Acrylonitrile Copolymerization with a NaClO₃/Na₂SO₃ Catalyst.   Part I.   Effect of 2-Methyl-5-Vinylpyridine*

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INTRODUCTION

The polymerization of acrylonitrile in dilute aqueous solution initiated by the chlorate–sulfite redox system has been previously studied both kinetically and with the aid of electron microscopy.[1]   In these studies, the monomer concentration was 5.3% ($1.0M$) or less so that all of the monomer was in solution at the start of reaction.   Particles of polymer separated from the start as spheroids less than 200 A. across and grew rather uniformly to 2000–3000 A.   The effects of higher monomer concentration or of the use of comonomers were not reported.

This paper is concerned with the investigation of batch copolymerization of acrylonitrile (AN) with vinyl acetate (VA) and 2-methyl-5-vinylpyridine (MVP), with the use of the chlorate–sulfite catalyst system and monomer concentrations in excess of the solubility of the monomers in water.   The polymerization is considered with respect to polymer molecular weight distribution, chemical distribution within the molecular weight distribution, grain size of polymer particles, and the manner in which these properties are affected in the early stages of reaction.

EXPERIMENTAL

Standard Batch Polymerization Procedure

Monomers (160 g.) in the desired ratio, hydrochloric acid sufficient to adjust pH to 2.0–3.0, and water to adjust monomer concentration to the desired level were charged into a three-necked, round-bottomed flask.   The flask was fitted with a condenser, stirrer, two additional funnels, thermometer and nitrogen inlet tube, and placed in a constant temperature bath.   The reaction mixture was heated at 40 ± 1.0°C. in a nitrogen atmosphere for 1 hr.   Sodium sulfite (2.24 g.) and sodium chlorate (0.630 g.) were dissolved in 150 ml. of deionized water and were placed in an addition funnel.

Hydrochloric acid (0.027 mole) was dissolved in 150 ml. of water and was placed in the second addition funnel. Acid and catalyst were added at 25-min. intervals in the following volume increments. The first addition was 60 ml. of each feed followed by 22.5, 22.5, 15, 15, 7.5 and 7.5 ml. additions. Additions were complete in 2.5 hr., after which the reaction mass was agitated for 1.5 hr. Polymer was collected by filtration. In order to interrupt polymerization at any point in the polymerization, sufficient aqueous ammonia was added to raise the pH to 7.0 or above. The catalyst reaction has been shown to cease at pH levels above 4.0.[2] Acid-soluble polymer present is insoluble at pH 7.0. The data in Figure 1 were obtained in the manner.

Separation of polymer into fractions of varied molecular weight was effected as follows. Polymer (1 g.) was dissolved in dimethylformamide (150 cc.) and ethyl alcohol (ca. 40 cc.) added until a slight turbidity, as measured by the Tyndall effect, developed. The mixture was centrifuged on a Spinco Model L preparative ultracentrifuge at 28,000 rpm. The supernatant liquid was poured off and the procedure was repeated, additional quantities of ethyl alcohol being used as required. In this way, the polymer was separated into 6 to 8 fractions.

Separation of polymers into fractions of varied grain size was effected as follows. Approximately 200 g. of wet polymer (100 g. dry) was slurried with methyl alcohol (500 ml.) for 0.5 hr. After filtration, the polymer crumb was slurried with methyl alcohol (500 ml.) to which 25 ml. of a 35% solution of antistatic agent Catanac SN (American Cyanamid Co.) had been added. The slurry was agitated for 1 hr., filtered and air dried. The dried polymer was screened through a series of screens of +35, +65, +100, +180, and +200, mesh until there was no change in weight from screen to screen. The crumb passing through the finest screen, +200, was placed in the smallest cone of an Infrasizer.[3] An Infrasizer was operated at an air pressure of 42 lb./in.[2] for two days. At the end of the run, the material in each cone was removed and weighed. The average particle size of each fraction was determined by direct microscopical examination.

The MVP content of the polymer was determined by ultraviolet absorption which was calibrated by a chemical method previously described.[4]

The molecular weights reported were determined from the following equation:

$$[\eta] = 2.27 \times 10^{-4} M^{0.75}$$

where $[\eta]$ is the intrinsic viscosity determined in dimethylformamide solution at 30°C. Since this equation was determined for homopolyacrylonitrile, it probably is not correct for the polymers dealt with in this paper. Therefore, the molecular weights reported herein should be considered only as relative to one another.

Preparation of Polymer Samples for Microscopical Study

A similar experimental technique was used in preparing samples for microscopic studies. Monomer, acid, and an amount of water necessary to

bring the batch to the desired monomer concentration were charged to a reaction vessel. The system, under agitation, was then purged with N_2 to insure exclusion of air during the subsequent catalyst addition. Samples were obtained at various times after catalyst addition by dipping the sampling tube into the reaction mixture and immediately withdrawing and quenching the sample. The quenching was accomplished by depositing the sample in water which was sparged with air. Samples were maintained at 0–5°C. until examined. Reaction was terminated by this method rather than addition of ammonia because the latter method caused aggregation of polymer particles.

Microscopical Procedures

For examination in the electron microscope, each sample was diluted approximately three-fold with water. After shaking to obtain uniform dispersion of any solids that might have settled, a drop of sample was dispersed on a carbon substrate supported by 200 mesh wire. The mount was air-dried with a low pressure air jet to insure representative distribution of all types that might be present in the dried residue. To remove catalyst salts, the dried mounts were gently flushed with 2 drops of water, strained, and again air-dried. Carbon substrates were selected because they are inert and have relatively little structure to interfere with the depiction of fine particles in the polymer. The electron micrographs in this paper, taken initially at a relatively low magnification, were photographically enlarged to 30,000 diameters to facilitate their study.

In a similar manner, drops of samples were dried on quartz slides for examination by ultraviolet microscopy. After drying, the residues were immersed in purified Nujol mineral oil and covered with quartz cover slips to minimize scatter, diffraction and other optical effects. The samples were also examined by visible light microscopical techniques to insure that what was observed in the ultraviolet spectrum was truly a result of absorption of the emitted radiation and not merely an artifact.

RESULTS

Polymer Composition and Molecular Weight

When acrylonitrile is polymerized in an aqueous suspension with a water-soluble redox initiator system (sodium chlorate and sodium sulfite in this case), the initial polymer is probably formed in solution prior to leaving the aqueous phase.[1,5,6] When MVP is one of the monomers used, a larger amount of polymer is formed in solution due to the increased solubility of the initial polymer molecules which are formed. Data for a typical batch polymerization are found in Figure 1.

A considerable amount of low molecular weight polymer containing a high concentration of MVP is formed during the early stages of polymerization. The molecular weight of the whole polymer continues to increase during the polymerization, while the average MVP concentration approaches the
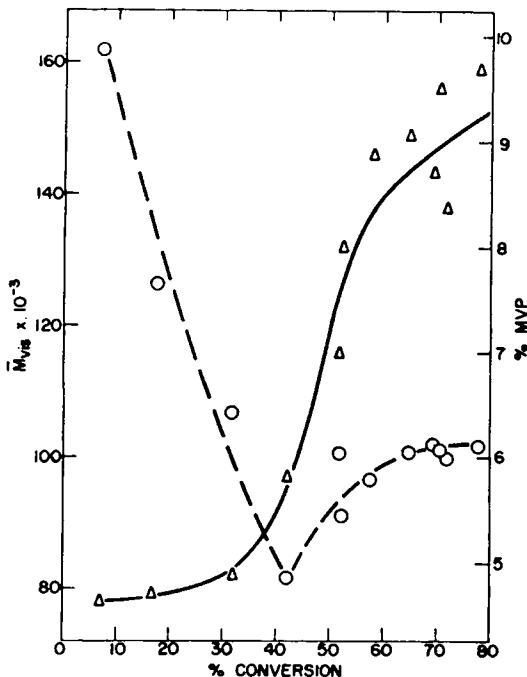
Fig. 1. Change in (△) polymer molecular weight and (O) MVP content with conversion, 14% monomers (85% AN, 7.5% VA, 7.5% MVP).

final average value. These data clearly point out that polymer formed in the latter stages of polymerization is considerably different in molecular weight and chemical composition compared with polymer formed initially. A reversal in average MVP content occurs with the second addition of catalyst, indicating that polymer containing a high concentration of MVP is again formed. At the end of the first 25 min. of reaction, the conversion of monomer to polymer is 40–45% of theory. About two-thirds of the total polymer produced is formed prior to the second addition of catalyst.

Fractionation and Grain Size Studies

Several terpolymers were fractionated by ultracentrifugation. Studies conducted on these fractions indicated that not only does a distribution of molecular weight exist, but also that a chemical distribution exists within the molecular weight distribution. The data plotted in Figure 2 indicate that as MVP content increases the molecular weight decreases. This relation points out the nonuniformity of chemical composition with respect to molecular weight. The chemical composition of each molecular weight fraction is different.

Polymer crumb was separated with respect to final grain size. The average molecular weight and MVP content of the polymer were found to be functions of grain size. Typical data are in Figure 3. For a given poly-

mer, the smaller grains contained more MVP and were of lower molecular weight. As the grains became larger, the MVP content decreased and the molecular weight increased. From these and other data, a mechanistic interpretation was deduced.
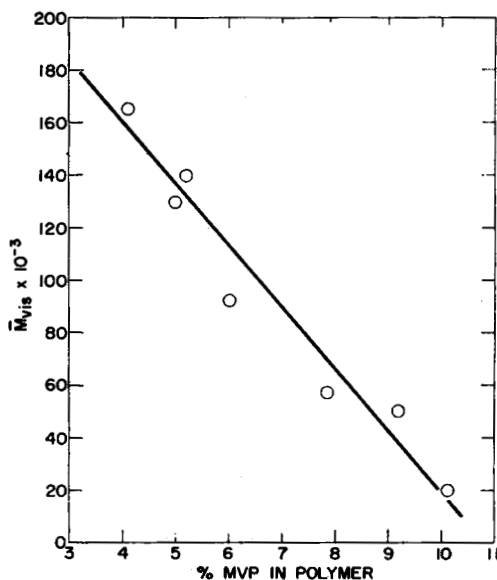

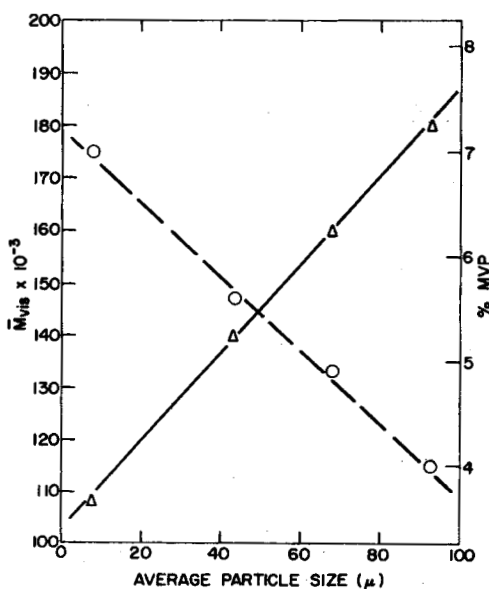Fig. 2. MVP content of polymer fractions as a function of molecular weight.

Fig. 3. Plot of (O) polymer MVP content and (Δ) molecular weight of polymer fractions as a function of grain size.

Polymerization Mechanism

The following mechanism is proposed to explain the observations. At the outset, two liquid phases, aqueous and organic, are present. Polymerization is conducted at pH 2.0–2.5, and all the MVP is in the aqueous phase as methylvinylpyridinium cation (MVPH$^+$). The acrylonitrile and vinyl acetate are distributed between the two phases. In the aqueous phase, the ratio of MVP to total monomer is greater than that calculated for the entire mass. The addition of aqueous catalyst solution initiates the growth of polymer in the aqueous phase. These macromolecules aggregate to form what will be termed fundamental particles.

The polymer formed initially contains a considerably larger amount of MVP than the final average for the whole polymer. Since polymers containing MVP are more soluble in acid media, the initially formed polymer remains in solution longer than polymers of similar molecular weight but without MVP. Those growing radicals which contain greater amounts of MVP not only will be more soluble but will probably possess a greater formal charge and thus more readily attract anions. The bisulfite anion which is a chain transfer agent,[1,7] is present in the aqueous phase. Thus, the polymer radicals which contain more MVP are sites of increased chain transfer activity. That the MVP itself is not a transfer agent is indicated by the fact that addition of pyridine or 2-methylpyridine plus sufficient acid to maintain the reaction pH does not alter the molecular weight of the polyacrylonitrile which is formed. The difference in the molecular weight of the polymer which forms may not be due entirely to transfer to HSO$_3^-$ but may also be due to variation of the rate constants in the two phases and the difference in monomer ratios in these phases. Due to both increased solubility and chain transfer, the initial polymer containing the most MVP tends to remain lowest in molecular weight. Therefore, the lack of growth to high molecular weight may be ascribed to the MVP content of a given polymer unit.

The growth of the initial polymer units continues in solution until they precipitate to form latex particles, having colloidal dimensions. Simultaneously with or immediately following the formation of latex particles, more rapid suspension polymerization commences. The molecular weight increases rapidly due to the reduction in the amount of chain transfer and the rate of termination. A reduced tendency to aggregate can be expected due to the relatively high formal charge carried by the particle. Aggregations of latex particles, which may exist in suspension, have been observed. Finally, the colloidal particles aggregate to form polymer grains which vary in particle size from several microns to 150 microns. Colloidal particles with the greatest charge aggregate less readily. Therefore, particles with the most MVP form the smallest grains.

From mechanistic considerations, it was concluded that solution polymerization is the major cause for both physical and chemical non-uniformity in the polymer. Observation of newly initiated polymerizations clearly

indicated significant differences between polymers containing MVP and those not containing MVP. The latter polymerizations exhibited a shorter "inhibition period," that is, polymer would appear more rapidly. It appeared that more information concerning the physical nature of the early formed polymer particles might lead to better understanding of this problem.

Electron Microscopical Studies

It was felt that the best approach to the study of the initial phases of polymerization was to use electron microscopical techniques. By these methods it would be possible to observe the size, shape, aggregation, and mode of growth of the polymer particles.

From the mechanistic interpretations it was felt that certain variables would have marked effects on the initial stages of polymerization, and they were therefore chosen for study. These variables were the effects of MVP concentration, total monomer concentration, and the weight ratio of acrylonitrile to MVP [AN/MVPH+] in the aqueous phase.

For purposes of comparison, a polymerization in which no MVP was present was carried out first. Figure 4 contains micrographs representing various sampling intervals. The bulk of this sample consisted of large
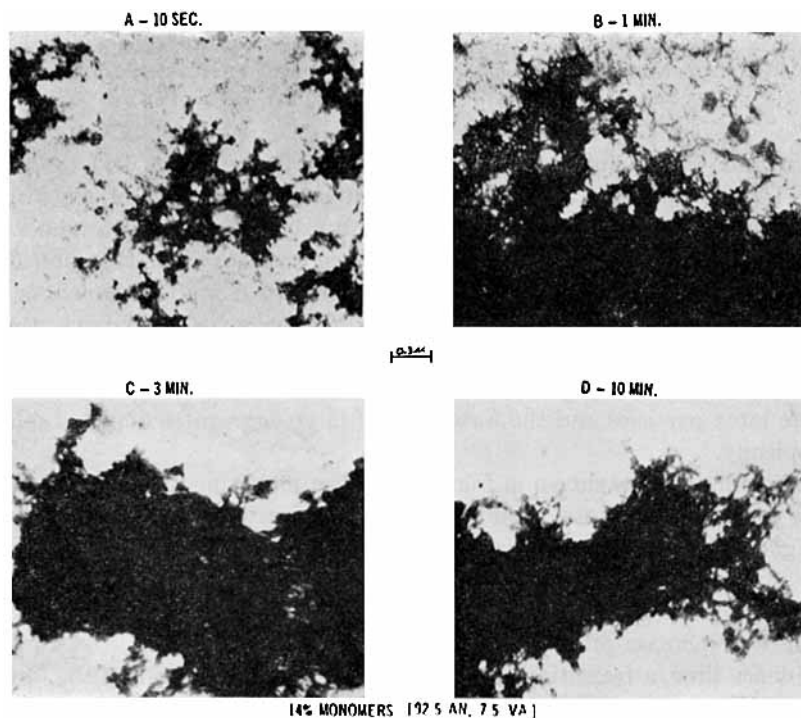

Fig. 4. Electron micrographs of experimental terpolymer at various stages of polymerization, 14% monomers (92.5% AN, 7.5% VA).

A – 20 SEC.   B – 1½ MIN.

C – 4½ MIN.   D – 10 MIN.
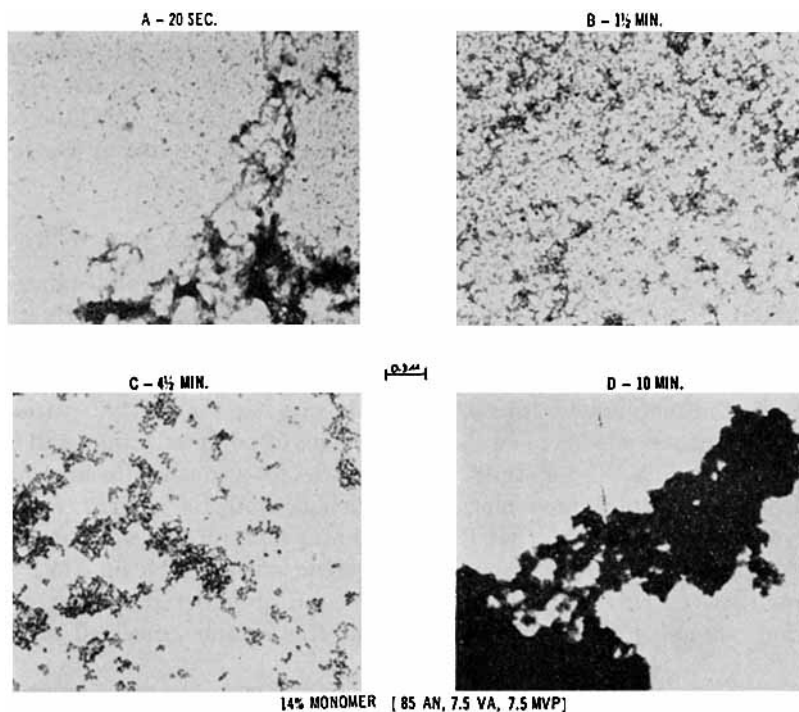
14% MONOMER [85 AN, 7.5 VA, 7.5 MVP]

Fig. 5. Electron micrographs of experimental terpolymer at various stages of polymerization, 14% monomers (85% AN, 7.5% VA, 7.5% MVP).

aggregates at all stages, forming as early as 10 sec. (Fig. 4A). Figures 4A–4D clearly show that these aggregates are composed of clusters of spheroidal, latexlike particles which apparently form in large numbers at the very start of reaction and then rapidly aggregate. Thus the precursor to the aggregate type of particle is probably an unstable latex. As the reaction continues up to 10 min., the aggregates grow to massive, three-dimensional particles (Fig. 4D). The water-clear supernatant and the heavy sediment formation is consistent with the observed absence of discrete latex particles and the formation of large aggregates depicted microscopically.

The micrographs shown in Figure 5 are those obtained when 7.5% MVP was present. The total monomer concentration was 14% based on total weight of materials in the reactor when polymerization is initiated, as in the above case. At the end of 20 sec., discrete spheroidal particles, resembling latex particles, were observed in great abundance. These continued to increase in size up to at least 4½ min. (Fig. 5C). At 10 min. residence time, a transition occurred (Fig. 5D) characterized by the formation of large, dense aggregates in the bulk of this sample. Between 4½ and 10 min., the charges on the latex particles could no longer prevent aggregation. The changes observed microscopically were consistent with
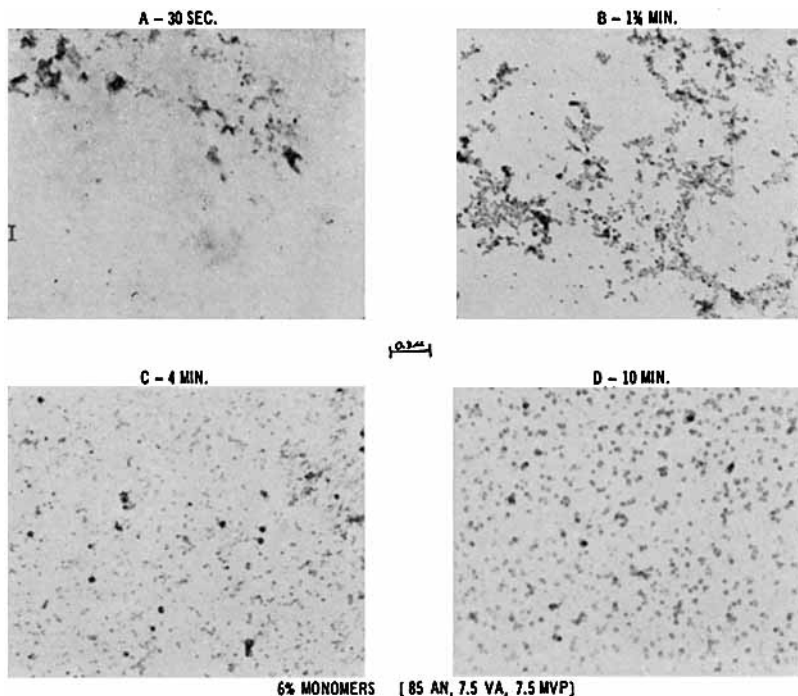
Fig. 6. Electron micrographs of experimental terpolymer at various stages of polymerization, 6% monomers (85% AN, 7.5% VA, 7.5% MVP).

the macroscopic appearance of the samples. The supernatant liquid was water clear at the start and had essentially no sediment, indicating no suspended material or presence of particles of such small size and low concentration that they did not visibly scatter light. The opacity of the supernatant increased with the residence time up to $4^1/_2$ min., indicating the presence of discrete, suspended particles of increasing size. For the 10-min. sample, the supernatant was water clear but a heavy sediment had formed which predominated in the micrograph (Fig. 5D). We conclude from these data that the MVP was responsible for the formation of a relatively stable latex. Aggregation does occur after longer residence periods, i.e., at higher conversion.

To study the effect of reduced monomer concentration, the total monomer concentration was reduced to 6%. At this concentration, all of the acrylonitrile was in solution as well as the MVP, so that the ratio of AN to MVP in the aqueous phase was increased. The micrographs obtained are shown in Figure 6. The outstanding characteristic of this polymerization was the early formation, the continued growth, and persistence of well-defined latex particles (Figs. 6B, 6C, 6D). At the early stage (Fig. 6A), only a few scattered, partially coalesced particles were found. At the end of 10 min. residence time, latex particles were still observed, without the formation of aggregates. The increasing opacity of the supernatant with
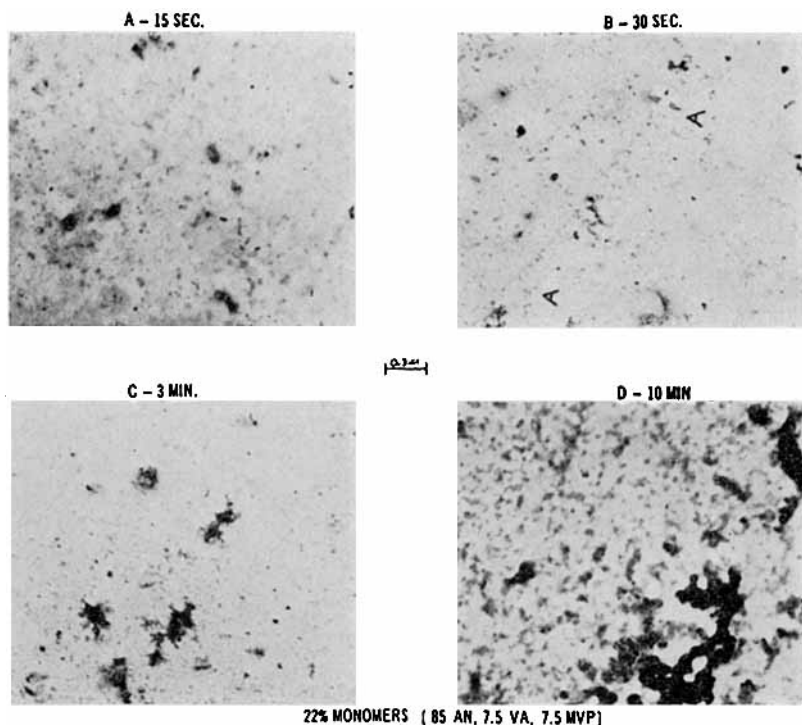
Fig. 7. Electron micrographs of experimental terpolymer at various stages of polymerization, 22% monomers (85% AN, 7.5% VA, 7.5% MVP).

time and the presence of essentially no sediment agrees favorably with the microscopical appearance of the dried residue.

The effect of higher monomer concentration was examined by reducing the amount of water so that the monomer concentration was 22%. In this case, the AN/MVP ratio at the start of reaction was much reduced since most of the AN was not in the aqueous phase. As in the previous cases, the monomer composition and polymerization conditions were maintained constant. Figure 7 contains micrographs characterizing this reaction. The samples obtained gave a polymeric material which had film-forming characteristics. Latex particles were also present, but they were significantly fewer in number, appeared poorly defined and were generally surrounded by a filmy matrix. The presence of this film is depicted in the micrographs as a hazy appearance and overall grey tone. Proof of the existence of the film is given in Figure 7B, which shows a break in the film indicated by the marked white area. The supernatant liquids from these samples were only slightly opaque. There was slight sediment in samples up to 30 sec. residence time and a gradual buildup to a heavy sediment at the end of 10 min. This microscopic observation correlates favorably with the relatively fewer latex particles that were found. The relatively high concentration of MVP in solution apparently inhibited formation of latex

particles. The presence of a film-forming polymeric material would tend to "tackify" and soften most of the latex particles, eventually causing them to coalesce and precipitate.

Ultraviolet Microscopical Studies

To substantiate further the chemical evidence and electron microscopical interpretation, several samples from a 6% monomer reaction were examined by ultraviolet microscopy. The photomicrographs in Figure 8 were taken at a wavelength of 2700 A. The dark areas represent the selective ultraviolet absorption of MVP.
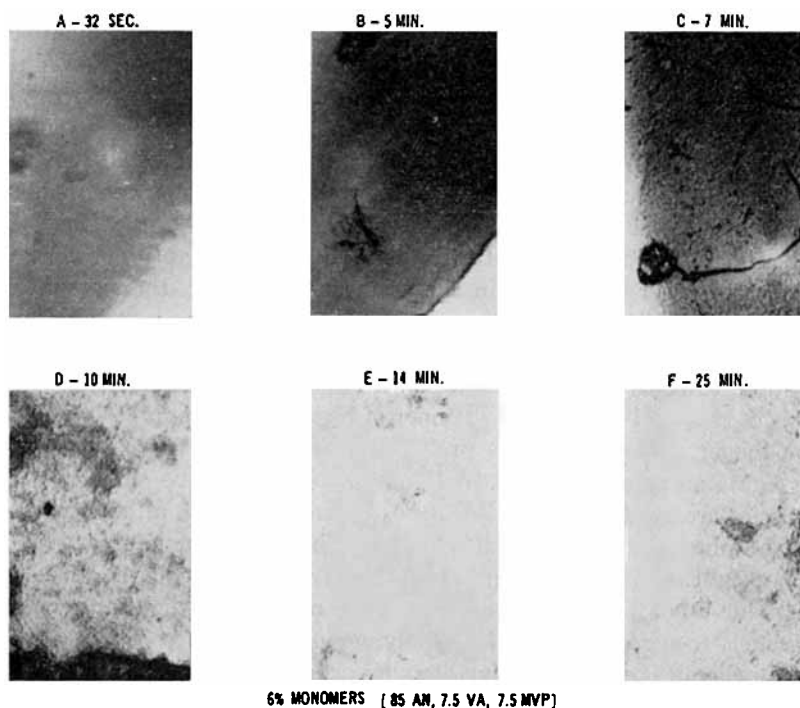

Fig. 8. Experimental terpolymer, 6% monomers (85% AN, 7.5% VA, 7.5% MVP). Samples drawn and quenched during polymerization. Photomicrographs taken with 2700 A. emanation.

Samples *A* and *B* represent residues from samples quenched at 32 sec. and 5 min., respectively; the findings agree favorably with electron microscopical observations. That is, at early stages the poorly defined latex particles partially coalesced on drying to form thin, almost continuous films. The overall grainy, particulate textures seen with the ultraviolet microscope agree with the electron microscope observation that there is a tendency for the latex particles to become larger, more clearly defined and to form loosely packed, secondary aggregates on drying. The $1/2$, 5, and 7 min. samples exhibit greater absorption than the 10, 14, and 25 min. samples, despite the

fact that polymer conversions are higher in the latter samples.   This indicates that the ratio of MVP to acrylonitrile in the early formed polymer is much higher than in the latter stages.   It will be remembered from Figure 1 that the chemical evidence showed that polymer formed at early stages of conversion contained more MVP than polymer formed at later stages MVP is present in sufficient amounts in the latter stages to delineate the secondary aggregates, or they would not be visible.   The highly absorptive area in Figure 8F is due most probably to the formation of a thicker film and not to excessive MVP.

DISCUSSION

Addition of MVP causes a major change in the polymerization of acrylonitrile with a chlorate-sulfite redox catalyst.   In an AN–VA polymerization, discrete latex particles form and then aggregate very quickly. Addition of MVP causes the initial polymer particles to come out more slowly.   Once formed, the latex particles containing MVP cluster poorly due to positive charges on the latex.   Lowering the total per cent monomers increases the ease of formation of latex particles at least partly because the reduction in monomer concentration also reduced the quantity of MVP with respect to other monomers in the aqueous phase, i.e., the site of initial polymer formation.   Increasing the total monomer concentration has the opposite effect.

These changes are in agreement with the mechanism proposed on the basis of chemical evidence.   Polymer of higher MVP content stay in solution longer.   These particles probably bear a higher charge and do not aggregate so readily.   Thus, the final grain size will be smaller.   These particles are sites of greater than average concentration of bisulfite anion, so that more chain transfer can occur, resulting in a polymer of lower molecular weight.   The result would be that particles of higher MVP content are made up of polymer molecules of lower molecular weight and would be less likely to aggregate into a large polymer grain.

The chemical evidence is further supported by ultraviolet microscopical examination which shows that, as polymerization progresses, the average MVP content of the polymer decreases.

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Synopsis

Batch copolymers, made by polymerizing acrylonitrile, vinyl acetate, and 2-methyl-5-vinylpyridine (MVP) with a chlorate–sulfite redox catalyst, are fractionated with respect to MVP content when they are fractionated with respect to molecular weight or polymer grain size. Polymer fractions of lowest molecular weight or smallest grain size contain the most MVP. A mechanism is proposed to explain these facts. To test the proposed mechanism, both ultraviolet and electron microscopes are used to study polymer formed during the early stages of batch polymerization. The effects of adding MVP, and of total monomer concentration, on the particles formed are determined. Interpretations of the microscopical observations are compared with the chemical interpretation. When MVP is present, the initial particles formed are more soluble, form colloidal particles less readily, and stabilize the colloidal particles, if formed, due to the charges on the polymer. Initial particles with highest MVP content form polymer of lowest molecular weight and aggregate into the smallest polymer grains.

Résumé

Les copolymères obtenus par polymérisation en masse d'acrylonitrile, d'acétate de vinyle et de 2-méthyl-5-vinylpyridine (MVP) au moyen d'un catalyseur rédox chlorate–sulfite, sont fractionnés en fait suivant leur teneur en MVP lorsqu'ils ont été fractionnés par rapport au poids moléculaire ou à la dimension des particules de polymère. Les fractions de polymère de plus bas poids moléculaire ou de plus petites dimensions des particules contiennent le plus de MVP. On a proposé un mécanisme pour expliquer ces faits. Pour tester le mécanisme proposé, on a employé les microscopes ultraviolets et électroniques afin d'étudier le polymère formé durant les premières étapes de la polymérisation en masse. L'influence de l'addition de MVP, et de la concentration totale en monomère sur les particules formées a été étudiée. On a comparé les interprétations des observations microscopiques avec l'interpretation chimique. Quand la MVP est présente, les particules formées initialement sont plus solubles, forment moins rapidement des particules colloïdales et stabilisent ces dernieres dans l'hypothèse où elles sont formées par la présence de charges sur le polymère. Les particules initiales à teneur en MVP les plus élevées forment un polymère de plus bas poids moléculaire et se rassemblent dans les grains de polymères les plus petits.

Zusammenfassung

Durch Polymerisation von Acrylnitril, Vinylacetat und 2-Methyl-5-vinylpyridin (MVP) mit einem Chlorat–Sulfit-Redoxkatalysator hergestellte Copolymere erfahren bei der Fraktionierung nach Molekulargewicht oder Polymerkorngrösse auch eine Fraktionierung nach dem MVP-Gehalt. Die Polymerfraktionen mit dem niedrigsten Molekulargewicht oder der kleinsten Korngrösse enthalten am meisten MVP. Ein Mechanismus zur Erklärung dieser Tatsachen wird vorgeschlagen. Um den vorgeschlagenen Mechanismus zu prüfen, wurde das im Anfangsstadium eines Polymerisationsansatzes gebildete Polymere ultraviolett- und elektronenmikroskopisch untersucht. Der Einfluss eines Zusatzes von MVP und der Gesamtmonomerkonzentration auf die gebildeten Teilchen wird gestimmt. Eie Vergleich der mikroskopischen Beobachtungen mit der chemischen Interpretation wird durchgeführt. Bei Gegenwart von MVP sind die anfänglich gebildeten Teilchen löslicher, bilden weniger leicht kolloide Teilchen und stabilisieren eventuell gebildete kolloide Teilchen infolge der Ladungen am Polymeren. Anfänglich gebildete Teilchen mit grösstem MVP-Gehalt bilden Polymere mit dem geringsten Molekulargewicht und aggregieren zu den kleinsten Polymerkörnchen.