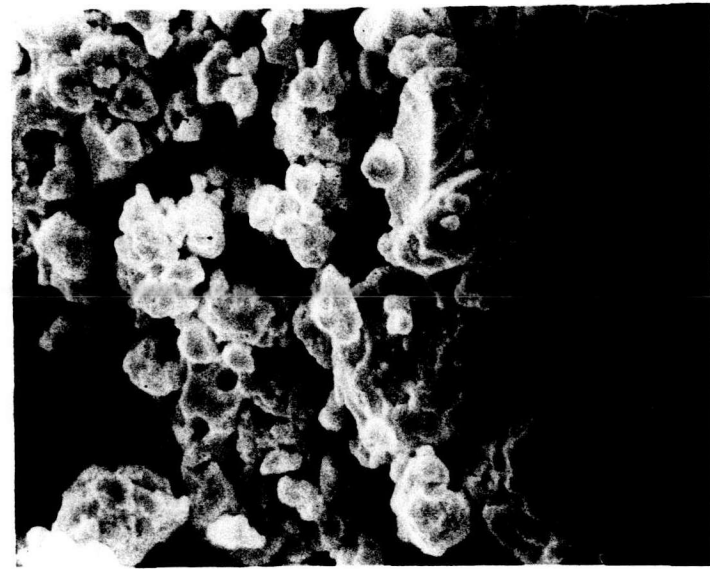
Figure 4.1 Schematic views of St monomer and PMVE matrix polymer in good and poor solvents

4.1 Characterization of Solution Copolymer

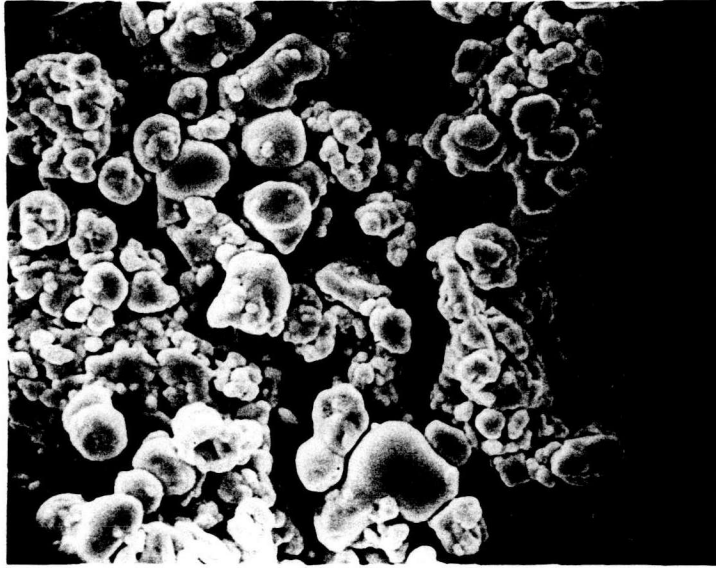
Solution polymerization was carried out in the mixed solvent of 80:20 weight% ethanol:n-hexane in the absence of PMVE matrix polymer. In the solution polymerization, the spherical shaped polymer particle was not obtained, in contrast, all of the polymers were aggregated and formed in random shapes to become a sheet form (Figures 4.2 and 4.3). In addition, the controlling of the particle size of solution polymer could not exist due to the absence of the PMVE matrix polymer.

In this work, poly(methyl vinyl ether) (PMVE) was not only used as the matrix polymer in dispersion copolymerization, but also was found to be a steric stabilizer and the particle size controlling agent. Particle stability is normally achieved by the interposition of repulsive forces of sufficient magnitude to overcome the inherent attractive forces of electromagnetic origin, which arise as particles approaching each other. In the absence of any repulsive forces, the particles rapidly aggregate. The repulsive force of the steric stabilizer was generated by the interaction of opposing dissolved polymer chains attached to dispersion polymer particles (17). Therefore, in the absence of the PMVE steric stabilizer which is equivalent to the solution copolymerization, the copolymer could not formed in spherical shaped polymer particles. Table 4.1 shows the copolymer properties obtained by solution copolymerization of styrene and methyl methacrylate.

Figure 4.4 shows the effect of feed composition of the comonomers on average molecular weights. The average molecular weights were obtained in the range of 10,000 to 40,000. The smallest values of molecular weights were found in the polystyrene by the solution polymerization. Figure 4.5 shows the copolymer composition of the solution copolymer obtained by the NMR method. This solution copolymer composition was used to compare with the bulk and dispersion copolymer compositions (Figure 4.18) as to obtain the information of particle formation.



PS



PMMA

Figure 4.2 Scanning electron micrographs of the polystyrene (left) and poly(methyl methacrylate) (right) by solution polymerization in the mixed solvent of 80:20 weight% ethanol/n-hexane



St 50% feed



St 75% feed

Figure 4.3 Scanning electron micrographs of the poly(styrene-co-methyl methacrylate) by solution copolymerization in the mixed solvent of 80:20 weight% ethanol/n-hexane at 50 and 75% feed of styrene

Table 4.1 Characterization of solution copolymer
(mixed solvent content: 80 wt% EtOH)

Sample No.	Styrene (mole%)	Yield (%)	\bar{M}_n	\bar{M}_w	$\frac{\bar{M}_w}{\bar{M}_n}$	F (%St)	
						NMR	EA
1s	0	58	17,000	27,000	1.56	0	0
2s	25	26	21,000	35,000	1.65	36	34
3s	38	24	16,000	26,500	1.65	50	46
4s	50	12	23,500	38,500	1.64	53	51
5s	62	18	16,000	27,000	1.68	62	63
6s	75	24	12,000	21,000	1.77	73	73
7s	100	20	10,000	16,000	1.54	100	100

F: copolymer composition

EA: elemental analysis

NMR: nuclear magnetic resonance spectroscopy

Solution Copolymer

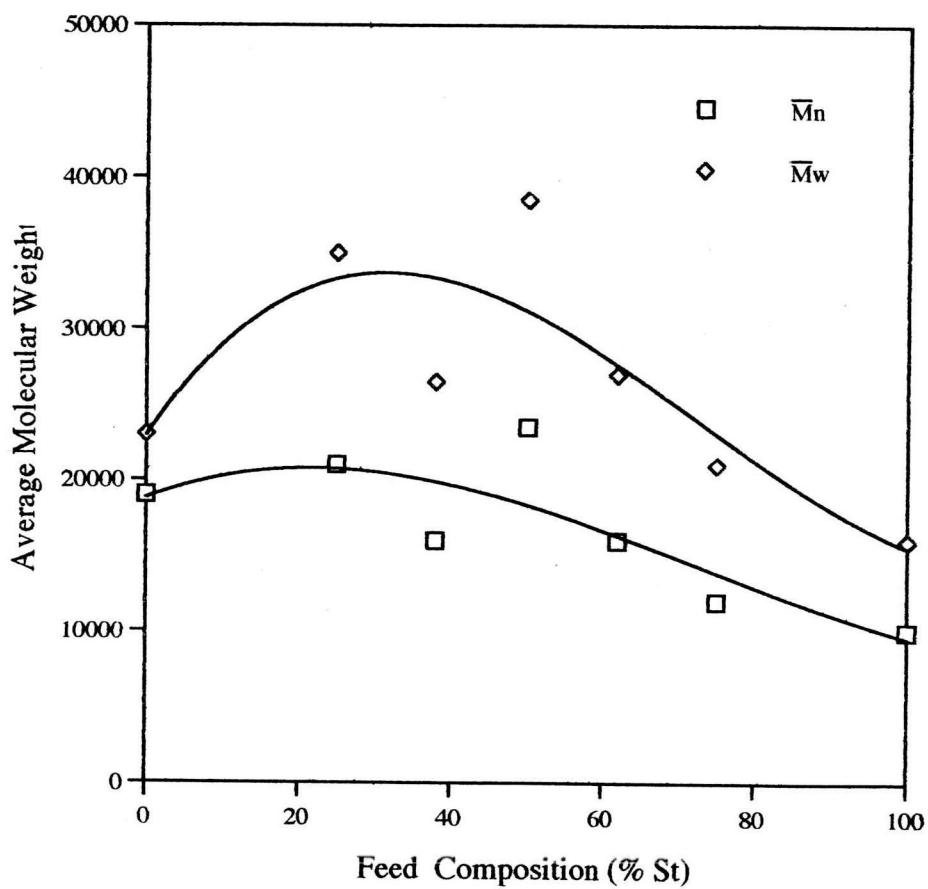


Figure 4.4 Effect of feed composition on average molecular weights of the solution copolymer; mixed solvent content: ethanol/n-hexane=80:20 weight%

Solution Copolymer

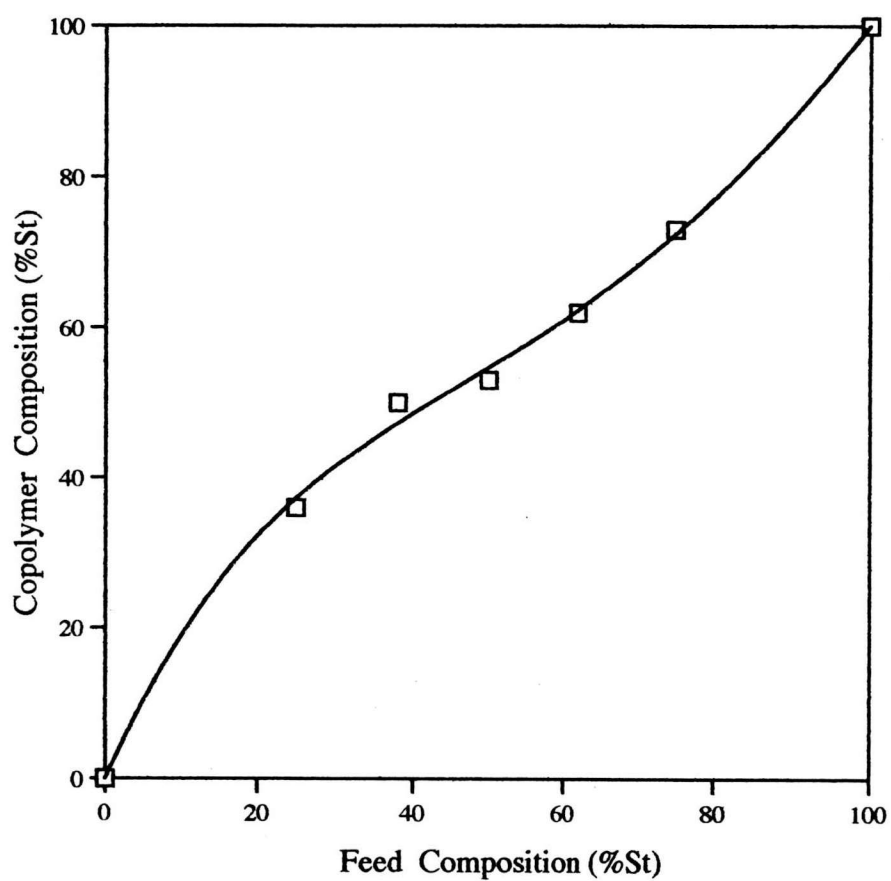


Figure 4.5 Copolymer composition of solution copolymer; mixed solvent content: ethanol/n-hexane 80:20 weight%

4.2 Characterization of Bulk Copolymer

Table 4.2 presents the copolymer properties obtained by bulk copolymerization. In bulk copolymerization, both of the number- and weight-average molecular weights of the copolymer were much higher than those obtained from dispersion and solution copolymerizations (Figure 4.6). In such cases, aggregative nucleation can possibly be the cause of the high molecular weight. In aggregative nucleation, oligomers grow to a certain critical size and reach a certain molecular weight in the continuous phase before precipitating out. The increase in the size and number of oligomers causes the oligomers to increasingly interact with each other thus forming high aggregates. Heat dissipation due to the bulk reaction can poorly evolve which causes an acceleration of oligomer aggregation and the higher molecular weights result.

Figure 4.7 shows the copolymer composition of the bulk copolymer. This bulk copolymer composition was used to compare with the solution copolymer composition and dispersion copolymer composition (Figure 4.18).

Table 4.2 Characterization of the bulk copolymer
(mixed solvent content: 80 wt% EtOH)

Sample No.	Styrene (mole%)	Yield (%)	\bar{M}_n	\bar{M}_w	$\frac{\bar{M}_w}{\bar{M}_n}$	F _a (%St)
1b	25	29	190,000	720,000	3.84	35
2b	38	17	195,000	420,000	2.14	47
3b	50	28	235,000	810,000	3.45	56
4b	62	18	200,000	390,000	1.90	65
5b	75	19	170,000	350,000	2.04	77

F_a: copolymer composition obtained from the NMR method

Bulk Copolymer

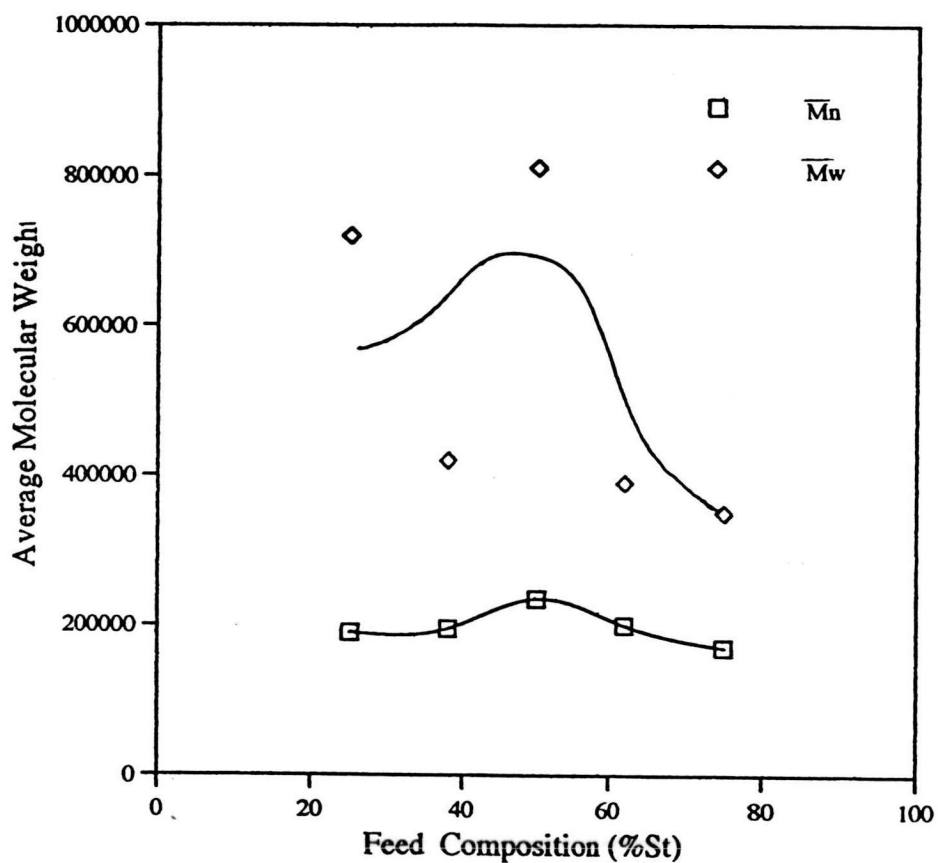


Figure 4.6 Effect of feed composition on average molecular weights of the bulk copolymer; mixed solvent content: ethanol/n-hexane=80:20 weight%

Bulk Copolymer

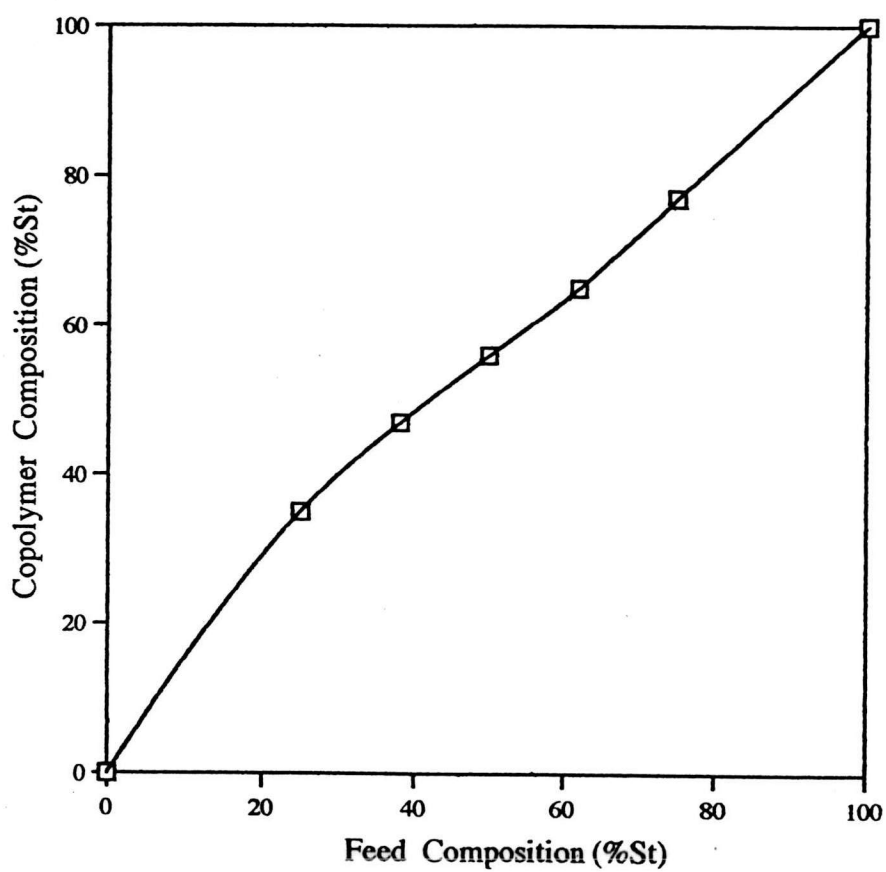


Figure 4.7 Copolymer composition of bulk copolymer; mixed solvent content: ethanol/n-hexane 80:20 weight%

4.3 Characterization of Dispersion Copolymer

Radical dispersion polymerization in a nonaqueous media is a process in which the monomer polymerizes in an organic liquid, which acts as a solvent for the monomer but as a precipitant for the polymer being formed. The mixture of monomer and solvent (or diluent) forms the disperse medium (continuous phase) that contains the required amount of initiator and stabilizing additive to prevent the polymer consequently formed from coagulation in the disperse medium. The composition of the dispersed medium changes gradually during polymerization because of the transformation of the monomer to polymer. The resulting reaction product is a polymer dispersion with a certain range of particle size in a disperse medium, which is, of course, the solvent (diluent) used. In the absence of a stabilizer, the primary polymer particles were produced by the aggregation of macromolecules with a rather low degree of polymerization (oligomers), their coagulation starts and results in formation of the polymer as a coagulate (precipitate) (35).

In a dispersion polymerization reaction, the reaction mixture starts out as a homogeneous solution that comprises the monomers, initiator, and stabilizer, which are all soluble in the solvent and that the resulting polymer precipitates as spherical particles during the reaction, which is stabilized by a steric barrier of dissolved polymer (15). This constrains the solvent that can be used in combination with a given monomer and stabilizer. The final polymer particle size is determined by the inherent polymer aggregation behavior under a given set of conditions. However, once the polymer particles nucleate, the initiator and monomer can be expected to partition between the solvent and polymer phases. The relative amount in each phase is then determined by the choice of solvent and temperature, among other factors (30).

Particle size control is therefore a function of several thermodynamic and kinetic factors. These include 1) monomer-polymer solubility, 2) reactant composition, 3) temperature, and 4) solvent medium. Temperature influences both the thermodynamic factors (i.e., solubility) as well as the kinetics of initiator decomposition which in turn determines the rate of polymerization and particle nucleation. It is important to note that, the monomers are a part of the solvent system and that their concentrations in the medium are being constantly diminished as polymerization proceeds. Thus, the role of the monomers which controls the success of the copolymerization is certainly not less important than that of the solvent (30).

4.3.1 Effect of PMVE Matrix Polymer

Figure 4.8 shows the effect of PMVE matrix polymer on the size of the copolymer. In the absence of the PMVE matrix as a steric stabilizer which is equivalent to the solution polymerization, it is found that the copolymer could not form a spherical shape because the particle could aggregate freely. In other words, to achieve permanent stabilization of the polymer particles, it is necessary to anchor strongly the dispersing agent onto the surface of the polymer particle, i.e. not to allow it to be released from the particle surface, or eventually, to be shifted on the low-energy particle surface. In the absence of a steric stabilizer (matrix polymer), unstabilized polymer (colloidal) particles in liquid media will rapidly coagulate owing to the effect of Van der Waals attractive forces between individual particles. Two ways of weakening the attractive forces between the particles, and thus hindering their coagulation, are known, i.e. (i) an electric double layer (EDL) or (ii) a steric barrier is formed on the particle surface. Both effects impede the necessary mutual approach of individual polymer particles. The electrostatic repulsion of particles with the same electric charge is very effective even in aqueous (polar) media; in media with a low relative permittivity (i.e. in nonpolar media), the steric stabilization of particles is more efficient (35).

The more precise explanation of the mechanism for steric stabilization of the polymer particles follows from an analysis of the changes in Gibbs free energy as a function of distance between the two sterically stabilized polymer particles. As the polymer particles approach, at a certain distance, compression (mutual penetration) of solvated (solubilized) parts (segments) on the surface of the particles of anchored molecules of steric stabilizer takes place. The effective concentration of the solubilized particles of steric stabilizer in the region between the polymer particles increases; at the same time, the chemical potential of the disperse medium decreases. The solvent therefore diffuses into this condensed space in order to reduce the concentration of the solubilized molecular segments of the steric stabilizer. This process causes mutual repulsion of the polymer particles until the penetration of the solubilized molecular segments of steric stabilizer anchored on the surface of both polymer particles is broken (35).

In this system, the polymer particles produced were stabilized in dispersion copolymerization by a steric barrier of the soluble polymer chains that was achieved by using the matrix polymer of PMVE. Consequently, the spherical styrene-co-

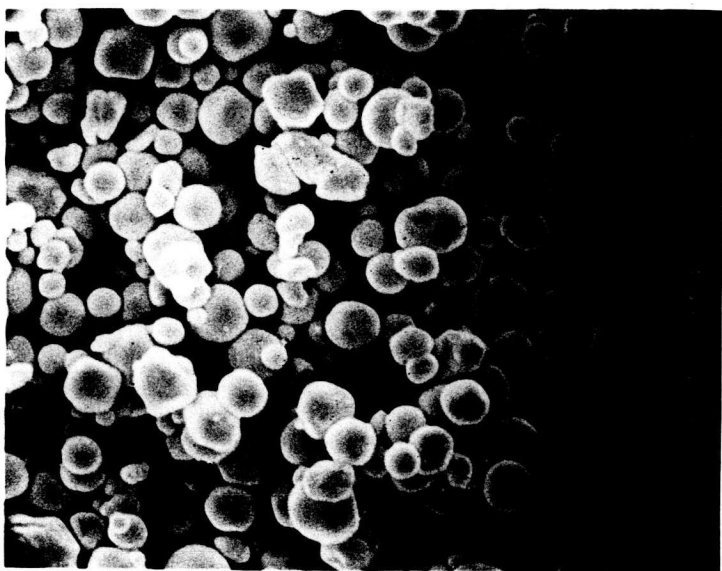


Figure 4.8 Scanning electron micrographs of the copolymers by solution copolymerization (left) and dispersion copolymerization (right) in the mixed solvent of 80:20 weight% ethanol/n-hexane

methyl methacrylate polymer can be synthesized by using the dispersion polymerization and a particle size stabilizer.

Figure 4.9 shows a schematic representation of particle formation and growth in nonaqueous dispersion polymerization (27). At the start of the process, St and MMA monomers, PMVE stabilizer and AIBN initiator are present in a homogeneous solution in the continuous phase (a). Upon heating, the initiator decomposes and the free radicals react with solute monomer to form oligomeric radicals (b). Growing oligomer chains associate with each other increasingly as their molecular weight and concentration rise. At a critical chain length, the oligomers precipitate and adsorb stabilizer to form stable particle nuclei (c). Once particles have been formed, they absorb monomer from the continuous phase. From this stage on, polymerization mainly takes place within the monomer-swollen particles till all of the monomer is consumed (d).

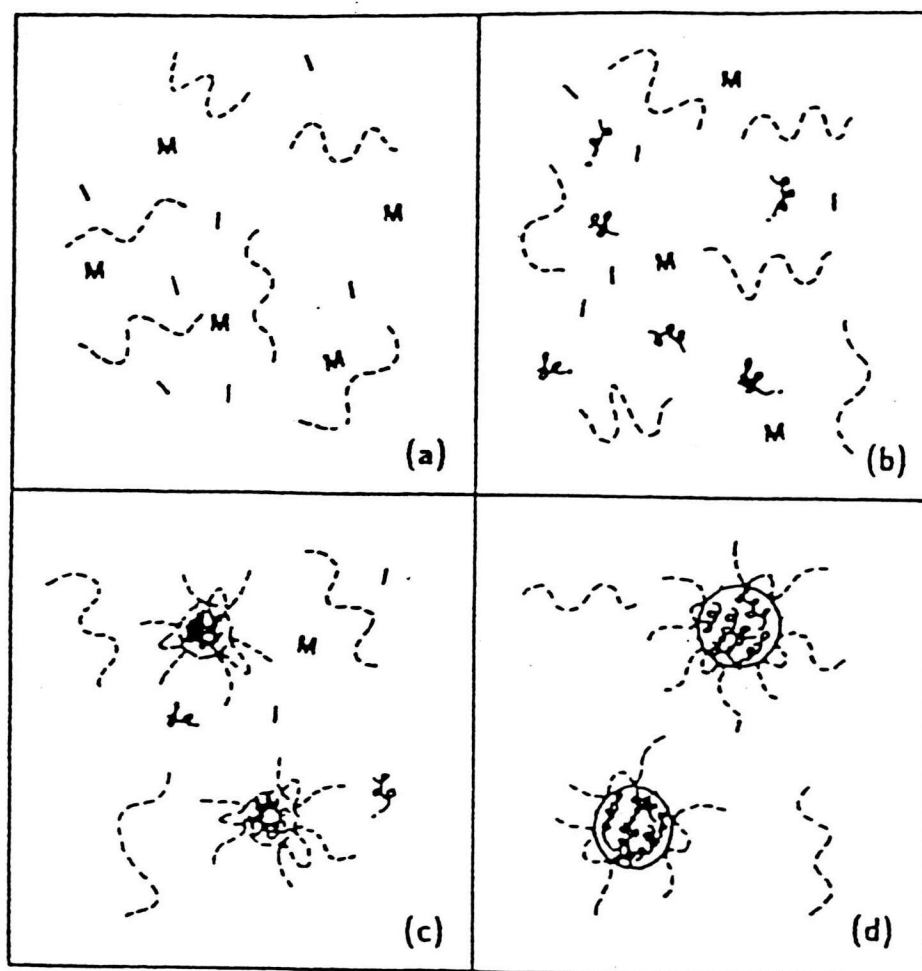
4.3.2 Effects of Styrene Feed Composition at 80 wt% Ethanol in Mixed Solvent

Styrene and methyl methacrylate were polymerized in the mixed solvent of ethanol and n-hexane in the presence of PMVE as a matrix polymer. By varying the styrene feed composition at 0 mole% St (100% MMA), 25, 38, 50, 62, 75 and 100 mole% styrene feed, the polymerization was started as a homogenous and clear system because the monomers and matrix polymer were soluble in the mixed solvent. After an induction period of about 30 minutes, a faint opalescence was obtained. It became a stronger opalescence after a while and turned into a white stable solution.

Considering the XPS analytical data (Appendix A), a small amount of oxygen (O) was found on the surface of PS which indicated that there was some PMVE matrix polymer still remained on the surface of the PS. However, the NMR and FT-IR spectra (Appendixes B and C) of PS did not indicate the presence of oxygen. This implied that the remaining PMVE was only found on the surface of the PS.

The yields of both homopolymers were relatively high, while those of the copolymers were smaller due to the formation of certain amount of the respective homopolymers.

The effect of styrene feed on the copolymer composition was summeried in Table 4.3.



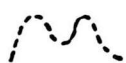



 Stabilizer
 Oligomer or polymer chain
 Initiator
 Monomer

Figure 4.9 Schematic representation of particle formation and growth in nonaqueous dispersion polymerization (27)

Table 4.3. Characterization of dispersion copolymer in various styrene feeds
(mixed solvent content : ethanol/n-hexane = 80:20 weight%)

Sample No.	Styrene (mole%)	Yield (%)	\bar{M}_n	\bar{M}_w	$\frac{\bar{M}_w}{\bar{M}_n}$	Particle Size(μm)	S.D. (%)	T _g (°C)	T _d (°C)	F (mole%Sty) NMR EA
1ds	0	90	25,000	63,000	2.47	2.78	2.08	111	347	0 0
2ds	25	69	27,000	55,000	2.06	1.88	1.18	107	344	35 34
3ds	38	39	22,000	40,000	1.79	1.76	0.88	102	350	38 38
4ds	50	73	24,000	48,000	1.99	1.73	0.74	99	348	55 54
5ds	62	38	18,000	34,000	1.92	1.69	0.72	98	353	61 60
6ds	75	57	18,000	37,000	2.02	1.59	0.58	98	357	71 70
7ds	100	86	39,000	200,000	5.12	1.05	0.24	96	378	100 100

S.D.: Standard Deviation

T_g: Glass Transition temperature

T_d: Decomposition temperature

F: Copolymer Composition

4.3.2.1 Effect of Styrene Feed in Dispersion Copolymerization on Average Particle Size and Particle Size Distribution

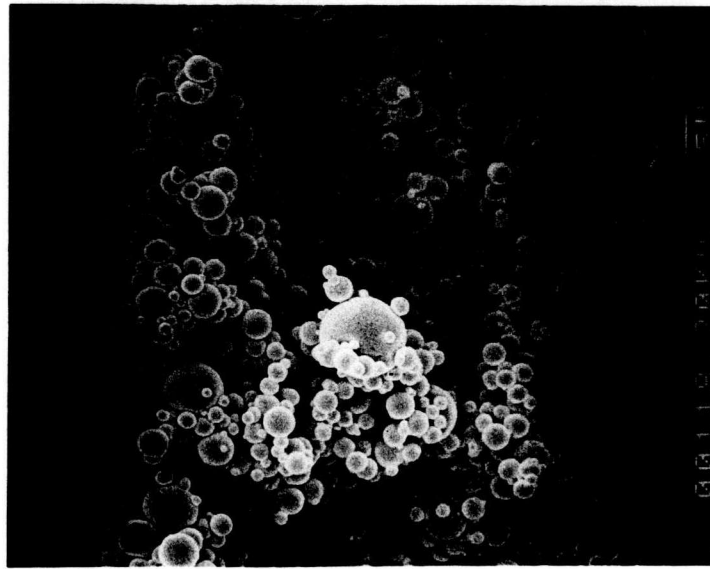
Figure 4.10 and Appendix D show the scanning electron micrographs of the styrene-co-methyl methacrylate polymer. It shows that, all the particles formed are in a spherical shape. The particle sizes obtained were in the range of 1-5 μm . The largest particle size was obtained for poly(methyl methacrylate) homopolymer whereas the smallest particle size was found for homopolymer of polystyrene. With increasing the styrene feed composition, the smaller particles were formed as shown in Figure 4.11.

Figure 4.12 shows the comparison of particle size distributions at low and high styrene contents. At high styrene content, the particles obtained were of a narrower size distribution.

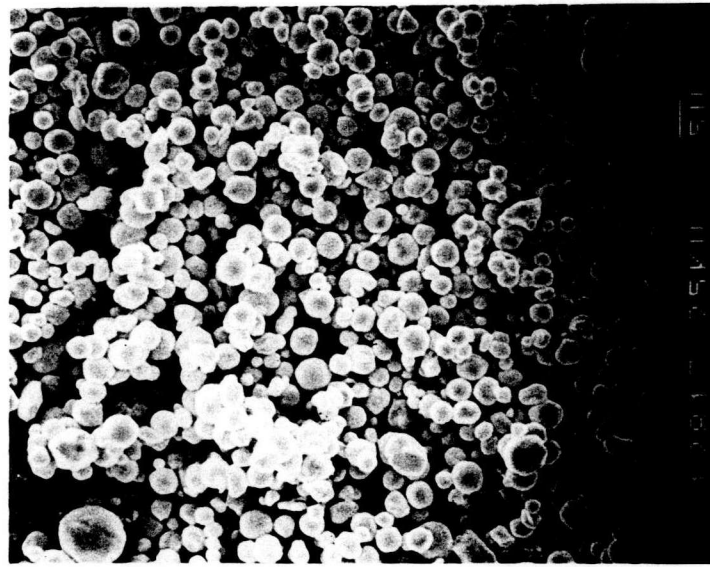
The styrene feed composition can effect the particle size and size distribution in that increasing the styrene feed, the smaller particles with narrower size distribution were formed. Comparing the polarity of the PMVE, MMA and St, the order of decreasing polarity is as follows: MMA>PMVE>St. In general, the type of polar effect is a general one often encountered in free radical reactions (36). One usually observes the reactivity of an electron-donor radical to be greater with an electron-acceptor substrate than with an electron-donor substrate, resulted in the different interactions between the two monomers with the matrix polymer. Based on the above-mentioned electron donating-electron accepting theory, the electron donating St could form a stronger interaction with the electron accepting PMVE, therefore, St radical was adsorbed much stronger on the PMVE matrix than the MMA radical. This contributes to the different sizes in both homopolymers and copolymers, i.e. polystyrene and the high styrene content in the copolymer are smaller in size.

4.3.2.2 Effect of Styrene Feed on Average Molecular Weights

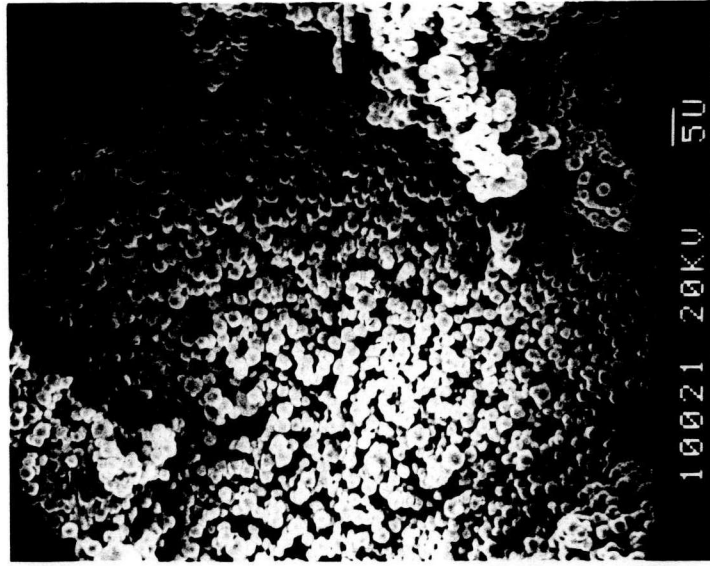
By considering the GPC charts (Figure 4.13), there was only one peak each of the copolymer product which indicated that, all of the



St 25% feed



St 50% feed



St 75% feed

Figure 4.10 Scanning electron micrographs of the poly(styrene-co-methyl methacrylate) by dispersion copolymerization in the mixed solvent of 80:20 weight% ethanol/n-hexane

Dispersion Copolymer

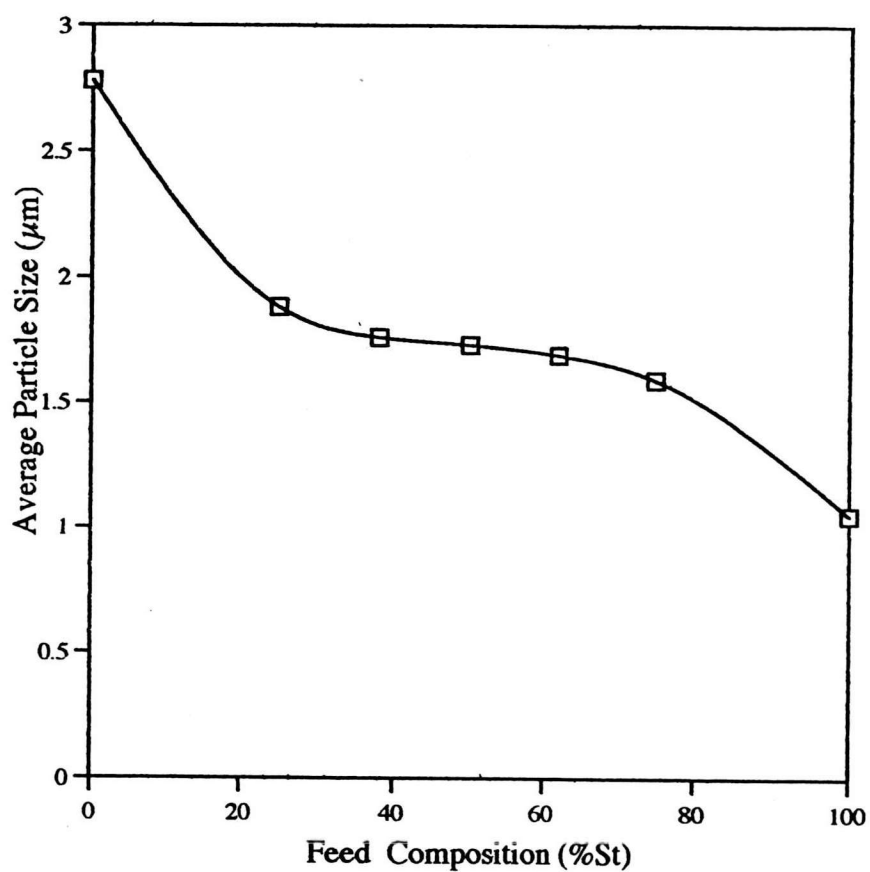


Figure 4.11 Effect of styrene feed composition in dispersion polymerization on average particle size; mixed solvent content: ethanol/n-hexane=80:20 weight%

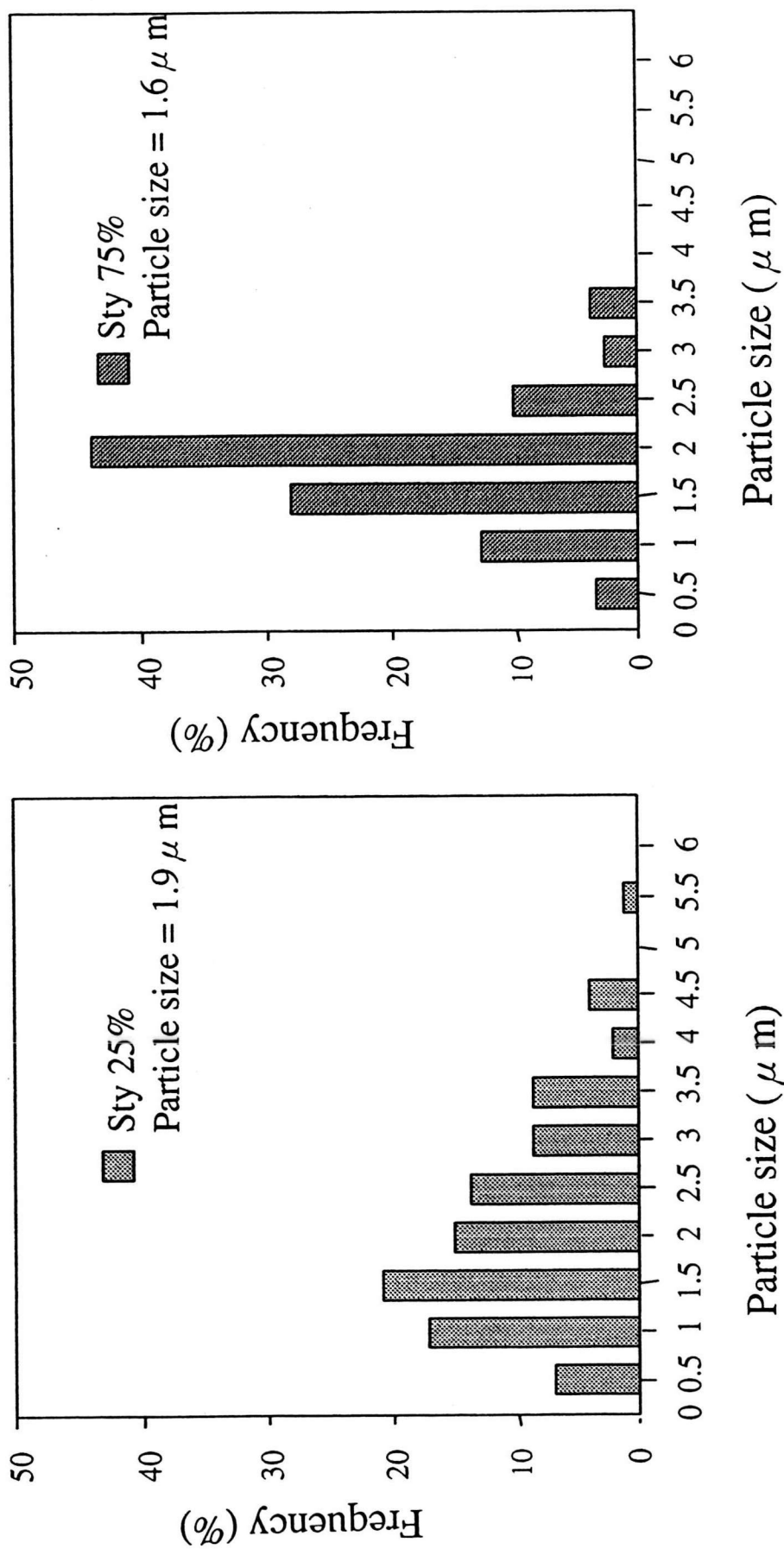


Figure 4.12 Particle size distribution of the poly(styrene-co-methyl methacrylate) by disperison copolymerization in the mixed solvent of 80:20 weight% ethanol/n-hexane

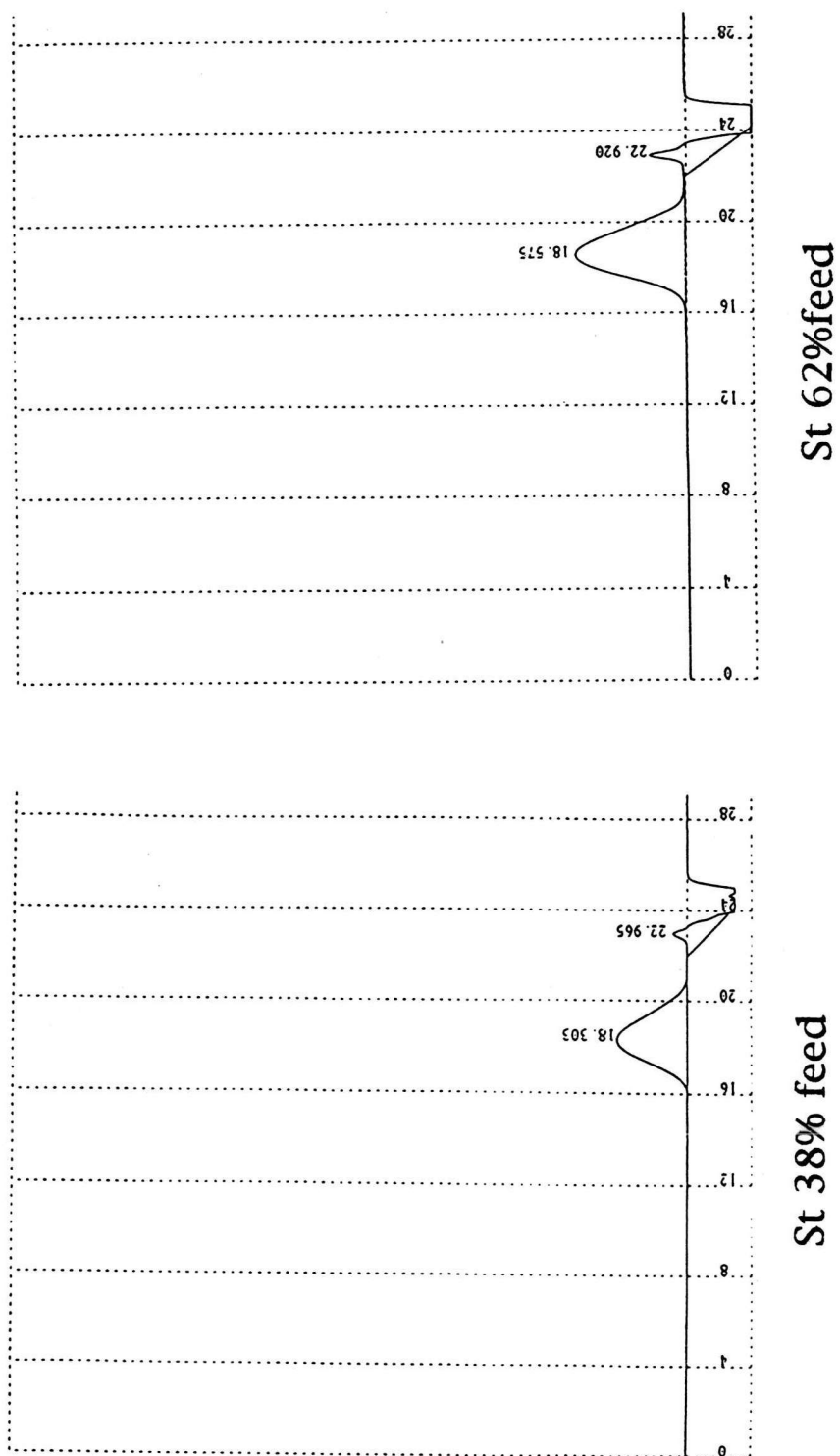


Figure 4.13 GPC Chromatograms of poly(styrene-co-methyl methacrylate) by dispersion copolymerization in the mixed solvent of 80:20 weight% ethanol/n-hexane

styrene and methyl methacrylate homopolymers were washed out from the copolymer product.

The weight-average molecular weights of the copolymer products were high, which were obtained in the styrene and methyl methacrylate homopolymerizations and decreased in the copolymerization. However, the number-average molecular weight of styrene-co-methyl methacrylate polymer was not significantly sensitive to the styrene feed (Figure 4.14). The reactivities of the two monomers (styrene and methyl methacrylate) in radical copolymerization are 0.52 and 0.46, respectively (37). Therefore, there were more styrene radicals than methyl methacrylate radicals in the reaction mixture leading to a higher styrene content in the copolymer composition.

4.3.2.3 Effect of Styrene Feed on T_g and T_d

In the six basic steps in the xerographic process, the fusing step is one of the most important steps for the dry toner design. The toner used should soften in the fuser roller and adhere to the paper without contaminating the fuser roller itself. In flash fusing, the toner is melt into the paper by a very short high intensity flash of light lasting less than 5 ms. Toner temperatures typically exceed 200°C in attaining the low viscosities required, and the thermal decomposition of the toner polymer is a significant problem (7). The thermal properties of the polymer resin which is the main component of the toner therefore must be examined.

Figures 4.15 and 4.16 show the effect of styrene feed on T_g and T_d , respectively. The T_g and T_d of copolymers were obtained within the range between the values of both homopolymers. The T_g was found in the range that can further modified to produce a toner. In addition, the T_d of the copolymers were also found in the higher temperature range than the typical toner temperatures. As the temperature of the fuser roller does not usually exceed 204°C.

Table 4.4 shows the comparison of the calculated- and observed-glass transition temperatures. An example of calculation was shown in Appendix E.

Dispersion Copolymer

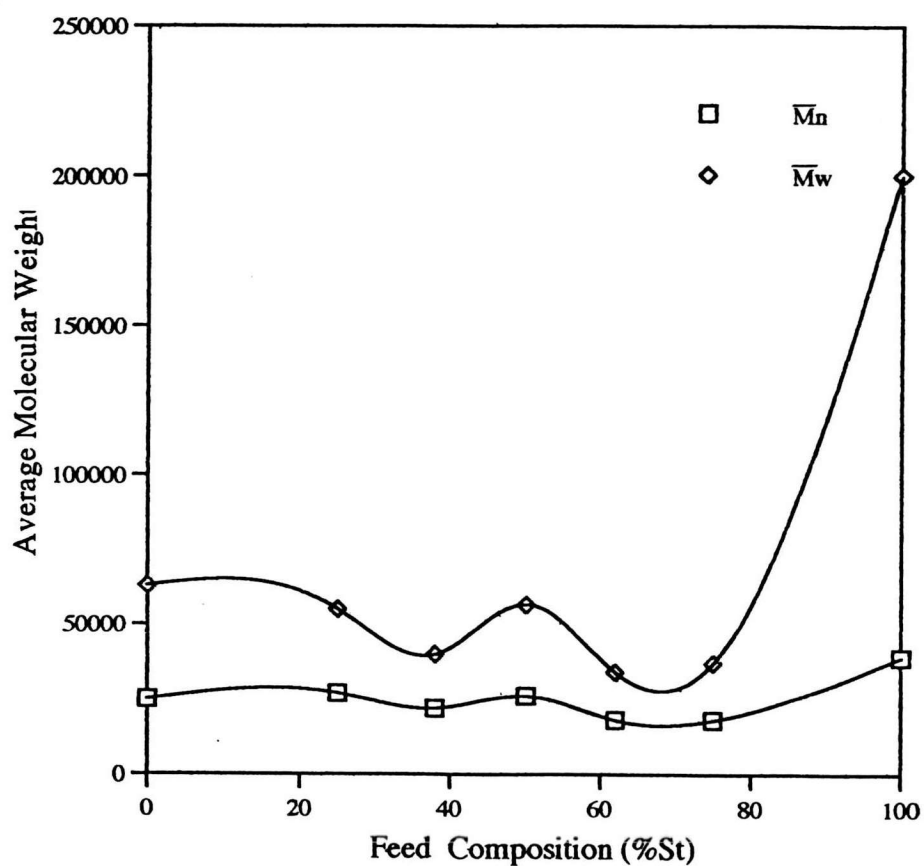


Figure 4.14 Effect of feed composition on average molecular weights of dispersion copolymer; mixed solvent content: ethanol/n-hexane= 80:20 weight%

Dispersion Copolymer

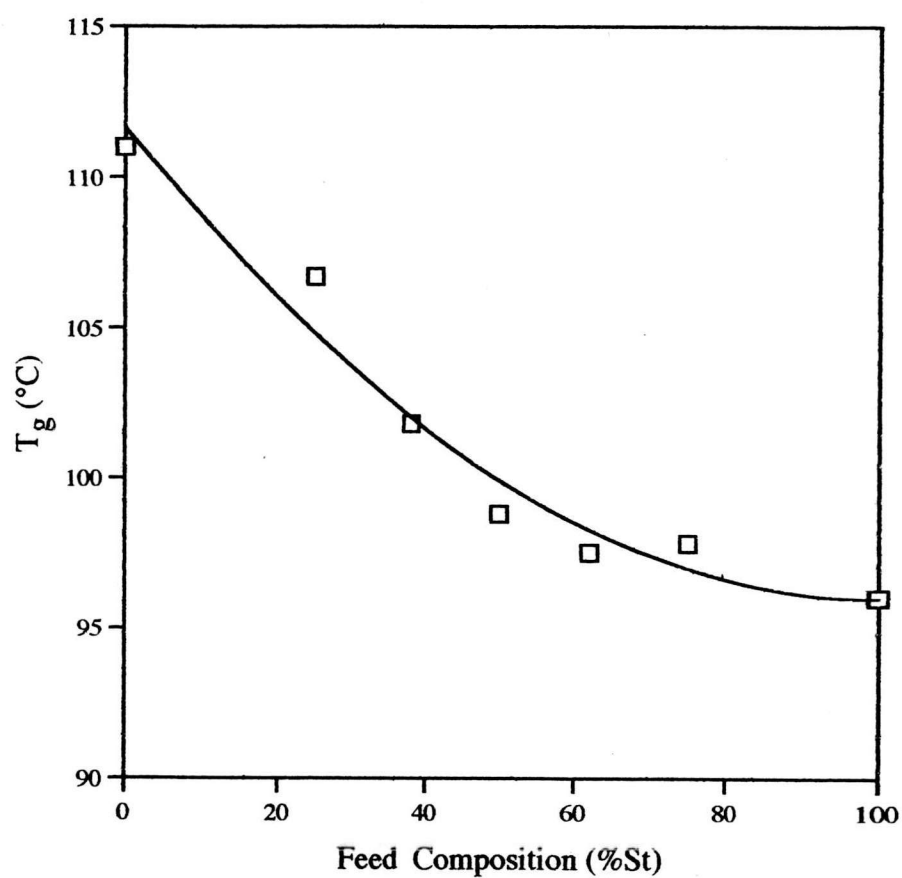


Figure 4.15 Effect of styrene feed on glass transition temperature of dispersion copolymer; mixed solvent content: ethanol 80 weight%

Dispersion Copolymer

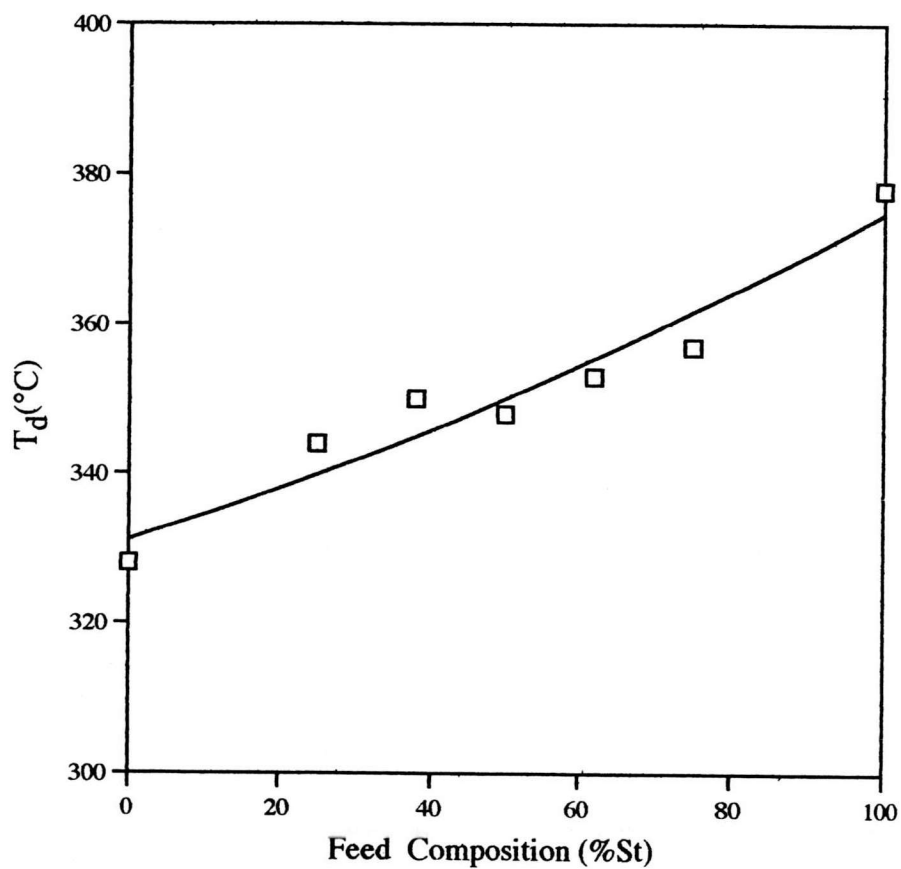


Figure 4.16 Effect of styrene feed on decomposition temperature of dispersion copolymer; mixed solvent content: ethanol 80 weight%

Table 4.4 Comparison of the calculated- and observed-glass transition temperatures

F (mole%St)	0	35	38	55	61	71	100
T _g , calculated ^a	---	105.6	105.2	102.6	101.7	100.2	---
T _g , observed	111	106.7	101.8	98.8	97.5	97.8	96
T _d , observed	328	344	350	348	353	357	378

F: mole% styrene in copolymer

^a: Calculated from the formula: $T_g = (w_1T_{g1} + Kw_2T_{g2}) / (w_1 + Kw_2)$,

4.3.2.4 Relationship between Feed Composition and Copolymer Composition

Copolymer composition was measured by using H¹ NMR and elemental analysis methods. Figure 4.17 shows the copolymer composition obtained from the H¹ NMR.

Figure 4.18 shows the comparison of the dispersion, solution and bulk copolymer compositions. It was found that, there was no difference in terms of mechanism of polymerization between these three polymerizations, because there were not any significant difference in the curve shown in Figure 4.17. Therefore, the copolymer composition may be not the major factor of particle formation mechanism.

Dispersion Copolymer

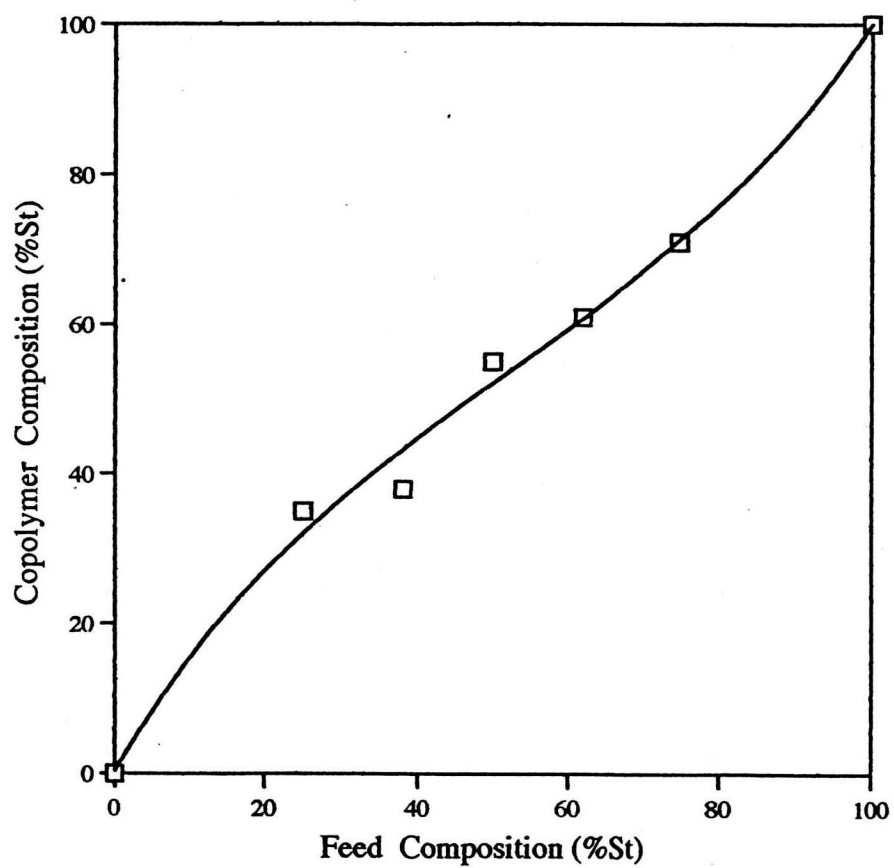


Figure 4.17 Copolymer composition of dispersion copolymer; mixed solvent content: ethanol 80 weight%

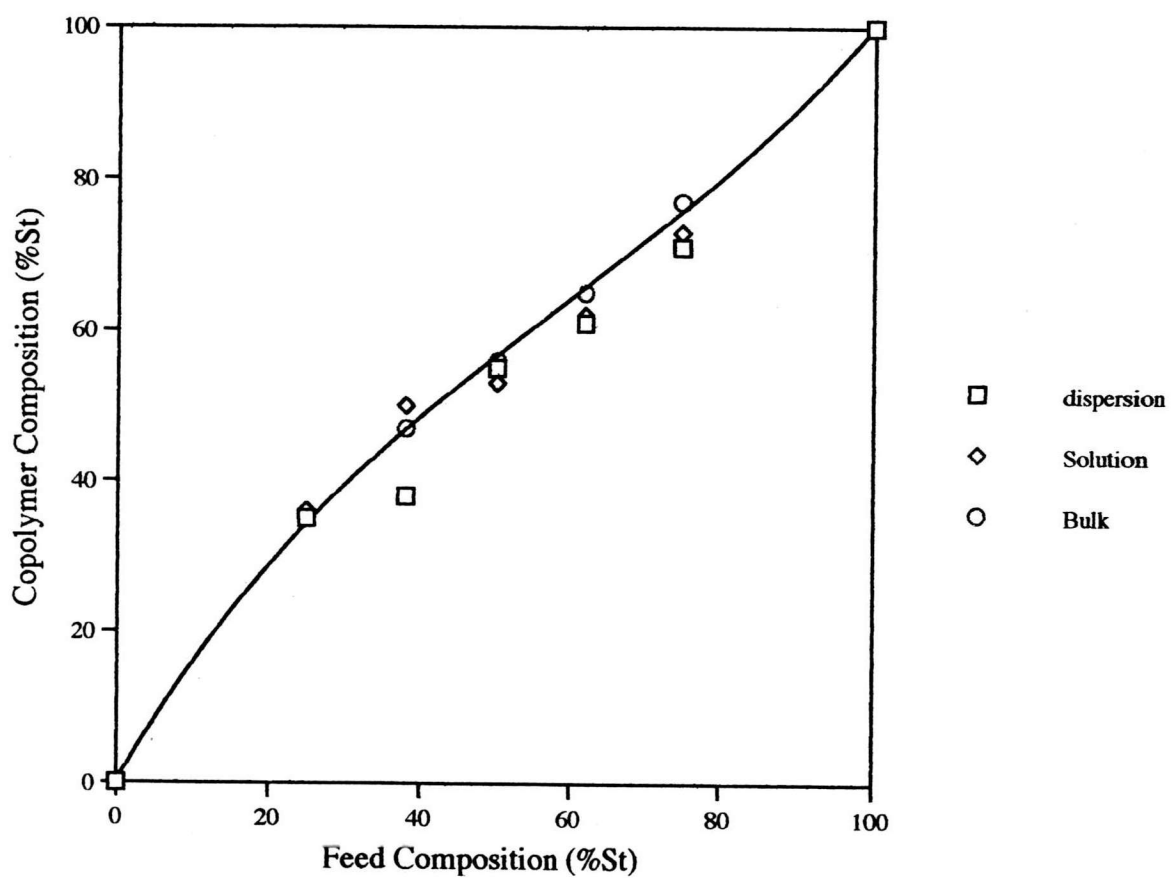


Figure 4.18 Comparison of the dispersion, solution and bulk copolymer compositions

4.3.3 Effects of Mixed Solvent Content at 25 Mole% Styrene Feed

25 mole% styrene feed together with other chemicals including the PMVE matrix polymer and the initiator in various concentrations of ethanol/n-hexane of 0, 20, 35, 50, 65, 80, and 100 weight% were polymerized. PMVE matrix polymer could not dissolve in the solvent concentrations of 0 and 20 weight% ethanol. It appears that a two-phased mixture occurred at these two concentrations of ethanol. N-hexane is a poor solvent for the PMVE. The appearance of two phases remained during the copolymerization. In contrast, the copolymerizations containing 35, 50, 65, 80, and 100 weight% ethanol were homogeneous for the whole course of copolymerization. Therefore, heterogeneous and homogeneous copolymerizations of styrene and methyl methacrylate will be considered separately.

4.3.3.1 Heterogeneous Systems

It is, therefore, impossible to explain the result of the heterogeneous system based on the theory of dispersion polymerization. Surprisingly, the particle size and size distribution of the copolymers, as shown in Table 4.5 and Figure 4.19, were of very small size (0.91 and 1.63 μm for 0 and 20% ethanol, respectively), and very narrow distribution (S.D.=0.27 and 0.42). The exact explanation of such a result is still unknown. The result might be due to the minute dissolution of the PMVE in the poor solvent of n-hexane. Copolymerization of styrene/methyl methacrylate perhaps occurred by the control of the small size of free volume of the dissolved and non-dissolved parts of PMVE. This might result in the smallest particle size at 0% ethanol. Considering the molecular weights, the high molecular weights were observed in the non-polar solvent of n-hexane especially in 100% n-hexane shown in Table 4.5. The unusually high weight-average molecular weight in n-hexane solvent might be due to the Trommsdorf-Norrish type I effect (locally gel effect).

Table 4.5 Characterization of dispersion copolymer in various concentrations of ethanol/n-hexane (monomer content: St/MMA=25:75 mole%)

Sample No.	Ethanol (wt%)	Yield (%)	\bar{M}_n	\bar{M}_w	$\frac{\bar{M}_w}{\bar{M}_n}$	Particle Size(μm)	S.D. (%)
1de	0	35	62,000	204,000	3.27	0.91	0.27
2de	20	21	23,500	49,000	2.08	1.63	0.42
3de	35	26	23,400	42,000	1.78	1.94	0.74
4de	50	33	23,000	42,000	1.82	2.18	0.99
5de	65	34	26,000	44,000	1.68	2.12	0.83
6de	80	69	27,000	55,000	2.06	1.88	1.18
7de	100	30	26,000	53,000	2.04	1.76	0.55

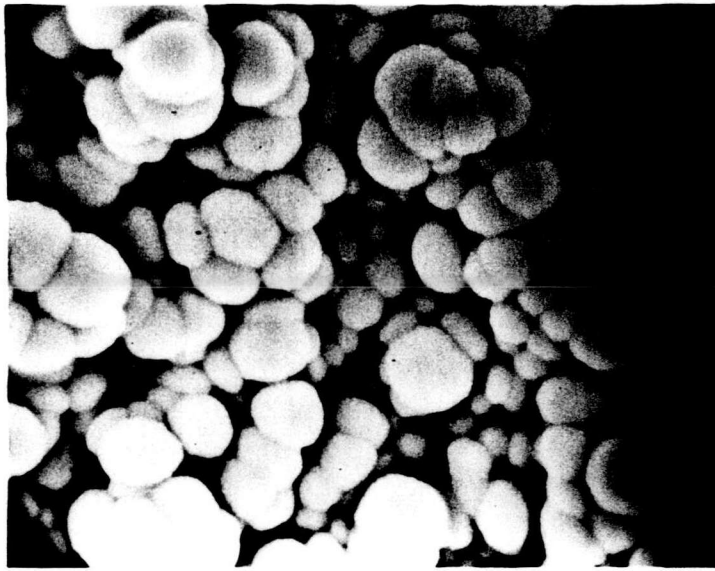
S.D. : Standard Deviation

4.3.3.2 Homogeneous Systems

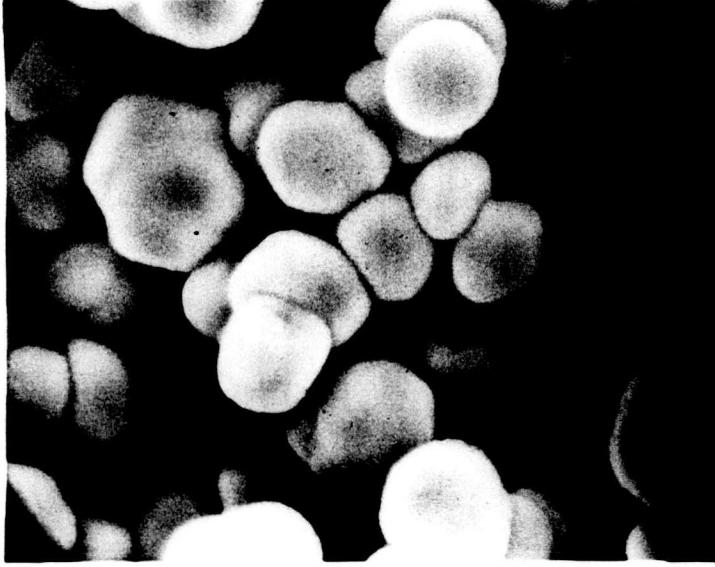
The homogeneous system was found in the solution containing 35 weight% ethanol onwards. One sees a rather uniformity of molecular weight distribution along with the influence of solvents on particle size and size distribution.

4.3.3.2.1 Effect of Ethanol Concentrations on Average Particle Size and Average Molecular Weights

Based on the previous works done elsewhere (10), controlling factors of the particle number and size includes the important effect of solvency of the medium and solubility of the polymer. The solvency of the medium, of course, depends as much on the nature of the polymer as on the nature of the diluent. They found that it was very difficult to prepare stable dispersion of polymers with high proportions of monomers at either of the extreme ends by dispersion polymerization in aliphatic hydrocarbons. Excessive amounts of the dispersant (matrix polymer) are needed to stabilize the large total surface area produced, then ultra-fine particles are formed. The less polar polymers are almost



EtOH 0%

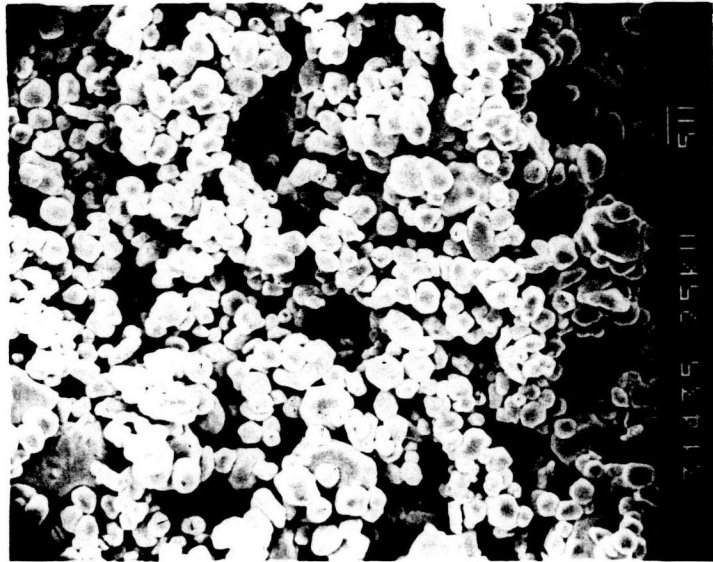


EtOH 20%

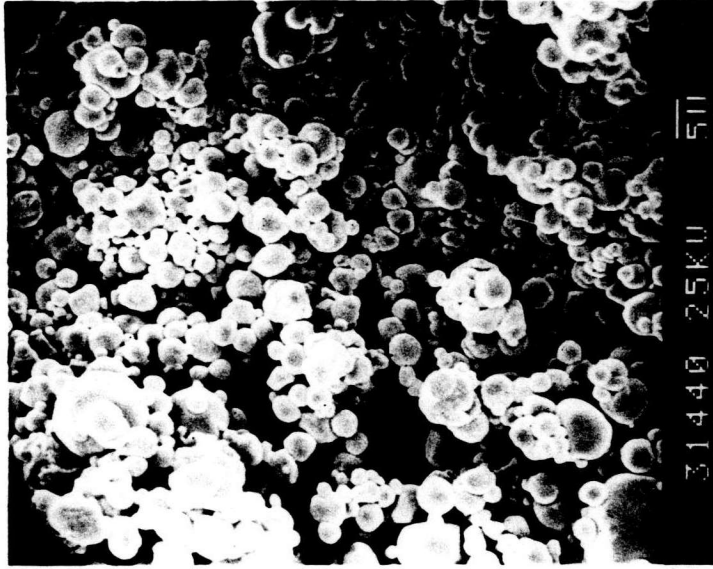
Figure 4.19 Scanning electron micrographs of the copolymers by dispersion copolymerization in the feed of 25:75 mole% St/MMA in the heterogeneous system

completely soluble, and their large particle readily aggregate because the dispersant is only weakly anchored to their surfaces. With more polar monomers, a correspondingly polar diluent such as ester or alcohol was used. There is another important effect of solvent in modifying the orientation of the dispersant and its influence on the number of particles formed. Their work have not as yet mention on sizes of the particles. Our present work is, therefore, the novel technique of preparing the super-fine polymeric particle size utilizing a new concept of free volume change of the matrix polymer solution depending to a very large extent on the solvency of the medium (ethanol and n-hexane) and solubility of the polymers (matrix polymer and the resulting copolymers produced).

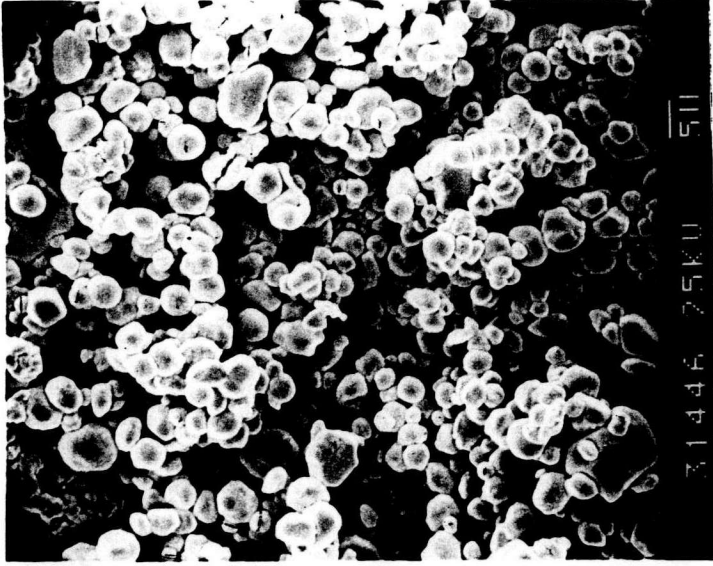
Table 4.5 shows the result of ethanol concentrations on particle size and size distribution. Increasing the ethanol concentrations, a smaller particle size was encountered. In other words, increasing the medium polarity resulted in a decrease in particle size and size distribution. According to Table 4.6 (38), at 100 weight% ethanol ($\delta = 12.92 \text{ (cal/cm}^3)^{1/2}$) which is a good solvent for the matrix polymer of PMVE ($\delta = 11.30 \text{ (cal/cm}^3)^{1/2}$) with a $\Delta\delta$ ($\delta_{\text{ethanol}} - \delta_{\text{PMVE}}$) value of about 1.6 units, the polymer can dissolve easily and its chains disentangle and then stretch in the medium. Solvation, a formation of solvent-solute complexes may also occur. For the poor solvent system, such as n-hexane, $\delta = 7.24 \text{ (cal/cm}^3)^{1/2}$ with a $\Delta\delta$ ($\delta_{\text{PMVE}} - \delta_{\text{n-hexane}}$) of about 4 units, polymer entangles or aggregates to become a coiled structure. These phenomena of both good and poor solvents entail a local modification of polymer structure and consequently gives a volume change in the polymer solution. Additionally, polymer chains in solution for both good and poor solvents repel one another as a result of Van der Waals forces. The change in polymer size due to that polymer-solvent solubility and repulsive force control the free-volume (space) of the polymer solution. As mentioned early that the chains of PMVE are the particle size steric stabilizer, the free space in the solvent controls morphologically the size of the particles in that the particle sizes are larger in high-concentrations of non solvent. Because there is a larger solvent volume available for copolymerization which is directly controlled by the PMVE chains and its conformation. Figure 4.20 depicts the scanning electron micrographs of poly(styrene-co-methyl methacrylate) particle size. The corresponding average particle size is shown as a function of ethanol concentration in Figure 4.21.



EtOH 35%



EtOH 50%



EtOH 65%

Figure 4.20 Scanning electron micrographs of the poly(styrene-co-methyl methacrylate) by dispersion copolymerization in the feed of 25:75 mole% St/MMA

Dispersion Copolymer

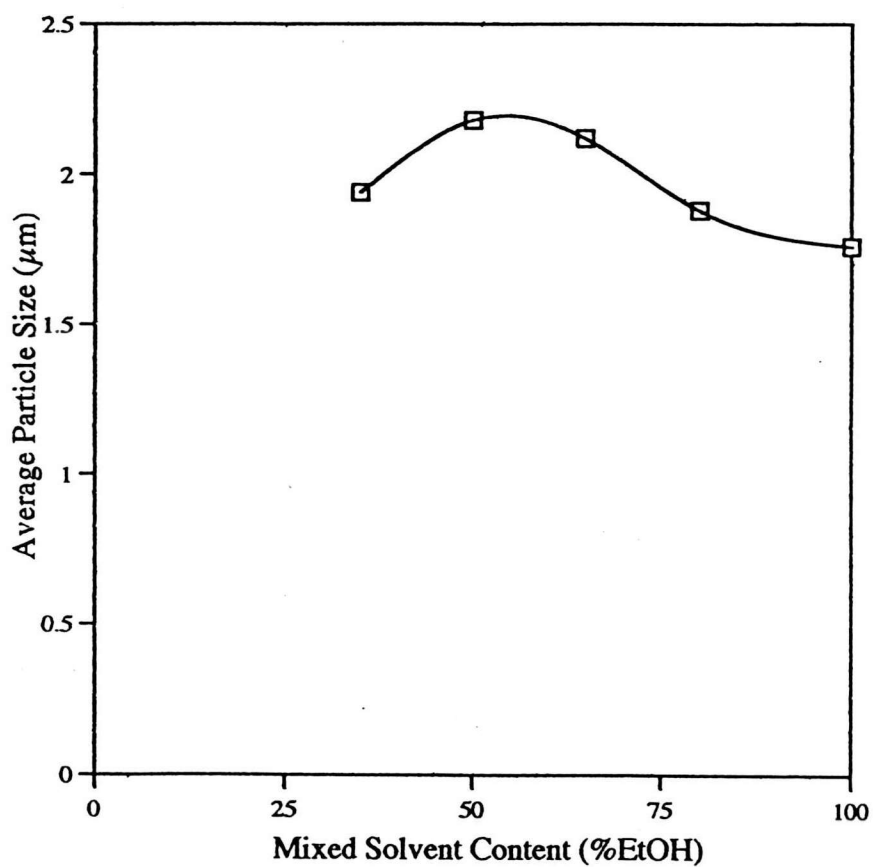


Figure 4.21 Effect of mixed solvent content on average particle size; feed: St/MMA=25:75 mole%

Table 4.6 Solubility parameters (cal/cm³)^{1/2} of selected chemicals

	∂_T	∂_d	∂_p	∂_h
St	9.30	9.07	0.5	8.5
PS	9.10	*	*	*
MMA	8.80	*	*	*
PMMA	9.08	*	*	*
PMVE	11.30	*	*	*
Ethanol	12.92	7.73	4.3	9.5
N-hexane	7.24	7.23	0	0
Methanol	14.28	7.24	6.0	10.9

*: Not available

$$\partial^2_T = \partial^2_d + \partial^2_p + \partial^2_h$$

∂_T = Total solubility parameter; ∂_d = component due to dispersion forces;

∂_p = component due to polar forces; ∂_h = component due to hydrogen bonding

Considering the trend of particle size and average molecular weights, one finds that average molecular weights increased with decreasing in particle size in more polar solvent ($\partial = 12.92$ (cal/cm³)^{1/2}). The more polar solvent produced more nuclei at the small particle sizes (15). These nuclei then spent much more time in a regime where they captured more oligomer growing radicals in the solution that a high molecular weight also resulted (Figure 4.22).

It is wondering that the 35 weight% ethanol system really comprised an absolutely homogeneous medium. It may contain some concentrations of heterogeneous droplets within the majority of the homogeneous phase. Therefore, solvent solubility and free volume aspect still could not be applied to this system containing 35 weight% ethanol as solvent. In addition, the same trend of particle size and molecular weight relationship is also observed as for the homogeneous system.

Dispersion Copolymer

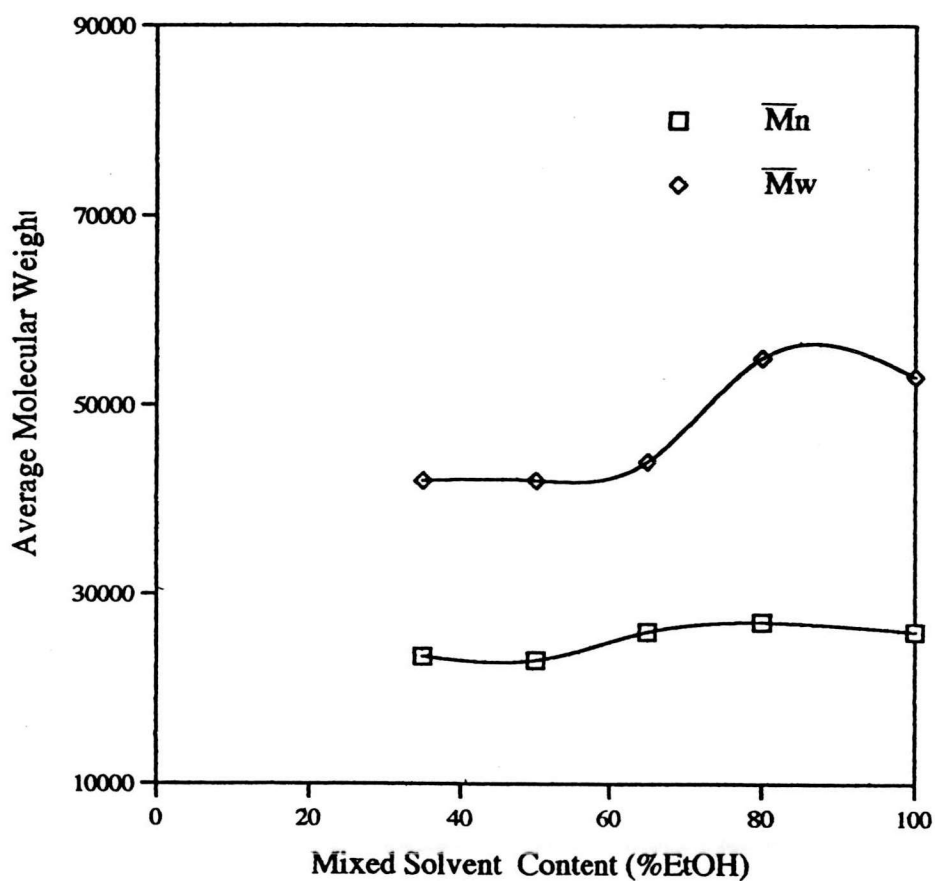


Figure 4.22 Effect of mixed solvent content on average molecular weights; feed: St/MMA=25:75 mole%

4.3.4 Effects of Temperature on Dispersion Copolymerization

A series of experiments were designed to investigate the effect of temperature on the particle size and size distribution. The ratios of St/MMA monomer feed and ethanol/n-hexane mixed solvent ratio were fixed at 75 mole% styrene feed and 80 weight% ethanol as before. The concentrations of AIBN initiator, PMVE matrix polymer were also fixed. The temperatures employed during the polymerization were between 40; and 73°C, and some characteristics of the resulting particles are listed in Table 4.7. It was found that, the reaction did not occur at 40 and at 73°C, the reaction gave the agglomerated particles and consequently the average particle size could not be determined. Therefore, the lower and upper temperatures limits for this dispersion copolymerization were 50°C and 64°C, respectively.

Table 4.7 Characterization of the dispersion copolymer at various reaction temperatures
(monomer feed content: 75 mole% St,
mixed solvent content: 80 wt% EtOH)

Sample No.	Temp. (°C)	Yield (%)	\bar{M}_n	\bar{M}_w	$\frac{\bar{M}_w}{\bar{M}_n}$	Particle Size(μm)	S.D. (%)
1dt	40	-----	-----	-----	-----	-----	-----
2dt	50	*	25,000	51,000	2.04	1.11	0.35
3dt	55	57	18,000	37,000	2.02	1.59	0.58
4dt	64	49	16,000	31,000	1.93	1.79	1.05
5dt	73	56	15,000	29,000	1.99	coagulate	coagulate

S.D.: Standard deviation

-----: The reaction cannot occur at 40°C

*: Not available

4.3.4.1 Effects of the Reaction Temperature on Average Particle Size and Particle Size Distribution

When increasing the reaction temperature of a radical chain copolymerization, the average particle size was increased and the size distribution became broader as shown in Figures 4.23 and 4.24. It is probably due to that the temperature is also another important parameter controlling the formation of particle. Basically, reaction temperature involves both thermodynamic and kinetic aspects of chain polymerization (31). On the thermodynamic aspect, increasing the temperature will increase the magnitudes of ΔH and ΔS , i.e. both are positive as more heat is given. The reaction will therefore, spontaneously proceed and more copolymer will be produced. Solubility of the copolymer is enhanced at higher temperatures until the copolymer has precipitated out. The particles will agglomerate and aggregate to become larger in size.

On the other hand, the higher temperature increases the decomposition rate of the initiator to produce a large amount of free radicals that can initiate to give many polymer radicals. As the temperature rises by 10°C, a two- or three-fold increase in the rate of polymerization usually occur (36). The small particles obtained by such a high temperature can be caused by a particle nucleation due to possibly that the soften particle surfaces can combine easily. Expansion of the small agglomerations of particles can occur spontaneously to form huge aggregates and finally a continuous film.

4.3.4.2 Effects of the Reaction Temperature on Average Molecular Weights

When the temperature of copolymerization was increased, the average molecular weights were decreased. At higher temperatures, more radicals were produced to initiate many short kinetic chains. These small kinetic chains can propagate to give many low molecular weight polymers. Table 4.7 and Figure 4.25 show the results of number- and weight-average molecular weights of the resulting copolymers. It is worthwhile mentioning that the reaction temperature of 40°C could not initiate the copolymerization because not enough activation energy was given that would not even decompose the thermal initiator like AIBN. In this particular reaction, the temperature for both producing smaller particle size, size distribution,

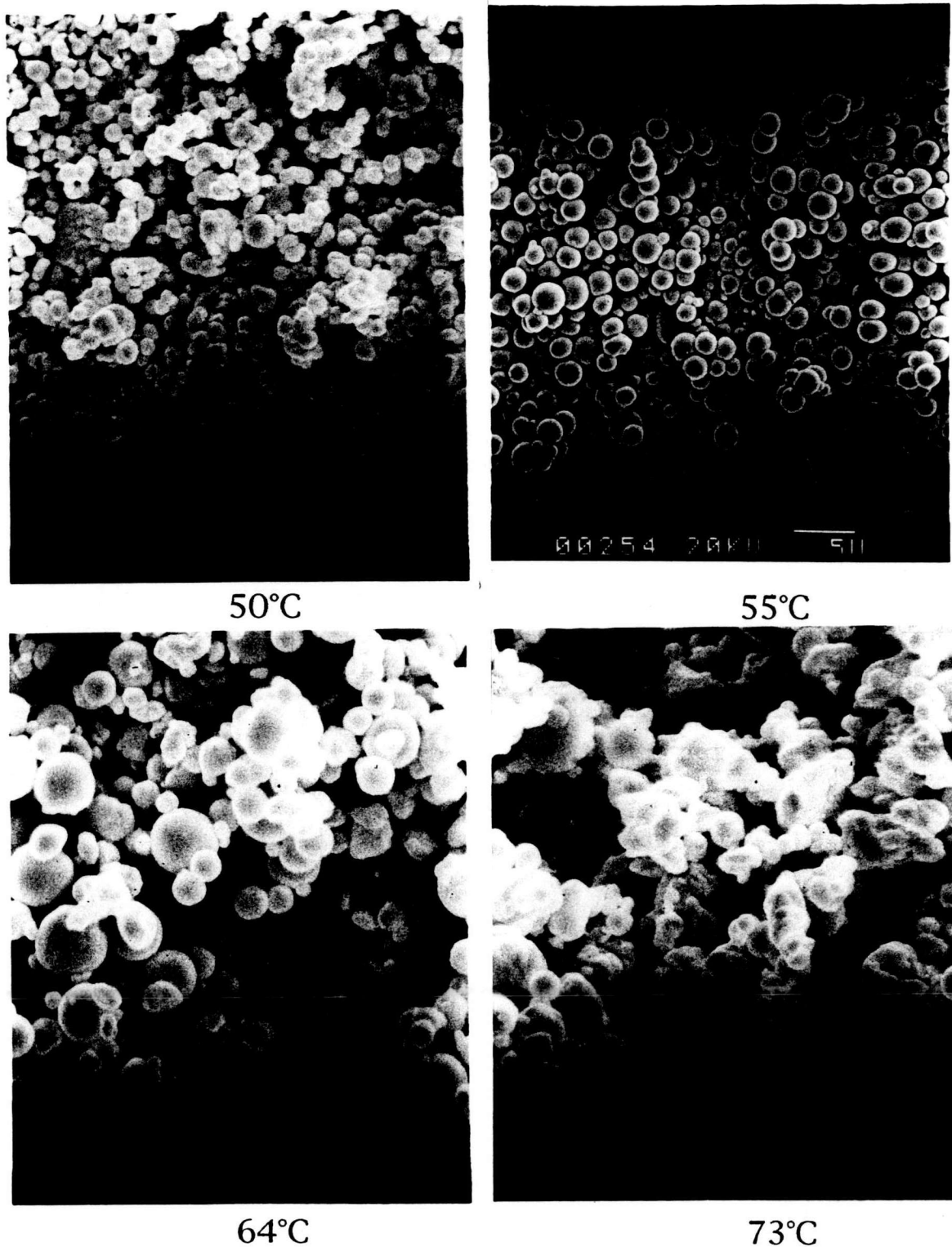


Figure 4.23 Scanning electron micrographs of the poly(styrene-co-methyl methacrylate) by dispersion copolymerization in 75:25 mole% St/MMA and 80:20 weight% ethanol/n-hexane

Dispersion Copolymer

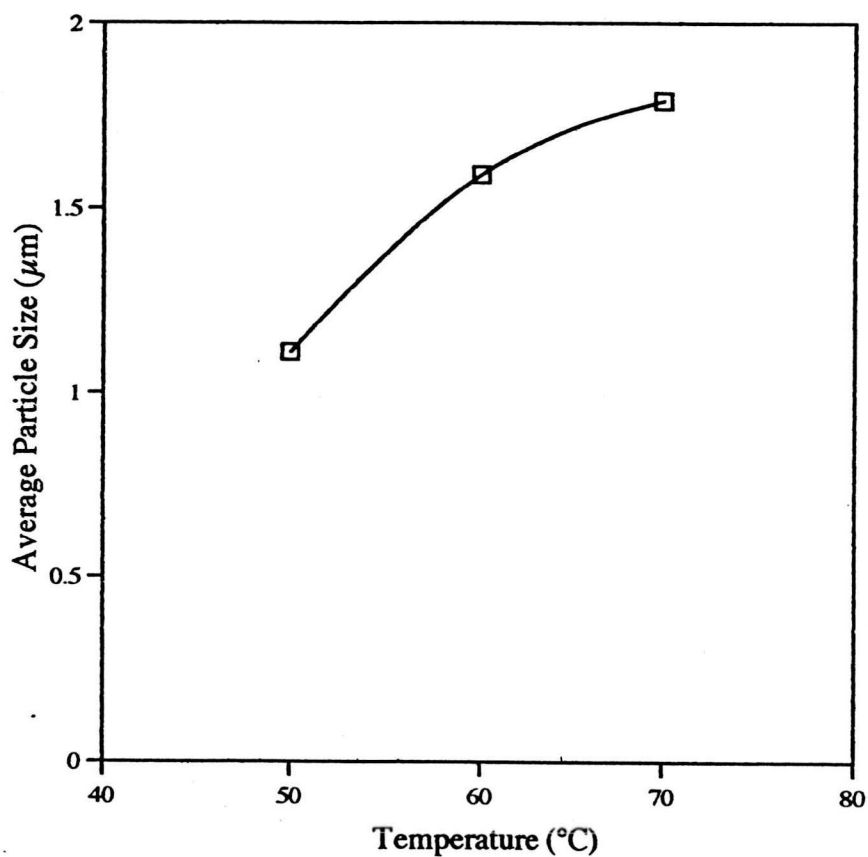


Figure 4.24 Effect of temperature on average particle size at styrene feed 75 mole%, mixed solvent of ethanol 80 weight%

Dispersion Copolymer

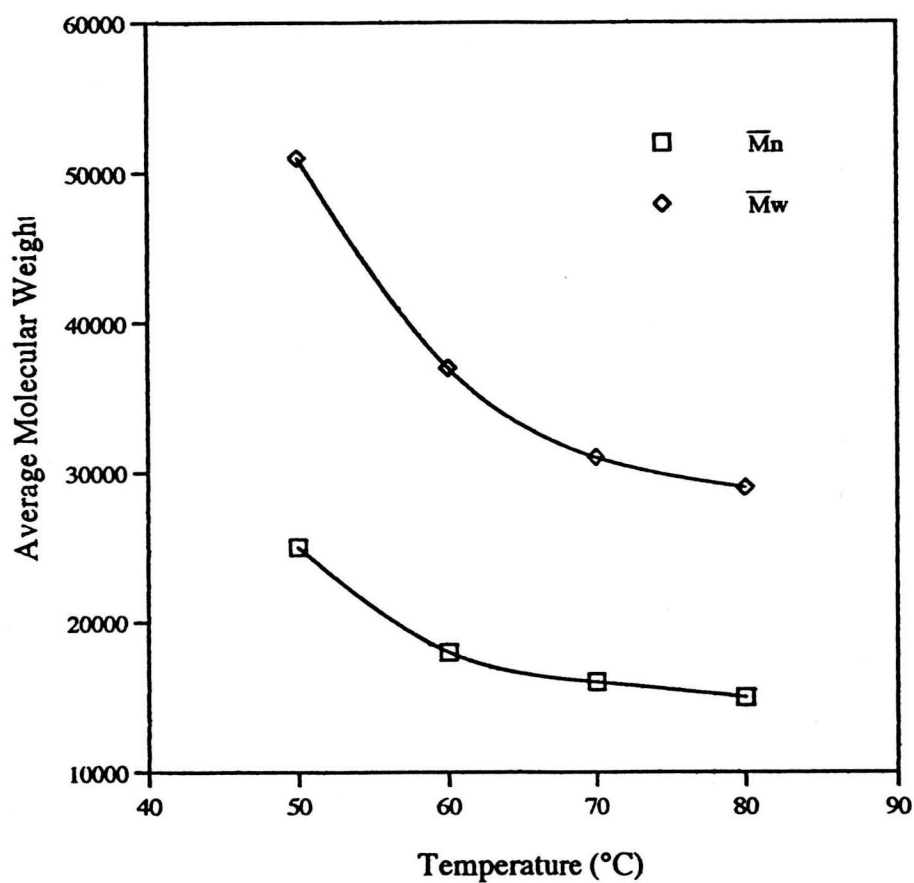


Figure 4.25 Effect of temperature on average molecular weights at styrene feed 75 mole%, mixed solvent of ethanol 80 weigh%

and high molecular weight copolymer should be carried out at around 50°C.

To conclude, the effects of temperature on particle size and average molecular weights suggest that the mechanism for particle nucleation depends on the molecular weights of polymer produced by polymerization before the initial precipitation. The initial rate of the polymerization is an important determining step for the final particle size as it is in the first short-time period that nucleation occurs. At higher temperatures, the kinetic chain length was short and low-molecular weight polymers were produced in the nucleation stage of the reaction. During the nucleation period, the less soluble (higher molecular weight) polymer chains are expected to precipitate and form the particle nuclei. However, at higher temperatures, a few high molecular weight polymers are produced due to the greater chain termination by chain transfer agent and initiator, then few nuclei will be produced, and the final diameter of the particles will consequently become larger (39).