Effect of Suspension Stabilizers on the Kinetics of Copolymerization of Acrylonitrile and Vinyl Acetate

INTRODUCTION

The principal problem in suspension polymerization is the formation of as uniform as possible monomer droplets in the aqueous phase and prevention of coalescence of these droplets during the polymerization process. Application of agitation helps to disperse the monomer in the aqueous medium. A typical organic, water-insoluble monomer usually has a lower surface tension than water. When such a monomer is agitated in water, an unstable dispersion is formed and continuous breakup and coalescence of the monomer droplets occur. If the agitation stops, the monomer-water system will separate into its respective two phases. During the polymerization process, the monomer globules tend to remain in a fairly stable dispersion until polymerization has proceeded to a point at which the droplets become tacky and agglomeration occurs upon globule collision. Such a stage is caused either by the presence of polymer in the residual monomer or coalescence of insoluble tacky polymer particles at a particular stage of growth. These insoluble polymer particles have a strong tendency to agglomerate.[1] At this stage, agitation must be sufficiently intense to separate all adhering monomer droplets and clusters. In general, agitation alone is not sufficient to carry the globules as individual units from the liquid monomer to the final rigid polymer state. Extensive use is therefore made of suspension stabilizers to prevent the globules from coalescing as the reaction proceeds. Water-soluble high polymers, such as gelatin, methyl cellulose, polyvinyl alcohol, polymethacrylamide, and salts of polyacrylic and polymethacrylic acid, have long been used as suspension stabilizers, as patented by Crawford and McGrath.[2] Rohm and Trommsdorff[3] also obtained the similar dispersing effects by addition of water-insoluble inorganic substances, such as talc, barium sulfate, magnesium carbonate, and aluminum hydroxide. Mark and Hohenstein[4] gave a thorough discussion including a review of research on suspension polymerization of olefins and substituted olefins, such as styrene, dichlorostyrene, and methyl methacrylate in the presence of talc, gelatin, and polyvinyl alcohol.

The effect of suspension stabilizers on the kinetics of polymerization of acrylonitrile was reported by Thomas et al.[5] The presence of polymeric stabilizers increases the rate of polymerization (R_p), whereas neutral salts have an opposite effect on the R_p of acrylonitrile. Izumi et al.[6] further reported the similar effect in their study on polymerization of acrylonitrile in the presence of high-molecular weight emulsifiers.

The present paper describes the copolymerization of acrylonitrile and vinyl acetate in the presence of water-soluble high polymers. An attempt has also been made to study the effect of polymeric stabilizers on the kinetics of acrylonitrile- vinyl acetate (An-VAc) copolymerization.

EXPERIMENTAL

The monomers AN and VAc (commercial) were dried over calcium chloride and purified by distillation at 77° and 73°C, respectively. Potassium persulfate, $K_2S_2O_8$ (Merck), was purified by recrystallization from water. Ferrous sulfate, $FeSO_4$ (BDH), was used without further treatment. Sulfur dioxide (SO_2) was prepared by reaction of sodium sulfite and concentrated H_2SO_4 in a two-necked round-bottom flask. Dropwise addition of H_2SO_4 was achieved by attaching a separating funnel to a flask containing Na_2SO_3. The SO_2 produced was collected in cold water through an adapter connected to a glass tube (by a rubber tube) and dipped in a volumetric flask containing cold water (5–10°C). This solution was stored in the refrigerator. The concentration of SO_2 in water was determined by titration with standard NaOH solution. Polyvinyl alcohol (PVA; Aldrich), 98% hydrolyzed, polyethylene glycol (PEG- 4000; BDH), and polyvinyl pyrrolidone type NP-K30 (GAF Corporation) were used without further treatment. Stock solutions of $K_2S_2O_8$, $FeSO_4 \cdot 7H_2O$, and stabilizers in distilled water were used for addition in the polymerization system.

POLYMERIZATION

Polymerization was carried out under a nitrogen atmosphere in a 1-L three-necked round-bottomed flask equipped with a Teflon paddle stirrer, nitrogen inlet, and condensor. The flask was immersed in a constant-temperature water bath at 45°C. Water was used as a polymerization medium. To the flask were added monomers (AN and VAc in the ratio 91:9), water (water-monomer ratio, 3.0), initiator ($K_2S_2O_8$), activator (SO_2 solution in water), and $FeSO_4 \cdot 7H_2O$. The pH of the system was maintained at 3.0 by addition of a small amount of H_2SO_4. The system was subjected to stirring, but this was accompanied by polymerization of AN and VAc, as indicated by development of a milky color in the system. The polymer was obtained as a water-insoluble slurry. It was filtered, washed thoroughly with cold distilled water, by hot water to remove unpolymerized monomer, and finally dried in a vacuum oven at 50°C.

The molecular weight of acrylic copolymers was expressed in terms of specific viscosity, measured in DMF at 25°C by a standard technique using a Ubbelohde suspension level viscometer.

The particle size distribution of polymers was determined by placing the wet polymer slurry on the mesh of the top sieve, which was fitted on a mechanical shaker. Water was allowed to spray over the polymer and was then shaken for a predetermined period of half an hour. The sample retained on each sieve was collected on a weighed crucible, dried, and weighed.

RESULTS AND DISCUSSION

Copolymerization of acrylonitrile and vinyl acetate in the ratio 91:9 (by weight) was carried out at 45°C under an inert atmosphere using $K_2S_2O_8$-SO_2-$FeSO_4$ redox initiator system in presence of polymeric suspension stabilizers such as polyvinyl alcohol, polyvinyl pyrrolidine (PVP), and polyethylene glycol (PEG). The amount of stabilizer was varied between 0.05 and 0.2% (based on monomer weight), and the results of these copolymerization studies are given in Tables I and II. The presence of stabilizer during copolymerization produces a AN-VAc copolymer of finer particle size. With increase in concentration of polyvinyl pyrrolidine and polyvinyl alcohol, the particle size of polymer further decreases. Similar effects were reported by Winslow and Matreyek[7] and Izumi et al.[6,8] in their studies on suspension polymerization

TABLE I
Particle Size Distribution of AN-VAc Copolymers (by Sieve Analysis)[a]

Stabilizer	Mesh no.	Particle size (μm)	Polymer retention at stabilizer conc.			
			0	0.05%	0.1%	0.2%
PVA	80	177	49.4	40.8	25.1	20.4
	100	150	22.6	20.4	19.8	20.8
	200	74	24.7	28.3	45.2	48.3
	325	44	2.9	6.4	8.0	4.2
	400	39	0.4	4.1	1.9	6.3
PVP	80	177	49.4	33.7	14.6	20.0
	100	150	22.6	7.8	26.0	11.9
	200	74	24.7	28.7	54.2	60.2
	325	44	2.9	27.4	4.0	6.3
	400	39	0.4	2.4	1.2	1.6
PEG	80	177	49.4	52.7	40.8	39.8
	100	150	22.6	7.8	15.2	34.5
	200	74	24.7	30.2	38.7	15.0
	325	44	2.9	8.7	1.4	9.9
	400	39	0.4	0.6	3.9	0.8

[a] Copolymers produced at 25% conversion by copolymerizing AN and VAc (91:9) at 45°C using 1% $K_2S_2O_8$, 3.0% SO_2, and $FeSO_4 \cdot 7H_2O$ (1.0 ppm) and water to a monomer ratio 3.0:1 (1 μm = 10^{-6}/cm).

of divinyl benzene and acrylonitrile, respectively. Incorporation of polyethylene glycol does not give the effect as observed by PVA and PVP. Copolymers of AN and VAc obtained at 25% conversion by the addition of ethylenediaminetetraacetic acid disodium salt (EDTA) were examined for stability of the dispersion. At 0.1% concentration of stabilizer, copolymer requires a maximum time to settle when PVP was used as a dispersion agent. Further addition of polyvinyl pyrrolidone, PVA, and PEG decreases the molecular weight of AN- VAc copolymers as indicated by the decrease in their specific viscosities (Table II). The drop in AN-VAc copolymer molecular weight may be explained by the action of stabilizers that act as chain transfer agents[8] for the copolymerization of AN and VAc. Furthermore, the presence of vinyl acetate in small amounts in the polymerization system (AN:VAc in the ratio of 91:9 by weight) does not change the overall kinetics of polymerization of acrylonitrile as explained later.

An attempt has been made here to explain and review the role of these stabilizers in suspension copolymerization. Some writers[1] have believed that increasing the viscosity of the medium is the mechanism by which good dispersion is achieved, whereas other investigators[4,7] have claimed that the adsorption of a stabilizer forms a tough skin around the globule and is the principal reason "gummy" globules do not stick together upon colloiding. Recently, stabilization mechanisms[9,10] by nonionic surface-active agents and polymeric stabilizers has been postulated to be due to a steric or solvation barrier caused by adsorption and dependent upon the factors affecting adsorption, that is, concentration and affinity. The low level of water-soluble polymers used in some suspensions makes it appear unlikely that the relatively small macroscopic increase in the viscosity of the aqueous phase could be the principal cause of stabilization of the suspended globules. The small increase in the viscosity of the water phase on the addition of water-insoluble minerals, which also serve to inhibit agglomeration, also seems to indicate that suspension stabilization is not due to an increase in the macroscopic viscosity per se in such a system. Rather, it is more likely that the monomer polymer granules are covered with an adsorbed layer of the polymer or insoluble inorganic salts and it is the adsorbed layer of suspension stabilizer that acts to inhibit coalescence and agglomeration. This adsorption mechanism was supported by microscopic examination of the granular resin particles.

Kinetics of AN and VAc Copolymerization

The use of suspension stabilizers in the polymerization system decreases the molecular weight of the polymers, as indicated by specific viscosity values at 25°C in DMF. To obtain acrylic polymers of spinnable fiber grade, it is desirable to have a higher viscosity (η_{sp}, 0.145–0.155) and higher molecular weight.

The kinetics of copolymerization of acrylonitrile and vinyl acetate was studied in order to eliminate the negative effect of stabilizers on specific viscosity (measure of molecular weight) of AN-VAc copolymer. As mentioned earlier, since PVP produces better dispersion and a large number of particles with finer sizes, it was selected as a natural choice for the kinetic studies. Copolymerizations of acrylonitrile and vinyl acetate were carried out at 45°C at different

TABLE II
Effect of Stabilizer on Viscosity of AN-VAc Copolymers

Stabilizer	Conc. of stabilizer (%)	η_{sp}[a]
PVA	0	0.147
	0.05	0.143
	0.1	0.140
	0.2	0.135
PVP	0.05	0.140
	0.1	0.136
	0.2	0.133
PEG	0.1	0.144
	0.2	0.138

[a] At 25°C in DMF.

TABLE III
Copolymerization of AN and VAc (91:9) in the Presence of 0.1% PVP at 45°C[a]

$K_2S_2O_8$ (%)	SO_2 (%)	$FeSO_4$ (ppm)	η_{sf}[b]
0.5	0.167	0.8	0.747
0.5	0.50	0.8	0.388
0.5	1.0	0.8	0.271
0.5	1.5	0.8	0.222
0.5	2.0	0.8	0.210
0.5	2.5	0.8	0.186
1.0	0.5	0.8	0.205
1.0	1.0	0.8	0.180
1.0	1.5	0.8	0.169
1.0	2.0	0.8	0.142
1.0	2.5	0.8	0.129
0.25	1.0	0.8	0.310
0.50	1.0	0.8	0.271
0.75	1.0	0.8	0.230
1.0	1.0	0.8	0.230
1.5	1.0	0.8	0.175
2.0	1.0	0.8	0.168
2.5	1.0	0.8	0.150
0.5	1.5	0.4	0.230
0.5	1.5	0.8	0.222
0.5	1.5	1.5	0.213
0.5	1.0	0.4	0.280
0.5	1.0	0.8	0.271
0.5	1.0	2.0	0.265

[a] Water-monomer ratio, 3:1.
[b] At 25°C in DMF.

concentrations of $K_2S_2O_8$, SO_2, and $FeSO_4$ to get polymers of desired viscosity range. The effect of variation in catalyst concentration ($K_2S_2O_8$ and SO_2) on the molecular weight of AN-VAc copolymer was studied. $FeSO_4$ was used as a promotor for the free radical generation in the $K_2S_2O_8$-SO_2 redox system. Experiments were carried out at a constant concentration of stabilizer (0.1% PVP based on monomer weight).

The results of kinetics of copolymerization of AN and VAc have been given in Table III. The table indicates that increasing the percentage of $K_2S_2O_8$ decreases the molecular weight of P(AN-VAc) at constant SO_2 and iron level. Similarly, at constant $FeSO_4$ and $K_2S_2O_8$ concentrations, a decrease in concentration of SO_2 increases the molecular weight of AN-VAc copolymer. The effect of change in $FeSO_4$ concentration was also studied. An increase in the amount of $FeSO_4$ lowers the molecular weight of polymers but does not change it significantly. Tsuda[11] reported the effect of $K_2S_2O_8$ and $NaHSO_3$ (sodium bisulfite) concentrations on the molecular weight of polyacrylonitrile. Peebles[12] has also reported the similar kinetic effect in his studies on the copolymerization of AN and VAc. In our present study vinyl acetate was selected and used in small amounts that do not change the overall kinetics of polymerization of acrylonitrile, as was suggested by work of Tsuda and Peebles. Furthermore, the presence of stabilizer does not vary the overall kinetics of AN-VAc copolymerization. The kinetic pattern is similar in both cases except that the presence of stabilizer decreases the molecular weight of the AN-VAc copolymer.

References

1. C. E. Schildknecht, *Polymer Processes*, Interscience, New York, 1957, p. 71.
2. J. C. W. Crawford and J. McGrath, U.S. Pat. 2,191,520 (1940).
3. O. Rohm and E. Trommsdorff, Ger. Pat. 735,285 (1943).

4. H. Mark and W. P. Hohenstein, *J. Polym. Sci.,* **1**, 127 (1946).

5. W. H. Thomas, E. H. Gleason and G. Mino, *J. Polym. Sci.,* **24**, 43 (1957).

6. Z. Izumi, H. Kiuchi, and M. Watanabe, *J. Polym. Sci. A-1,* **5**, 455 (1967).

7. F. H. Winslow and W. Matreyek, *Ind. Eng. Chem.,* **43**, 1108 (1951).

8. Z. Izumi, *J. Polym. Sci., A-1,* **5**, 469 (1967).

9. H. F. Mark, N. G. Gaylord, and N. M. Bikales, *Ency. Polym. Sci. Technol.* Interscience, **13**, 562 (1964).

10. W. Black, *Chem. Ind.* (London), **1**, 450 (1968).

11. Y. Tsuda, *J. Appl. Polym. Sci.,* **5**, 104 (1961).

12. L. H. Peebles, *J. Appl. Polym. Sci.,* **17**, 113 (1973).

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