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Reactions of Transformation of Polyacrylamide Obtained by Polymerization in Inverse Suspension

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ABSTRACT

Some results on the polymerization of acrylamide in heterogeneous systems are presented. The first part presents the polymerization of acrylamide in inverse suspension; the steps of the reaction and the part played by each factor that influences the advancement of the reaction are discussed. Some aspects whose elucidation was required throughout the investigation are presented, together with a hypothesis and the experimental results obtained. The second part presents reactions of the modifications achieved with the polymers obtained in inverse suspension and the properties of modified polymers. The final section reports some attempts to entrap some enzymes in polyacrylamide gel. The results of entrapment by copolymerization of acrylamide with methylenebisacrylamide in a homogeneous system are presented comparatively with those yielded by the same reaction in a heterogeneous system.

Three specific connected areas on which our research on heterogeneous system acrylamide polymerization has focused are presented:

- I. Polymerization of acrylamide in inverse suspension
- II. Polyacrylamide modification reactions
- III. Utilization of modified polyacrylamide as support for enzyme entrapment

I. POLYMERIZATION OF ACRYLAMIDE IN INVERSE SUSPENSION

The polymerization of acrylamide in inverse suspension is achieved by dispersion under stirring of an acrylamide solution in white spirit or cyclohexane in which a nonionic emulsifier (ethoxylated stearin, MYRJ 45, or ethoxylated nonylphenol, IGEPAL CO 430) is dissolved.

In previous work [1] (see Fig. 1) it was shown that polymerization in inverse suspension occurs as follows. First a water/oil type emulsion is formed (possibly a double emulsion, i.e., the organic medium can be microemulsified [2] in an aqueous medium and this latter emulsified in turn as drops in an organic medium) which is unstable and tends to separate when stirring is stopped. Following the start of the reaction, the inversion of phases occurs (the monomer containing the aqueous phase becomes the continuous phase) and is accompanied by a marked increase in the viscosity of the medium which attains the consistency of a gel whose properties are those of a viscoelastic gel. At higher conversion, under stirring, the gel breaks into small particles ranging from 0.5 to 1.5 mm in size, which remain as such until the end of the polymerization reaction.

Inversion of phases was proved by low magnification optical microscopy and conductometry (Figs. 2 and 3).

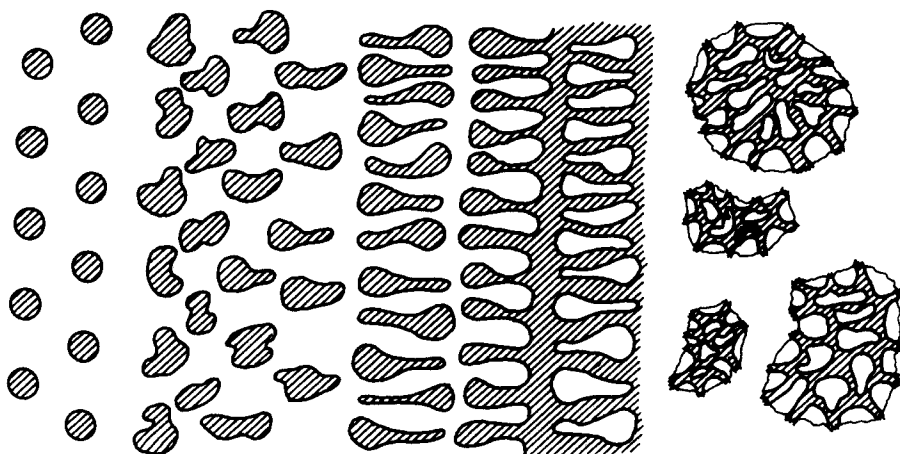


FIG. 1. Schematic representation of acrylamide polymerization in inverse suspension.

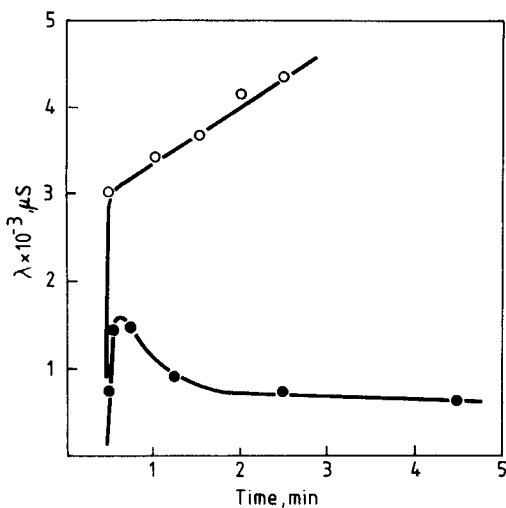


FIG. 2. Conductometric evidence of the inversion of phases during the polymerization reaction: (\circ) moles acetate/moles acetate + moles acrylamide = 0.02, (\bullet) moles acetate/moles acetate + moles acrylamide = 0.1.

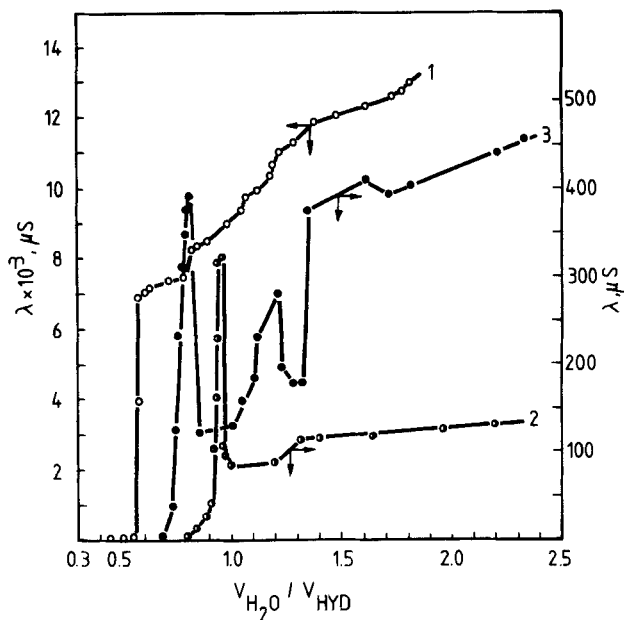


FIG. 3. Conductometric titration of the organic dispersion medium (white spirit + MYRJ 45 = 3%) with: (1) acrylamide and sodium acetate solution ($H_2O/AA = 1$, moles/moles acetate + moles acrylamide = 0.1); (2) water; (3) acrylamide solution ($H_2O/AA = 1$).

Figure 2 shows the inversion of phases as evidenced by conductometry during the polymerization reaction. After a few moments, the reaction starts (Fig. 2).

The conductivity suddenly rises (with a magnitude proportional to the salt content in the reaction medium), which is direct proof of phase inversion in the system. A similar conductivity jump was also observed during titration of the inverse suspension with a water-acrylamide-salt mixture (Fig. 3), which produces a change in conductivity when phase inversion occurs.

Previous investigations have shown that the parameters which govern the polymerization of acrylamide in inverse suspension (characterized by evolution of the polymerization reaction, the morphology of particles, or the molecular weight of the polymers obtained) are the nature of the organic phase and the aqueous/organic phase ratio, the nature and concentration of the emulsifier, and the nature and concentration of the electrolyte present in the system.



FIG. 4. Scanning electron micrograph of a polyacrylamide sample obtained by polymerization using MYRJ 45 as emulsifier. Sample prepared by graphite deposition. 250 \times .

The ratio of the aqueous phase to the organic phase is directly related to the compactness of the gel, whose structure becomes looser as the content of the organic phase increases.

The nature of the emulsifier affects both the structure of the gel and the morphology of polymer particles, given the fact that the breaking of the gel at the interface is facilitated by the presence of a surface-active substance.

Scanning electron microscopy provides (Figs. 4 and 5) evidence of the existence of ductile fractions on the surface of the polymer particles. Scanning electron microscopy of polyacrylamides with various emulsifiers has also shown that: the surfaces are smooth, with flat and gentle contours, in the case of ethoxylated stearin (Fig. 6), and polyacrylamide particles exhibit a fiberlike surface texture in the case of ethoxylated nonylphenol (Fig. 7).

In the latter case transmission electron microscopy at a greater magnification (40,000 \times , Fig. 8) showed that each fiber has a micro-lamellar structure. The fiberlike structure of the surface is achieved

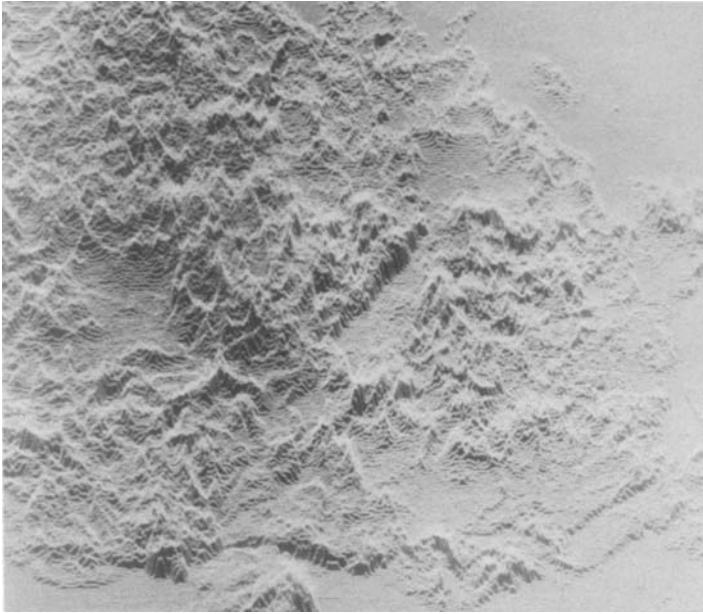


FIG. 5. Scanning electron micrograph of the same sample as in Fig. 4; y modulation.

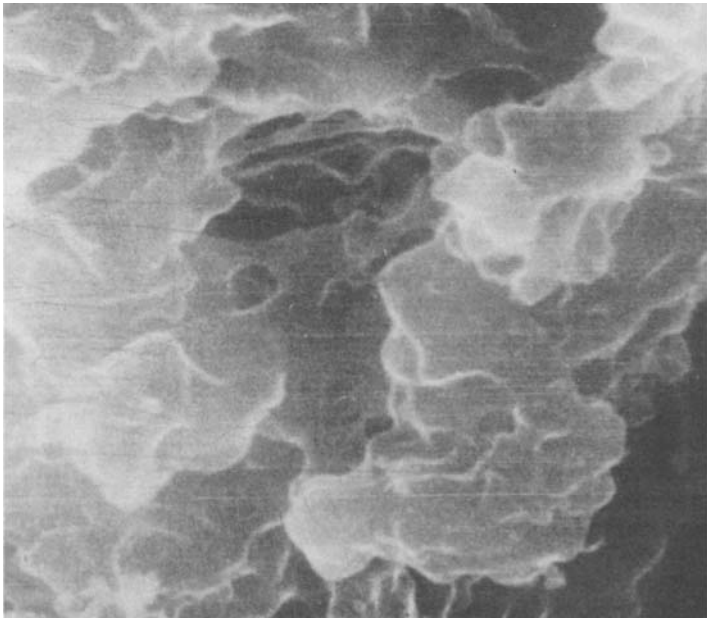


FIG. 6. Scanning electron micrograph of a polyacrylamide sample obtained by polymerization using MYRJ 45 as emulsifier. 7700 \times .

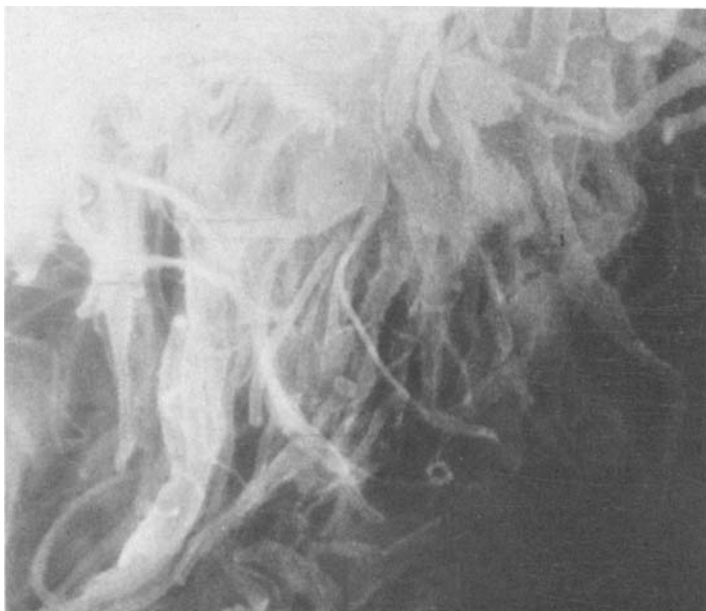


FIG. 7. Scanning electron micrograph of a polyacrylamide sample obtained by polymerization using IGEPAL CO 430 as emulsifier. 2800 \times .

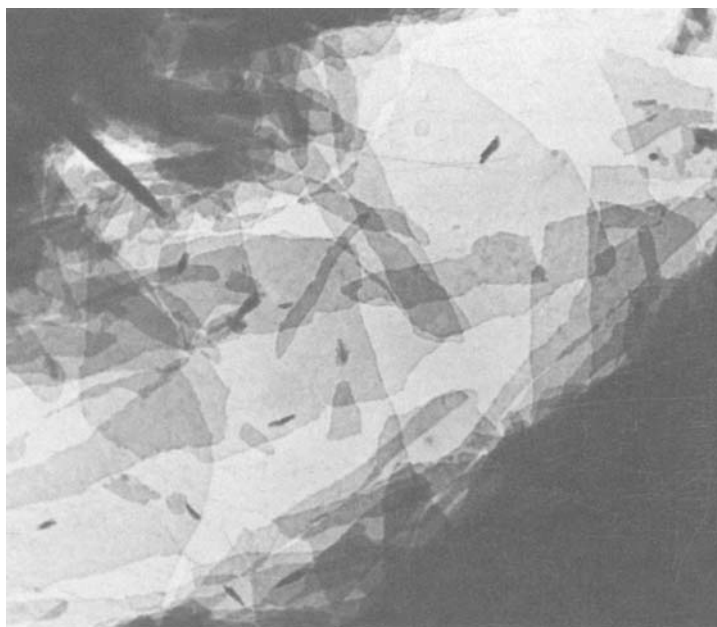


FIG. 8. Transmission electron micrograph of the same sample as in Fig. 7. 40,000 \times . Black of the figure: fibril border.

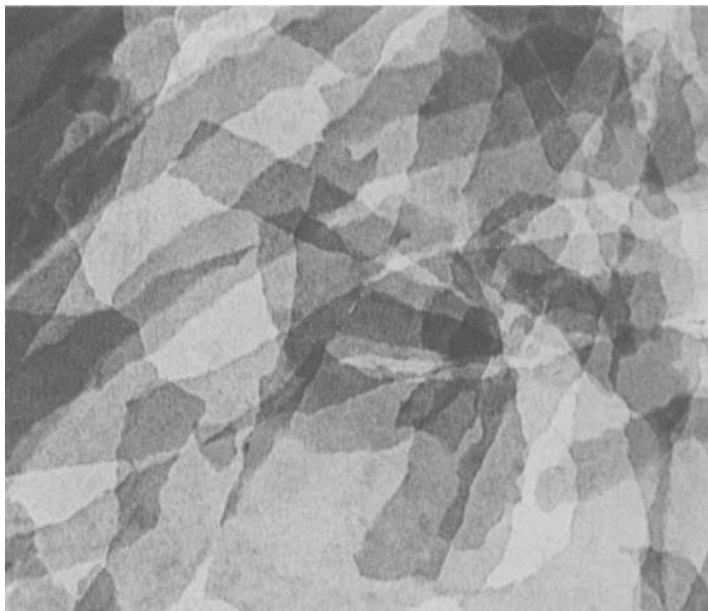


FIG. 9. Detail of the micrograph in Fig. 8.

in this case by superposition of some microlamellae of irregular shapes and various sizes (Fig. 9).

The presence of these microlamellae suggest that the reaction advances along certain preferred planes, probably imposed by the specific monomer-emulsifier-salt interaction at the molecular level. This interaction results in a particular arrangement of the microheterogeneities of the system.

The presence of an electrolyte of the organic salt type influences the polymerization of acrylamide in inverse suspension in a completely unexpected way. While the inorganic electrolytes exert no important influence [3, 4], such organic electrolytes as sodium acetate, fumarate, oxalate, amilate, and polyacrylate, when present in the reaction medium, cause a substantial increase of the molecular weight of the polyacrylamide obtained (Fig. 10). This figure shows the influence of organic salt concentration upon the polyacrylamides obtained in the presence of the organic electrolytes mentioned.

At zero salt concentration, inverse suspension polymerization leads to molecular weights smaller than those obtained in solution, (Fig. 11). The results in Fig. 11 also demonstrate the nondependence of the inversion emulsion polymerization process on initiator concentration in the reaction medium.

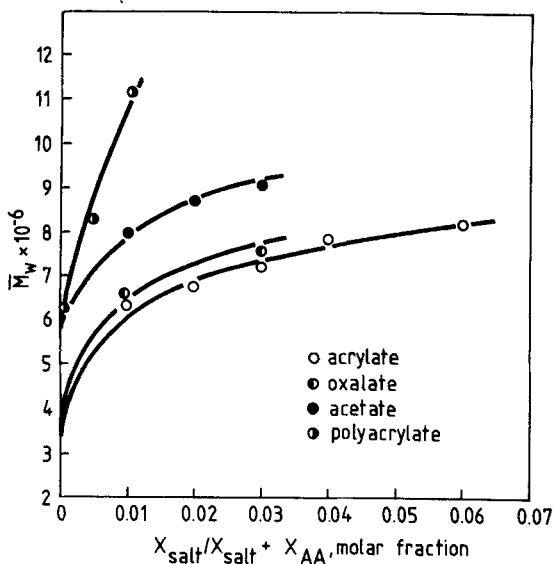


FIG. 10. Dependence of polyacrylamide molecular weight on some organic salt concentration. The emulsifier used was MYRJ 45.

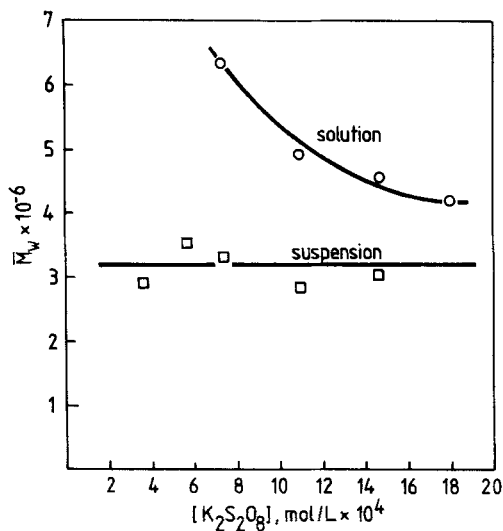


FIG. 11. Dependence of polyacrylamide molecular weight on initiator concentration: $H_2O/AA = 1$, $K_2S_2O_8/NaHSO_3 = 2/1$ molar ratio, temperature = 30°C .

These experimental data have led us to ask the following questions:

1. How does the organic electrolyte act?
2. What is the part played by the nature of the emulsifier? Is the nature of the emulsifier the only determinant or is there a conjugate action of the emulsifier and the dispersion medium upon the process?
3. What is the action of the polymer already formed in the system, since it is known that in case inversion of phases occurs accidentally before a reaction is started, polymerization may not be initiated?

We answer these questions briefly in what follows.

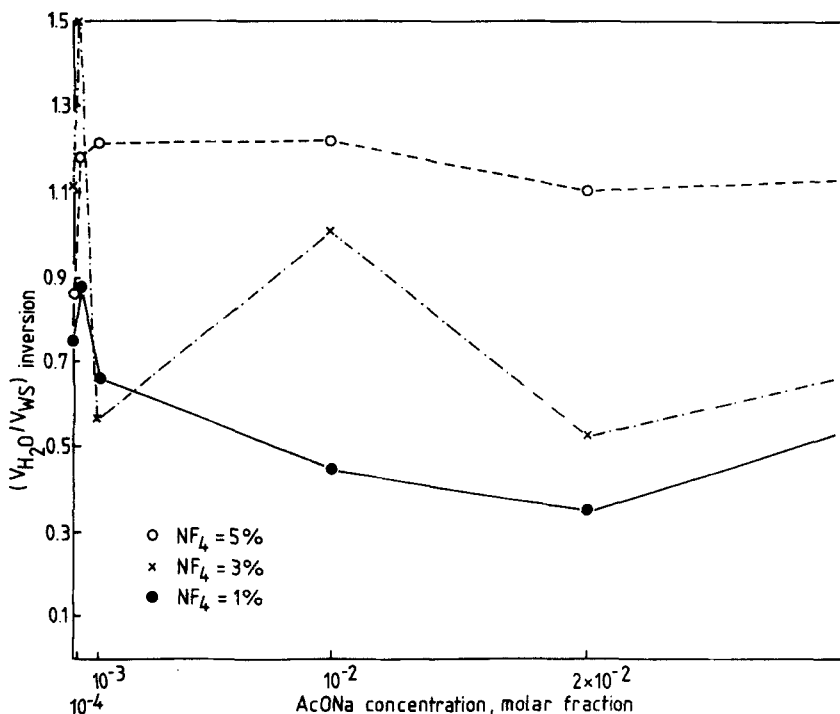


FIG. 12. Dependence of the volume phase ratio (V_{H_2O}/V_{WS}), measured by conductometric titrimetry, on the sodium acetate concentration in the system: WS = white spirit, NF_4 = IGEPAL CO 430.

1. There are two possible answers regarding the electrolyte. (1A) The electrolyte influences the physicochemical properties of the disperse system suitable for polymerization. (1B) The electrolyte interferes directly with the reaction through chemical interaction with the components of the system.

(1A) Regarding the role of the physicochemical properties of the system in polymerization, data were obtained on the disperse systems under study from conductometric titration and interfacial tension measurements.

Conductometric titration has supplied the following information: the phase ratio at the time of phase inversion in the system [1] (Fig. 3), and the value of jump conductivity at the same moment of titration (Fig. 3).

The experiments have thus shown that in the range of usual emulsifier concentration there is an optimum content of organic electrolyte which ensures the maximum molecular weight of the polyacrylamide obtained.

Examination of the influence of organic electrolyte concentration upon molecular weight and conversion shows that, while conversion decreases monotonously with an increase of salt content, the molecular weight records a maximum at about 2×10^{-2} mole fraction of salt [5].

It is worth remarking that in conductometric titration curves the volume jump ratios (Fig. 12) (as well as the conductivity at jump) exhibit a minimum at the same salt concentration. Moreover, interfacial tension measurements in the same systems reveal an effect similar to that of the organic electrolyte whose presence causes interfacial tensions to drop to a minima located at $1-2 \times 10^{-2}$ sodium acetate mole fraction (Fig. 13).

The existence of these optimal values of organic salt concentration may be accounted for by the optimum stabilization of the interface at these salt concentrations, perhaps through electrostatic and interfacial molecular interactions which occur there.

This seems to be the action of the emulsifier and electrolyte upon the interface, and how the state of this interface determines polymerization.

(1B) To clear up the role of the electrolyte as a chemical factor in polymerization, kinetic measurements of acrylamide polymerization in concentrated (50%) aqueous solutions were performed by a dilatometric technique.

The results show that an increase of salt concentration in the reaction medium causes the molecular weight to increase, and at the same time the conversion levels off (Fig. 14).

This leveling off is stronger in solution than in inverse suspension. The problem arises as to whether the influence of salt upon the process is associated with a modification of the pH of the medium caused by the salt [6, 7].

To clear up this problem, we carried out polymerizations in phosphate buffer solutions whose pH was equal that of a salt (sodium acetate) solution in the reaction medium.

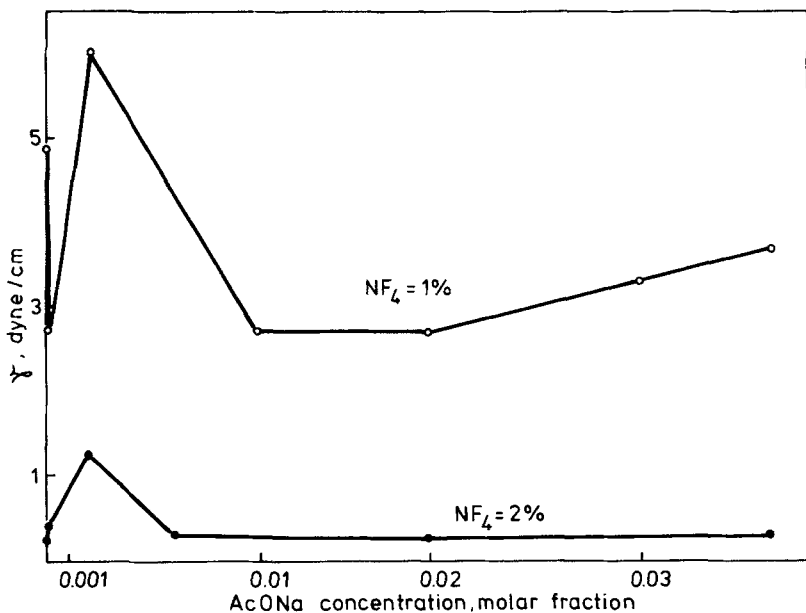


FIG. 13 Interfacial tension dependency on the sodium acetate concentration in the system AA: $H_2O/WS = 30/70$ by weight, $NF_4 =$ IGEPAL CO 430.

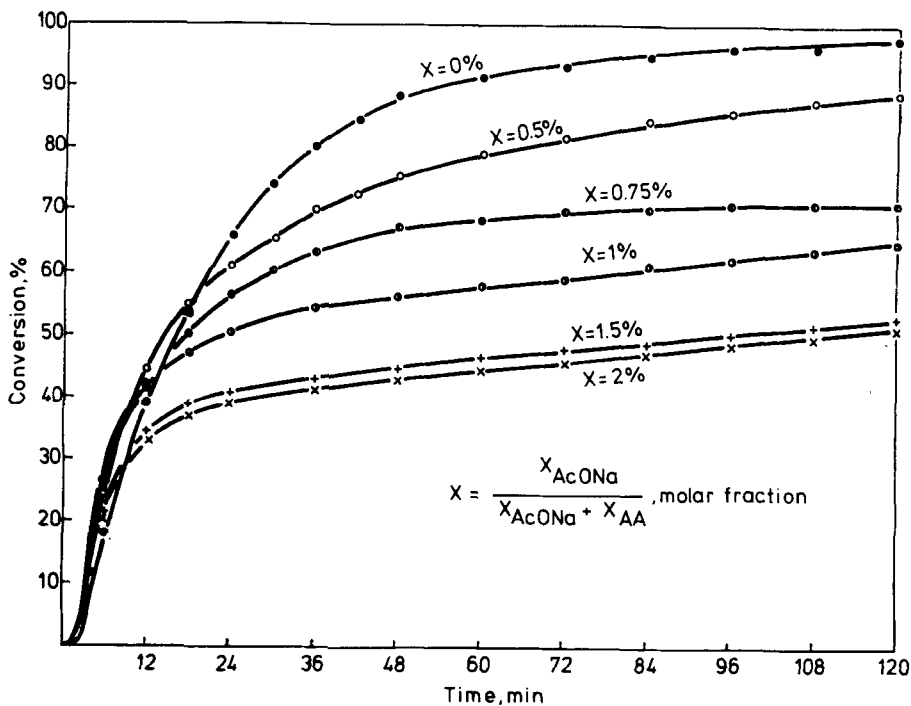


FIG. 14. Kinetics of acrylamide polymerization in homogeneous aqueous solutions in the presence of various concentrations of sodium acetate.

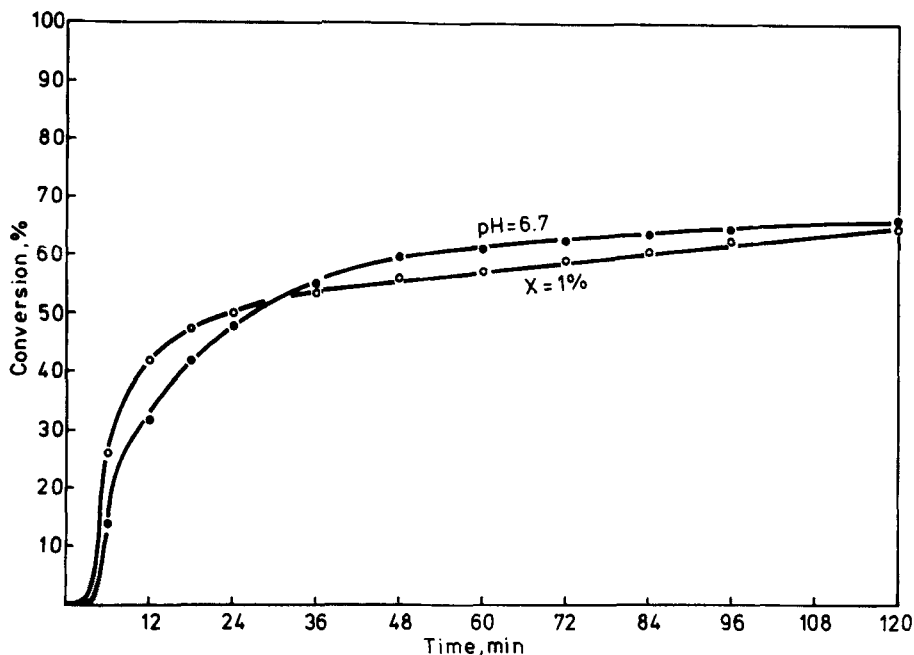


FIG. 15. Kinetics of acrylamide polymerization in the presence of 0.02 M phosphate buffer ($\text{pH} = 6.7$) and of 0.01 molar fraction sodium acetate solution ($X = 1\%$).

It turns out that the kinetics are identical in both cases at equal pH's (Fig. 15). The result that pH is a factor explains the influence of electrolyte upon the polymerization process. pH may influence polymerization in two ways: 1) by altering the rate of initiation through diminishing the concentration of active centers, and 2) by altering the conformation of macromolecules already formed in solution. Our experimental results suggest that the second factor is far more important (Fig. 14).

The initial rates of polymerization are identical no matter what the concentration of electrolyte in the system (Fig. 14), and the leveling off of conversion does not occur unless appreciable amounts of polymer accumulate in the system.

Examination of Fig. 16 shows that the plots of intrinsic viscosity/sodium acetate concentration ratios versus polyacrylamide concentration have different slopes for various concentrations of sodium acetate in solution. The variation of slope with the concentration of organic electrolyte indicates that the role of salt is to determine the reformation of the macromolecular spool. The salt gathers and agglomerates the macromolecules of polyacrylamide and increases the average hydrodynamic volume, which is equivalent to the increase of viscosity noticeable in Fig. 16.

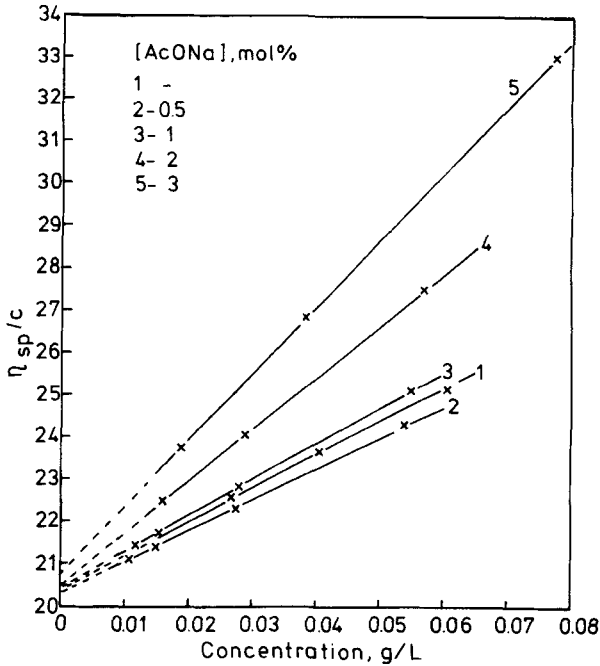


FIG. 16. Specific viscosity/concentration ratio variation with polyacrylamide concentration in the presence of various concentrations of sodium acetate in polymerization media where the respective polymers were obtained.

Thus, both the growth reaction rate and the termination reaction rate are affected by the presence of an organic salt, which accounts for the increase of conversion and the increase of molecular weight with the concentration of the electrolyte.

The effect is stronger with polymerization in solution, because with polymerization in inverse suspension the electrolyte migrates to the interface and the effective concentrations in the aqueous phase are lower.

In conclusion, electrolyte influence on inverse suspension polymerization leads to three main effects: the organic electrolyte partially migrates to the interface and produces stiffening, the electrolyte limits the chain transfer reaction, and the electrolyte increases the molecular weight of the polyacrylamides obtained due to a pH effect.

2. A separate set of runs was used to deal with the role of the emulsifier and that of the dispersion medium in the polymerization process. We have studied some characteristics of the polyacrylamides ob-

TABLE 1

Surfactant	Dispersion medium	Conversion, %	$M_w \times 10^{-6}$	Notes
Ethoxylated nonylphenol, 4 EO IGEPAL CO 430 (NF ₄)	Dibutyl-phtalate (DBP)	100	6.25	Without phase inversion
	White Spirit (WS)	50	8.0	With phase inversion
	Cyclohexane (CH)	85	19.0	With phase inversion
	Ethyl acetate	2	2.5	With phase inversion
	CCl ₄	20	Crosslinked polymerization	With phase inversion
	Benzene	-	-	Complete phase separation
Ethoxylated stearine (MYRJ 45)	DBP	100	6.7	Without phase inversion
	CH	65	9.25	With phase inversion
	WS	98	8.25	With phase inversion

tained, i.e., conversion, molecular weight, and the way the reaction, with or without the inversion of phases, occurs (Table 1). We have employed some other dispersion media (for example, dibutyl phtalate, whose density and polarity are higher). Polymerization occurred without phase inversion, reflecting the importance of the dispersion medium in the polymerization reaction.

If a solvent is employed whose chain transfer activity is high, the polymer is strongly crosslinked. Taking into account that the two phases are hardly miscible (even in the presence of an emulsifier), it turns out that polymerization occurs at the interface where both the organic and aqueous phases are present.

Depending on the emulsifier, HLB, and on the emulsifier partition coefficient between the aqueous and organic phases, when polymerization starts, the system may either separate completely into two dis-

TABLE 2

Dispersion medium	Surfactant	Notes
Benzene	NF ₄	Complete phase separation
	NF ₆	Complete phase separation
	NF ₁₀	Suspension polymerization
	NF ₁₅	Suspension polymerization with initial inversion of phases

tinct phases or advance normally with phase inversion and dispersion into particles of the gel formed (Table 2).

Thus, the two factors (dispersion medium and emulsifier) conjugate their action upon the acrylamide polymerization reaction. Attention should be drawn to the effect of the HLB balance of surfactant between the organic and aqueous phases.

3. The answer to the question concerning the action of the polymer is still being sought.

One can offer as preliminary information the following: The random presence of the polymer in the system modifies its structure so that it comes close to that of a viscoelastic gel. It is likely that it blocks the interface and severely lowers the interfacial tensions which, once more, explains why once the phases are inverted, the reaction no longer starts.

II. POLYACRYLAMIDE MODIFICATION REACTIONS

The following reactions (Fig. 17) were conducted in polyacrylamide obtained in inverse suspension: 1) The partial hydrolysis of the amide group, 2) the Mannich reaction, and 3) the imidization reaction.

1. The Basic Hydrolysis of Polyacrylamide

The basic hydrolysis of polyacrylamide particles obtained in inverse suspension was carried out in an heterogeneous system.

Hydrolysis in suspension offers technological advantages compared to hydrolysis in solution: high polyacrylamide concentrations in the system (up to 25%), and easy separation of the polymer from the reaction mixture.

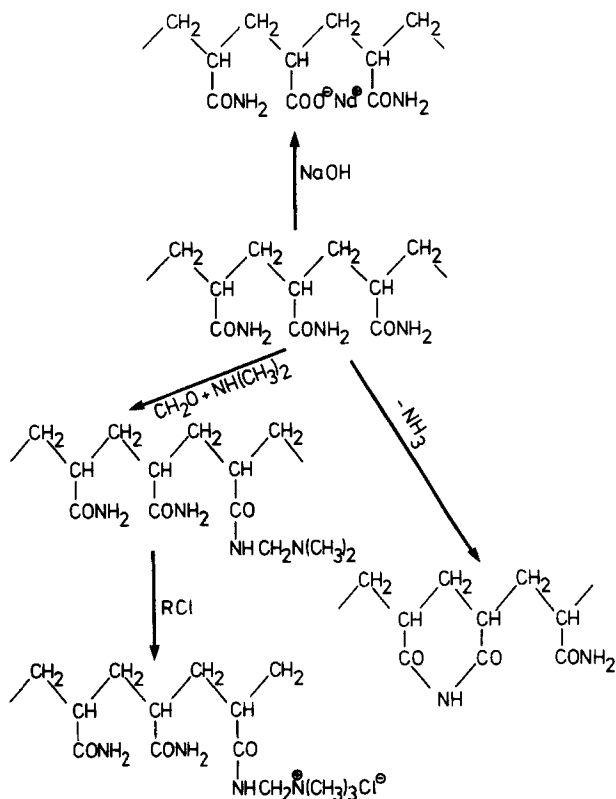


FIG. 17. Reactions of transformation of polyacrylamide.

The polyacrylamide particles were suspended in a methanol-water mixture in the presence of a soluble catalyst, NaOH or KOH.

The porosity of particles due to polymerization of acrylamide in inverse suspension ensures improved contact between the liquid and the polymer. Moreover, the presence of water in the system causes swelling of particles and allows access of the catalyst to the inside of the polymer particles.

Figure 18 shows the dependence of the degree of transformation (hydrolysis) on the catalyst/polymer mole ratio for hydrolysis in suspension and solution. For the reaction times employed (6 h), the difference between solution and suspension is small. This affirms that hydrolysis in suspension is not diffusion controlled.

That diffusion does not have a larger share in the hydrolysis of polyacrylamide in suspension is probably due to the morphology of the

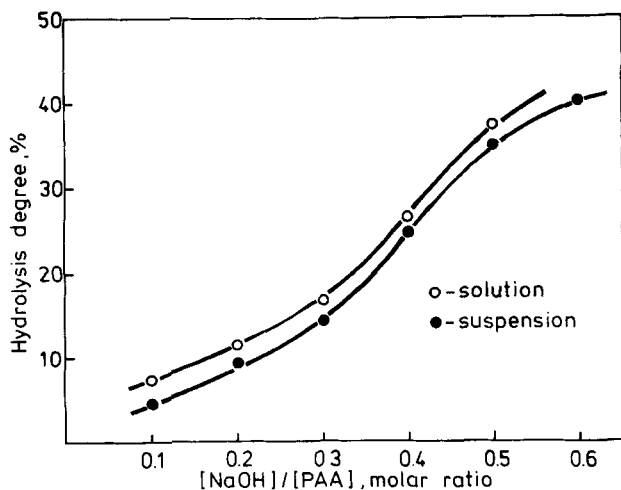


FIG. 18. Hydrolysis degree dependence on NaOH/PAA ratio, mole/mole: $M_w = 7.3 \times 10^6$; $H_2O/CH_3OH = 1/5$, g/g; temperature = $30^\circ C$.

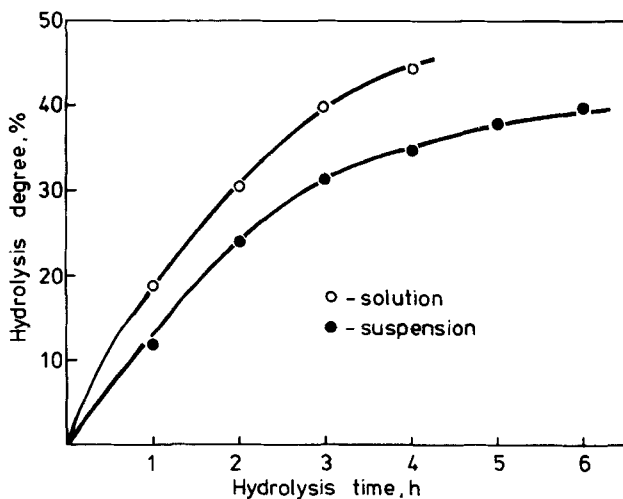


FIG. 19. Hydrolysis degree variation with reaction time.

particles. Because they are porous and therefore of larger specific surface, the diffusive factor is limited.

The variation of the degree of hydrolysis during the reaction can be observed in Fig. 19. The difference between hydrolysis in suspension and in solution is not very important.

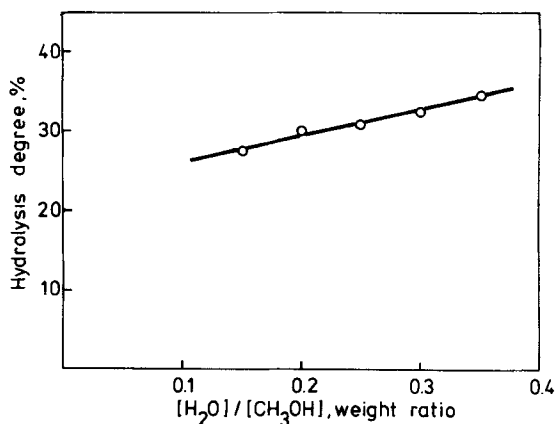


FIG. 20. Inverse suspension hydrolysis degree variation with the $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ weight ratio.

The degree of hydrolysis in suspension depends on the water/methanol ratio (Fig. 20); this ratio should not be too high (above 0.4) because the particles coalesce and there is a loss in the efficiency hydrolysis.

According to data in the literature [8], the kinetics of the reaction obeys a quadratic relationship:

$$\frac{1}{b-a} \ln \frac{a(b-x)}{b(a-x)} = kt$$

where a = initial molar concentration of amidic groups

b = initial molar concentration of NaOH

x = concentration of hydrolyzed groups at time t

It is surprising that the basic hydrolysis of polyacrylamide in inverse suspension obeys the same quadratic relation. However, in this case the rate constant is about four times smaller (Fig. 21). We believe that the hydrolysis reaction rate in suspension is lower than in solution due to the different mobilities of the macromolecular segments.

2. Mannich Reaction in Polyacrylamide

The Mannich reaction of polyacrylamide in solution or emulsion has been investigated previously in order to establish the optimum conditions for obtaining the modified product and to improve the technology [9, 10].

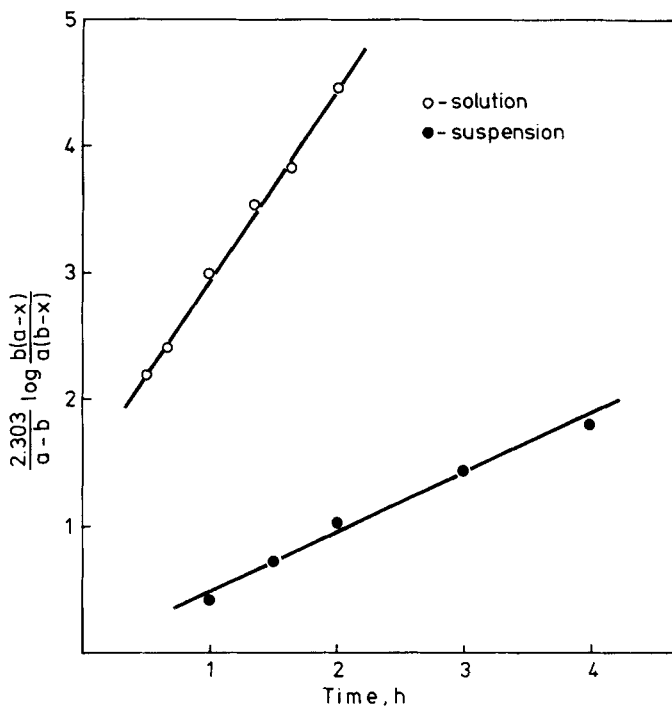


FIG. 21. Agreement of the data for solution [8] and suspension polyacrylamide hydrolysis with the second-order kinetic equation cited in the text.

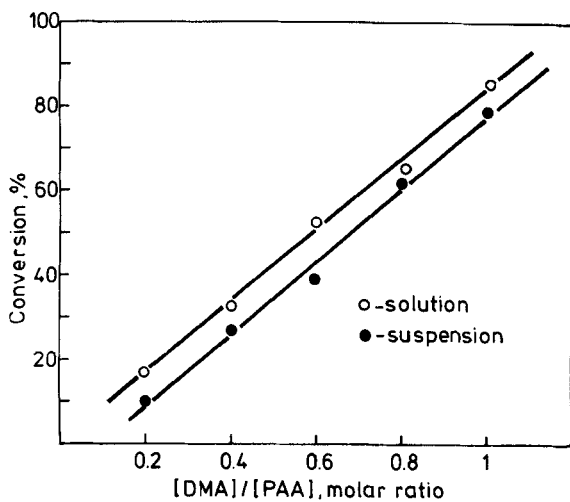


FIG. 22. Conversion in the Mannich reaction versus dimethylamine/polyacrylamide molar ratio.

As shown earlier (Fig. 17), polyacrylamide was treated with formaldehyde and dimethylamine and reached a final conversion of about 95%.

In Fig. 22 are presented the degrees of conversion of Mannich transformed polyacrylamide versus the dimethylamine/polyacrylamide molar ratio. Note that the difference between the results of the Mannich reaction in solution and in suspension are small.

Spectra were recorded of the polymer obtained by the Mannich reaction. The absorption characteristic of the $-N(CH_3)_2$ group is found again in the IR spectrum ($1030-1240\text{ cm}^{-1}$ range), and it increases as the degree of transformation rises.

After the Mannich reaction the product was quaternized with methylene chloride or treated with HCl solution to a pH value of 3.

The increase of the viscosity of the treated solution is evidence of the existence of positive electric charges (Fig. 23).

As with hydrolysis, the Mannich reaction leads to polyacrylamides with special properties (high solubility, viscosities much higher than in ordinary polyacrylamides).

Some examples will illustrate how these modified polymers act as flocculants. Figure 24 shows the variation of average times of sedimentation of 3% suspensions of bentonite and 1% suspensions of cellulose fibers by polyacrylamide with various degrees of hydrolysis. Figure 25 presents various sedimentation curves of a 3% bentonite suspension for various concentrations of polyacrylamide and degrees of

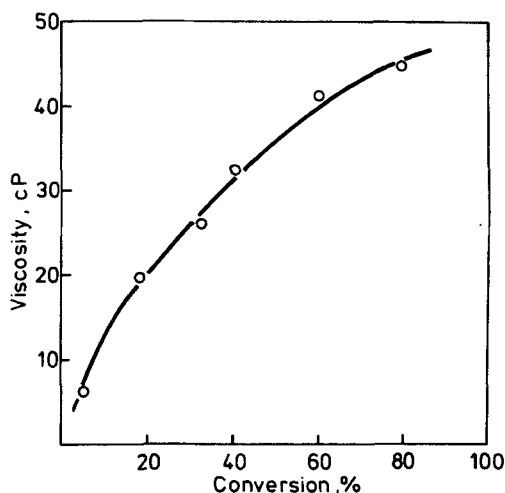


FIG. 23. Variation of the viscosity of Mannich transformed and quaternized polyacrylamide with conversion by the Mannich reaction.

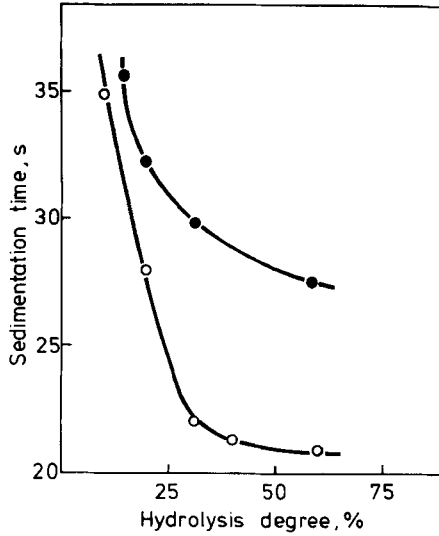


FIG. 24. Dependency of the average sedimentation times with the degree of hydrolysis of polyacrylamide utilized for the flocculation of (●) 3% bentonite suspension and (○) 1% cellulose fiber suspension.

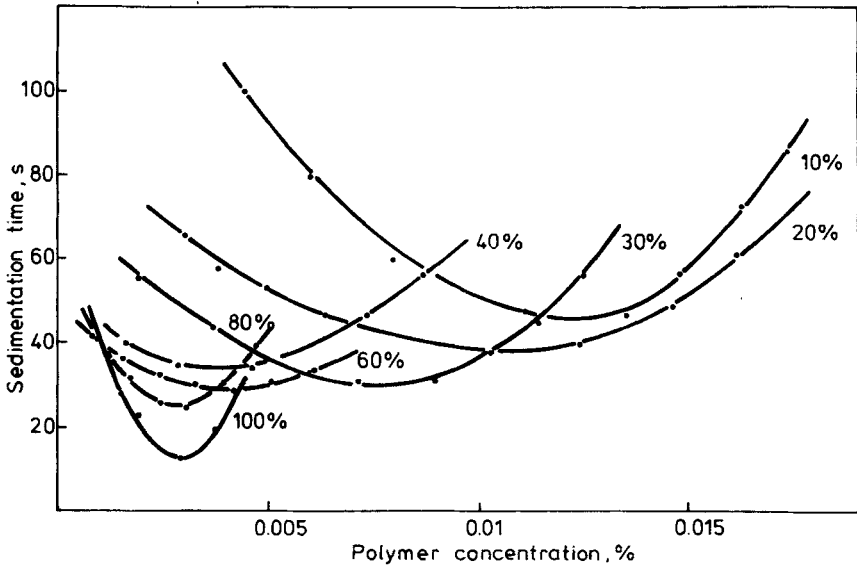


FIG. 25. Sedimentation curves of a 3% bentonite suspension for different Mannich modification degrees of polyacrylamides utilized in flocculation. The minimum of each curve represents the optimum sedimentation time.

Mannich modification. The minimum of each curve is taken as the optimum sedimentation time.

3. Imidization Reactions

Films were evaporated at 30°C from solutions of polyacrylamide or polyacrylamide transformed by Mannich reactions. If the initial solutions are acid (pH value of 3-4), the films evaporated at a temperature smaller than 40°C are always water insoluble [13].

The nitrogen content of these films ranges within 15-17%, proving the existence of inter- and intramolecular imidizations [11, 12].

The imide functions were also evidenced by IR spectra of the polymer films.

III. UTILIZATION OF MODIFIED POLYACRYLAMIDE AS SUPPORT FOR ENZYME ENTRAPMENT

Our results regarding the polymerization of acrylamide in inverse suspension were developed in a study of the copolymerization of acrylamide with methylenebisacrylamide in the same system as described in Section I. We utilized this reaction for enzyme entrapment.

The advantages of supporting enzymes come from the handiness and sometimes from the stability it achieves.

The principle of the utilization of polyacrylamide as a support for enzymes is the obtaining of insoluble polymers of adequate porosity.

Copolymerization of acrylamide and methylenebisacrylamide in solution results in gels which entrap the enzyme, perhaps as drops. However, for monomer concentrations and comonomer ratios that allow retention of the enzyme, the enzymatic activity is low. Moreover, with copolymerization in aqueous solution the thermal transfer is poor and the particles formed are too large and of irregular shape.

Copolymerization of acrylamide and methylenebisacrylamide in inverse suspension offers some advantages. Variation of the parameters mentioned earlier (i.e., the nature and concentration of the emulsifier, the nature of the organic phase and the phase ratio, the monomer concentration in the aqueous phase, and the comonomer ratio) can lead to insoluble particles whose size is controllable and whose morphology and porosity are adequate.

The enzymatic activity of some oxidoreductases (peroxidase from horseradish and catalase from bovine liver) entrapped at various comonomer molar ratios by copolymerization in inverse suspension is presented in Fig. 26. The two enzymes show different behaviors. Catalase, a bulky enzyme (of molecular weight 250,000), whose functionality requires more space, prefers larger networks, that is, lower comonomer ratios. Peroxidase is a smaller enzyme (molecular weight 50,000) and shows higher activity at larger comonomer ratios, i.e., smaller cell networks.

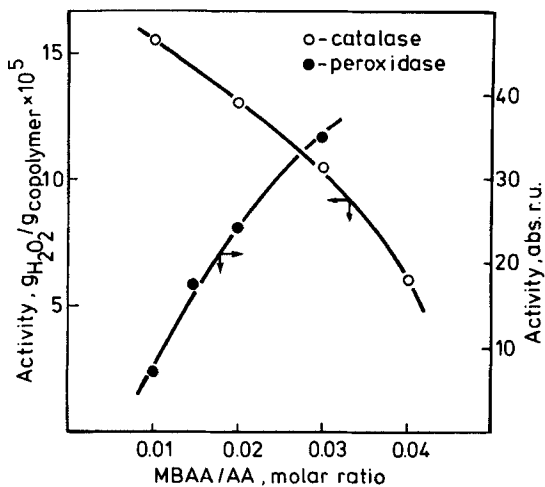


FIG. 26. The enzymatic activity of catalase and peroxidase entrapped at different comonomer molar ratios.

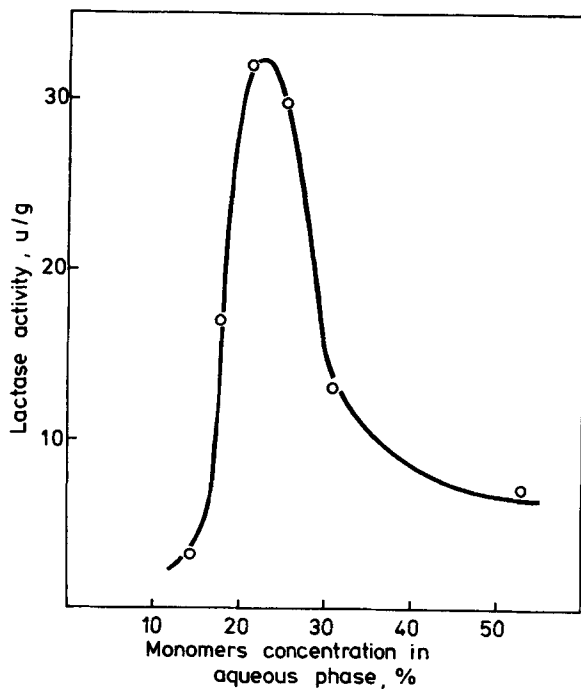


FIG. 27. The enzymatic activity of lactase entrapped at various concentrations of comonomers in the aqueous phase of the polymerization medium.

Figure 27 shows the activities of another enzyme, β -galactosidase (lactase), entrapped by copolymerization in inverse suspension at various concentrations of monomer in the aqueous phase. At a concentration of about 25% monomer, there is a maximum of activity (Fig. 27), but there are also some inconveniences. The copolymer particles are not very stable under repeated washings or transfer from one reaction medium to another.

Therefore, we resorted to another type of entrapment, that by seeded polymerization. The copolymer particles resulting from a previous polymerization, without enzyme, were polymerized again with comonomers in the presence of the enzyme. There are two steps (Fig. 28): 1) obtaining seed particles and 2) obtaining particles with the supported enzyme.

The activity of lactase entrapped by seeded copolymerization is presented in Fig. 29. The supported enzyme is entrapped under identical conditions. Only the seed particles are obtained under different conditions; the concentration of comonomers in the aqueous phase is variable.

Note the increase of lactase activity with monomer concentration in the aqueous phase of the copolymerization medium of the seed particles. The polymerization yield is a maximum at 50% monomer concentration in the aqueous phase. This concentration has been chosen as optimum.

The activity of polyacrylamide particles with entrapped lactase and the entrapment efficiency vary with the concentration of the enzyme in the aqueous phase. This variation is presented in Fig. 30. It is seen that when the enzyme concentration rises, the efficiency of polymerization drops to zero, which is probably due to the fact that in high concentration the enzyme interacts with the redox initiator system.

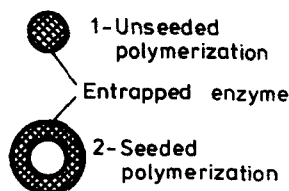


FIG. 28. Schematic representation of the unseeded and seeded polymer particles obtained by polymerization in 1 and 2 steps, respectively.

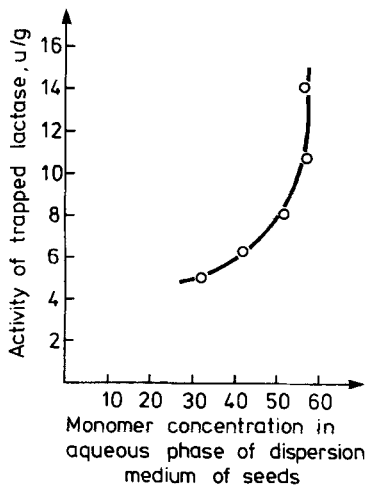
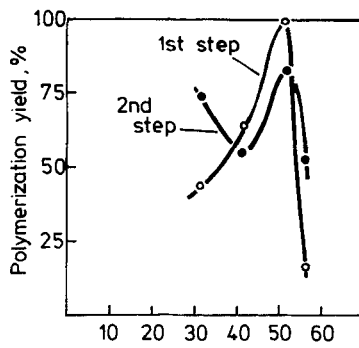


FIG. 29. The dependency of lactase activity and polymerization yield of each copolymerization reaction step on the monomer concentration in the aqueous phase of the seed particle reaction medium.

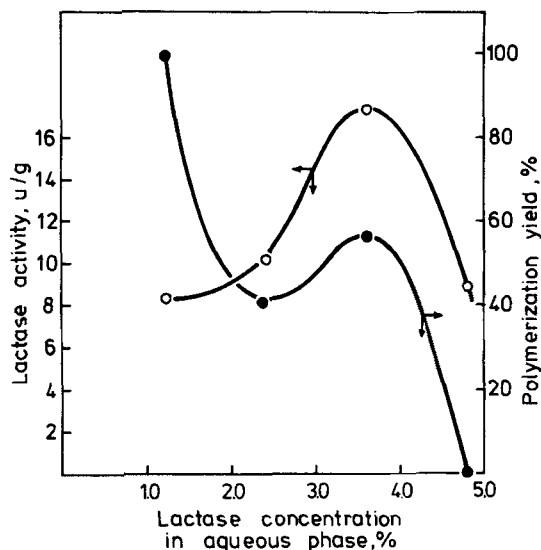


FIG. 30. Efficiency and activity of entrapped lactase versus enzyme concentration in the reaction medium.

CONCLUSIONS

Polymerization of acrylamide in inverse suspension has features which distinguish it from other polymerization procedures reported in the literature.

The characteristics of the polymers obtained include the qualities required for their further modification, either by other reactions (hydrolysis, Mannich) or by copolymerization. This diversity of the final properties of these polymers increases their possible applications.

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